

# Development of a selective absorbent SiAlON/Si-Al thin film system for radiative cooling

by

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Under the supervision of

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I

### Preface

This work is under the supervision of Dr. Hao Chen, Prof. Hongtao Cao, and Dr. Ming Li. The author declares that all the work is original. Research publications from this thesis are listed as follows:

- Yuxin Jiang, Zhilin Chen, Hui Xiong, Qiuju Zhang, Hao Chen<sup>\*</sup>, Junhua Gao<sup>\*</sup>, Hongtao Cao<sup>\*</sup>, SiAlON Composite Films with Strengthened Chemical Intermixing for Wide Infrared Absorption Band." Appl. Surf. Sci., 640 (23) (2023) 158341. doi: 10.1016/j.apsusc.2023.158341.
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## Abstract

Radiative Cooling (RC), which can reduce the surrounding temperature with no extra energy input, has attracted much attention in recent decades. The key principle of this approach involves the development of a system that selectively emits the light within the Atmosphere Window (AW) in a wavelength of  $3 \sim 5 \,\mu m$ and  $8 \sim 13 \,\mu\text{m}$ , while minimizing the absorption in the region from 400 nm to 2.5 µm. Traditionally, RC films have employed organic materials as the absorbent layer, characterized by intrinsic transparency in the short wavelengths and absorption in the InfraRed (IR) range due to the vibrational and rotational modes of abundant chemical groups presented within their molecular structures. However, they have inherent limitations, including large film thickness, unavailable spectrum selectivity and limited lifetime. Conversely, contemporary system design based on inorganic materials also faces challenges related to the complex film structures. These complexities mainly stem from either the fixed, narrow absorption band, or the limited Refractive Index (RI) of the materials. Presently, the foremost challenge in the development of inorganic film systems lies in simplifying their structural composition while preserving the cooling efficiency as much as possible. Hence, the primary objective of this research project is to demonstrate an ultrathin coating for RC by designing and preparing novel materials used in the absorbent and light confinement layers.

Thus, this research is separated into three parts. Firstly, SiAlON composite is fabricated through magnetron co-sputtering method (Si<sub>3</sub>N<sub>4</sub> and AlN targets are used), enabling the formation of multiple absorption bonds through chemical intermixing. This composite exhibits broadband absorption characteristics ranging from 8 to 16 µm, which can be readily manipulated by tuning the film composition in response to the deposition parameters. Extensive analyses suggest that regulation upon the absorption feature is attributed to the precise control over chemical composition as well as the chemical bonding states. Secondly, the spacer is based on Al NanoWire (NW) arrays-embedded Si metamaterial film, serving to confine incident light and establish Fabry-Pérot (F-P) resonance. Molecular Dynamics (MD) simulations are conducted to reveal the forming mechanism of vertical aluminum nanowire arrays, which is ascribed to the mobility variance between the two phases (Si and Al). Additionally, ion bombardment due to the substrate bias supplies external energy, facilitating adatom diffusion and reevaporation during the deposition process, thereby increasing the upper limit of aluminum filling fraction required for the formation of the metamaterial structure. The Si-Al NWs system exhibits metallic behavior within the Visible (Vis) to near-IR region, characterized by high reflectivity (up to 70%). Besides, the composite demonstrates dielectric properties within the mid-IR range because of its deep-subwavelength NW structure, marked by a tunable high RI ranging from 6 to 8. Finally, a double-layer RC coating is developed by combining the two materials mentioned above onto a 120 nm thick aluminum mirror. The thickness of each layer is optimized through the application of a Particle Swarm Optimization (PSO) algorithm, taking the theoretical performance in 8~13 µm computed by the Transfer-Matrix Method (TMM) program executed by MATLAB as the criterion. The film system shows an average emissivity of 0.806 in the AW and achieves a maximum temperature reduction of approximately 20°C compared to the bare Cu plate under lowhumidity conditions.

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Many thanks to all!

## Nomenclature

| $	heta_0$             | Incident angle                           |
|-----------------------|--|
| $	heta_1$             | Refractive angle                         |
| Ε                     | Electric field intensity vector          |
| Н                     | Magnetic field intensity vector          |
| S                     | Poynting vector                          |
| $N_{0}$               | Refractive index of free space and air   |
| $N_x(x=1,2,3)$        | Refractive index of layer <i>x</i>       |
| $d_x$ (x=1,2,3)       | Film thickness of layer <i>x</i>         |
| $\eta_0$              | Optical admittance of free space and air |
| $\eta_x(x=1,2,3)$     | Optical admittance of layer x            |
| I <sub>0</sub>        | Incident light                           |
| I <sub>1</sub>        | Reflective light                         |
| <i>I</i> <sub>2</sub> | Refractive light                         |
| <i>I</i> <sub>3</sub> | Transmitted light                        |
| Т                     | Temperature in K                         |
| λ                     | Wavelength                               |
| k <sub>B</sub>        | Boltzmann's constant                     |
| h                     | Planck's constant                        |
| С                     | Light speed in vacuum                    |
| f                     | Volume Filling Fraction of Nanowires     |
| V                     | Light speed in the medium                |

| ρ                    | Polarization state                                       |
|----------------------|--|
| Е                    | Permittivity; Dielectric constants                       |
| μ                    | Permeability   |
| h <sub>c</sub>       | Non-radiative heat coefficient                           |
| $n_{ m eff}$         | Effective refractive index                               |
| ε                    | Emission   |
| α                    | Absorption coefficient                                   |
| $r_x$                | Reflective lights of x order                             |
| t                    | Transmission light                                       |
| $t_{\lambda}$        | Atmospheric transmittance                                |
| φ                    | Phase shift  |
| δ                    | Phasor thickness   |
| $\int d\Omega$       | Angular integral   |
| $I_{AM1.5}(\lambda)$ | Intensity of solar illumination when the air mass is 1.5 |
| $I_{BB}(T,\lambda)$  | Spectral emission of blackbody at T, $\lambda$           |
| $P_{net}(T)$         | Net cooling power at T                                   |
| $P_{rad}(T)$         | Radiated power of the sample at T                        |
| $P_{atm}(T)$         | Atmospheric absorbed power at T                          |
| P <sub>sun</sub>     | Absorbed solar power                                     |
| $P_c(T)$             | Absorbed power caused by nonradiative factors at T       |
| Δ                    | Phase difference, ellipsometric parameter                |
| Ψ                    | Intensity difference, ellipsometric parameter            |
| A                    |  |
|                      | Absorptance  |

| Т      | Transmittance                                    |
|--------|--|
| 1D     | One-Dimensional                                  |
| 2D     | Two-Dimensional                                  |
| 3D     | Three-Dimensional                                |
| 2DFFT  | Two-Dimensional Fast Fourier Transform           |
| AW     | Atmospheric Window                               |
| CVD    | Chemical Vapor Deposition                        |
| DBR    | Distributed Bragg Reflector                      |
| DFT    | Density Functional Theory                        |
| DMF    | N,N-DiMethylFormamide                            |
| EAM    | Embedded Atom Method                             |
| EMA    | Effective Medium Approximation                   |
| EMT    | Effective Medium Theory                          |
| FDTD   | Finite-Difference Time-Domain                    |
| F-P    | Fabry-Pérot                                      |
| FTIR   | Fourier Transform Infrared                       |
| GGA    | Generalized Gradient Approximation               |
| HRTEM  | High-Resolution Transmission Electron Microscopy |
| HVAC   | Heating, Ventilation and Air Conditioning        |
| IR     | InfraRed   |
| KK     | Kramers-Kronig                                   |
| LAMMPS | Large-scale Atomic/Molecular Massively Parallel  |
|        | Simulator  |
| LSP    | Localized Surface Plasmon                        |
| LSPR   | Localized Surface Plasmon Resonance              |

| MC       | Monte-Karlo  |
|----------|--|
| MD       | Molecular Dynamics                                     |
| NIR      | Near InfraRed  |
| NVT      | canonical ensemble (fixed amount of atoms N, volume V, |
|          | and temperature T)                                     |
| NW       | NanoWire   |
| PAN      | PolyAcryloNitrile                                      |
| PCMFs    | Phase-Change Microstructure Fibers                     |
| PE       | PolyEthylene   |
| PECVD    | Plasma Enhanced Chemical Vapor Deposition              |
| PEG      | Poly(Ethylene Glycol)                                  |
| РЕО      | PolyEthylene Oxide                                     |
| PES      | PolyEther Sulfone                                      |
| PET      | PolyEthylene Terephthalate                             |
| PDMS     | PolyDiMethylSiloxane                                   |
| PLD      | Pulsed Laser Deposition                                |
| PMMA     | PolyMethyl MethAcrylate                                |
| PMP/TPX  | PolyMethyl Pentene                                     |
| PS       | PolyStyrene  |
| PSO      | Particle Swarm Optimization                            |
| PSP      | Propagating Surface Plasmon                            |
| PVC      | PolyVinyl Chloride                                     |
| PVD      | Physical Vapor Deposition                              |
| PVDF-HFP | Poly(VinyliDene Fluoride-co-HexaFluoro Propene)        |
| PVF      | PolyVinyl Fluoride                                     |

| Q factor | Quality factor                            |
|----------|---|
| RC       | Radiative Cooling                         |
| RI       | Real part of the complex Refractive Index |
| SAED     | Selected Area Electron Diffraction        |
| SCCM     | Standard Cubic Centimeter per Minute      |
| SEM      | Scanning Electron Microscopy              |
| SPR      | Surface Plasmon Resonance                 |
| SW       | Stillinger-Weber                          |
| TE       | Transverse-Electric                       |
| TEM      | Transmission Electron Microscopy          |
| ТМ       | Transverse-Magnetic                       |
| UV       | UltraViolet                               |
| VASP     | Vienna Ab initio Simulation Package       |
| Vis      | Visible                                   |
| WGM      | Whispering-Gallery-Mode                   |
| TMM      | Transfer-Matrix Method                    |
| XPS      | X-ray Photoelectron Spectroscopy          |
| XRD      | X-Ray Diffraction                         |
| XRR      | X-Ray Reflectivity                        |

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### **Chapter 1 Introduction**

#### **1.1 Background**

The energy consumption in the thermal comfort sector is experiencing dramatic growth due to the increasing demand in temperature control [1, 2]. This demand places a substantial strain on electricity resources and contributes significantly to greenhouse gases emissions [3]. Over the past few decades, passive RC, a concept predicated on the thermal exchange between the Earth and outer space, has caught considerable interest. The significance of RC systems lies in the capacity to reduce ambient temperatures without external energy inputs [4]. Therefore, this technology has become a global research hotspot although its cooling power is limited. Once it is widely implemented, the existing paradigm of human cooling methods will undergo a revolutionary change, and many of the existing problems in cooling technology will be effectively addressed. As shown by Figure 1.1, the RC productions have great potential in building cooling [5-7], condensers [8], purified water collection [9], wearable clothing [10]. Besides, the RC devices are also widely applied in agriculture [11] and solar panels [10].



Figure 1.1 The utilization of RC system in (a) Heating, Ventilation and Air Conditioning (HVAC) system [7]; (b) wearable clothing [10]; (c) air cooled condenser for CSP plants [8]; (d) water collection [9].

#### 1.2 Problem definition

Objects above absolute zero are able to continually emit heat in the form of electromagnetic radiation to their surroundings, constituting the heat output of the system. Typically, this thermal radiation falls within a wavelength range of 0.1 to 100  $\mu$ m [12]. Most of the emission from objects is absorbed by greenhouse gases, vapor, ozone, and atmospheric particulate matter with a diameter smaller than 2.5 mm (PM2.5) in the atmosphere, as depicted in **Figure 1.2** [13]. Conversely, radiation within the AW (ranging from 3~5, 8~13, to 16~28  $\mu$ m) can be emitted into outer space due to the high transmittance of air [14]. Thus, high emission in the AW is a crucial criterion for achieving effective cooling.



Figure 1.2 The absorption spectra of the atmosphere [13].

Meanwhile, most natural materials exhibit pronounced absorption of solar irradiance within the range of 0.3 to 2.5  $\mu$ m, leading to substantial heat input. Additionally, atmospheric radiation and incoming energy induced by nonradiative factors also contribute to the temperature rise. According to this model, the heat flow of a system is illustrated in **Figure 1.3**. An RC system can only achieve temperature reduction when the output energy resulting from thermal radiation surpasses all the input energy.



Figure 1.3 Heat flow of the RC system.

According to Kirchhoff's law, the emission and absorption of a material are equal when the system is in thermodynamic equilibrium [15]. Hence, materials with strong absorption within the AW, such as polymers [16, 17], metallic materials [18], and dielectrics [19], are commonly employed in the design of radiative coolers. Based on their absorption characteristics, radiative coolers can be classified into two categories: selective emitters, which emit only within the AW, and broadband emitters, which emit across the entire mid-IR range, as depicted in **Figure 1.4**. Selective emitters are typically composed of inorganic systems with optical cavities and/or artificial structures (i.e., metasurfaces and photonic crystals), preventing heat input from the atmospheric radiation, thereby achieving greater temperature reduction. In contrast, thick organic films often perform as broadband emitters, demonstrating higher net power and quicker ambient temperature reduction [20].



**Figure 1.4** The ideal spectral characteristics of two emitter types, and commonly implemented methodologies for accomplishing dual-band

modulation in the context of RC.

Moreover, the heat input via solar irradiance should be minimized to achieve an effective temperature drop. Thus, radiative coolers also need to selectively prevent the absorption from 0.3 to 2.5  $\mu$ m. As illustrated in the left part of **Figure 1.4**, this is typically achieved by constructing a transparent or scattering system with Vis-transparent materials [21], or employing reflective mirrors such as

Distributed Bragg Reflectors (DBRs) [22] or selective solar reflectors [23] atop Vis-absorbent materials. Moreover, some transparent RC systems also integrate metallic reflective mirrors, such as Al and Ag, to enhance high solar reflectivity [24].

In summary, the development of an effective radiative cooler requires the system to simultaneously achieve high absorption within the AW and high reflectivity or transmittance in the 0.3~2.5 µm range, with particular emphasis on the visible light region (400~780 nm), where the majority of solar irradiance is concentrated. To address this issue, a single thick film composed of a material transparent to visible light yet capable of IR absorption, can inherently deliver this dual-band light modulation [25-27]. However, the challenge arises from the considerable film thickness, resulting in a lack of selectivity and a relatively low temperature reduction. Many efforts have focused on optimizing the structures of film systems to attain selective absorption in the AW, but the RC coatings still faces issues related to substantial film thickness [28], complex construction [29], and limited integration capacity [30]. In this context, material optimization, including the materials constituting the absorbent layer and the spacer for optical resonance, becomes pivotal in simplifying the design of a radiative cooler. Furthermore, the design of the testing apparatus must be carefully optimized to

accurately measure and report the experimental temperature reduction. Both the temperature of the sample and the control group are either measured by

thermocouples [31-33] or directly with IR cameras [34, 35], and the typical testing setups of the two measurements are shown in **Figure 1.5** [36, 37].



Figure 1.5 The apparatus for temperature assessment involves (a) the use of a heat sink [36] and (b) the application of a straightforward IR camera for measurement [37].

#### 1.3 Aims and objectives

This project aims to develop a simple and IR-selective daytime RC structure. The concept of system design is inspired by a simple three-layer radiative cooler consists of a 70 nm-thick Si<sub>3</sub>N<sub>4</sub> layer, a 700 nm-thick Si layer, and a 150 nmthick Al reflective mirror [38], indicated in **Figure 1.6**. Herein, the top layer of Si<sub>3</sub>N<sub>4</sub> is designed as the IR absorbing layer, given by the robust photon-phonon coupling inherent in the Si-N bond. A high-RI Si spacer is introduced to establish F-P resonance, thereby effectively confining the incident light and enhancing the absorbing performance. Meanwhile, the bottom Al layer functions as the
reflective mirror, guaranteeing zero transmittance.



Figure 1.6 Three-layer RC film system designed by Chen et al. [38], and its principle.

However, this film system is highly limited by the narrow absorption band of  $Si_3N_4$  and high Si cavity thickness. Besides, the intrinsic absorption of Si before 0.4  $\mu$ m results in a relatively high solar energy input, greatly restricting the cooling performance of the film system. To optimize the structure, the present work is divided into the following four main objectives:

# • Objective 1: Extend the bandwidth of the absorbing dielectric via chemical bond intermixing

Considering the limited and fixed absorbing capabilities of the natural existed IR materials, the development of a novel absorbent material with high absorption in the 8~13  $\mu$ m range offers significant potential for simplifying RC designs. Therefore, this objective consists of: (i) understanding the absorbing mechanisms for the naturally existed materials; (ii) establishing the absorption broadening strategy; (iii) fabricating a material with an absorption band that covering the whole AW from 8 to 13  $\mu$ m, peaking at ~10  $\mu$ m; (iv) exploring the structural and absorbing characteristics of the SiAlON composite; (v) analyzing

the principal chemical composition and absorbing bonds in the SiAlON composite; (vi) revealing the absorption broadening mechanism; and (vii) manipulating the contents of chemical bonds through the introduction of reaction gases and ion impact, thereby regulating the absorbing features of SiAlON.

# • Objective 2: Enlarge the RI and solar reflectivity of the spacer via introducing metallic nanostructures

Enhancing the RI value of the spacer is an effective approach to reducing the thickness of the film system. The strategy for introducing metallic nanostructure into the dielectric to control the RI of the material is derived from Kramers-Kronig (KK) relations and "f-sum rule" [39], which indicate the dielectric index of the material is closely linked to its electron density. Additionally, metals naturally exhibits high solar reflectivity due to their ability to generate induced field when responding to the incident light. Hence, the introduction of metallic nanostructure benefits the raise of the short-wavelength reflection. This objective comprises the following tasks: (i) understanding the mechanisms for RI modification; (ii) establishing the material system with an effective RI of at least 6.8 (twice of the Si RI value) to compress the thickness to half of the Sibased system; (iii) theoretically modeling the Si-Al system under diverse conditions, including varying Al volume filling fractions and temperatures; (iv) establishing the conditions for the phase separation of Si and Al, specifically the criteria for the formation of vertically aligned Al NWs; (v) validating the theoretical simulations by experimentally fabricating the Si-Al system with varied Al volume filling fractions; (vi) producing the Si-Al NWs system with a high Al filling fraction and analyzing both the structure and the formation mechanism of the Si-Al NWs; (vii) conducting broadband optical analyses for the Si-Al NWs system; and (viii) investigating the optical tunability of the Si-Al NWs system by altering the occupation of Al.

# • Objective 3: Deposit the double-layer radiative cooler

An optimized ultrathin inorganic radiative cooler with highly selective IR absorption and a simplified fabrication process is developed by integrating the updated broadband absorbing material with the high- RI spacer. The optimization process is guided by experimentally tested and simulated optical and cooling performances, focusing on parameters such as film thickness and the composition of each layer. Thus, this objective contains: (i) establishing a predictive model for cooling performance using MATLAB; (ii) determining the target full-spectrum absorption for the film system – an average emission of 0.8 in the AW and an average reflectivity of 90% in the short-wavelength range; (iii) optimizing the thickness of each layer in the double-layer film system based upon the optical targets; (iv) the overall thickness of the film system being less than the thickness of the Si<sub>3</sub>N<sub>4</sub>/Si system from the literature in Section 1.3 (770 nm without Al reflective mirror); (v) experimentally fabricating the film system and evaluating its absorbing properties; (vi) addressing the optical contribution of each layer; (vii) optimizing its IR absorbing selectivity by adjusting the film structure, and (viii) achieving a temperature reduction of at least 3 °C under clear sky conditions with a minimum humidity of 50%.

# • Objective 4: Cooling performance testing

To accurately assess the cooling performance of the designed film system and identify influencing parameters through both IR photography and thermal measurements, the development of testing apparatuses for temperature drop measurements is essential. This objective includes: (i) designing thermally insulated testing apparatuses tailored for IR photography and thermal measurements, including the selection of appropriate construction materials and the definition of testing points; (ii) determining testing periods under various weather conditions, and (iii) constructing the testing apparatus and completing the cooling performance testing.

# 1.4 Thesis outline

This section presents the structure of the thesis, with a brief description of each chapter.

• Chapter 1 provides a concise introduction to the RC project. This chapter covers the principles underlying passive cooling and qualified the requirements into optical parameters. Through this introduction, the significance of the present work is explained. Moreover, based on this

comprehensive background research, aims and objectives are concluded, covering four main parts of the research.

- Chapter 2 comprises an extensive literature review. It firstly focuses on the historical development of radiative coolers and their present advancements. Then, principles of light absorption, the design of optical absorbers, mechanisms of refractive index (RI) modulation, and absorbing principle of IR materials are reviewed, followed by the analysis of both organic and inorganic RC systems. Additionally, the manufacturing processes employed in the construction of inorganic radiative coolers are systematically summarized and compared.
- Chapter 3 provides a systematic description of the methodology employed in this research, including the selection of the material system, the mathematical models and simulation programs used for system analysis, optimization, and performance prediction, as well as the sample fabrication procedures. It also details the optical and microstructural measurements conducted for sample characterization. Furthermore, a comprehensive explanation of the design of the IR photography and the 24-hour outdoor thermal testing apparatuses is presented.
- **Chapter 4** contains the investigation of the novel broadband selective IR absorbing SiAlON composite. A detailed analysis of the broadening effect in its absorption is conducted by examining its band structure, composition,

and chemical bonding. The relationship between the optical properties of the material and its chemical contents is further explored through introducing reactive gas and ion impact. A simulation of the absorption spectral selectivity of SiAlON composite-based absorber is also implemented.

- Chapter 5 establishes Si-Al NWs composite to attain the optical modulation. Specifically, the forming mechanism of vertically aligned Al NWs embedded in Si is investigated via MD simulation and experimental validation. The microstructure of the Si-Al NWs is analyzed, revealing the relationship between the Al filling fraction, the diameter, and the interwire gap of the NWs. The full-spectrum light response of the NW system is studied through near-field simulation to clarify its extraordinary electromagnetic behavior. Furthermore, the optical tunability of the Si-Al system is explored, along with its significant capabilities in dual-band manipulation.
- Combining the new established material SiAlON and Si-Al NWs, Chapter 6 shows the performance of the double-layer cooling system. This chapter discusses the optical contributions of each layer and examines the relationship between the parameters of each layer (e.g., thickness and Al filling fraction) and full-spectrum absorption. Additionally, the actual temperature drops under different weather conditions are measured using

both IR photography and 24-hour outdoor direct thermal measurements.

- Chapter 7 serves as the conclusion to the entire project, providing a concise overview of the research and describing the noteworthy contributions made in each of the preceding chapters.
- Chapter 8 engages the discussions regarding the completed work, offering insights into potential areas for future research.

# **Chapter 2** Literature review

From the analysis in Section 1.2, radiative coolers are essentially dual-band modulated IR absorbers characterized by low solar irradiance absorption and high IR emission in the AW. Following the introduction to the development of radiative coolers, the subsequent sections focus on explaining the principles of light propagation and the design strategies for five representative optical absorbers. These foundational concepts are crucial for understanding how to achieve selective absorption within target wavelength ranges. Subsequently, this chapter explores the IR absorption mechanisms relevant to both organic and inorganic materials. This comparative analysis serves to identify the research gap in the development of absorbing materials for RC. Moreover, recent advancements in radiative cooler technology are reviewed, including their design strategies, fabrication processes, and cooling performances. As a culmination of this assessment, an optimized film system is proposed to achieve selective IR absorption within a double-layer structure.

#### 2.1 Radiative cooling

The historical journey of RC, as illustrated in **Figure 2.1**, spans a diverse range of developments. The use of RC materials can be traced back ancient times, when people in arid and desert regions employed specific building materials and

architectural designs that released heat during the night, utilizing clear skies to radiate heat into space. A significant step forward occurred in 1828 when Arago firstly discussed the scientific concept of RC and achieved a temperature drop of 6~8 °C with a small amount of grass, cotton, and quilt, paving the way for further exploration [8]. Starting from the mid-20th century, researchers made notable progress in achieving nighttime cooling with substantial temperature reductions, due to the improved energy efficiency [40]. In recent times, RC has gained renewed attention in the 21<sup>st</sup> century due to advancements in materials science. Materials designed for daytime RC have been well developed, capable of efficiently releasing heat while reflecting incoming solar radiation [41]. The resurgence reflects the growing importance of RC in modern energy-efficient and sustainable technologies. Among them, polymer-based organic radiative coolers, typically in the form of flexible thick films or coatings, are characterized by their broadband IR absorption. Besides, polymers have undergone rapid development in recent decades for use in radiative cooling applications, owing to their high transparency to short wavelengths and strong IR absorption. However, the lack of IR spectral selectivity and challenges associated with thickness compression greatly limit their temperature drop in real-world application. Conversely, inorganic radiative coolers mainly manifest in the form of salt-based coatings, dielectric- and metal-based photonic crystals. Benefiting from their flexibility in optical modulation, the inorganic system are preferred in

the working scenarios that need higher temperature drop. However, the complexity of the inorganic RC structures and their relatively high thickness (micro-level) make them hard to be scaled up and integrated. Thus, the investigation in the design simplification and miniaturization of the inorganic radiative coolers with high IR selectivity can further promote the utilization of this passive cooling approach.



Figure 2.1 The development of radiative cooling project.

#### 2.2 Light propagation

As the project aims at constructing a system to achieve dual-band regulation (solar reflective & IR selective absorbent), the propagation of light should be studied to understand the light response mechanism and complete the optical design. Considering the light propagates through a single-layer film placed in the free space with optical constants  $N_1$ , the corresponding reflective and transmitted light are depicted in **Figure 2.2**.



Figure 2.2 Light propagation in a single-layer film.

When the incident light meets the interface, a portion is reflected back to the original medium. The reflection intensity (R) is defined by the ratio of the normal component of reflective light intensity  $I_1$  to incident light intensity  $I_0$  using **Equation 2.1**:

$$R = \frac{I_1 \times \cos\theta_0}{I_0 \times \cos\theta_0} = \left( \left( \frac{N_0 \cos\theta_1 - N_1 \cos\theta_0}{N_0 \cos\theta_1 + N_1 \cos\theta_0} \right)^2 + \left( \frac{N_0 \cos\theta_0 - N_1 \cos\theta_1}{N_0 \cos\theta_0 + N_1 \cos\theta_1} \right)^2 \right) / 2$$
 Equation 2.1

where  $\theta_0$  is the incident angle,  $\theta_1$  is the refractive angle, and  $N_0$  is the optical constant of the incident medium (i.e., free space in this case). Meanwhile, the remainder is refracted, propagating forward but in a different direction. The reflective angle is equal to the incident angle, and the refractive angle follows Snell's law [42]:

$$\frac{\sin\theta_0}{\sin\theta_1} = \frac{N_1}{N_0}$$
 Equation 2.2

This refracted light eventually reaches the bottom surface, where part of it undergoes secondary reflection, and the rest transmits into the free space. Similar to the reflection case, the intensity of transmitted light (T) is determined by the ratio of the normal component of transmission light intensity  $I_3$  to incident light intensity  $I_0$  through Equation 2.3:

$$T = \frac{I_3 \times \cos\theta_1}{I_0 \times \cos\theta_0} = \left(\frac{4N_0N_1\cos\theta_0\cos\theta_1}{(N_0\cos\theta_1 + N_1\cos\theta_0)^2} + \frac{4N_0N_1\cos\theta_0\cos\theta_1}{(N_0\cos\theta_0 + N_1\cos\theta_1)^2}\right)/2 \quad \text{Equation 2.3}$$

Absorption (A) can be calculated using **Equation 2.4**, since the sum of R, T, and A of a system always equals 100%:

$$A = 100\% - T - R$$
 Equation 2.4

According to the above analysis, the optical constants of the medium play a crucial role in influencing the optical properties of the interface, expressed as

$$N = \frac{c}{v} = \frac{\sqrt{\varepsilon_0 \times \mu_0}}{\sqrt{\varepsilon_1 \times \mu_1}}$$
 Equation 2.5

where *N* is the ratio of light speeds in vacuum (*c*) and a certain medium (*v*), involving the permittivity values in free space  $\varepsilon_0$  and the medium  $\varepsilon_1$ , and permeability values in free space  $\mu_0$  and the medium  $\mu_1$ . For absorbent materials, *N* is a complex number N = n + ki, with *n* representing the refractive index (RI) and *k* representing the extinction coefficient. The optical constants vary with wavelength, directly impacting the optical designs.

# 2.3 Structures and principles of absorbers

Optical absorbers exhibit a broad range of applications across the electromagnetic spectrum, serving pivotal roles in diverse fields, including photovoltaic and photochemical cells [43], photodetectors [44, 45], thermal light sources [46, 47], solar desalination [48-50], and display technologies [51, 52]. Essentially, radiative coolers are also selective IR absorbers whose target

wavelength range is located in  $8 \sim 13 \mu m$ . Given that the intrinsic optical properties of the materials are often fixed and deviate from the desired wavelength band, current progress mainly concentrates on refining microcavity designs to enhance the performance. This section summarizes the structure and principle of five common optical cavity designs and makes comparison between them, aiming at determining a suitable structure to realize the simplification and miniaturization of RC devices with high spectral selectivity.

# 2.3.1 Whispering-Gallery-Mode (WGM) resonators

Whispering-Gallery-Mode (WGM) resonators, which based upon the total internal reflection effect along the circular boundary (see **Figure 2.3**), demonstrate capabilities for achieving ultrahigh quality factors, high optical density, and extraordinary small mode volume [53].



Figure 2.3 Schematic view of the WGM microcavity.

The resonant wavelength can be modulated by the ratio between the inner and outer mediums  $n_{\text{eff}}$ , and the radius of the cavity R:

where *m* is the angular mode number [54]. This resonant mode is first observed in acoustic application [55], and it has found widespread optical applications in areas such as sensors [56-58], light trapping [59], lasers [60, 61], *etc.* For instance, Jin et al. found that the WGM resonance in the Zn doped hexagonal CuGaO<sub>2</sub> nanoplates greatly enhanced nonlinear optical response due to its strong photon trapping capability, leading to a higher optical-optical conversion efficiency [62]. Ha et al. integrated a GaAs solar cell system with SiO<sub>2</sub> nanosphere arrays, achieving an enhancement of 24% in power conversion efficiency due to the WGM resonance within the spherical resonators [63]. However, the suitability of WGM-based structures for large-scale integration is highly constrained, thus restricting their potential application scenarios.

# 2.3.2 Scattering systems

Scattering systems that consist of highly lossy nanoparticles are well developed due to their simple process [64, 65] and high integration capability [66, 67]. The extinction capability of the scattering systems is derived from the combination of absorption and scattering [68], as shown in **Figure 2.4**. Considering that the light-matter interactions and the corresponding optical properties of the system, are determined by the inserted nanoparticles [69], the absorption band can be flexibly tuned by the size, distribution, morphology, material type of the nanoparticles.



Figure 2.4 Schematic view of scattering system.

The scattering system is widely applied in the solar radiation band. Sakurai et al. demonstrated a tungsten core-shell nanoparticle embedded SiO<sub>2</sub> thin film, realizing high selectivity with desirable efficiency [70]. In addition, the metal oxides nanoparticles-based light absorbers can have wideband absorption from deep ultraviolet (UV) to visible regime, offering a metal-to-metal charge-transfer induced electron transfer to support water oxidation in the application of solar fuel conversion [71, 72]. However, according to Mie theory, large particle sizes are required to match the wavelength and achieve forward scattering in IR region [73]. Therefore, the development in subwavelength IR scattering media (i.e., the miniaturization of the system) became the mainstream in current researches for IR absorbers, including the introduction of forward-scatterer [74] and anisotropic particles [75]. Nevertheless, the reduction in the size of scattering media is limited, resulting in an average scatterer diameter at the micrometer scale in RC applications. Consequently, the challenge of high film thickness persists in scattering system-based radiative coolers.

#### 2.3.3 Photonic crystals

Photonic crystals, designed to create photonic band gaps or manipulate incident electromagnetic fields, offer a promising approach for achieving dual-band regulation with flexible Quality factors (Q factors) [76]. Structurally, photonic crystals exhibit periodic arrangements in one to three dimensions, see **Figure 2.5**. One-dimensional (1D) photonic crystals consist of periodically layered materials with different refractive indices (n<sub>1</sub> and n<sub>2</sub>), where the thicknesses (d<sub>1</sub> and d<sub>2</sub>) of each material are carefully designed based on the target wavelength. The central photonic band gap is determined by **Equation 2.7**:

$$n_1 d_1 = n_2 d_2 = \lambda_0 / 4$$
 Equation 2.7

Two-dimensional (2D) photonic crystals feature periodical microstructures with various shapes, typically microholes or columns [77-79], where resonances and waveguide cut-offs of Transverse-Electric (TE) and Transverse-Magnetic (TM) modes are highly influenced by the periodicity. Additionally, three-dimensional (3D) photonic crystals offer increased degrees of freedom in optical parametric processes through phase-matching conditions introduced by the 3D nonlinear microstructure [80, 81], enabling optical modulation with greater flexibility.

As outlined in **Section 1.2**, the use of DBRs as solar irradiance filters represents a typical application of photonic structures integrated into radiative coolers. For instance, a SiC-based radiative cooler achieves plateau-like reflective performance from 460 to 800 nm, with a maximum reflectivity of 98% at 500 nm, by employing two pairs of alternate 145-nm-thick nanoporous SiO<sub>2</sub> layer (n=1.08) and 40-nm-thick Si layer (n=3.5) as the reflecting system [22]. Moreover, a hybrid structure combining a double-layer 2D photonic crystal with an overlapped 1D photonic crystal has been developed to attain dual-band regulation in RC with high selectivity [29]. In this configuration, the top 2D photonic crystal utilizes silica and SiC to exploit photon polariton resonance in the AW, while the bottom 1D photonic crystal comprises alternating TiO<sub>2</sub> and MgF<sub>2</sub> layers to inhibit solar absorption. However, optimizing the absorbing performance for a wideband target wavelength range remains challenging [82]. Furthermore, the complex structure of photonic crystal-based absorbers presents integration difficulties and impedes large-scale manufacturing processes.



Figure 2.5 Typical photonic structures (a) 1D photonic crystal; (b) 2D photonic crystal; and (c) 3D photonic crystal.

# 2.3.4 Metasurfaces

Metasurfaces, constructed from sub-wavelength periodic structures, offer the potential to achieve near-perfect absorption [83]. As illustrated in **Figure 2.6**, a typical metamaterial comprises a three-layer Metal-Dielectric-Metal structure,

consisting of a top periodic metallic layer, a middle resonant dielectric, and a bottom metallic reflective mirror. The absorptive characteristics stem from the light response of the periodic structures, such as impedance matching [84, 85], electric and/or magnetic resonance [86-88], Surface Plasmon Resonance (SPR)/LSPR [89], negative permittivity and permeability value [90], *etc.* Due to their full-spectrum optical regulation capabilities, metasurface absorbers find wide applications in microwave [91], terahertz [92, 93], and optical [94-97] bands.



Figure 2.6 (a) Cross section and (b) surface morphology of typical

#### metasurface-based absorbers.

Herein, Hao et al. introduced an ultrathin metasurface absorber composed of rectangular Au patterns and an Al<sub>2</sub>O<sub>3</sub> spacer using standard microfabrication techniques, achieving a maximum absorption of 0.88 at 1.58  $\mu$ m [98]. The absorption mechanism of their near-IR absorber relies on localized electric and magnetic dipole resonance, which exhibits insensitivity to the incident angle. Similarly, Zou et al. demonstrated a metal-loaded dielectric radiative cooler comprising Ag and n-type doped Si fabricated via electron beam lithography and

electron beam evaporation [99]. The doped Si supports appropriate impedance matching for high IR absorption, while the Ag layer contributes to reflection beyond the resonant band, thereby ensuring high selectivity. Notably, the rectangular unit cells are orthogonally oriented, enabling the excitation of resonance modes along both the length and width directions and resulting in broadband absorption with distinct resonant peaks observed at 8.8 and 11.3 μm. However, the unit cell dimension of metasurface-based optical absorbers undergoes a continuous reduction as the target wavelength decreases. Consequently, advanced nano-fabrication techniques (e.g., lithography) are required to realize unit cells at the micrometer-scale or even nanoscale. Moreover, the open framework of metasurfaces significantly compromises their resistance to mechanical damage, such as scratching or friction, resulting in poor environmental durability in practical applications.

# 2.3.5 Optical thin film systems

The design of optical thin-film systems is multidisciplinary, encompassing material science, optics, and advanced fabrication technologies. It involves the reflection, transmission, and polarization characteristics of light through layered media during its propagation. Employing the interference effects of light, these films can be tailored to either reduce reflection and transmission to enhance absorption in the target wavelength range or increase surface reflection to minimize losses. Due to its superior optical modulation capability, many multilayer thin film system perfectly achieve broadband and/or selective absorption across electromagnetic spectrum, applying in photodetectors [100-102], structural coloring [103, 104], solar selective absorber [105-107], and optical filters [108, 109]. **Figure 2.7** illustrates the schematic, phasor, and vectoral diagram depicting the propagation of light from the first medium with refractive index  $n_1$  through a single layer with refractive index  $n_2$  and thickness h to the substrate with refractive index  $n_3$ . This propagation involves reflective lights of various orders ( $r_0, r_1, r_2...$ ). The reflectivity of the layer can be theoretically calculated with **Equation 2.8** [110]:

$$r = \sum_{x=0} r_x = r_1^+ + t_1^+ r_2^+ t_1^- e^{-2i\delta_1} + t_1^+ r_2^+ r_1^- r_2^+ t_1^- e^{-4i\delta_1} + \cdots$$
  
=  $(r_0 + r_1 e^{-2i\delta_1})/1 + r_0 r_1 e^{-2i\delta_1}$  Equation 2.8

Here,  $r_0$  and  $r_1$  represent the polarization-dependent Fresnel coefficients, and  $\delta_1 = \frac{2\pi}{\lambda} n_2 d\cos\theta$ , where *d* denotes the film thickness. The primary mechanism behind thin film absorption is rooted in the destructive interference effect, which requires the first-order and higher-order reflections to have the same amplitude and a phase difference of  $\Delta \phi = (2m + 1)\pi$ , (m = 0, 1, 2...). Hence, the perfect absorption condition for a single lossy film on a reflecting substrate is expressed as:

$$r_0 + r_1 e^{-2i\delta_1} = 0$$
 Equation 2.9

Accordingly, the amplitude and phase conditions can be separately represented

as follows [111]:

$$|r_0| = |r_1|e^{-4\pi \frac{h}{\lambda} Im(n_2)} = |r_1|e^{-h\alpha_2}$$
 Equation 2.10  
 $\phi_{23} + 2\phi_{prop} - \phi_{12} = 2\pi m$  Equation 2.11

where  $\alpha$  denotes the absorption coefficient, and  $\phi$  is the phase shift as plotted in

# Figure 2.7b.



Figure 2.7 (a) Schematic, (b) phasor, and (c) vectoral diagram for a single-

#### layer film system.

In the context of multilayer films, an effective layer is utilized to characterize the optical response of the entire system based on the optical properties of each individual layer. This approach is further explained in the Transform Matrix Method (TMM) described in **Section 3.3.5**. Consequently, spacers are often introduced to effectively modulate the optical properties of the effective layer, thereby enabling functionalities such as dual-band regulation [112], band broadening [113-115], high selectivity [116, 117], absorption enhancement [118], etc. For instance, Toudert et al. incorporated a transparent  $Al_2O_3$  spacer into a single Bi layer-based absorber, creating a three-layer Bi/Al<sub>2</sub>O<sub>3</sub>/Reflective mirror structure [119]. In this case, the  $Al_2O_3$  spacer acts as a fractal phasor resonant cavity, effectively reducing the effective extinction coefficient of the system without compromising the high RI provided by the Bi layer. Moreover, the impedance mismatch between the Bi/air and Bi/Al<sub>2</sub>O<sub>3</sub> spacer interfaces ensures efficient multiple reflections, enhancing light confinement and leading to nearperfect absorption. Consequently, the insertion of the spacer strengthens interactions between the layers, further enhancing the overall absorbing performance of the system. Moreover, Gao et al. demonstrated a perfect visible absorber comprising three pairs of alternating SiO<sub>2</sub> and Cr layers, achieving an average absorption of 99.6% across the Vis to near-IR spectrum through destructive interference effects [120]. Interestingly, the SiO<sub>2</sub> play a crucial role in anti-reflection and phase accumulation, while the absorption mainly occurs in the Cr layers. Overall, optical thin film systems exhibit significant potential for spectral modulation and integration of materials with various optical characteristics. Their simple structure enables large-scale manufacturing, and their angle insensitivity and compatibility with flexible substrates render them applicable across a wide range of fields. Therefore, effort has been made to

construct an RC film in a simple multilayer film system in this work.

#### 2.3.6 Optical modulation of spacer materials

According to **Section 2.3.5**, optical characteristics of the spacer material play a pivotal role in determining the structural configuration of the film system and influencing the interference. The principle of destructive interference indicates that the resonance band, or absorption band, for a single homogeneous layer occurs at a wavelength determined by **Equation 2.12** [121]:

$$\lambda = (4 \times n_{\rm eff} d)/N$$
 Equation 2.12

where  $n_{\text{eff}}$  represents the effective RI of the layer, d is the film thickness, and N is an odd integer. Specifically, the effective optical constants of the system are governed by the properties of the spacer material. Thus, maximizing the refractive index of the spacer material is beneficial for reducing the overall thickness, as it enhances the effective refractive index of the system. Meanwhile, the spacers must exhibit low absorption (i.e., low *k* value) within the target wavelength range to ensure that the amplitudes of the first-order and higher-order reflected light are equal. Non-absorptive spacers are employed between the upper absorptive layer and the reflective mirror to achieve phase accumulation and performance optimization [122-124]. Among them, Silicon (Si) and Germanium (Ge), both of which exhibit refractive indices approaching the upper limit of IR transparent materials, are frequently utilized as spacers of

IR absorbers [125, 126]. However, the fixed intrinsic properties of natural material, such as its optical constants and absorption/transmission band, results in the limitation in meeting the complex optical regulation requirements. Therefore, to investigate the materials for various target wavelength ranges and applying scenarios, the optical modification becomes a mainstream in its development. Great efforts have been made to realize wideband optical property modulation through introducing metasurface [127], microstructures [128, 129], and photonic crystals [130]. But the corresponding system complexity becomes a barrier to further applications.

Recently, making optical modifications is mainly focusing on the adjustment towards band structure, atomic and electronic polarization, dipolar relaxation, and ionic conduction [131]. Chemical doping can modify the material band structure and directly influence the interband response to the external electromagnetic field [132-134]. However, IR properties that depend on the intraband transition and vibration mode resonances are hard to be precisely controlled via simply doping [135]. Besides, in terms of property stability and large area uniformity [136, 137], there are still close concerns for chemical doping. Therefore, considerable efforts have been dedicated to achieve optical property modulation by introducing meta surfaces [138], microstructures [139, 140], photonic crystals [130], and so on. Taking low index material (i.e. polymers [140, 141], air [39]) as the matrix, artificial metal-based arrays allow remarkable RI increase at the plasmonic resonant wavelength, along with a slight influence upon the extinction coefficient. The insertion of metals with large electron density contributes to the change of high-frequency response of mediums, hence efficiently modifies the system properties. Herein, metallic NWs or nanotubes embedded dielectrics have the extraordinary hyperbolic features [142], further enabling a broadband wavelength tuning. In addition, the enhanced light confinement and light-matter interactions resulting from the inclusion of metal nanowires are crucial for optical modifications of the dielectric matrix. Fortunately, an Ag NWs array-SiO<sub>2</sub> system with deepsubwavelength characteristic structure has been reported, demonstrating optical anisotropy nature and a progressive shift from dielectric behavior to hyperbolic dispersion one [142]. In addition, the growth of Ag filling fraction contributes to the expansion of the hyperbolic region. Consequently, increasing the range of metal nanowire filling fractions is considered beneficial for finely tuning optical modifications within the dielectric matrix.

Previous research highlights that the low eutectic temperature and low solubility of the Si-Al system facilitate precise phase separation between Al and Si, ensuring that a relatively high Al filling fraction and vertical growth of Al can be obtained [143]. Besides, an Al NWs-embedded silicon system has been extensively investigated due to its ability to achieve a broad NW formation window with a straightforward fabrication procedure [144-146]. Similar to Ag NWs system, the Al NWs structure can be easily controlled under different conditions [147]. For example, substrate bias, utilized for ion-assisted deposition, enhances surface diffusion length (i.e., the diameter of Al NWs) under a specific Al fraction [148]. However, the impact of ion bombardment to govern the NW forming window is underestimated, resulting in a maximum Al atomic ratio of 56 at.% [149]. This research gap presents a method for exploring a broader regulation band of optical constants. In **Chapter 5**, a detailed investigation into a Si-Al nanowire system featuring an aluminum atomic percentage (at.%) of 61 at.% will be provided.

# 2.4 Principles of IR absorption

For decades, advanced IR photonic materials and structures have been extensively explored, where selective broadband absorption is gradually becoming a hot topic. Apart from RC (8~13  $\mu$ m selective absorption), military IR camouflage coatings can meet the need of high absorption over 5~8  $\mu$ m [150-155], while thermal management or IR detection strongly relies on frequencyselective extinction across ultra-broad wavelength region from 0.8 to 30  $\mu$ m [156, 157]. Various designs have been proposed and developed for constructing IR absorbers with broadband absorption [158-162]. Among them, the compositiondependent intrinsic response always plays a critical role in these photonic structure schemes. In this section, the IR absorbing properties and principles of both organic and inorganic materials are analyzed, providing a comprehensive summary of the characteristics of commonly used IR materials. Based upon these absorbing mechanisms, strategies for tailoring material absorption bands are explored. Finally, a potential method for developing selective, broadband absorptive materials tailored for RC applications is proposed, which benefits the structure simplification in the following RC film system design.

# 2.4.1 Organic material absorption

As is well known, conventional organic polymers exhibit great broadband intrinsic IR absorption nature, which derives from vibration and/or rotation of abundant chemical groups in their molecular chains, see **Figure 2.8**. Specifically, the stretching-induced absorption bands of functional groups such as N-H, C=O, and C-N are observed at wavelengths ranging from 2 to 4  $\mu$ m, 6  $\mu$ m, and 6 to 8  $\mu$ m, respectively [163]. Moreover, alkyl groups exhibit intrinsic absorption bands typically between 3 and 3.7  $\mu$ m, while carbonyl groups are prominent in the range of 5.3 to 6.5  $\mu$ m [164]. Additionally, C-Y groups (where Y represents halogen elements) exhibit bending vibration absorption within the range of 6.7 to 16.7  $\mu$ m [165]. Owing to the flexible nature of polymer chains, it is feasible to combine various functional groups to achieve absorption within specific target wavelength ranges. Consequently, polymers find widespread applications in IR technology, such as photodetector [166-168], solar cells [169, 170], and photovoltaics [171]. For instance, Li et al. demonstrated a 500  $\mu$ m thick radiative cooler based on PolyEthylene Oxide (PEO), exhibiting selective absorption induced by combined bond vibrations located around ~5  $\mu$ m and 6 to 13  $\mu$ m [172]. Moreover, the broadening and enhancement of the absorption band can be achieved by physically combining multiple polymers. Yu et al. utilized a 70  $\mu$ m thick layer of PolyDiMethylSiloxane (PDMS), featuring stretching vibrations at 8  $\mu$ m (-CH<sub>3</sub>), 9.38  $\mu$ m (Si-O), and 12.5  $\mu$ m (Si-C), as well as in-plane rocking vibrations at 10.9  $\mu$ m (Si-O) and 11.8  $\mu$ m (-CH<sub>3</sub>), to significantly enhance the IR absorption of a PolyStyrene (PS)-based colored radiative cooler [173].



Figure 2.8 Vibration modes and vibration-induced absorption regions of

groups in polymers [165].

However, polymers typically struggle to achieve flexible IR absorption with ultrahigh spectral selectivity in AW due to the vibrational absorption of C-C and C-H bonds [174]. Furthermore, achieving near-perfect absorption often requires a relatively large optical path length for polymers, which is typically realized through high film thickness [175, 176] or by combining with scattering nanoparticles [177-179].

#### 2.4.2 Inorganic material absorption

The metals present intraband-transition induced IR absorption due to their complex band structure and rich energy levels, resulting in the unselective nature [180]. Meanwhile, the surface plasmon resonance absorption of metallic materials (i.e., metals and metallic compounds) can only respond at the fixed excitation wavelength, along with a narrow bandwidth [181, 182]. In addition, lots of inorganic dielectrics having phonon-polariton excitation ability are also commonly employed in constructing IR absorbers, such as silicides [183], nitrides [184], oxides [185], salt compounds [186], etc. Similarly, the referred photon-phonon coupling is still strongly related to the corresponding chemical bonds in these dielectrics, which brings limitations to the tuning flexibility in the absorption bandwidth. Among them, metallic compounds such as In<sub>2</sub>O<sub>3</sub> [181] and  $CrO_2$  [187] exhibit IR absorption because of surface plasmon resonance. Moreover, Si<sub>3</sub>N<sub>4</sub> is commonly chosen as the absorbing material, whose intrinsic absorption peak starts at 7.7  $\mu$ m and ends at 14.3  $\mu$ m with a maximum magnitude at ~10 µm [188], illustrated by Figure 2.9a [189]. Besides, according to Dimitrova et al., the absorption peak of AlN covers  $8 \sim 15 \,\mu m$  (see Figure 2.9b) [190]. Furthermore, Si-O and Al-O bonds have their absorption peak at  $\sim 9 \,\mu m$ 



and ~12 µm, respectively, shown in Figure 2.9c and Figure 2.9d [191].

Figure 2.9 Absorption peaks for (a) Si<sub>3</sub>N<sub>4</sub> [189], (b) AlN [190], (c) SiO<sub>2</sub>, and (d)



8 10 12 Wavelength (μm) Figure 2.10 Extinction coefficient comparison between typical IR absorbing

polymers (PET and PDMS [192], PMMA [193]), metals ([194]), and

dielectrics (SiO<sub>2</sub> [195] and Si<sub>3</sub>N<sub>4</sub>, experimentally extracted).

The extinction coefficients of the typical IR materials, including polymers [192, 193], dielectrics [195], and metals [194] are plotted in Figure 2.10. Comparing the extinction feature of the material types mentioned above, there is still a great demand for exploiting novel composite films, with higher flexibility and widerband absorption ability to realize the desirable spectral selectivity.

Simply physical piles of different dielectrics are efficient to combine their behaviors on intrinsic absorbing for broadening the absorbing bandwidth of the whole stack system. As reported, multilayer stacks consist of SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>/Ag and Si<sub>3</sub>N<sub>4</sub>/SiC/SiO<sub>2</sub>/BaSO<sub>4</sub> can present broad spectral absorption across the 8~13 µm range, mainly resulting from the linear superposition of relatively narrow intrinsic response from each sublayer [196]. Compared with the superposition scheme, chemical intermixing in a single-layer film would bring about plentiful bonding interactions with more dopant energy levels, which is conducive to further extend the absorbing capability along with flexible tunability. The strategy is similar to the alloying behavior for tailoring optical response of metallic mixtures [197]. Based upon an extended selectivefrequency extinction range from 9 to 12  $\mu$ m, a silicon oxynitride (SiO<sub>x</sub>N<sub>v</sub>) composite layer recently has served as the critical absorbing layer for realizing high-efficiency cooling radiation [198]. Nevertheless, due to related composition and structure limitations, the magnitude of its extinction coefficient k and the corresponding bandwidth is hard to be further extended to cover the AW. Incorporating additional chemical bonds that exhibit strong responses in the 12~13 µm range can facilitate the development of materials with broadband absorption and high spectral selectivity, thereby advancing their applicability in RC systems with simplified structures.

# 2.5 Organic radiative cooling film systems

#### 2.5.1 Design strategies

According to the preceding review in **Section 2.4.1**, polymers stand out as desirable materials for RC owing to the diverse functional groups that offer multiple intrinsic IR absorption bands within the AW. Among them, PDMS [199], Poly(Methyl MethAcrylate) (PMMA) [200], PolyEthylene Terephthalate (PET) [201], PS [202], PolyVinyl Chloride (PVC) [203], PolyVinyl Fluoride (PVF), PolyMethyl Pentene (PMP/TPX), and even natural fibers like silk and cellulose [204, 205] are commonly employed as the primary absorbing body. Besides, polymers barely absorb solar irradiance due to their transparency, thereby greatly reducing the complexity associated with short-wavelength reflectors. Consequently, organic radiative coolers typically manifest as single-layer films, coatings, or are simply integrated with reflective metallic mirror (e.g., Al and Ag) [206], as well as scattering structures such as nanoparticles [207] and nanovoids [208].

Based upon the flexibility inherent in polymers, numerous deformable polymerbased radiative coolers have been devised for applications in clothing or packaging [209]. For example, Wu et al. developed a wearable textile with phase-change microstructure fibers (PCMFs) and PDMS for personal thermoregulation (Figure 2.11a) [210]. Herein, the PCMFs consist of microporous fibers and a phase-change material poly(ethylene glycol) (PEG), coated with PDMS to prevent PEG leakage and enhance IR emission. Moreover, organic RC systems are often integrated with micro-nanostructures to optimize cooling performance. Zhang et al. fabricated a hybrid film comprising Al<sub>2</sub>O<sub>3</sub> nanoparticles dispersed in a PDMS matrix with a periodic pyramid surface, where the Al<sub>2</sub>O<sub>3</sub> nanoparticles contribute to scattering-induced absorption to enhance emission [211], as indicated in Figure 2.11b. The pyramid structure facilitates a gradual refractive index transition from air to PDMS, thereby enhancing impedance matching compared to a bare surface. Furthermore, Wu et al. devised a rhombic PDMS film with triangular air gaps at the base, see Figure **2.11c.** By employing total internal reflection, the film successfully attains the increase in short wavelength reflectance (300~1600 nm) of 17% and in AW emissivity of 11% [212]. Additionally, Song et al. investigated a PDMS-based metasurface with a finely designed surface grating, shown in Figure 2.11d [213]. Benefiting from the wavelength-comparable rectangular units, narrowband cavity resonance was excited, greatly enhancing the spectral emission across whole mid-IR regime ( $3 \sim 15 \,\mu$ m) and overcoming the problem of low emissivity region of PDMS in  $9 \sim 11 \,\mu\text{m}$  and  $12 \sim 14 \,\mu\text{m}$ .



**Figure 2.11** Morphology of (a) PDMS coated PCMFs textile [210]; (b) hybrid Al<sub>2</sub>O<sub>3</sub>-PDMS pyramid film [211]; (c) rhombic PDMS film with triangular air

gap [212]; (d) PDMS film patterned with rectangular gratings [213].



Figure 2.12 Schematic diagram of (a) temperature-adaptive PMMA-VO2 RC

film [214]; (b) colorful radiative cooler integrated with pigment and PE membrane [215]; (c) fluorescent RC coating [216]; (d) Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> coated UV resistant PES RC film [217]; and (e) UV resistant BST nanorods embedded Furthermore, organic radiative coolers that contain functional nanoparticles are able to perform unique properties. Figure 2.12a illustrates a temperatureadaptive RC film by embedding VO<sub>2</sub> nanoparticles in PMMA developed by Zhao et al. [214]. Meanwhile, Figure 2.12b indicates organic radiative coolers can meet aesthetic requirements by integrating pigments or photoluminescent materials [215]. Xue et al. integrated a polystyrene-acrylates emulsion with a fluorescent pigment (SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>,Yb<sup>3+</sup>), resulting in a green appearance due to fluorescent excitation [216], see Figure 2.12c. Considering the UV sensitivity of polymers, nanoparticles that reflect and/or absorb UV radiation can be employed in organic RC systems to enhance durability. As shown in Figure **2.12d**, Li et al. applied a 4 µm thick layer of Al<sub>2</sub>O<sub>3</sub> nanoparticles as UV reflective layer and a 0.1 µm thick layer of TiO<sub>2</sub> nanoparticles as UV absorbing layer to cover a polyether sulfone (PES) cooler, obtaining an effective organic cooler with extremely high UV resistance [217]. The film system exhibited a high systematic solar reflectance of 97.2%, with negligible change in reflective performance after exposure to 1000 hours of UV radiation (equivalent to 280 days of UV radiation in Hong Kong). Furthermore, Li et al. engineered a UVtolerant membrane by combining the thermoplastic polyurethane (TPU)-based absorbing main body with UV absorbent strontium barium titanate (BST) nanorods (Figure 2.12e) [218]. The BST@TPU membrane demonstrated a slight decrease in short-wavelength reflectance from 97.2% to 92.1% after exposure to UV radiation for 216 hours, whereas the reflective performance of the bare TPU membrane dropped significantly to 84.2% under the same experimental conditions.

# 2.5.2 Optical and cooling performance

The performances of the reported organic RC systems are compared and visualized, shown in Table A.1 and Figure 2.13.



Figure 2.13 Experimental IR emission and temperature drop of the reported organic RC film in Table A.1.

In summary, organic radiative coolers experimentally exhibit solar reflectivity and IR emissivity within the desirable range from 80% to 100%. However, the limited spectral selectivity arising from the presence of multiple functional groups in the polymers constrains their cooling performance, leading to relatively low temperature drop ( $\Delta$ T) values. Consequently, considerable
attention has been directed towards inorganic RC films with selective IR absorption, aiming to attain greater daytime temperature reductions.

## 2.6 Inorganic radiative cooling film systems

### 2.6.1 Design strategies

The designs of inorganic radiative coolers primarily rely on absorber structures, as discussed in Section 2.3. In contrast to organic systems, inorganic cooling systems offer higher selectivity due to controllable intrinsic absorption bands and geometry-dependent structural resonances, thereby exhibiting greater cooling potential. A fundamental inorganic RC system may consist of a doublelayer structure comprising a visible-transparent IR absorbing layer, whose absorbing band lies in the AW, and a metallic mirror to prevent full-band light transmission, as illustrated in Figure 2.14. For example, Yalçın et al. simultaneously achieved high solar irradiance reflectivity and near-perfect IR absorption with only a 500 µm thick SiO<sub>2</sub> layer and an Ag substrate [219]. Similarly, Ao et al. deposited a thin Ag reflecting mirror on a 3mm thick ultrawhite glass-based radiative cooler, achieving a solar reflectivity of 94% and an IR emissivity of 90% [220]. Notably, the composition and structure of the top layer directly influence the light response of the entire system. The IR absorbing bandwidth and intensity can be enhanced by combining multiple absorbing materials [221], while nanoporous structures can increase the visible reflectivity

of the system [222]. Moreover, the absorbing layer comprised of self-disciplined sphere arrays exhibits scattering-induced structural color [223]. However, radiative coolers with such absorber layers/reflective mirror structures often meet the challenge of high film thickness, limiting their further integration or flexible applications.



Figure 2.14 Schematic diagram of a double-layer inorganic RC system.

Therefore, thickness reduction and device miniaturization are main stream in the development of inorganic RC systems, promoting the investigation of ultra-thin film systems with artificial structures [224]. In 2014, Raman et al. designed a photonic structure comprising multiple SiO<sub>2</sub> and HfO<sub>2</sub> layers, where SiO<sub>2</sub> serves as the low-index material and HfO<sub>2</sub> as the high-index material [225]. The structure, as shown in the SEM image in **Figure 2.15a**, can be divided into two parts based on their optical function. The upper three layers contribute to strong selective IR emission in the AW, while the middle four alternate high- and low-index layers result in 97% reflectivity of incident solar irradiance. Subsequently, in 2019, Liu et al. reported a geometry-independent metamaterial selective radiative cooler with Al-MgF<sub>2</sub>-Ge stacks, as depicted in **Figure 2.15b** [226].

Light trapping and absorption are attributed to the slow-light effect in each metal-dielectric pair waveguide, where the slow-light wavelength is determined by the waveguide width (W, the diameter of the unit cells) and the perpendicular component of effective permittivity ( $\varepsilon_{\perp}$ , the thicknesses of metal  $t_m$  and dielectrics  $t_1$  and  $t_2$  in each pair). Hence, absorption can be controlled by varying the metal-dielectric layer thicknesses, achieving a wideband absorbing band in the AW through the combination of blocks with different slow-light wavelengths. Additionally, inorganic film systems can realize additional functions through integration with extra layers or light cavities, such as structural color display [227] and self-adaptive cooling [228]. However, the design of these structures still faces challenges related to structural simplification and thickness reduction, limiting large-scale production.



**Figure 2.15** (a) SEM photo of the ultrathin photonic radiative cooler [225]; (b) Detailed structure of hyperbolic metamaterial emitter with selective absorption

Combining intrinsic and resonance-induced absorbing peaks provides a solution to further simplify cavity design, involving only a three-layered F-P resonance cavity. Similar to the structure designed by Chen et al. mentioned in Section 1.3, Zhou et al. investigated a sandwich-structured Ti/Ge/Ti absorber (Figure 2.16) [161], with an absorption band ranging from 8 to 12  $\mu$ m. Propagating Surface Plasmon (PSP) and Localized Surface Plasmon (LSP) modes are excited at the top square Ti grating, contributing to effective light trapping at the resonance wavelength. Moreover, destructive interference (i.e., F-P resonance) in the middle Ge cavity further reduces reflection and broadens the absorbing band, leading to selective wideband absorption. Compared to the structures above, this three-layer design is thinner and simpler, offering significant potential for integration and cost reduction in fabrication.



Figure 2.16 Schematic of the three-layer Ti/Ge/Ti radiative cooler [229].

## 2.6.2 Manufacturing process

Pulsed Laser Deposition (PLD) is an efficient approach to form inorganic films with well controlled stoichiometric ratio [230]. This technique employs highenergy pulsed lasers to bombard solid ceramic targets, resulting in target ablation and the generation of a plasma plume, which then deposits onto a substrate and forms a dense film. The growth parameters in PLD primarily include substrate temperature, laser energy, background pressure, and laser frequency [231]. The attainment of high-quality films via PLD hinges on striking a dynamical balance between plasma motion and chamber atmosphere, requiring careful exploration to achieve optimal growth parameters. However, pulsed laser-deposited thin films often contain melted small particles or target fragments splattered during the laser-induced explosion process, thereby compromising film quality.

Thus, the deposition of homogeneous thin film systems mainly relies on Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD), both offering precise control over film thickness, composition, and uniformity [232, 233]. Therefore, these two approaches find wide application in high-quality thin film or coatings production. Both the two process involves vacuum chamber with complex evaporation system, and **Figure 2.17a** [234] and **Figure 2.17b** [235] separately display the schematic diagrams of CVD and PVD processes. Notably, CVD involves three main stages: (i) diffusion of reactant gases; (ii) adsorption of reactant gases onto the substrate surface; and (iii) formation of reactive products and release of gaseous byproducts. Common CVD reactions include thermal decomposition, chemical synthesis, and chemical transport reactions. Moreover, this technique facilitates the deposition of complex materials with tailored properties like composition, stoichiometry, and crystallinity. Through Plasma Enhanced Chemical Vapor Deposition (PECVD), Ma et al. deposited 7 alternated stoichiometric  $SiO_2$  and  $Si_3N_4$  layers with thicknesses precisely matching those of the optimized structure in simulations, demonstrating the accuracy up to 1 nm [236].



**Figure 2.17** Schematic diagram of (a) CVD [234] and (b) PVD [235] process. In comparison, PVD is more about the physical transfer of material from a solid source to a substrate through methods such as evaporation or sputtering. The material is vaporized in a vacuum environment and adsorbs on the substrate,

constructing a dense, adherent film with high purity and good mechanical properties [237, 238]. Furthermore, the high vacuum condition of PVD ensures the production of highly pure deposited films, which is advantageous for the growth of metallic reflective mirrors [239]. The approach is also widely used in dielectric thin film growth. For example, Cunha et al. fabricated a multilayer Al/SiO<sub>2</sub>/SiN<sub>x</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> film system via straightforward Direct Current (DC) magnetron sputtering [240], while Tazawa et al. deposited a uniform SiO film atop Ag using the vacuum evaporation technique [241]. The properties of films produced via PVD are subject to the influence of multiple parameters:

- Supply power: The higher power levels correspond to improved film density and deposition rates. In the context of co-deposition, elevated supply power levels result in a greater abundance of the constituent element contained within the target material.
- Depositing atmosphere: The ambient atmosphere during deposition plays a crucial role in determining the composition and structure of the films deposited. Introducing reactive gases, such as oxygen, nitrogen, and hydrogen, during the depositing process alters the bonding environment, thereby influencing the stoichiometric ratio and morphology of the products.
- Substrate bias: By introducing substrate bias during the deposition, charged particles within the plasma accelerate towards the substrate surface, leading to enhanced adhesion, higher density, and microstructures of the deposited

film. This process can influence the growth of kinetics and stress within the film, impacting its mechanical and electrical properties. Furthermore, substrate bias can facilitate the formation of a preferred orientation or phase structure in the film.

- Chamber pressure: The influence of depositing pressure is rooted in its control over gas density within the chamber, thereby affecting the mean free path of particles from the targets and their energy distribution upon substrate interaction. Enlarged chamber pressure fosters collisions between particles and plasma, leading to diminished particle energies and potential degradation in film quality.
- Substrate temperature: Elevated substrate temperatures facilitate adatom mobility and interfacial diffusion, promoting denser film packing and higher crystallinity. This can result in improved film adhesion, reduced defect density, and enhanced film uniformity. Conversely, excessively high temperatures may induce thermal stress, grain growth, or even phase transformations, compromising film integrity. Substrate cooling, conversely, can mitigate these effects, though potentially at the expense of reduced film adhesion or crystallinity. Therefore, careful control of substrate temperature is critical to optimize film quality and properties.

All these parameters should be well balanced to precisely control the final film properties, including its composition, structure, thickness, and morphology.

Additionally, photolithography finds widespread use in metasurface fabrication [158], while chemical etching and phase inversion are effective methods for achieving homogeneous inorganic nanoporous structures [229].

# 2.6.3 Optical and cooling performance

The performances of the reported inorganic RC systems are summarized and compared in Figure 2.18 and Table A.2.



Figure 2.18 Experimental IR emission and temperature drop of the reported

inorganic RC film in Table A.2.

Compared to the performance of organic systems illustrated in Figure 2.13, inorganic RC films with high IR selectivity demonstrate the potential to achieve higher  $\Delta T$ . For example, study [1] in Figure 2.18 reported a temperature reduction of approximately 8°C with an average AW emissivity of only ~50% [29]. However, some reported inorganic structures exhibit high solar absorption

because their designs prioritize IR emissivity optimization without adequately addressing solar reflectivity. Achieving dual-band modulation for daytime RC remains a substantial challenge in inorganic systems. To address this limitation, radiative coolers utilizing short-wavelength-absorbing materials require integration with solar irradiance reflectors to enhance short-wavelength reflectivity and improve overall cooling performance. However, this approach increases structural complexity. In summary, achieving dual-band selective modulation within a simplified ultrathin structure to meet radiative cooling requirements is a critical challenge in the development of inorganic radiative cooling films and constitutes the primary focus of this study.

#### 2.7 Summary

In this chapter, the evolution of the radiative cooling project was firstly discussed, followed by a fundamental exposition on light propagation. Given the frequency-selective absorption characteristics requisite for radiative coolers (i.e., low solar irradiance absorption and high emissivity in the AW), five typical structures of absorbers and their underlying absorption mechanisms are detailed. Among these designs, WGM resonators are unsuitable for integration, scattering-based systems fail to achieve significant film thickness reduction, and photonic crystals and metasurfaces pose challenges in mass fabrication and/or integration due to their structural complexity. In contrast, thin-film systems offer the potential to achieve strong optical responses with high selectivity, thereby facilitating the simplification and miniaturization of radiative cooling systems. Besides, the optical modulation of the spacers that contribute phase accumulation is also reviewed since they fundamentally shape the designed structures and corresponding performance outcomes. Subsequently, the absorption mechanisms of materials are elucidated and compared. Specifically, the broadband IR absorption of polymers is attributed to the vibrational modes of their constituent chemical groups. Conversely, absorption in metals and dielectrics is delineated by phenomena such as SPR and photon-phonon polariton interactions, resulting in controllable narrowband absorption. Finally, design strategies, fabrication methodologies, and performance evaluations of both organic and inorganic RC systems are explored and analyzed.

Organic systems have witnessed significant advancements in daytime RC applications owing to their remarkable visible transparency and IR absorption properties. Moreover, the simple manufacturing processes greatly benefit largearea production of polymer-based device, thereby facilitating the development of the corresponding research achievements. However, their integration capability and durability are comparatively restricted, limiting their applications. Conversely, inorganic systems with delicately designed cavities offer enhanced integration capabilities owing to their thin-film thickness and compact size. Nevertheless, the concurrent realization of dual-band regulation involves complex structural designs.

## 2.7.1 Research gap

Previous studies have made significant advancements in the development of RC systems. However, none have simultaneously achieved the critical goals of optimizing optical performance, reducing film thickness, and simplifying structural design – factors essential for advancing RC applications. This research may stem from limitations of naturally occurring materials with fixed optical properties, which need additional optical designs to meet RC performance requirements. To address these challenges and bridge this gap, the following two strategies are proposed. It is believed that employing these approaches will resolve the primary issues, paving the way for further advancements in RC systems.

- RC-customized wideband selective absorbent material. The challenges related to IR selectivity and structural complexity arise from the insufficient compatibility between the absorbent material and RC application. In most cases, the development of novel RC systems focuses on creating optical cavities that confine light in the AW using materials with absorption bands that are either too narrow to cover the AW or extend beyond it. To achieve selective absorption within a simple system, an absorbent material that exhibits a strong optical response specifically within the AW is crucial.
- RI enlargement of the spacer material. Spacers are required to have a

high RI while maintaining low absorption in the target wavelength range to enable phase accumulation, thereby dramatically compressing the film thickness with minimal impact on the amplitude of higher-order reflected light. However, natural IR-transparent materials such as Si (RI = 3.4) and Ge (RI = 4.0) approach the upper limits for RI values and are insufficient for further reducing the thickness of RC devices when the target wavelength is within 8~13  $\mu$ m. Additionally, both materials suffer from high solar absorptivity, which is undesirable in RC applications. Therefore, there is a strong need for novel spacer materials that possess both high RI and high solar reflectivity.



Figure 2.19 Schematic view of the double-layer RC film.

The following chapters will describe a double-layer thin inorganic radiative cooler, encompassing the exploration of a broadband IR-absorbing material SiAlON and a visible-reflective but IR-transparent high refractive index Si-Al NWs spacer, shown in **Figure 2.19**. The optical and cooling performance of the double-layer radiative cooler will also be analyzed. Before delving into these specifics, the methodology employed for system optimization and testing is firstly clarified.

# **Chapter 3 Methodology**

This chapter contains the selection of materials, math models used in optical & cooling performance simulations, experimental procedures, and tests to conduct the property analyses. It highly relates to the arrangement of the whole research.

## 3.1 Methodology background

To design and fabricate an RC film system, the first step involves selecting suitable materials for each layer, including the absorbent layer, spacer, and reflective mirror. Subsequently, the target parameters, such as average IR emission and solar reflection, are determined using a cooling power prediction model. The next phase optimizes the thickness of each layer, which defines the film system structure. This optimization process incorporates theoretical calculations of optical constants, absorption characteristics, and algorithmic approaches. Additionally, theoretical electromagnetic field simulations are performed to elucidate the absorption mechanisms of the film system.

Following these steps, a comprehensive research procedure is implemented to investigate the properties of both the newly designed materials and the complete film system, focusing on formation mechanisms and optical performance of the materials. To experimentally determine the temperature reduction of the sample, an initial IR photography test is conducted to validate the feasibility of the system. Subsequently, a custom apparatus is designed and constructed to enable 24-hour outdoor temperature measurements.

Overall, the methodology of this project is organized into four primary stages to achieve the objectives outlined in Section **1.3**, as visualized in **Figure 3.1**: (i) identify suitable material systems to construct a broadband absorbing layer and a high-RI spacer; (ii) theoretically evaluate the film system and optimize its structure; (iii) experimentally deposit and analyze the materials for each layer and the overall film system; (iv) design and build the apparatus for temperature measuring, including the apparatus for IR photography and outdoor temperature test.



Figure 3.1 Flow chart of the methodology.

## 3.2 Material systems

According to the literature review in **Section 2.4.2**, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and AlN exhibit intrinsic absorption bands in the AW due to their Si-N, Si-O, and Al-N bonds with absorption peaks at different wavelengths. To combine the absorbing characteristics of all the bonds and achieve wideband response in the AW, a SiAlON composite was formed by co-sputtering Si<sub>3</sub>N<sub>4</sub> and AlN. Herein, the reactions between the sputtered fragments and residual oxygen also involved during the sputtering process to introduce O-related bonds, aiming at chemical bonding enrichment and bandwidth broadening.

Besides, a light confinement spacer with high RIs and low visible absorption is required to enhance the IR absorption without introducing the solar irradiance energy input at relatively thin film thickness. Considering the insertion of Al NWs efficiently raises the effective RIs of the system, a Si-Al NWs composite with high Al volume fraction was fabricated to be the phase accumulation spacer. The phase separation between Si and Al was firstly theoretically studied using MD simulations, which will be detailed in **Section 3.3.1**. Based upon the simulation results, ion impact was applied during the film growth, facilitating the adatom diffusion and reevaporation to further increase the Al volume fraction. Finally, the composites above were integrated to form a double-layer film system, with SiAION acting as the top absorbing layer and Si-Al being the bottom light confinement cavity.

#### 3.3 Math model

#### 3.3.1 Molecular Dynamic (MD) model

MD simulation was held to theoretically study the principle of the phase separation between Si and Al. The model dimensions were set to  $30\text{\AA} \times 30\text{\AA} \times$ 70Å, comprising 343 Al atoms and 290 Si atoms. Aluminum was described using the common Embedded Atom Method (EAM) potential, while silicon employed the widely used Stillinger-Weber (SW) potential. The Al-Si interactions were governed by the Morse potential function, [242] with the Morse potential parameters listed in Table 3.1. The bottommost four atomic layers were kept immobile to serve as the substrate, with the neighboring atoms defined as the thermostatic layer. A canonical ensemble (fixed amount of atoms N, volume V, and temperature T, NVT) thermostat was applied to maintain a temperature of 300 K in the model. Simultaneously, the remaining atoms were also under NVT temperature control. The deposition rates of silicon and aluminum atoms were configured as follows: 4, 3, 1.86, 1, 0.49, and 0.25, corresponding to aluminum atom proportions of 20%, 25%, 35%, 35%, 50%, 67%, and 80%, respectively. The velocity Verlet algorithm with a time step of 1 fs was employed to numerically integrate the Newtonian equations of motion. Throughout the simulation, the built-in command "fix atom/swap" in LAMMPS was employed, coupled with Monte Carlo (MC) probability. This hybrid "MC+MD" simulation approach was utilized to enhance overall accuracy. Furthermore, the substrate temperature was enlarged from 300, 500 to 1300 K to promote adatom diffusion and reevaporation, mimicking the external energy introduced by ion impact.

| System | Parameter         | Morse potential |
|--------|-------------------|-----------------|
|        | D <sub>0</sub>    | 0.07            |
| Al-Si  | A(1/Å)            | 1.12            |
|        | $r_0(\text{\AA})$ | 3.36            |

 Table 3.1 List of Morse Potential Parameters.

#### **3.3.2** Density Functional Theory (DFT)

To reveal the broadening absorption mechanism of the chemical intermixing in the SiAION composite, a first-principles calculation was applied. Theoretical band structures of three materials (a crystalline Si<sub>3</sub>N<sub>4</sub> and AlN model extracted from Materials Project [243], and a constructed SiAION composite model with the tested stoichiometric ratio (Si:Al:O:N = 2:1:1:3) were investigated based upon first-principle Density Functional Theory (DFT) and calculated via Vienna Ab initio Simulation Package (VASP). Crystal models were employed in the simulations to simplify calculations, as doping can induce additional orbital hybridization in both amorphous and crystalline structures. The Generalized Gradient Approximation (GGA) [244] using Perdew-Wang 91 [245] was adopted to describe the exchange-correlation function. The projector augmented wave method was employed with a cut-off energy of 500 eV. The conjugate gradient method was used for geometry optimizations. The Brillouin zone was sampled 11×11×11 k-point mesh using the Monkhorst-Pack method.

#### 3.3.3 Finite-Difference Time-Domain (FDTD) method

The Finite-Difference Time-Domain (FDTD) method is a numerical modeling technique used to solve Maxwell's equations for electromagnetic wave propagation and interaction with materials. FDTD programs were employed to analyze energy distribution within the materials, including the optical response mechanisms of the Si-Al spacer and the double-layer film system. As an example, the program setup for a single Si-Al layer is illustrated in **Figure 3.2**. The film structure aligned with the microscopy measurements detailed in Chapter 5 and Chapter 6, with the boundary condition beneath the substrate in the z-direction configured as a Perfectly Matched Layer (PML). The boundary in the xy-plane was defined as periodic, simulating an infinitely large film to prevent boundary effects. The light source was modeled as a plane wave positioned approximately 10 µm above the surface, mimicking vertical incidence conditions. Additionally, an infinite detector was placed 2 µm above the light source to measure the reflected wave from the system.



Figure 3.2 Setup of the FDTD simulation for calculating power dentisy distribution in Si-Al NWs layer.

## **3.3.4** Effective Medium Theory (EMT)

Effective Medium Theory (EMT), a widely applied numerical method in materials science, was employed to determine the effective optical properties of composite materials. It derives the optical characteristics of composite materials by combining the optical properties of all the phases. Typically, the Bruggeman (BR) approximation model [246] and the Maxwell Garnett (MG) approximation model [247] are the two primary EMT models employed for determining the effective dielectric constant of nanowire layers. The key difference between these models lies in the characterization of the host phase, where the BR approximation assumes a dielectric host phase and the MG approximation assumes an air or vacuum host phase. In the context of this study concerning Si-Al NWs array, the solution for the effective dielectric constant under the BR approximation for the xy- and z-directions is represented by **Equation 3.1** and **Equation 3.2**:

$$\varepsilon_{x,y} = \frac{1}{2} \Big[ (1 - 2f)(\varepsilon_d - \varepsilon_m) \pm \sqrt{(2f - 1)^2(\varepsilon_d - \varepsilon_m)^2 + 4\varepsilon_d \varepsilon_m} \Big] \qquad \text{Equation 3.1}$$

$$\varepsilon_z = (1-f)\varepsilon_d + f\varepsilon_m$$
 Equation 3.2

Here, f denotes the volume filling ratio of nanowires, calculated as  $f = \pi d^2/4p^2$ , while d and p are the diameter and periodicity of the nanowires. Additionally,  $\varepsilon_d$ and  $\varepsilon_m$  represent the dielectric constants of the host medium and the metal, respectively. It is noteworthy that the imaginary part of the calculated  $\varepsilon$  should be greater than or equal to 0.

# 3.3.5 Transform Matrix (TMM) model

TMM is an approach for theoretically predicting the optical performance of a film system. The characteristic matrix of the whole system is

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{ \prod_{x=1}^{K} \begin{bmatrix} \cos \delta_x & \frac{1}{\eta_x} \sin \delta_x \\ 1 \eta_x \sin \delta_x & \cos \delta_x \end{bmatrix} \right\} \begin{bmatrix} 1 \\ \eta_{K+1} \end{bmatrix}$$
Equation 3.3

where  $\begin{bmatrix} \cos \delta_x & \frac{i}{\eta_x} \sin \delta_x \\ i \eta_x \sin \delta_x & \cos \delta_x \end{bmatrix}$  is the characteristic matrix of a single layer (x=1,

see Figure 3.3).  $\delta_x$  is phasor thickness that describes the phase change, given by

$$\delta_x = \frac{2\pi}{\lambda} N_x d_x \cos\theta_x \qquad \qquad \text{Equation 3.4}$$

 $\lambda$  is wavelength,  $N_x$  is complex refractive index the layer,  $d_x$  is the film thickness, and  $\theta_x$  is the incident angle.

As defined in **Equation 3.5**, the optical admittance  $\eta_x$  is characterized as the ratio of the magnetic field intensity to the electric field intensity. This parameter

encapsulates the optical response of the medium and holds significant importance in the TMM program.

$$H_x = \eta_x (S_x \times E_x) = \eta_x E_x$$
 Equation 3.5

Given that the incident light is normalized to a unit wave vector, the intensity of the Poynting vector **S** is equal to 1 in this context. The optical admittance of air  $\eta_0$  equals to  $\frac{1}{377}$ , and  $\eta_x$  can be calculated as

$$\eta_x = N_x \times \eta_0$$
 Equation 3.6

Besides, the optical admittances of the media,  $N_x$ , are polarization-dependent under conditions of oblique incidence. Shown in the inset of **Figure 3.3**, the magnetic field **H** is oriented perpendicular to the plane of incidence, while the electric field **E** is inclined at an angle  $\theta$  in the *p*-polarized direction. Based on the continuity of the electromagnetic field at the interface, the intensities of the electromagnetic field components in the *p*-polarization direction, before and after encountering the interface, can be expressed as:

$$H_0 = H_t$$
 Equation 3.7  
 $E_0 = E_t / cos \theta_0$  Equation 3.8

Take Equation 3.7 and Equation 3.8 into Equation 3.5, the transmitted *p*-polarized magnetic field can be calculated as

$$H_t = H_0 = \eta_x \left( S_0 \times \frac{E_t}{\cos \theta_0} \right) = \frac{\eta_x}{\cos \theta_0} \left( S_0 \times E_t \right)$$
 Equation 3.9

Therefore, the optical admittance in the *p*-polarized direction can be determined as

$$\eta_p = \eta_x / \cos \theta_x$$
 Equation 3.10

Similarly, in the *s*-polarized direction, the magnetic field **H** is inclined at an angle  $\theta$ , and the electric field **E** is normal to the plane of incidence, satisfying the following boundary conditions:

$$H_0 = H_t / cos \theta_0$$
 Equation 3.11  
 $E_0 = E_t$  Equation 3.12

Thus, the optical admittance in s-polarized direction is

$$\eta_s = \eta_x \times \cos\theta_x$$
 Equation 3.13



Figure 3.3 Sketch of light propagation in a single layer system.

The polarized reflection of the designed film system is

$$R_{s/p} = \frac{\eta_0 B - C}{\eta_0 B + C} \times \left(\frac{\eta_0 B - C}{\eta_0 B + C}\right)^*$$
 Equation 3.14

For a system with a metallic bottom layer, its transmittance can be assumed as 0,

thus, the polarized absorption/emission is

$$A_{s/p} = 100\% - 0 - \frac{\eta_0 B - C}{\eta_0 B + C} \times \left(\frac{\eta_0 B - C}{\eta_0 B + C}\right)^*$$
 Equation 3.15

The output absorption spectrum of the absorber is given by

$$A = \frac{A_s + A_p}{2}$$
 Equ

**Equation 3.16** 

## 3.3.6 Particle Swarm Optimization (PSO) model

Kennedy and Eberhart introduced PSO model in 1995 as a population-based optimization algorithm wherein individuals, termed particles, navigate the solution space by adjusting their positions based on their personal experiences and those of their neighboring particles [248]. The movement of each particle is guided by its current position, velocity, and the best-known position of both itself and its neighbors. In the context of this study, a PSO algorithm obtained from the MathWorks Toolbox was employed to iteratively optimize the thickness of each layer, thereby achieving selective absorption within the AW band with desirable intensity. Initially, a TMM program was applied, with the film thicknesses of SiAlON and Si-Al layers treated as variables, to compute the theoretical wideband absorption spectrum of the film system. To emphasise the weight of selectivity in the optimization process, the resultant spectrum was multiplied by the transmittance of the atmosphere. The optimized film thicknesses were ascertained when the sum of the adjusted absorptivity reached its maximum value.

## **3.3.7** Cooling performance prediction model

With the input average visible reflectivity and IR emission determined, the

program for predicting the cooling power of the designed film system was established. The net cooling power served as a criterion to evaluate the efficiency of a RC device, defined as the difference between the emitted energy and the absorbed energy at a specific temperature *T*.

The energy input can be categorized into absorbed atmospheric radiation, solar irradiance, and non-radiative heat [221]:

$$P_{net}(T) = P_{rad}(T) - P_{atm}(T_{amb}) - P_{sun} - P_c$$
 Equation 3.17

The emitted radiation of the film system is determined by:

$$P_{rad}(T_{dev}) = \int d\Omega \cos(\theta) \int d\lambda I_{BB}(T_{dev}, \lambda) \epsilon_{dev}(\lambda, \theta) \qquad \text{Equation 3.18}$$

Here,  $I_{BB}(T_{dev}, \lambda)$  is the blackbody emission at temperature T, calculated by:

$$I_{BB}(T_{dev}, \lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda k_B T)} - 1}$$
 Equation 3.19

where *h* is Planck's constant,  $k_B$  is Boltzmann's constant, and *c* is the speed of light in vacuum. The integral  $\int d\Omega$  in **Equation 3.18** represents the angular integral, expressed as  $2\pi \int_0^{\frac{\pi}{2}} d\theta \sin\theta$ . The term  $\epsilon_{dev}(\lambda, \theta)$  denotes the angular-dependent emission of the device at wavelength  $\lambda$ , which is the ratio of the input emission (i.e., absorptivity) to the blackbody emission.

The absorbed solar irradiance is calculated by:

$$P_{sun} = \cos(\Psi) \int d\lambda \,\epsilon_{dev}(\lambda, \Psi) I_{AM1.5}(\lambda) \qquad \text{Equation 3.20}$$

where  $\Psi$  is the solar elevation,  $I_{AM1.5}(\lambda)$  is the solar illumination intensity at an air mass of 1.5, and  $\epsilon_{dev}(\lambda, \Psi)$  represents the emission of device at the solar

elevation angle.

The absorbed atmospheric radiation is given by:

$$P_{atm}(T_{amb})$$

$$= \int d\Omega \cos(\theta) \int d\lambda I_{BB}(T_{dev}, \lambda) \epsilon_{dev}(\lambda, \theta) \times \epsilon_{atm}(\lambda, \theta)$$
Equation 3.21

where  $\epsilon_{atm}(\lambda, \theta)$  is the angular-dependent atmospheric emissivity, calculated by **Equation 3.22**:

$$\epsilon_{atm}(\lambda, \theta) = 1 - t(\lambda)^{1/\cos\theta}$$
 Equation 3.22

 $t(\lambda)$  is the atmospheric transmittance, as reported by MODTRAN [249]. This transmittance is strongly influenced by factors such as humidity, geographic location, and cloud cover.

Additionally, the absorbed non-radiative heat is described by:

$$P_c(T_{amb}, T_{dev}) = h_c(T_{amb} - T_{dev})$$
 Equation 3.23

where  $h_c$  is heat transfer coefficient, typically varying from 0 to  $10 W/m^2 \cdot K$ .  $T_{amb}$  and  $T_{dev}$  are the ambient and device temperatures, respectively. The system reaches equilibrium when the net cooling power equals zero, and the temperature drop is the difference between the device temperature and the ambient temperature.

### **3.4 Magnetron sputtering**

In this project, all the samples were fabricated via magnetron sputtering since it is a technique used to accurately deposit thin films with specific thickness and chemical compositions (discussed in Section 2.6.2). As illustrated in Figure 3.4, this process involves depositing thin films onto a substrate by creating a plasma. The plasma is generated by introducing an inert gas, typically argon, into a vacuum chamber and ionizing it using an electrical discharge. Magnets placed behind the target material within the chamber create a magnetic field to confine the electrons in circular orbits near the target surface, thereby attracting the gas atoms towards the targets and accelerating the deposition. When positively charged ions in the plasma collide with the target material, they transfer their energy to the target atoms, causing them to be ejected from the surface in a process known as sputtering. These sputtered atoms then travel through the chamber and deposit onto the substrate, forming a thin film.



Figure 3.4 Photo and working principle of the magnetron sputter.

## 3.4.1 Fabrication of SiAlON composite

SiAlON composite thin films were deposited on single/double polished Si (100) and aluminum foil substrates through Radio Frequency (RF) magnetron sputtering of AlN (purity 99.99%) and Si<sub>3</sub>N<sub>4</sub> (purity 99.99%) targets. Substrates were cleaned successively with acetone, ethanol, and deionized water in an ultrasonic wave bath for 10 mins each.

| Sample                         | Supply Power (W)               |     | Bias | N <sub>2</sub> flow rate | Sputtering speed |
|--------------------------------|--------------------------------|-----|------|--------------------------|------------------|
| Ì                              | Si <sub>3</sub> N <sub>4</sub> | AlN | (W)  | (SCCM)                   | (nm/min)         |
| Si <sub>3</sub> N <sub>4</sub> | 80                             | 0   | 10   | 0                        | 0.95             |
| AlN                            | 0                              | 75  | 10   | 0                        | 0.6              |
| SiAlON                         | 80                             | 75  | 10   | 0                        | 1.61             |

Table 3.2. Sputtering speed of single-layer Si<sub>3</sub>N<sub>4</sub>, AlN, and SiAlON films

The sputtering was implemented when the base pressure reaches approximately  $1 \times 10^{-4}$  Pa, taking pure Ar (99.999%) with various pure N<sub>2</sub> (99.999%) feeding as reactive gas. The gas flow rate of Ar was maintained at 6.5 Standard Cubic Centimeter per Minute (SCCM), while the N<sub>2</sub> flow rate was varied between 0 and 3 SCCM. At the beginning of each deposition, a 40-mins pre-sputtering procedure was held to ensure a fresh surface of all the targets. A comparison of the sputtering rates for single-layer Si<sub>3</sub>N<sub>4</sub>, AlN, and SiAlON films is presented in **Table 3.2**, with the deposition parameters for all SiAlON samples listed in **Table 3.3**.

| Sample  | Supply Power (W)               |            | Bias (W)  | N <sub>2</sub> flow rate |
|---|--------------------------------|------------|-----------|--------------------------|
| -   | Si <sub>3</sub> N <sub>4</sub> | AlN        |           | (SCCM)                   |
| Broadband SiAlON                              | 80                             | 75         | 10        | 0                        |
| Si <sub>3</sub> N <sub>4</sub> for Raman test | 80                             | 0          | 10        | 0                        |
| SiAlON with various                           | 80                             | 75         | 10        | 0.0, 1.5, 3.0            |
| N <sub>2</sub> feeding                        | 00                             | 10         | 10        |                          |
| SiAlON with various                           | 80                             | 75         | 0, 10, 20 | 0                        |
| substrate bias                                | 00                             | 10         | 0, 10, 20 | -                        |
| Si <sub>3</sub> N <sub>4</sub> and AlN with   | 0                              | 85         | 10        | 0.2                      |
| various N <sub>2</sub> feeding                | 80                             | 0          | 10        | 0, 3                     |
| SiAlON with various                           |                                |            |           |                          |
| AlN target supply                             | 80                             | 65, 75, 85 | 10        | 0                        |
| power   |                                |            |           |                          |

Table 3.3. Sputtering parameters for a series of compound films deposition.

## 3.4.2 Fabrication of Si-Al NWs samples

Single polished Si (100), quartz, and aluminum foil substrates were selected as the substrate for fabricating the ~107 nm thick Si-Al NWs composite. Prior to the deposition, silicon and quartz substrates were ultrasonically cleaned for 10 mins in acetone, ethanol, and deionized water, respectively. The vertical NW structure was obtained through direct current (DC) magnetron co-sputtering using Si (purity 99.99%) and Al (purity 99.99%) as targets. When the base pressure was lower than  $1 \times 10^{-4}$  Pa, pure argon gas (purity 99.999%) was fed into the chamber with a gas flow rate of 6.5 SCCM to ensure a stable sputtering pressure of 0.2 Pa. The substrates were further cleaned by Ar plasma for 10 mins in vacuum, followed by a 20-mins pre-sputtering procedure. The filling fraction, as well as the structure of the NW array, was carefully controlled by the sputtering time, supply power and substrate bias. As a reference, all the depositing parameters are listed in **Table 3.4**.

|                       | Target Power |         |          | Sputtering     |  |
|-----------------------|--------------|---------|----------|----------------|--|
| Sample                | (W)          |         | Bias (W) |                |  |
|                       |              | ( )<br> | 2102 ()  | speed (nm/min) |  |
|                       | Si           | Al      |          |                |  |
| Nanoparticle          | 80           | 15      | 0        | 1.26           |  |
| Nanoscale network     | 80           | 70      | 0        | 3.07           |  |
| 0 vol.% nanowire (Si) | 80           | 0       | 0        | 1.87           |  |
| 29 vol.% nanowire     | 85           | 30      | 0        | 2.18           |  |
| 34 vol.% nanowire     | 85           | 36      | 0        | 2.11           |  |
| 45 vol.% nanowire     | 80           | 37      | 0        | 2.10           |  |
| 50 vol.% nanowire     | 80           | 46      | 13       | 1.78           |  |
| 64 vol.% nanowire     | 65           | 65      | 30       | 1.75           |  |

Table 3.4 Sputtering parameters for a series of Si-Al nanowire films deposition.

## 3.4.3 Fabrication of double-layer film systems

The film system fabrication process was separated into two steps, including the deposition of the Si-Al spacer and the SiAlON composite. The substrates were single polished Si (100) and aluminum foil. Silicon substrates were ultrasonically cleaned for 10 mins in acetone, ethanol, and deionized water before the deposition. Pure argon gas (purity 99.999%) was fed into the chamber with the flow rate of 6.5 SCCM when the base pressure was lower than  $1 \times 10^{-4}$  Pa.

| Sample   | Target Po        | ower (W) | Bias (W) | Time  |
|--|------------------|----------|----------|-------|
| -  | SiO <sub>2</sub> | AlN      | -        | (min) |
| 282 nm SiAlON layer in the final sample (e=0.81) | 80               | 110      | 10       | 200   |
| 113 nm SiAlON layer                              | 80               | 110      | 10       | 70    |
| 217 nm SiAlON layer                              | 80               | 110      | 10       | 140   |
| 322 nm SiAlON layer                              | 80               | 110      | 10       | 210   |
| 427 nm SiAlON layer                              | 80               | 110      | 10       | 280   |

 Table 3.5 Sputtering parameters for SiAlON composite deposition.

The substrates were further cleaned by Ar plasma for 10 mins in vacuum, followed by a 20 mins pre-sputtering procedure. The Al NW structure was obtained through direct current (DC) magnetron co-sputtering using Si (purity 99.99%) and Al (purity 99.99%) as targets, while the SiAlON layer was grown

with Radio Frequency (RF) magnetron co-sputtering of AlN (purity 99.99%) and SiO<sub>2</sub> (purity 99.99%) targets. All the depositing parameters are listed in **Table 3.5 and** 

#### **Table 3.6**.

 Table 3.6 Sputtering parameters for Si-Al spacers deposition.

| Sample                      | Target Power (W) |    | Bias (W) | Time (min)  |  |
|-----------------------------|------------------|----|----------|-------------|--|
| -                           | Si               | Al | -        |             |  |
| Spacer in the final sample  | 63               | 38 | 23       | 301         |  |
| (e=0.81)                    | 03               | 38 | 23       | 501         |  |
| Spacer with 50 vol.% NW     | 65               | 45 | 23       | 220         |  |
| Spacer with 53 vol.% NW     | 60               | 50 | 23       | 215         |  |
| Spacer with 56 vol.% NW     | 60               | 54 | 23       | 203         |  |
| Spacer with 60 vol.% NW     | 60               | 57 | 23       | 200         |  |
| Spacer in the samples with  | 62               | 20 | 22       | 205         |  |
| various top layer thickness | 03               | 30 | 25       | 303         |  |
| Spacers with various F-P    | 62               | 29 | 22       | 225/261/205 |  |
| resonant wavelengths        | 03               | 30 | 23       | 223/201/303 |  |

# 3.5 Optical property measurements

Optical properties were important parameters in evaluating the performance of the newly designed materials and the film system, and they directly influenced the optimization of sputtering parameters during the material development process. In this study, optical constants were extracted using ellipsometry. Additionally, wideband spectra were characterized using multiple techniques: ellipsometry for short-wavelength reflection under oblique incidence, Fourier-Transform InfraRed (FTIR) spectrometry for infrared reflection/absorption under near-normal incidence, and UltraViolet-Visible-Near-InfraRed (UV-Vis-NIR) spectrometry for short-wavelength reflection/absorption under nearnormal incidence.

### 3.5.1 Ellipsometry

Ellipsometry is an optical technique used to measure the structural and optical properties of thin films. Its output – optical constants – played a critical role in this project, as it directly influenced the design of the film structure during the simulation steps. Additionally, the instrument can measure the reflection and transmittance spectra under oblique incidence, with an incident angle range from 45° to 75°. As schematically indicated in **Figure 3.5** [250], this method relies on the analysis of alterations in the polarization state of light upon reflection from a sample surface. Incident light, polarized in the p- and s-planes, is directed onto the sample surface at a predetermined angle, and the polarization state of the reflected light, denoted as  $\rho$ , is analyzed. The expression for  $\rho$  is described by the amplitude variation  $\psi$  and phase variation  $\Delta$ , defined as **Equation 3.24** [250]:  $\rho = tan(\psi)e^{i\Delta} = r_p/r_s$  **Equation 3.24** 

Here,  $r_p$  and  $r_s$  respectively symbolize the Fresnel reflection coefficients for the

p-plane and s-plane, computed through Equation 3.25 and Equation 3.26 [110]:

$$r_s = \frac{N_0 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1}$$
 Equation 3.25

$$r_p = \frac{N_1 \cos \phi_0 - N_0 \cos \phi_1}{N_1 \cos \phi_0 + N_0 \cos \phi_1}$$
 Equation 3.26

According to the above model, critical information regarding the optical properties of the sample can be derived, including the wideband reflection and transmittance, complex optical constants N (refractive index and extinction coefficient), film thickness, and surface roughness. In the structural and optical constants fitting process, theoretical models (e.g., Cauchy model and Drude model) or databases are employed to fit the measured ellipsometric parameters, thereby determining the properties of the material under investigation. Additional refinement is achieved through fitting with physical oscillators (Lorentz/Gaussian for transparent dielectrics, Drude for metals) to ensure the conformity to the Kramers-Kronig model [251].



Figure 3.5 Photo and optical path in an ellipsometry test [250].

In this study, ultra-broadband RI n and extinction coefficient k, along with the film thickness of the samples were evaluated via combining two separated ellipsometric measurements on account of testing ranges, namely, one for the

UV-Vis-NIR region (Woollam M-2000DI, from 0.3 to 1.7  $\mu$ m) and the other for the IR case (Woollam IR-VASE Mark II, from 1.7 to 20  $\mu$ m).

During the extraction of optical constants for the SiAlON composite, a Cauchy model was taken for the measured ellipsometric parameters fitting in the transparent range (before 7  $\mu$ m) to confirm the film thickness. This was followed by the incorporation of oscillators to finalize the determination of the optical constants. Concerning the possible strong IR phonon absorption of the composite film, the fitting model was converted to a B-spline function for firstly fitting the ellipsometric spectra (beyond 7  $\mu$ m), and it was consequently replaced by Gaussian oscillators to extract the corresponding *n* and *k*.

To get the accurate NW filling fraction, the Si-Al NWs film was etched in a 50% HCl solution for 2h to selectively remove the aluminum. Due to the transparent nature of the nano porous Si film, the air volume fraction of the etched product (i.e., Al volume fraction) was easily obtained with the ellipsometeric parameter  $\Delta$  and  $\psi$  fitting. An effective medium approximation (EMA) model, which took air as the first phase and silicon as the second phase, was applied in the fitting process, with the thickness and filling fraction set as variables [252]. Furthermore, a surface roughness fitting process was conducted to confirm the flatness of the sample surface and to eliminate the factors caused by diffuse reflection during testing. With the fixed model structure, the first phase in EMA model was shifted to Al during the further fitting steps to obtain the complex

optical constants of the Si-Al composite.

#### 3.5.2 Fourier-transform infrared (FTIR) spectrometry

To optically analyze the performance of the materials and the film system, one of the most important criteria was their absorption/reflection spectrum. Herein, Fourier-transform infrared (FTIR) spectrometer (Nicolet 6700) was utilized to measure the reflection and absorption of IR radiation by a sample across a range of wavelengths or frequencies. The fundamental principle of FTIR spectroscopy involves directing IR light onto the sample, where it interacts with the molecular vibrations present in the material, see **Figure 3.6**. The sample may reflect or absorb specific wavelengths of the incident light, depending on its molecular composition and structure. The reflected or transmitted radiation is then collected and directed onto a detector. The interferometer within the FTIR spectrometer modulates the incoming light and generates an interferogram, which contains information about the intensity of the reflected, transmitted, or absorbed IR light at different wavelengths.

Relative IR absorptions of all the samples on double-polished silicon substrate were obtained from the difference between the transmittance of the silicon substrate  $T_0$  and the samples with substrate  $T_x$ , calculated through  $T_0 - T_x$ . Besides, absorptivity of the samples on the aluminum foil was determined through A = 1 - R, while R is the tested reflectivity.


Figure 3.6 Photo and working principle of the FTIR.

# 3.5.3 UltraViolet-Visible-Near InfraRed (UV-Vis-NIR) spectrometry

Due to the RC project is related to dual-band regulation (i.e., UV-Vis-NIR reflective & IR absorbing), the UV-Vis-NIR reflectivity under near vertical incidence condition should also be measured to evaluate the short-wavelength optical performance of the film systems. Therefore, a UV-Vis-NIR spectrometer (Lambda 950, Figure 3.7) with a testing range from 200~2000 nm is used to accomplish the test. The principle of UV-Vis-NIR spectrometry is based on the absorption of light by molecules in a sample. When the light passes through or reflects off a sample, specific wavelengths are absorbed by the sample's molecules, causing electronic transitions. These transitions correspond to the energy difference between the ground and excited electronic states of the molecules, allowing for qualitative and quantitative analysis. During the test, the incident angle was set as  $\sim 8^{\circ}$ , which was small enough to be equivalent to normal incidence. The reflective signal R was collected with a step of 2 nm. Given by the opaque nature of the Al foil substrate, the absorption of the sample was calculated through A = 1 - R.



Figure 3.7 Photo of the UV-Vis-NIR spectrometer

#### 3.6 Structure analysis

Structural analyses are essential for understanding the optical behavior of materials, since optical properties of the materials and the film system are the response to their structures. To this end, composition analyses that identify chemical bonds were conducted using X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. The microstructure of the samples was examined through Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The crystal structure of the newly designed materials was investigated via X-ray Diffraction (XRD), which provided insights into their growth mechanisms. Additionally, a density measurement was performed using X-ray Reflectivity (XRR) to study the effects of ion bombardment on film growth and the corresponding changes in optical properties.

#### **3.6.1** Composition analysis

Element concentrations and their chemical valences in SiAlON samples were analyzed by X-ray Photoelectron Spectroscopy tests (XPS, Axis Ultra DLD, **Figure 3.8a**). The resultant concentrations were acquired through relative XPS spectra analysis after a linear background correction. Besides, to avoid the error in stoichiometry caused by surface contamination, the tests were implemented before and after 2 mins Ar<sup>+</sup> etching. The C 1s core-level spectra of samples before Ar<sup>+</sup> etching were aligned to 284.8 eV to get the chemical shift of Si 2p, and the core-level spectra after etching were calibrated with Si 2p spectrum and analyzed. Furthermore, to inspect the chemical bonding states of a 490 nm thick SiAlON composite film, its Raman spectra were also collected through a spectrometer (Renishaw inVia Reflex, **Figure 3.8b**) with a HeCd laser (325 nm).



Figure 3.8 Photo of the (a) XPS spectrometer and (b) Raman spectrometer.

#### 3.6.2 Microscopy

Both the plane-view and cross-sectional morphologies of the composite were investigated through Scanning Electron Microscopy (SEM, Verios G4 UC, **Figure 3.9a**) under the voltage of 10 kV and current of 25 pA. To enhance the electroconductivity of the samples, a 60-s platinum deposition was implemented before the test. The detailed cross-sectional microstructure of the vertical Al nanowires embedded in the Si matrix was investigated by Transmission Electron Microscopy (TEM, Talos, **Figure 3.9b**) and High-Resolution Transmission Electron Microscopy (HRTEM) with an acceleration voltage of 200 kV.



Figure 3.9 Photos of (a) scanning electron microscope and (b) transmission

electron microscope.

## 3.6.3 Phase analysis

The phase of the samples was identified by X-Ray Diffraction (XRD, Vantec500 D8 Discover, **Figure 3.10**) measurement at 2θ angles from 10° to 90° with a step of 0.02°. Furthermore, to supplement the XRD findings and provide microscopic insights into crystalline structure, Selected Area Electron Diffraction (SAED) and HRTEM were employed. These techniques were instrumental in enhancing the examination of the structural characteristics of Si-Al nanowire configurations.

# 3.6.4 Density measurement

The equivalent densities of films were measured through grazing incidence X-

Ray Reflectivity (XRR, Vantec500 D8 Discover, Figure 3.10), with the incident

angle starting from 0° to 4° and a step of 0.05°.



Figure 3.10 Photo of XRD spectrometer.

# 3.7 Cooling performance test and apparatus design

After the optical properties and structural characteristics of the sample were detailed, an IR photography test was held to first validate the feasibility of this sample for achieving RC, and the setup is presented in **Figure 3.11**. An IR camera (FLIR E5-XT) is employed to capture IR imaging of a 10 cm  $\times$  10 cm sample under sunny winter conditions on January 2<sup>nd</sup>, 2024, at 3:00 PM in Ningbo, China, with a relative humidity of 40% (reported by China Meteorological Administration). The results were analyzed using FLIR Tools provided by Teledyne FLIR, with the ambient temperature during the test maintained at 4 °C and the sample emission set at 0.8 (experimental tested average IR emission).

Three outdoor temperature tests were conducted under varying ambient conditions to evaluate the cooling performance of the sample by monitoring the temperatures at four specific points over a 24-hour period. The tests were performed in Ningbo, China, under three different weather conditions: a dry sunny day (May 10th, 2024, relative humidity 50~65%), a dry cloudy day (November 13<sup>th</sup>, 2024, relative humidity 50~65%), and a humid cloudy day (November 19<sup>th</sup>, 2024, relative humidity 80~90%), with humidity data provided by the China Meteorological Administration. The measured temperatures included the temperatures of ambient temperature  $T_0$ , the chamber temperatures  $T_1$ , temperature of the Cu plate under the sample  $T_2$  (i.e., the temperature of the sample), and the temperature of control group  $T_3$ . Notice that weak sunlight was present during cloudy days between 8:00 and 16:00. The testing apparatus design is illustrated in Figure 3.12, comprising two heat isolation shells made of acrylic and foam, a PE cover to prevent heat conduction and convection over the sample, and a copper (Cu) heat conducting plate beneath the film. An additional Cu plate was placed next to the sample as a control group. The temperatures at four points, namely, were measured using k-type thermocouples.



Figure 3.11 Photo and schematic view of the test apparatus for IR photography.



Figure 3.12 Schematic view and photos of the outdoor temperature test

apparatus.

# Chapter 4 Development of advanced selective wideband absorbing material - SiAlON composite

In this chapter, a new IR-absorbing composite dielectric material with broad intrinsic absorption and tunable optical constants is developed and successfully fabricated through co-sputtering of Si<sub>3</sub>N<sub>4</sub> and AlN. This material is designed to meet the requirements of a wideband absorbing material with strong extinction characteristics in the AW range, simplifying the design of selective radiative coolers. The optical properties, phase, and composition of the composite is studied. Further, based upon the change in stoichiometric ratios and chemical bonding, the absorption band and optical constants of the composite film can be flexibly regulated. The investigation mainly concentrates on the composition adjustment through controlling the sputtering atmosphere, supply power, and substrate bias, and the corresponding optical responses are also analyzed. Moreover, a theoretical investigation on the absorption spectral flexibility of this composite film is also implemented, showing a great promising application prospect compared with other reported counterparts.

#### 4.1 Morphology and optical property analysis

## 4.1.1 Composite morphology

As mentioned in Section 2.6.2, cosputtering deposition schemes are superior to fabricate composite films with flexibly controllable chemical mixing. Based upon this strategy, a co-deposition process of  $Si_3N_4$  and AlN has been proposed to construct a composite film SiAlON, as schematically shown in Figure 4.1 from both macro and micro views. Specifically, the co-sputtering configuration of the two sputtering cathodes are beneficial for the uniform and easy-control mixture of the component fragments from each target. Meanwhile, during the growth process, the oxygen incorporation is derived from the residual oxygen in the chamber.



Figure 4.1 Sketch of co-sputtering configuration in macro view and compound formation in micro view.

Without intentional heating to the substrate, the thermodynamic nonequilibrium deposition condition cannot form crystalline nitrides and oxynitrides. Thus, the as-deposited SiAlON film shows the amorphous feature, as clearly illustrated by its XRD spectrum depicted in **Figure 4.2a**. And its transparent appearance is similar to those of the Si<sub>3</sub>N<sub>4</sub> and AlN films, see the inset in **Figure 4.2a**. Further, the homogenous and compact microstructural characteristics of the composite film can be clearly observed, as shown by the SEM images in **Figure 4.2b**, along with a smooth surface. These results indicate that the as-deposited composite does not exhibit evident clusters of separated phases, signifying its good composite feature. According to the cross-sectional SEM observation in the inset of **Figure 4.2b**, the thickness of the composited film is around 200 nm, which is well consistent with the thickness of ~192 nm extracted from corresponding ellipsometry analysis. Based upon this mutual confirmation, ellipsometry measurements would be utilized reliably for film thickness determination below.



Figure 4.2 (a) XRD pattern of the composite SiAlON film on SiO<sub>2</sub> substrate;

(b) Plane-view and cross-sectional morphologies of the SiAlON film on a

silicon substrate.

## 4.1.2 Wideband optical properties

For further examining the intrinsic optical property of the composite film, its

optical constants are calculated and depicted in **Figure 4.3**. Note that the optical constants of the single-layer AlN and Si<sub>3</sub>N<sub>4</sub> are also given as control groups. Similar to the AlN and Si<sub>3</sub>N<sub>4</sub>, the near-zero extinction coefficient *k* dominates the experimental short-wavelength region. In contrast, the SiAION film has a broadband intrinsic absorption feature across  $8\sim16$  µm, nearly gathering the intrinsic absorption characteristic of AlN and Si<sub>3</sub>N<sub>4</sub> whose extinction capability lies in the range of  $8\sim12$  µm and  $12\sim17$  µm, respectively. Moreover, the RI curve of the composite film is located almost entirely between those of AlN and Si<sub>3</sub>N<sub>4</sub>, maintaining a relatively high magnitude compared to most conventional inorganic absorbing dielectrics.



Figure 4.3 Optical constants of the SiAlON film ranging from 0.2 to 20 μm.
The distinct broaden tendency on the *k* of the SiAlON layer (shown in Figure 4.3) perfectly meets the absorbent broadening tendency, i.e., the composite film

presents a broadband absorption peculiarity across from 8 to 16  $\mu$ m, compared to those of the Si<sub>3</sub>N<sub>4</sub> and AlN case which is largely concentrated on the 8~12  $\mu$ m

and  $12 \sim 17 \mu m$  regime respectively, see Figure 4.4.



Figure 4.4 Comparison on the relative absorptivity of Si<sub>3</sub>N<sub>4</sub>, AlN, and SiAlON

films.

# 4.1.3 Composition and chemical bonding

A comparison on Raman spectra between Si<sub>3</sub>N<sub>4</sub> and the SiAION composite film has also been implemented to understand the widened feature, as demonstrated in **Figure 4.5a** and **Figure 4.5b**. There are two typical Raman bumps for the composite layer, as separately marked by light orange (from 300 to 700 cm<sup>-1</sup>) and lilac (from 700 to 900 cm<sup>-1</sup>) patches in **Figure 4.5a**, showing broadened Raman scattering signals due to its amorphous nature [253]. As magnified images shown in the insets of **Figure 4.5a**, two weak peaks centered at ~450 and ~600 cm<sup>-1</sup> can be found with the magenta and orange column labels in the profile, which are assigned to the Si-O [254] and the distorted Al-O structure [255] respectively. Besides, the acoustical and optical phonons of Al-N bonds might contribute to two additional shoulders located at ~350 and ~650 cm<sup>-1</sup> [253], marked via yellow marks. Moreover, another peak at 840 cm<sup>-1</sup> marked with purple color columns are mainly due to the vibration of the Si-N bonds, in terms of the one-phonon density of states in crystalline Si<sub>3</sub>N<sub>4</sub> [189]. Based upon the above Raman analysis, the spectral bump feature also indicates the abundant chemical mixing involved in the composite film to a great extent and makes several gathered characteristic peaks less distinguishable. In comparison, the Raman spectrum of Si<sub>3</sub>N<sub>4</sub> also has broadband smooth performance as that of the composite SiAlON (**Figure 4.5b**), due to its amorphous nature. Herein, the signal of Si-N at ~ 840 cm<sup>-1</sup> is obvious. Besides, the signal bump at ~450 cm<sup>-1</sup> caused by Si-O still exists, indicating the residual oxygen contributes to the enrichment of chemical bonding in the sputtering product. Moreover, compared to SiAlON, the wide peaks that represent Al related bonds (Al-N and Al-O) cannot be found in this case.



**Figure 4.5** Raman spectrum of (a) the SiAlON film and (b) the Si3N<sub>4</sub> film. The elemental chemical states of the SiAlON film are examined in XPS, and the resultant composition concentration is listed in

Table 4.1. The composite manifests a nitrogen-dominated constitution (~40.8

at%), and the proportion of Si is higher than Al. Further, as demonstrated via the N 1s core-level spectrum depicted in Figure 4.6, two major peaks appear at around 397.4 and 397.8 eV, which are ascribed to the nitrogen atoms in Si-Al-ON [256, 257] and N-Si-O [258]. Note that the additional shoulder centered at ~399.2 eV can also be observed, which might be attributed to the C-H-N derived from inevitable environmental adsorption [257]. Consistently, as illustrated via the Si 2p and O 1s core-level spectra shown in Figure 4.6, the peak of the Si-Al-ON and N-Si-O appears at 101.6 and 102.2 eV in the Si 2p spectrum [259], while three peaks in the O 1s case locate at 531.5, 532 and 533.4 eV, respectively, corresponding to the Si-Al-ON, Al-O [260], and N-Si-O bonds [258]. Moreover, in addition to the Al-O signal, the peak centered at 74.5 eV attributes to the Si-Al-ON [256] dominates the whole Al 2p core-level spectrum. Combining the Raman inspection with the XPS analysis, it is speculated that instead of the inheritable chemical bonds from the target materials, the co-sputtering procedure would tend to bring about random bonding interactions (because of its nonstoichiometric nature), and thus introduce evident chemical mixing in the composite layer.

 Table 4.1 Element concentrations of the SiAlON film in Figure 4.4.

| Element composition (at. %) |      |      |      |
|-----------------------------|------|------|------|
| Si                          | Al   | Ν    | 0    |
| 24.3                        | 19.5 | 40.8 | 15.4 |



Figure 4.6 XPS core-level spectra of N 1s, O 1s, Si 2p, Al 2p in the SiAlON

film.

#### 4.1.4 Band broadening mechanism

To further explain the connection between the enriched bonding constitution and absorption broadening, theoretical electronic energy band structure has been calculated via first-principles DFT simulation. As is described by crystal field theory, both the doping in crystal and amorphous structure can introduce extra orbital hybridization, hence complicate the band level [261]. Therefore, crystalline models of  $Si_3N_4$ , AlN, and a corresponding doped composite model are analyzed to simplify the calculation although the deposited films are of amorphous state, and the calculated band structures are plotted in **Figure 4.7**, where the horizontal dashed lines represent the Fermi level ( $E_F$ ) of the materials.

For the pure Si<sub>3</sub>N<sub>4</sub> and AlN, no intermediate energy level locates in the band gap according to **Figure 4.7a** and **Figure 4.7b**. In comparison, many intermediate energy levels are introduced into the band of the composite material **Figure 4.7c**, making its band gap diverging from those of the insulated Si<sub>3</sub>N<sub>4</sub> and AlN. Undoubtedly, the evident discrepancy in the band structure signifies the strong chemical mixing in the composite. Thus, the additional bonding brings more vibration/rotation energy levels into the composite film, which can account for the broadband IR absorption behavior for the SiAlON film (see **Figure 4.4**).



Figure 4.7 Theoretical electronic band structure of the crystalline compounds:

(a)  $Si_3N_4$ , (b) AlN, and (c) SiAlON.

# 4.2 Optical tunability and mechanisms

## 4.2.1 Introducing reactive gas

As mentioned above, in view of the nitrogen bond-dominated optical features, the corresponding properties of the SiAlON films can be flexibly adjusted based upon tuning its sputtering process. Similarly, previous reports have revealed that the optical properties of magnetron sputtered Si<sub>3</sub>N<sub>4</sub> are sensitive to its stoichiometric ratio, which is significantly determined by the N<sub>2</sub> partial pressure of the sputtering atmosphere [262, 263]. This similar situation can also be found in the composite films, namely, the mid-IR intrinsic absorption band varies with changing the gas flow rate of N<sub>2</sub> from 0, 1.5 to 3.0 SCCM. As shown in **Figure 4.8a**, without introducing the N<sub>2</sub> flow, the sample presents a significant broadband extinction coefficient within 8~20  $\mu$ m. In comparison, the peak of the sample with 3 SCCM N<sub>2</sub> feeding experiences a blue shift from 11.8 $\mu$ m to 10.9 $\mu$ m, while the overall magnitude of *k* value is also reduced. Besides, RI values in near IR range, as well as visible range experiences a significant drop with the growth of N<sub>2</sub> feeding, e.g., from 2.02, 1.90, to 1.82 at the wavelength of 1000 nm in





**Figure 4.8** (a) IR RI of sample fabricated with 0 SCCM and 3 SCCM nitrogen feeding; (b) refractive index in Vis-NIR range of the sample deposited under 0,

1.5, and 3.0 SCCM N<sub>2</sub> feeding rate.

More interestingly, as shown by **Figure 4.9**, a continuing compression in the absorption occurs at the wavelength range beyond 12  $\mu$ m through gradually raising the N<sub>2</sub> flow rate. On the contrary, the absorption at 9~10  $\mu$ m experiences

a slight increase with the growing N<sub>2</sub> feeding.



Figure 4.9 Relative IR absorptivity of samples fabricated with 0, 1.5, and 3 SCCM nitrogen feeding.

To find the underlying reasons for the flexible regulation on their optical property, the element concentrations of the 3 SCCM-N<sub>2</sub> sample obtained from XPS analysis is listed in **Table 4.2**, and the change in atom concentrations with the growth of N<sub>2</sub> flow rate is also plotted in **Figure 4.10**.



Figure 4.10 Change in atomic concentrations with increasing N<sub>2</sub> flow rate.

**Table 4.2** Element concentrations of the SiAlON film in Figure 4.8 with 3SCCM  $N_2$  feeding.

| Element composition (at. %) |      |      |      |
|-----------------------------|------|------|------|
| Si                          | Al   | Ν    | 0    |
| 25.0                        | 16.3 | 39.6 | 19.1 |

Compared to the sample without N<sub>2</sub> feeding (in **Table 4.1**), the atomic concentrations of the element N and Si remain nearly constants, along with a slight increase in oxygen by 3.7 at.% and a corresponding decrease of the Al content from 19.5 to 16.3 at.%. Herein, the opposite variation between O and Al might be due to the significant reduction in the deposition rate (listed in **Table 4.3**) of the composite film, which allows the adsorbed species on the growing surface to have extended opportunities to contact and react with the residual reactive oxygen. It is further proved by the optical performance variation on single-layer Si<sub>3</sub>N<sub>4</sub> and AlN with and without N<sub>2</sub> feeding, as indicated in **Figure 4.11**.



Figure 4.11 Short-wavelength RIs (a) and IR absorptivity (b) of the as-

deposited  $Si_3N_4$  and AlN film with/without 3 SCCM  $N_2$  feeding.

| Sample | N <sub>2</sub> flow rate (SCCM) | Pressure (Pa) | Rate (nm/min) |
|--------|---------------------------------|---------------|---------------|
| 1      | 0.0                             | 0.20          | 1.6           |
| 2      | 1.5                             | 0.25          | 1.2           |
| 3      | 3.0                             | 0.32          | 1.0           |
|        |                                 |               |               |

**Table 4.3** Sputtering pressures and corresponding depositing rates of samples in **Figure 4.8** and **Figure 4.9** with various N<sub>2</sub> feedings.

In comparison, although the deposition of the two materials both encountered distinct changes with input N<sub>2</sub>, the induced influence on the RI and IR absorption was lower for the Si<sub>3</sub>N<sub>4</sub> case than that of the AlN counterpart, which might be because of the higher deposition rate of Si<sub>3</sub>N<sub>4</sub> (see **Table 4.4**). Thus, the continuous decline in the RIs and absorption in  $12\sim17$  µm of the composite film with more N<sub>2</sub> flow can also be attributed to the lower sputtering yield of the AlN component under the nitrogen-rich sputtering atmosphere.

Table 4.4 Sputtering pressures and corresponding depositing rates of singlelayer  $Si_3N_4$  and AlN with and without  $N_2$  feeding.

| N <sub>2</sub> flow rate | Pressure (Pa) | Si <sub>3</sub> N <sub>4</sub> | AlN           |
|--------------------------|---------------|--------------------------------|---------------|
| (SCCM)                   |               | Rate (nm/min)                  | Rate (nm/min) |
| 0.0                      | 0.20          | 1.2                            | 0.7           |
| 3.0                      | 0.32          | 0.8                            | 0.5           |

As confirmed by the deconvolution of the N 1s, O 1s and Si 2p core-level spectra (Figure 4.6 and Figure 4.12), there is more N-Si-O bonding under nitrogen-rich

environment, indicating the extra-introduced oxygen has the preference to bond with silicon compounds. The preference for incorporated nitrogen in forming silicon oxynitrides is further evidenced by the enhanced absorption observed in  $9\sim10 \ \mu\text{m}$  (**Figure 4.9**). On the contrary, the generation of aluminum oxynitride is greatly suppressed, meeting the significant drop in the content of Al. Besides, a weak shoulder centered at around 404 eV appears in the N 1s spectrum, indicating that additional environmental oxygen is introduced to react with nitrogen and form -(NO)<sub>x</sub> bonding [264] in the composite. In all, the introduction of N<sub>2</sub> is beneficial to the formation of N-Si-O bond that contributes absorption from 8 to 12 µm, but reduces aluminum-related bonds that response in 12~17 µm, resulting in the corresponding adjustment in the absorption band and extinction coefficient.



Figure 4.12 XPS core spectra of N 1s, O 1s, Si 2p, Al 2p in the sample with 3

SCCM nitrogen feeding.

## 4.2.2 Varying supply power

The IR optical properties of the composite film have a tight connection with these intermixing changes. This is further proved by the IR absorption and the short-wavelength RI change towards AlN with increasing AlN power supplies (from 65 W to 85 W), i.e., enlarging the amount of Al-related bonds (Al-N and Al-O), as shown in **Figure 4.13**.



Figure 4.13 Short wavelength RIs (a) and relative IR absorptivity (b) of SiAlON films deposited with 65, 75, and 85 W AlN power supplies.

## 4.2.3 Applying ion bombardment

The chemical intermixing can also be tailored by applying bias ion-assist. It is worth noting that the atomic concentration of O has the opposite varying trend to that of N as increasing the energy of the ion bombardment. Its composition change presented in **Figure 4.14** clearly proves the impact of the RF substrate bias with varying the power from 0, 10 to 20 W. The element N still dominates in the composite, but its concentration fluctuates obviously (from 34.2%, 40.8% to 38.8%) with the increasing bias. On contrast, the atomic concentration of O

experiences an opposite change, and the lowest concentration of 15.4% appears in the 10 W case.



**Figure 4.14** Change in atomic concentrations with increasing substrate bias. Meanwhile, the IR refractive index, as well as the intensity and location of the absorption peak are also changed with the bias (see **Figure 4.15a** and **Figure 4.15b**). Specifically, the overall absorption ranges from 8 to 16  $\mu$ m is dramatically enhanced in the 10 W-bias case, while only the absorption in 9~13  $\mu$ m is slightly increased after further adjusting the substrate bias to 20 W (**Figure 4.15b**). Thus, the ion-assisted preparation routine is also efficient for compositional adjustment, as well as corresponding optical performance control. For the bias-dominated interatomic bonding, as illustrated in **Figure 4.16a**, a weak shoulder in the N 1*s* spectrum approximately located at 404 eV is assigned to -(NO)<sub>x</sub>, which only presents in the film without substrate bias. And the density of the film is increased from 2.8 g/cm<sup>3</sup> to 3.3 g/cm<sup>3</sup> with the 10 W substrate bias (see **Table 4.5**), indicating that the blocking of the oxygen-related bonds

formation under appropriate ion-bombardment is benefiting from film densification.



Figure 4.15 (a) IR RIs of the samples fabricated with 0, 10, and 20 W substrate

bias and (b) their relative IR absorptivity.

Table 4.5 Effective density of films with various substrate biases in Figure

| Sample | Substrate bias (W) | Density (g/cm <sup>-3</sup> ) |
|--------|--------------------|-------------------------------|
| 1      | 0                  | 2.8                           |
| 2      | 10                 | 3.3                           |
| 3      | 20                 | 2.9                           |
|        |                    |                               |

4.15.

The XPS results presented in **Figure 4.16c** and **Figure 4.16d** show that the formation of Si-Al-ON and N-Si-O bonds predominates throughout the deposition process at 10 W, thereby contributing to the overall enhancement of the absorption capability of the material (**Figure 4.16c**). However, with the substrate bias up to 20 W, the relative amount of the Si-Al-ON structure and film density is reduced (from 3.3 to 2.9 g/cm<sup>3</sup>), along with the increase in N-Si-O and

Al-O bonds, as presented in **Figure 4.16b-d**. This phenomenon is in line with the content change of N and O shown in **Figure 4.14**. Considering the dissociation energy of the chemical bonds demonstrated in **Table 4.6**, the nitrogen bonds are more likely to be broken or even reevaporated via the excessive ion-bombardment, which can well explain the chemical change presented in **Figure 4.16** and thus the absorption peak shift in **Figure 4.15b**.



Figure 4.16 XPS core-level spectra of N 1s (a), O 1s (b), Si 2p (c) and Al 2p

(d) for SiAION films deposited under different substrate bias conditions.

According to the above-mentioned analysis, the schematic diagram of the ionbombardment-induced dynamic behaviors is demonstrated in **Figure 4.17**. Specifically, the structural defects such as atom vacancies and micro voids can be partially eliminated via the ion-bombardment-assisted migration of adsorbed particles on the film surface, producing a "nitride-friendly" forming and film densifying environment. Thus, both the absorption and extinction coefficient of SiAlON experience a distinguishable enlargement. On the contrary, higherenergy ion-impact would bring about the breaking of nitrogen bonds with relatively low dissociation energies and facilitate the corresponding replacement by the competitive oxygen counterparts, along with the slight increase in oxygen bond induced absorption in  $9\sim13$  µm.

| Chemical bond                                      | Dissociation energy (kJ/mol)   |
|--|--|
| Al-N   | 297  |
| Si-N   | 439  |
| Al-O   | 512  |
| Si-O   | 798  |
| Ar particle<br>Bond breakage<br>(High energy case) | Al Si N O<br>Al Si N O<br>Filling<br>(Ralatively low<br>energy case) |

Table 4.6 Dissociation energy of different chemical bonds [265].

Figure 4.17 The schematic diagram depicting the ion-bombardment-induced

dynamic processes on the growing surface under RF-bias.

#### 4.3 Absorbing capability

#### 4.3.1 Simulation setups

Based upon the optical properties of SiAlON, the IR absorbing performance of two absorbers are numerically studied for further exploring its capacity. Firstly, as shown in **Figure 4.18**, there is an evident absorption band across 8~16 µm for a single-layer SiAlON absorber (~460 nm-thick SiAlON film atop on a 120 nm Al mirror, see **Figure 4.19**).



Figure 4.18 Experimental and theoretical absorption of a 490 nm-thick

SiAlON film.



Figure 4.19 Structure models of the (a) single-layer absorber and (b) the

Fabry-Pérot resonant multilayer stack.

Note that the deposition condition of the SiAlON layer is the same as that of the sample in **Figure 4.13** with 85 W supply power on AlN target. With the experimental optical constants extracted from ellipsometry analysis (**Figure 4.20**), the theoretical absorption is also depicted in **Figure 4.18**, which is calculated through TMM.



Figure 4.20 The IR *n* and *k* of the SiAlON,  $Si_3N_4$ , AlN,  $SiO_2$ , and  $Al_2O_3$ .

Despite the intensity difference caused by testing errors (detailed analysis is listed in the **Appendix B**), the simulated and experimental results meet with each other very well. Herein, the spectra of SiAlON films with the thickness of 200 nm and 490 nm are also plotted to explain the thickness limitation upon the low absolute absorption of the single-layer absorber. According to **Figure 4.21**, the position of the peaks remains the same, while the absorption intensity is increased by  $\sim$ 20% after the thickness. From the above, the absorbing performance can be simply enhanced with increasing the thickness of the

absorber.



Figure 4.21 Absorptions of SiAION films with the thickness of 200 and 490

nm.

## 4.3.2 Simulated performance of the absorbers

To further indicate the significant broadband absorbing characteristic, the simulated SiAlON layer is thickened up to 2000 nm. As illustrated in **Figure 4.22a**, the absorption intensity is greatly enhanced compared to the 460 nm case. Meanwhile, the whole absorber performs as a near plateau across  $8\sim16 \mu m$  with an average up to 90.4% in its absorption spectrum since it combines two optical interference peaks appearing at ~8 and ~14.4  $\mu m$ . The above results indicate the SiAlON film with simple single-layer scheme has great potential in constructing wideband IR absorption. Further, the optical performance of the SiAlON film for IR selective absorption is also investigated. To be specific, a typical multi-layer stack is proposed and prepared, which consists of a 300 nm-thick absorbing

top layer (SiAlON, Si<sub>3</sub>N<sub>4</sub>, AlN, SiO<sub>2</sub>, or Al<sub>2</sub>O<sub>3</sub>), a 700 nm-thick Si cavity layer, and a 120 nm Al bottom mirror layer (**Figure 4.19b**). The corresponding IR performances are simulated by TMM and depicted in **Figure 4.22b**. Due to the combination of intrinsic absorption and Fabry-Perot resonant confinement, the ultra-thin stack presents a highly selective absorption plateau ranging from 9 to 12  $\mu$ m (96.6% in average), with a near-unit absorptance of 99.7 % at 9.9  $\mu$ m. However, both the spectral selectivity and broadband extinction capability are not ideal when replacing the top layer by the other materials (Si<sub>3</sub>N<sub>4</sub>, AlN, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>).



**Figure 4.22** (a) Comparison on the theoretical absorption of a 2000 nm-thick SiAlON, Si<sub>3</sub>N<sub>4</sub>, AlN, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> film and (b) The theoretical absorption spectra of multi-layer stacks consisting of a SiAlON (or a Si<sub>3</sub>N<sub>4</sub>, AlN, SiO<sub>2</sub>, or Al<sub>2</sub>O<sub>3</sub> single layer) absorbing layer, a Si cavity layer and an Al mirror layer on

Si substrate.

#### 4.3.3 Optical tunability of the SiAlON-based absorbers

Considering the optical tunability of SiAlON composite, the absorbing properties of the two absorbers above that take SiAlON films with various optical performance are also calculated, showing that the control upon SiAlON can be further extended to the SiAlON-based absorbers. The input optical constants are experimentally extracted, as plotted in **Figure 4.8a** and **Figure 4.15a**. The thickness of the single-layer absorber is set as 1000 nm in this case to prevent the resonance and present a clearer view of its absorbing capability. Herein, the difference in the intensity of resonant peaks within 2~8 µm are attributed to fitting errors (see the insert of **Figure 4.23a**).

According to **Figure 4.23a**, the absorption peak of sample without N<sub>2</sub> feeding locates at 13.5  $\mu$ m, achieving a maximum of 65.5%. In comparison, the peak experiences obvious blue shift to 11.6  $\mu$ m in the 3 SCCM case, along with a decrease of ~10% in intensity. This is attributed to the introduction of N<sub>2</sub> compresses the formation of Al-related bonds that have response in 12~17  $\mu$ m. Similar trend is also observed in the cases with ion-assist control. The absorber with largest oxygen content (0 W case) has its absorption peak located at 12.3  $\mu$ m, while the 20 W sample with large Si-Al-ON bond and N-Si-O bond contents shows high absorption intensity up to 74.3% at 13.5  $\mu$ m.



Figure 4.23 (a) simulated performance of single-layer absorbers taking the SiAlON composites produced under various N<sub>2</sub> feeding and various substrate bias as absorbing material, the insert shows the errors in extinction coefficient from 4 to 8 μm; (b) simulated performance of three-layer Fabry-Perot resonant multilayer stack taking the SiAlON composites produced under various N<sub>2</sub>

feeding and various substrate bias as absorbing material.

Absorbing performance of the Fabry-Pérot resonant absorbers cannot be simply determined by the absorbing property of SiAlON since impedance matching and phase accumulation are also considered. Despite the higher absorption capability of the 0 SCCM sample, absorber with 3.0 SCCM sample presents higher absorbing intensity (96.9% at 10.9  $\mu$ m), indicated in **Figure 4.23b**. The same phenomenon is also observed when shifting the bias, as 0 W case shows greatest

absorption above 98% from 10 to 12  $\mu$ m, while the extinction of the corresponding sample is relatively low (**Figure 4.15a**). On the other hand, the broader band absorbing material-based absorbers (i.e., 0 SCCM, 10 W and 20 W cases in **Figure 4.23b**) have an extended bandwidth from 8 to 16  $\mu$ m. Therefore, the bandwidth and peak position of the absorber is still highly linked to the corresponding property of the absorbing material.

Therefore, the composite SiAlON film can meet both broadband and high selective IR absorption requirements based upon appropriate absorber design, endowing it with more potential in practical applications.

## 4.4 Discussion

This work investigates the IR absorption principles of the SiAlON composite and effectively manipulates its absorption band by controlling the relative content of its constituent chemical bonds. Generally, the intrinsic absorption band of the SiAlON composite, ranging from 8 to 16  $\mu$ m, is derived from the photon-phonon coupling of the N-Si-O bond, Si-Al-ON bond, and Al-O bond. The composition of these chemical bonds can be easily tuned by varying the sputtering environment. Herein, oxygen bonds are more stable due to their large dissociation energy, leading to a preference for forming oxygen-related bonds. By introducing reactive N<sub>2</sub> gas, the nitrogen content is increased with growing chamber pressure, promoting the formation of N-Si-O bonds dominant in film growth while compressing the bonding of Si-Al-ON by reducing the deposition rate of Al-related bonds. Additionally, the densifying effect induced by ion impact at relatively low energy creates a "nitride-friendly" environment by removing defects, resulting in an enrichment of Si-Al-ON bonds.

In comparison to physical piling, which broadens the bandwidth by combining multiple absorbent layers with various materials and requires impedance matching to minimize reflections at interface [266, 267], chemical intermixing simplifies the structure to a single layer and enhances the extinction capacity of the system [268]. For example, Dolado et al. embedded the Tobermorite (Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) into an amorphous nanostructured hydration product (C-S-H gel), achieving selective intrinsic absorption in 8~11 µm by combining the stretching vibration mode of Si-O, Ca-O, and Calcite (CaCO<sub>3</sub>) [269]. Similarly, this method of optical property regulation can be extended to different wavelengths, providing the composite contains corresponding chemical bonds exhibiting vibrational modes at the required range. Furthermore, the extinction feature can be tuned according to the weight of different target wavelength ranges by adjusting the content of the chemical bonds, offering an additional degree of freedom in material and system design.

However, the existence of residual oxygen results in the formation of oxygenrelated bonds. In this context, reducing the oxygen content is challenging due to the high dissociation energy of oxides, which greatly limits the control of the absorption feature. This challenge could be mitigated by enhancing the vacuum level, thereby reducing the residual oxygen and suppressing its reaction with the sputtered fragments. But this approach sacrifices mass production capabilities, as such high vacuum levels are impractical for industrial fabrication.

Considering the target regime for radiative cooling, which focuses on the 8 to 13  $\mu$ m range, and the fact that the SiAlON composite fabricated by co-sputtering Si<sub>3</sub>N<sub>4</sub> and AlN targets exhibits strong absorption in the 10 to 14  $\mu$ m range, the content of Si-O bonds, which have intrinsic absorption at ~8  $\mu$ m, should be increased to enhance performance at shorter wavelengths. Therefore, using a SiO<sub>2</sub> target instead of a Si<sub>3</sub>N<sub>4</sub> target can form a composite dominated by Si-O and Si-Al-ON bonds in the subsequent film system construction. Similarly, the IR optical performance should be optimized through compositional adjustments, targeting a broadband absorption peak that encompasses the entire AW. This can be achieved by modulating the power supply to the two targets.

## 4.5 Summary

In this chapter, an absorbent material with a broad intrinsic absorption band spanning the entire AW is developed. This novel composite enables effective RC with a significant temperature reduction in a relatively simple structural design, owing to its selective IR-absorbing properties. The innovative approach of combining specific absorbing chemical bonds to form a new composite overcomes the limitations of naturally occurring materials, addressing the challenge of structural complexity associated with achieving a wide IR absorption bandwidth in the design of inorganic radiative coolers. During the material development process, the influence of magnetron sputtering deposition parameters on the properties of the SiAlON composite was systematically investigated. This study aimed to reveal the relationship between chemical intermixing and the resulting optical properties of the composite. Based upon it, the absorption peak covering  $8 \sim 16 \mu m$  can be flexibly tuned, including its intensity, location, and bandwidth. As adjusting the sputtering atmosphere, the peaks of IR extinction coefficient and absorption can be narrowed to 8 to 13 µm with the stoichiometric change. Further composition and valence analyses show that such an optical response is attributed to the preference for the formation of silicon oxynitride and the reduced deposition rate of Al compounds in a nitrogenrich environment. Then, substrate-bias-assisted deposition is also applied to tune the relative proportion of the chemical bonds in the composite film, and ion bombardment with appropriate energy is effective to harvest the oxynitriderelated chemical bonding and densify the film. Finally, the two theoretical absorbers illustrate the high flexibility of its optical performance and suitability in various designs for different applying scenarios, such as optical sensing and IR energy harvesting. In all, the SiAlON composites with tunable and wideband absorption is adaptable for both selective and broadband applications, which is
beneficial for the further structural simplification in IR absorber design.

# Chapter 5 Development of high refractive index spacer - Si-Al nanowires metamaterial

In this chapter, a novel Si-Al nanowire metamaterial with a high effective RI value is developed to address the challenge of excessive film thickness caused by phase accumulation in RC film system designs. As discussed in Section 2.3.6, the incorporation of metallic arrays can lead to a significant increase in the RI at specific plasmon resonance wavelengths. Among these, the nanowire-embedded dielectric structure is an optimized configuration, as the enhanced capacitive coupling within the metal/matrix/metal cavity facilitates a broadband expansion of the RI with low dispersion. Additionally, the strong electromagnetic coupling between the nanowires imparts the material with a hyperbolic dispersion feature, exhibiting reflectivity in the short-wavelength range and transparency in the long-wavelength range. This characteristic has the potential to enhance solar reflectivity, thus enabling dual-band optical regulation in RC applications. To construct the nanowire structure, an MD simulation is first employed to reveal the mechanism underlying the broadening of the Al nanowire formation window. This approach aims to differentiate the effects of various interaction forces, including adatom attraction, diffusion, and re-evaporation, on the movement of sputtered particles, thereby facilitating the formation of a vertical Al NWs array. Based upon the simulation results, the Al NWs embedded Si composite is experimentally deposited, and its forming mechanism and optical properties are analyzed. Besides, the composite microstructure is precisely regulated by manipulating the Al volume fraction, which is realized through adjusting the target supply power and the substrate bias (i.e., ion impact energy). Additionally, the control upon broadband optical properties of the Si-Al NWs composite is studied, including the adjustment of its optical constants and full-band reflecting performance. Finally, the full spectrum optical performance of the Si-Al NWs with an Al volume fraction of 50% is discussed, showing the potential of the composite in constructing selective high IR emission.

## 5.1 MD simulation

#### 5.1.1 Filling fraction-dependent phase separation

The inherent low eutectic temperature in the Si-Al system allows phase separation to take place spontaneously, and appropriate mobility of adatoms enables the formation of vertical NW arrays at specific Al at.%, as schematically shown in **Figure 5.1a**.

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [270] was utilized to simulate the motion of the Si and Al phases during the phase separation (details in **Section 3.3.1**). It is indicated from **Figure 5.1b** and **Figure** 



5.2 that complete phase separation only occurs within the range from 25% to 50%

**Figure 5.1** Simulated phase separation cases with and without ion impact: (a) schematic model of the filling fraction-dependent phase separation case; (b) Three-dimensional models for filling fraction-dependent phase separation

cases; (c) schematic model of the ion-assisted phase separation case; (d) Three-

dimensional model for ion-assisted phase separation case.

To further validate the model and prove the NW formation window, three samples with 20%, 45%, and 60% (Al at.%) were prepared, see **Figure 5.3**. Herein, Al was selectively removed by acid etching to enhance the contrast in SEM images and reveal the microstructure character.

The sample with an aluminum atomic percentage of approximately 20% exhibits no significant etched holes, indicating the discrete particle structure is formed. With an increased ratio of aluminum to 45%, vertical growth of aluminum is observed, evidenced by the columnar and separately distributed normal tracks. The remaining matrix features a web-like structure when the aluminum atomic percentage is further increased to 60%, aligning with the simulation prediction in **Figure 5.1b**. Therefore, aluminum tends to form as nanoparticles at low Al at.% (below 25%), while nanoscale network emerges at high Al at.% (beyond 50%). This phenomenon is attributed to the unbalanced arrival of adatoms, which disrupts the phase equilibrium and limits their separation.



Figure 5.2 MD simulated filling-fraction dependent phase separation (without



ion assist).

**Figure 5.3** SEM photo of the etched samples with (a) 20 at.% Al that forms

nanoparticles; (b) 45 at.% Al that forms nanowires; (c) 60 at.% Al that forms

nanowebs (under no ion assist condition).

## 5.1.2 Ion-assisted phase separation

To further expand the operation window for the formation of NW structures, ion bombardment is introduced to provide external energy for promoting adatom migration. The procedure is experimentally realized by applying substrate bias during deposition. As depicted in **Figure 5.1c**, ion-assisted deposition enhances adatom diffusion, enabling phase separation at a higher aluminum concentration, up to 67%, i.e., the window for NW formation is significantly expanded from 25% to 67% (**Figure 5.1d** and **Figure 5.4**).



Figure 5.4 MD simulated ion-assisted phase separation.

However, according to **Figure 5.5**, excessive adatom mobility induced by overhigh ion impact energy has the opposite effect, causing the aggregation of the aluminum phase and promoting the formation of network instead of NW structures.



Figure 5.5 Simulated phase distribution with overhigh ion impact energy.

#### 5.2 Microstructure

#### 5.2.1 Geometry of the Si-Al NWs composite

Overall, the theoretical maximum filling fraction of the metallic nanowire can be increased when the adatom diffusion is enhanced during the film growth, as proved by the experimentally achieved closely packed nanowire structure shown in **Figure 5.6a** and **Figure 5.6b**. The sample fabrication procedures are described in **Section 3.4.2**. The as-deposited Si-Al composite film (high fraction of Al NW) is highly reflective with an average reflection of  $\sim 72\%$  (**Figure 5.7b**) in a metallic color (the insert in **Figure 5.6b**). As revealed by the 2D fast Fourier Transformation (FFT) image in the insert of **Figure 5.6b**, the average diameter of the ring equals  $\sim 0.227$  nm<sup>-1</sup>, corresponding to an average radius of  $\sim 0.1135$ nm<sup>-1</sup>. By taking the inverse of the radius, the center-to-center spacing is calculated to be  $\sim 8.8$  nm.



**Figure 5.6** (a) Cross sectional view of the as-deposit Si-Al film and (b) Surface view of the as-deposit Si-Al film, the inserts are 2DFFT result and the optical photograph of the as-deposit film.

In addition, the aluminum NWs can be completely eliminated through a 2-h etching process, resulting in a nano-porous silicon column structure, as depicted in **Figure 5.7a**. The bright silver color fades away after the removal of aluminum (see the insert in **Figure 5.7a**), and the etched sample exhibits a faint yellow color with a substantial decrease in reflection (**Figure 5.7b**).



**Figure 5.7** (a) Cross section and optical photograph of the etched film and (b) reflectivity of the NW sample in **Figure 5.6** before and after etching process. Due to the transparent nature of the etched sample, the volume fraction of air column (i.e., volume fraction of Al NWs), about 64%, can be easily extracted via ellipsometry method (explained in the **Section 3.5.1**). Moreover, according to the dark-field transmission electron microscopy (TEM) images in **Figure 5.8**,

the average diameter of the NWs is  $\sim$ 7 nm. Considering its geometry, the aluminum volume fraction approximates 62%, in line with the fraction determined by ellipsometry fitting. Given that the aluminum nanowire arrays in the actual samples do not exhibit the perfect periodicity assumed by the EMA model, errors arise between the filling fraction obtained from ellipsometric fitting and that calculated from the structural parameters.



Figure 5.8 Dark-field TEM photo of the Si-Al NWs.

# 5.2.2 Crystalline structure of the Si-Al NWs composite

Remarkably, the Al nanowires exhibit (111)- and (200)- preferred orientation, whereas the Si matrix is with amorphous structure, as evident from the X-ray diffraction (XRD) patterns in **Figure 5.9**.

The preferred orientation of Al is further evidenced by the SAED patterns and HRTEM images. This is shown by the diffraction rings with a radius of 2.37 and 2.09, as well as the measured lattice spacing of 2.17 and 2.03 (refer to **Figure 5.10a-c**). Additionally, the amorphous state of Si is proved by the halo rings in **Figure 5.10b** [271].



Figure 5.9 XRD spectra of the Si-Al film before and after acid etching.



Figure 5.10 (a, c) high resolution TEM photo of the Al NWs; (b) SAED result

of the composite.

# 5.3 Forming mechanism

According to the above analysis, the vertically aligned aluminum NWs growth

mechanism is illustrated in Figure 5.11.



Figure 5.11 The sketch of the growth of Al NWs with ion impact.

Specifically, ion bombardment is employed to achieve a dynamic equilibrium between the growth of silicon and aluminum phase, thereby enhancing phase separation. Furthermore, the enhanced migration of sputtered Si and Al clusters leads to preferential attraction to the neighboring clusters of the same phase, reducing the overall system energy. Meanwhile, Al adatoms are etched at energetically active sites, followed by their reassembly into (111) and (200) planes. Meanwhile, the growth of the surrounding amorphous Si matrix hinders the dispersion of Al clusters, ensuring the growth of the aluminum nanowireembedded silicon composite. It is worth noting that the adatom reevaporation will gradually dominate the film growth with the increase of the ion impact energy. Besides, the reevaporation-induced low deposition rate contributes to an increase of the Al NW diameter, further enlarging the Al filling fraction within the system. However, excessive ion impact energy disrupts the dynamic balance between surface migration and reevaporation, giving rise to a constrained spatial confinement of the silicon matrix and the formation of Al network.

# 5.4 Optical characterization and modulation

# 5.4.1 Wideband optical properties

The Si-Al NWs exhibits high reflectivity across a wide wavelength range from 0.2 to 20  $\mu$ m, with a noticeable valley located at approximately 4  $\mu$ m (**Figure 5.12**).



Figure 5.12 Broad spectrum reflectivity of the high Al fraction Si-Al NWs.



Figure 5.13 FDTD simulation model.

For further analysis, the spatial electromagnetic field distribution in Si-Al NWs system at 0.4, 4, and 8  $\mu$ m is calculated by using Finite-Difference Time-Domain

(FDTD) method. The model contains two NW units, and the dimension completely follows that of the NW sample in Figure 5.6, as presented in Figure 5.13.

The incident field is concentrated at the top of the surface, while the electric field only penetrates the Si matrix (**Figure 5.14a**). Consequently, the exceptional broadband reflection observed in Si-Al composite can be attributed to the migration of free electrons within the Al nanowires towards the surface, generating an induced field that cancels the incident field, as depicted in **Figure** 





Figure 5.14 (a) Simulated electromagnetic field of the NWs material at 0.4

μm; (b) Schematic light response of NWs material at 0.4 μm.



Figure 5.15 (a) Simulated electric field and power density distribution of the NWs material at 4 μm; (b) Schematic light response of NWs material at 4 μm.
Meanwhile, the Si-Al NWs composite becomes a homogenous dielectric

material in the IR region due to its deep-subwavelength-scale structure, whose F-P resonant wavelength can be calculated with **Equation 2.12**. The resonanceinduced absorption band is located at ~4  $\mu$ m both in the tested spectrum (**Figure 5.12**) and the simulated power density distribution (**Figure 5.15a**), which is attributed to the interference between the plasmon polaritons waves propagate forward and backward along the surface of Al NWs in z-direction, as shown in **Figure 5.15b**.

However, the confinement of light is limited to the resonant band. Thus, the light trapping effect resulting from interference diminishes when the wavelength becomes 8  $\mu$ m, as illustrated in **Figure 5.16b**. The simulated near electromagnetic fields at 8  $\mu$ m in **Figure 5.16a** and **Figure 5.17** also reveal that the light response of Si-Al NWs material is similar to that of silicon in the non-resonant band. In summary, the incorporation of Al NWs structure into silicon allows the material to exhibit metallic properties from 0.2 to 1.7  $\mu$ m, while the composite material demonstrates dielectric characteristics with a selective absorption band in mid-IR wavelength range.



Figure 5.16 (a) Simulated electromagnetic field of the NWs material at 8 µm;

(b) Schematic diagram illustrating light response of NWs material at 8 μm.



**Figure 5.17** Full spectrum reflectivity of the silicon film, the insert is the FDTD simulated electromagnetic field distribution in Si at 8 μm.

# 5.4.2 Structure-based optical regulation

The controllable optical performance of Si-Al system is also investigated since the interior structure can be flexibly controlled with varying Al filling fraction range. Herein, as a response to the shifting of optical constants and inner structure, the reflection spectrum of the Si-Al composite also reveals the state of aluminum phase. In this context, nanoparticle sample shows typically dielectric characteristic with relatively low dispersion, see the insert of **Figure 5.18a**. In addition, the broadband high transparency is also observed due to its nearly zero k value, which benefits from the deep-subwavelength particle structure. Notice that the baseline of the reflectivity for nanoparticle sample is lower than the reflectivity of the Si substrate in **Figure 5.17**. This is attributed to the wellmatched impedance since the RI of the nanoparticle sample is lower than Si. On contrast, the nanoscale network performs more like metals in the shortwavelength range, see **Figure 5.18b**. According to **Figure 5.3c**, the dimension of aluminum network is comparable to the wavelength, leading to a scatteringinduced solar absorption.



**Figure 5.18** Wide spectrum reflectivity and sketch of (a) nanoparticle (the insert is the refractive index of nanoparticle sample) and (b) nanoscale network

# samples.

Furthermore, for the NWs cases, it is observed that an increase in the Al filling fraction corresponds to an increase in the diameter of Al NWs, while the internanowire spacing has an opposite trend, as evidenced in **Figure 5.19**. As a result of the Al filling fraction dependent structure control, the metallic-to-dielectric transition point experiences a significant red shift from 335, 345, 536, to 958 nm with respectively increasing the Al NW volume fraction from 29%, 34%, 50%, to 64%, as shown in **Figure 5.20**.



Figure 5.19 Surface view of the Si-Al NWs material with an Al volume

fraction of 29%, 34%, 50%, and 64%.

Meanwhile, due to the homogenization effect achieved within the subwavelength structure, the optical properties of the Si-Al composite within the dielectric region agree with the principles of the effective medium theory. This effect is mathematically described by:

$$\frac{f(\varepsilon_m - \varepsilon_{\text{eff}})}{\varepsilon_{\text{eff}} + g(\varepsilon_m - \varepsilon_{\text{eff}})} + \frac{(1 - f)(\varepsilon_d - \varepsilon_{\text{eff}})}{\varepsilon_{\text{eff}} + g(\varepsilon_d - \varepsilon_{\text{eff}})} = 0$$
 Equation 5.1

where f is the volume fraction of the metal Al, the geometry factor g equals to 0.5 for the case of NWs,  $\varepsilon_m$  the dielectric constant of Al, and  $\varepsilon_d$  the dielectric constant of the host matrix Si. It can be inferred that the change in  $\varepsilon_{eff}$  is highly related to f. As predicted by the theoretical calculation, the ellipsometric fitted refractive index in the IR band is increased from 4.6 to 8 (@12 µm), corresponding to the Al volume fraction from 29% to 64% as presented in **Figure** 



Figure 5.20 Complex dielectric constants of Si-Al NWs samples with Al

volume fractions of 29%, 34%, 50%, and 64%.

This phenomenon is attributed to the strengthened capacitance coupling, stemming from the decreased interwire gap [272]. Meanwhile, the enhanced capacitance coupling causes concomitant Ohmic losses, resulting in a notable extinction coefficient increase, from 0.2 to 1.39.



Figure 5.21 IR optical constants of Si-Al NWs samples with Al volume

fractions of 29%, 34%, 50%, and 64%.

**5.21**.

To investigate the optical properties in response to structural variations, the reflection spectra covering visible light to mid-IR region were measured (**Figure** 



**5.22a** and **Figure 5.22b**).

Figure 5.22 Reflectivity of Si-Al NWs samples at Al volume percentages of

29%, 34%, 50%, and 64% in the (c) 300 to 1200 nm and (d) 1.5 to 6  $\mu m$ 

spectral ranges.

From **Figure 5.22a**, it is observed that the average reflectance in the shortwavelength regime exhibits a consistent upward trend, increasing from 39%, 45%, 65% to 72%, in line with the increasing volume fraction of aluminum. This phenomenon can be ascribed to the significant contribution of the growing strength of the induced electromagnetic fields generated within the NWs structure. In the mid-IR range, due to the raise of Al content and RI value, a continuous red shift of the reflection valley caused by destructive interference (i.e., F-P resonance) is observed. This phenomenon perfectly matches the TMM simulated result, as seen in the colormap of reflection spectra in **Figure 5.23**.



Figure 5.23 full-spectrum performance of Si-Al NWs-based single-layer absorber.

Additionally, there is a notable decrease in the reflection valley intensity as the Al fraction increases from 29% to 34%, followed by an increase as the Al fraction is further increased from 34% to 50%, as illustrated in **Figure 5.22b**. This is also reflected in the nonlinear variations in the simulated absorption peak magnitude (**Figure 5.23**). The heightened reflection (i.e., the reduced absorption) happens due to an inappropriate extinction coefficient value, leading to a mismatch between the intensity of the first-order and the higher-order reflection [119].

# 5.4.3 Si-Al NWs-based controllable absorber

The Si-Al NWs material demonstrates substantial potential for developing a selective IR absorber, owing to its high refractive index and dual-band (metallic and dielectric) modulation characteristics. However, careful considerations on the Al filling fraction are crucial to balance the IR absorbing performance and

the absorber thickness reduction. As schematically shown in the inset of **Figure 5.24**, a Si-Al-based IR selective absorber, tailored for the wavelength range of  $5 \sim 8 \mu m$ , is formulated. The Al% is set at 50% to enhance absorbing intensity while maintaining a relatively high refractive index. The reflectance in the short wavelength remains flat with an average value of 65%, while the F-P resonanceinduced absorption peak at 6.2  $\mu m$  approaches a maximum value of 94%, as depicted in **Figure 5.24**. The overall thickness of the absorber is optimized to be 217 nm using the TMM program, as shown in the insert of **Figure 5.24**. T his result indicates that selective absorption within the atmospheric window can be effectively achieved with a single-layer Si-Al structure by adjusting its film thickness. Additionally, taking Si-Al spacer with an Al volume fraction of  $\sim$ 50% holds potential for optimizing the solar reflectivity of the RC system, thereby improving its overall cooling performance.



Figure 5.24 full-spectrum performance of Si-Al NWs-based single-layer absorber.

# 5.5 Discussion

This study focuses on the optical manipulation of Si by incorporating Al NWs array, resulting in a significant increase in RI due to the enhanced capacitance coupling. During the film growth, Al can spontaneously form vertically aligned NWs within a Si matrix due to the low solubility and mobility differences in the system. However, the Al NW formation window is relatively narrow due to the unbalanced sputtering rates of the Si and Al phases, while the enlargement of the Al volume fraction is crucial for RI maximization since the strength of this coupling is inversely proportional to the interwire gap. To address this issue, ion impact is introduced during material formation to increase the surface diffusion length of aluminum. Consequently, the Si-Al NWs system achieves an ultrahigh experimental Al volume fraction of 64% (61 at.%), surpassing previously reported works (56 at.%).

Previous research on high-index metamaterials with self-aligned metallic arrays has revealed several limitations. These materials typically achieve their maximum RI value only at plasmonic resonant wavelengths. The drawbacks include: (1) the matrix materials of these metamaterials, usually polymers or air, have relatively low RI values, leading to low RI in the non-resonant range [273]; (2) the plasmonic resonance-induced RI increases exhibit high dispersion and high extinction capacity, making them unsuitable for spacer applications [274]; and (3) the self-aligned metal arrays have a relatively short lifecycle [141]. In contrast, the Si-Al NWs array employs high-index Si as the matrix, significantly enhancing the achievement of ultrahigh RI values in the non-resonant band with low dispersion.

The composite can shift the destructive interference-induced absorption band to longer wavelengths (e.g.,  $\sim 11 \ \mu m$ ) by simply increasing its thickness, thereby meeting the requirement for light emission within the AW. It has been previously demonstrated that the high RI value, achieved by increasing the Al volume fraction, facilitates complete phase accumulation within an ultrathin structure. However, the Si-Al NWs composite with a high aluminum volume fraction also exhibits a large extinction effect due to its high Ohmic losses, which significantly reduces the intensity of the absorption peak. Thus, the balance between thickness reduction and performance optimization is required for further investigation to find the appropriate Al filling fraction.

Moreover, the broadening of the nanowire formation window through ionassisted deposition offers a method for obtaining low-dispersion materials with varying RI values. Experimentally, the RI of Si-Al varies from 4.5 to 8 with increasing aluminum filling fraction. Additionally, one can achieve ultrahigh porous Si with a low RI value (from 1.4 to 2.5) by removing the Al phase through an acid etching process, which is desirable for antireflection applications. The ability to flexibly adjust the optical constants of the material makes this Si-Al composite system suitable for a wide range of applications.

#### 5.6 Summary

In this work, the optical properties of silicon by inserting vertically aligned Al nanowires are manipulated. The resulting Si-Al NWs system manifests dualband properties, transitioning from a metallic nature with high reflectivity in the short-wavelength range to a dielectric one with a high refractive index in the long-wavelength range. Substrate bias-induced ion impact provides fine control of the nanowire structure, particularly the volume fraction, diameter and interwire gap. This facilitates the adjustment in the metal-to-dielectric transition point as well as the optical constants. Subsequently, an ultrathin single-layer Si-Al NWs-based absorber was developed, demonstrating high short-wavelength reflectivity (~65%) and selective absorption approaching 94% within the 5~8 µm range. This finding demonstrates that the Si-Al NWs composite material can be effectively integrated into RC systems through simple thickness control. The peak induced by the F-P resonance offers considerable potential for enhancing emission within the AW. Additionally, the high solar reflectivity of the Si-Al NWs spacer ensures superior dual-band modulation compared to pure Si spacer, thereby presenting the potential for achieving a greater temperature drop during the daytime.

# Chapter 6 Performance of ultrathin double-layer SiAlON/Si-Al nanowire radiative cooling system

In this chapter, a double-layer inorganic radiative cooler is designed to realize highly selective absorption with a simplified film structure. This work achieves optical optimization of the film system through material innovation and in-depth understanding, demonstrating significant potential for advancing the development of RC systems. The system is deposited on a full-spectrum reflective aluminum foil substrate and consists of a top SiAlON layer and an IR low-loss Si-Al NWs spacer. The full-band performance of the film system is well analyzed, including the optical contribution of both the layers. Based on the calculated target IR emission required to achieve effective temperature reduction, the Al filling fraction and the thickness of each film layer are optimized. This optimization process clarifies the mechanism behind the broadening of the absorption band, providing a deeper insight into the absorption characteristics of the film system. Finally, the cooling performance of the film system was evaluated using both an IR camera and k-type thermocouples, demonstrating the

actual temperature drop of this ultrathin radiative cooler.

#### 6.1 Film system structure

#### 6.1.1 Design strategy



Figure 6.1 Schematic illustration of (a) the top selective absorbing SiAlON material layer and its optical constants, (b) the high-index Si-Al NWs composite spacer and its optical constants, and (c) the complete film system and its wideband optical performance.

An F-P cavity is constructed to address the challenge of structure simplification in selective inorganic radiative cooler design. As illustrated in **Figure 6.1a**, the SiAION composite film is the top layer due to its wideband intrinsic absorption, which perfectly matches the AW. Additionally, the Si-Al NWs spacer enables phase accumulation within a low film thickness due to its high refractive index of up to 6.3 (see the insert of **Figure 6.1b**). An aluminum foil substrate is employed to prevent any incident light from penetrating the system. The entire film system is schematically illustrated in **Figure 6.1c**. By combining the two layers, the system achieves an average emission of approximately 0.81 in the AW, as depicted in the inset of **Figure 6.1c**.

#### 6.1.2 Structure of the film system

Taking the TMM calculated absorption of the film system as the critical criterion, the film structure is optimized via PSO program. Herein, SiAlON composite with high extinction coefficient in  $8{\sim}16$  µm (deposited under 0 SCCM N<sub>2</sub> feeding and 10 W substrate bias) and Si-Al NWs with an Al volume fraction of 50% (RI value ~6, near perfect IR absorption) are selected. The optical constants of these materials, as previously illustrated in Figure 4.3 and Figure 5.21, serve as the inputs for the analysis. The result in PSO program suggests the film system should be constructed of a top SiAlON layer as thick as the upper limit in the setting and a spacer with a thickness of ~400 nm. In consideration of both the thickness reduction and IR absorbing performance optimization, the overall thickness of the system is 682 nm, with a 282 nm top layer and a 400 nm spacer. Based upon the design, the film system is experimentally deposited with a twostep magnetron co-sputtering process, as shown in Figure 6.2. The top SiAlON layer is homogeneous without noticeable particles. Meanwhile, the Si-Al spacer exhibits an interwire gap of ~4.4 nm and an average nanowire diameter of 5.6 nm, corresponding to an Al volume fraction of approximately 50%.



Figure 6.2 Cross-sectional view of the film system.

### 6.2 Absorbing capability

# 6.2.1 Wideband optical performance

In the IR range, the film system exhibits a main absorption band with a full width at half maximum of 6.3  $\mu$ m and a peak value of 97.6% at 10.8  $\mu$ m, as illustrated in **Figure 6.3**. The emission peak aligns well with the AW range of 8 to 13  $\mu$ m, maintaining an average value of 0.81. Additionally, a high-order resonance around 3.6  $\mu$ m meets the secondary AW (3 to 5  $\mu$ m), further enhancing the emitted radiation and contributing to a lower equilibrium temperature. These resonance-induced absorption peaks also extend into the short-wavelength range, contributing to the structural color appearance of the sample (as shown in the insert of **Figure 6.2**).



Figure 6.3 Full-spectrum absorptivity of the film system.

## 6.2.2 Optical contribution of each layer

To assess the contribution of each layer to the overall system performance, the absorptivity of individual layers was tested separately and compared with the performance of the film system. **Figure 6.4** shows that both the Si-Al layer and the complete film system exhibit three main absorption peaks at 2.2  $\mu$ m, 3.6  $\mu$ m, and 10.8  $\mu$ m, respectively, with closely matched locations. The minor differences (less than 0.2  $\mu$ m) are attributed to the thickness variations between the Si-Al NWs sample and the spacer in the film system. Thus, the F-P resonance in the Si-Al layer directly influences the positions of the absorption bands in the film system. Furthermore, the intrinsic absorption of the SiAlON layer ranging from 8~10  $\mu$ m is greatly enhanced due to the light confining effect of Si-Al spacer, leading to an additional peak around 9.5  $\mu$ m. It is combined with the resonance at 10.8  $\mu$ m, significantly broadens the overall bandwidth. Moreover, the top layer

also acts as a multiple reflector, enhancing destructive interference at 2.2  $\mu$ m, 3.6  $\mu$ m, and 10.8  $\mu$ m, thereby increasing the intensity of these three peaks.



Figure 6.4 IR absorption spectra of single Si-Al layer, SiAlON layer and the

film system.

To further validate this analysis, the power density distribution at 10.8  $\mu$ m, 9.5  $\mu$ m, and 3.6  $\mu$ m was calculated using FDTD, as shown in **Figure 6.5**. The model dimensions are perfectly in line with that in **Figure 6.2**, and the input optical constants are experimentally extracted by ellipsometric method. Herein, the Si-Al NWs was homogenized into a uniform dielectric material for simplicity. From **Figure 6.5**, the electromagnetic field at 3.6  $\mu$ m is confined to the Si-Al spacer, indicating secondary-order resonance is excited within the spacer. Conversely, the field at 9.5  $\mu$ m mainly concentrates in the top layer, with incident light penetrating the whole film system and experiencing an extinction with increased depth. This phenomenon suggests that both layers contribute to the absorption, with the SiAlON layer being the primary site due to its higher *k* value. It is noted that most of the incident energy is confined to the top of the Si-Al spacer at 10.8

µm, indicating that absorption predominantly occurs within the spacer. Additionally, a region of relatively low-intensity fields is observed in the top layer, which can be attributed to the intrinsic absorption properties of the SiAlON material.



Figure 6.5 Simulated power density distribution at 3.6 µm, 9.5 µm and 10.8

μm.

The reflectivity of Si-Al, SiAION, and the film system from 200 nm to 1600 nm were tested and plotted in **Figure 6.6**. According to the spectra, the single Si-Al layer has a stable reflectivity of ~60%. Despite the broadband transparency of SiAION (as discussed in **Chapter 4**), its sample on a single polished silicon substrate exhibits strong resonance characteristics. The absorption of the SiAION sample in 200~1000 nm is derived from the extinction feature of Si substrate, with the top SiAION layer acting as a multiple reflector to construct interference and confine the light. Based upon the above analysis, the solar irradiance absorption of the film system is attributed to the silicon matrix in the Si-Al spacer. This is further supported by the factor that the locations of reflection valleys in SiAION sample match that in the film system.



Figure 6.6 Reflectivity spectra of single Si-Al layer, SiAlON layer and the film system.

The simulated power density distribution at 642 nm in **Figure 6.7** indicates the incident light is confined at the top of the effective homogenized spacer, further demonstrating that the Si in the Si-Al layer is the main absorbing body, as **Chapter 5** proves the incident electromagnetic field is shielded by the Al nanowire. Besides, the increase in the reflectivity for the film system sample arises from the insertion of Si-Al spacer (from 44% to 67% at 470 nm), and this enhanced reflectivity contributes to the reduction of input solar energy.



Figure 6.7 Simulated power density distribution at 642 nm.

#### 6.3 Full-band performance control

#### 6.3.1 Target solar reflectivity and IR emissions

A MATLAB program is used to hold the theoretical calculation that predicts the temperature of the radiative cooler with various average emissions in 8~13 µm. This simulation helps to determine the target emission for the film system to achieve an effective temperature drop, thereby guiding the corresponding structure design of the double-layer thin film. The mathematical model is detailed in **Section 3.3.7**, with the nonradiative factor set at 8  $W \cdot m^{-2} \cdot K$  to match common serving conditions. According to **Figure 6.8**, the system can realize an effective temperature drop only if the average reflectivity reaches 90%, even with perfect absorption in the IR regime. Thus, further optimization of the solar irradiance reflectivity of approximately 50% (see **Figure 6.6**).



**Figure 6.8** Net cooling power of the system with average short-wavelength reflectivity of 90%, 80%, 70%, and 60% and unit average AW emission.

Thus, the average reflectivity is primarily set at 90% to guide the regulation of IR absorbing properties. Simulated results in **Figure 6.9** reveal that the temperature of the system approaches the ambient temperature (293 K) when the average emission is 0.6, while a significant temperature reduction can be observed when the system achieves an average emission of 0.8.



**Figure 6.9** Calculated net cooling power of the system with average AW emission of 0.2, 0.4, 0.6, 0.8, and 1.0 and 90% average short-wavelength reflectivity.

# 6.3.2 Control via Al filling fraction variation

The regulation of the Si-Al structure, particularly the Al volume fraction and film thickness, directly affects the optical response of the spacer, including its visible reflectivity, wideband optical constants, and the location of its resonance band. Therefore, the adjustment upon the structural parameters of the Si-Al NWs layer allows for flexible control of the full-band absorbing performance of the film system. The IR absorption of the film system taking Si-Al spacers with Al volume fraction from 53%, 56% to 60% is investigated, as illustrated in **Figure 6.10**. The resonance band is fixed at approximately 11  $\mu$ m, and the absorbing properties of the SiAlON layer remain constant. The intensity of the absorption peaks for both the Si-Al layer and the film system significantly drops with the increase in Al filling fraction, from 87%, 78%, to 69%. This trend aligns with the investigation in **Chapter 5**, attributed to the large extinction coefficient of the spacer. Hence, the reduction in Al filling fraction benefits the IR emission optimization.



**Figure 6.10** IR absorbing performance of the SiAlON absorbing layer, the SiAl spacer, and the film system integrated with spacers having Al volume fractions of 53%, 56%, and 60%.

In addition, the short-wavelength reflectivity (200~1600 nm) of the film system incorporating spacer with Al% of 60% and 50% is also tested, see Figure 6.11. The reflection intensity of the film system decreases in line with the reduction

of the Al%, leading to a correspondingly higher solar absorption. From the above, careful consideration of the structure of the Si-Al NWs layer is essential to achieve a balance between visible and IR performance.



**Figure 6.11** Short-wavelength reflectivity of (a) the film system and (b) a single Si-Al NWs layer with aluminum volume fractions of 60% and 50%.

# 6.3.3 Control via SiAlON layer thickening

Regarding light confinement conditions simulated in **Figure 6.5**, SiAlON layer contributes to the bandwidth broadening in the AW. To analyze the influence of the top layer thickness, which closely linked to the absorbing capability of SiAlON, the film thickness of the SiAlON composite is increased from 113 nm, 217 nm, 322 nm, to 427 nm. Based upon **Figure 6.12**, the strength of intrinsic absorption increases progressively with the film thickness. Specifically, the absorption intensity in the  $10~14 \mu m$  range, corresponding to the vibration-induced absorption of the Si-Al-ON bond, shows a remarkable enhancement. This is attributed to the initially low quantity of Al-related counterparts capable of forming Si-Al-ON bonds when the film thickness is insufficient (due to short
deposition times and the low deposition rate of AlN). The lack of Al elements is mitigated by extending the deposition time, which in turn promotes the formation of Si-Al-ON bonds during film growth, leading to a stronger response from 10 to 14  $\mu$ m. Additionally, the absorption peak at approximately 8  $\mu$ m increases linearly with film thickness, suggesting a proportional increase in the number of Si-O bonds with deposition time.



Figure 6.12 IR absorptivity of the SiAlON composite with various film

thickness.

According to **Figure 6.13**, an obvious bandwidth broadening is observed with the top layer thickness growth, resulting in a continuous enlargement in the average emission in the AW, as listed in **Table 6.1**. This matches the guidance of the PSO program, indicating a thicker top layer benefits the raise of average emission within the AW by improving the absorbing capability in the  $10\sim14 \,\mu\text{m}$ range. The film system achieves an average emission of 0.8 with a 217 nm SiAlON layer, with potential for further optimization by increasing the film thickness to 427 nm, resulting in an emission of approximately 0.82. In this case, the top layer thickness is chosen to be approximately 300 nm to balance device miniaturization and emission performance enhancement.

 Table 6.1 Average AW emissions of the film system with various SiAlON layer

 thicknesses.

| Average emission in the AW (%) |
|--------------------------------|
| 79.21                          |
| 80.15                          |
| 80.62                          |
| 81.78                          |
|                                |

Moreover, increasing the top layer thickness results in a slight red shift of the peak location from 10.5  $\mu$ m (113 nm case) to 10.9  $\mu$ m (427 nm case). However, the absorption at approximately 9.5  $\mu$ m decreases significantly, contrary to the trend observed in single SiAlON layer testing.



Figure 6.13 IR absorptivity of the film system with a top layer thickness of 113

nm, 217 nm, 322 nm, and 427 nm.

### 6.3.4 Control via F-P resonance shifting

The performance of film systems taking Si-Al spacers with F-P resonant wavelength varies from 8.3  $\mu$ m to 10.8  $\mu$ m was measured, as shown in **Figure 6.14**. This is realized by changing the thickness of spacer from 330 nm to 400 nm, while remaining other structural parameters almost the same. The peak at 9.5  $\mu$ m appears in all cases, and the sample with a 380 nm thick spacer (F-P resonance at 10.1  $\mu$ m) shows the greatest intensity of ~94%. However, the intrinsic absorption-induced peak decreases to ~80% when the F-P resonance is moved to 8.3  $\mu$ m and 10.8  $\mu$ m. Thus, the significant decline in absorption at 9.5  $\mu$ m in **Figure 6.13** is derived from the red shift of the resonant wavelength. Additionally, **Figure 6.14** demonstrates that increasing the distance between these two peaks (i.e., intrinsic absorption and F-P resonance) broadens the absorption, thereby enlarging the average emission in the AW.



Figure 6.14 IR absorptivity of the film system with a spacer thickness of 330

nm, 380 nm, and 400 nm.

## 6.4 Cooling performance

Based on the previous analysis, the film with a simple double-layer structure exhibits great potential for cooling due to its highly selective IR emission within the atmospheric transparent window. To determine the actual temperature drop of the system, IR photography was employed to assess its cooling performance. The setup for IR photography is shown in **Figure 3.11**, wherein the sample was positioned 80 mm below the upper surface of a foam box to shield against direct sunlight and minimize absorbed solar irradiance. As illustrated in **Figure 6.15**, the average temperature of the sample was approximately 0.1°C, while the ambient temperature of approximately 4°C.



Figure 6.15 IR image of the film system.

According to **Figure 6.16**, this study achieves an average emissivity exceeding that of over half of the works listed in **Appendix A**. However, while the majority of reported studies demonstrate a temperature reduction of approximately 10°C, the temperature drop of this work remains suboptimal. This result further emphasizes the critical importance of optimizing short-wavelength reflectivity, as the high solar absorption of the sample significantly restricts its cooling

performance.



Figure 6.16 Comparison of cooling performance and emissivity between this study and previously reported works.

To further evaluate its cooling performance under different weather conditions, an apparatus was designed for the 24-hour outdoor direct thermal measurement, as depicted in **Figure 3.12**. Similar to the IR photography setup, the acrylic box was covered with aluminum foil to reflect the sunlight, and both the sample and the control group were positioned 120 mm below the PE cover.

Temperature data for the ambient, the chamber, the control group, and the sample during the 24-hour testing period in a dry sunny day (relative humidity 50~65%) were collected and plotted in **Figure 6.17a**. Due to its high emissivity in the AW, the film system sample maintained a temperature approximately 3°C lower than the ambient temperature during the night, as shown in **Figure 6.17b**. The wideband absorbent nature and high thermal conductivity of the Cu plate contributed to maintaining its temperature approximately 1.5°C lower than that

of the sample during the night. In contrast, the temperature of the Cu plate rose rapidly from 9°C to 50°C between 6:00 and 9:00 AM, while the film sample exhibited a comparatively gradual temperature increase in the morning, resulting in a maximum temperature difference of approximately 20°C by 10:00 AM. However, the destructive interference in 200~1600 nm (**Figure 6.6**) greatly limits the cooling performance of the film system. According to **Figure 6.17c**, the sample temperature reached approximately 60°C by 12:10 PM, coinciding with the peak solar irradiance intensity at noon.



Figure 6.17 (a) 24-hour temperature variation data for the ambient

environment, chamber, copper plate, and film system sample on a dry sunny day; (b) night-time temperature data from 20:00 to 02:00; and (c) day-time

temperature data from 08:00 to 14:00.

As illustrated in the insert of Figure 6.18, the atmospheric transmittance within

the 8~13 µm range significantly decreases as humidity rises from 40% to 90%. Specifically, the average transmittance drops from 70% (with a maximum value of 85%) to 33% (with a maximum value of 58%). This decline highlights the limitations of RC film performance under high-humidity conditions, which is further corroborated by theoretical temperature drop results obtained using a cooling performance prediction program (details in **Section 3.3.7**). In the simulation, the solar reflectivity was set at 90%, the target value, and the IR emissivity was 0.806, matching the experimentally measured value of the double-layer RC film sample. From **Figure 6.18**, the temperature difference between the sample and the ambient environment keeps decreasing from 2.8°C to -0.6°C as relative humidity increases from 40% to 90%, demonstrating that the efficiency of the RC film is significantly compressed under wet conditions.



Figure 6.18 Theoretical temperature drop under various relative humidity.

In addition, the experimental cooling performance of the RC sample was evaluated under dry cloudy day (relative humidity of 50~65%) and wet cloudy

day (relative humidity of 80~90%) to further investigate the impact of the testing environment. Notably, the impact of wind speed during the testing period was negligible, as the testing apparatus with PE cover and two-layer heat isolator (acrylic and foam boxes) was designed to prevent heat convection.



**Figure 6.19** 24-hour temperature variation data for the ambient environment, chamber, copper plate, and film system sample under two conditions: (a) dry

cloudy day and (b) wet cloudy day.

Similar to the dry sunny day conditions, the sample achieves a temperature drop of approximately 3°C during the nighttime on a dry cloudy day, see **Figure 6.19a**. In the early morning and late afternoon, the sample reaches a maximum cooling effect of about 1.5°C. However, during midday, the temperature of the sample slightly exceeds the ambient temperature due to sunlight, with a maximum temperature difference of 2°C. In contrast, the copper plate consistently exhibits temperatures higher than the ambient environment throughout the daytime, with a maximum temperature difference of 6°C at midday. As depicted in **Figure 6.19b**, the sample exhibits a temperature approximately 2°C lower than the ambient environment during the nighttime on a wet cloudy day. This diminished cooling effect is primarily attributed to the high humidity, in line with the simulated result in **Figure 6.18**. Additionally, the increased humidity contributes to a rapid temperature rise for both the sample and the copper plate under midday sunlight, resulting in temperature differences of 7°C and 14°C above the ambient temperature, respectively. Consequently, reducing the operating humidity represents an effective strategy for improving the cooling performance of the double-layer RC film.

### 6.5 Discussion

The double-layer film system integrates the intrinsic absorption of the SiAlON composite material with the F-P resonance generated in the Si-Al spacer. This combination produces wideband selective emission across the AW. Specifically, the intensity of the F-P resonance-induced absorption decreases with higher Al filling fraction and shifts in wavelength as the spacer thickness increases, directly influencing the overall system performance. Furthermore, the intrinsic peak around ~9.5  $\mu$ m shows a significant enhancement as it aligns with the F-P

resonance. Therefore, achieving selective emission within the AW hinges on precise control of the Al filling fraction in the spacer and the spacing between these two peaks (i.e., the thickness of both layers).

This work overcomes the complexity associated with achieving selective absorption across a broad bandwidth of 5 µm (8~13 µm) [275], thereby enhancing the potential for mass production. Reducing the overall thickness of the film system to 682 nm marks a breakthrough in device miniaturization, contrasting with most reported radiative coolers operating at micrometer scales due to longer target wavelengths [276]. Compared to the three-layer (Si<sub>3</sub>N<sub>4</sub>/Si/Al mirror) RC structure in Section 1.3 [38], whose selective IR absorption peak ranges from 8~13 µm has its maximum value ~90% at 9.5 µm, the optimized double-layer radiative cooler (SiAlON/SiAl) manifests higher peak value (97.5%) and average emission (0.806). Besides, as shown in Section 6.2.2, Figure 6.6, the absorptivity of the SiAlON/Si system from 400~1600 nm is approximately 20% higher than the SiAlON/Si-Al system, indicating SiAl spacer greatly optimizes the solar reflectivity. From the optical performance points of view, this work improves both the IR average emission and shortwavelength reflection through material updating.

However, the performance of the film system in the short wavelength range is still suboptimal due to the significant reflection valley induced by the Si matrix in the Si-Al spacer. Minimizing solar absorption, particularly in the visible range, is crucial to achieving a more substantial temperature drop. Addressing the challenge of reducing solar absorption has traditionally focused on two methods: integrating an IR-transparent solar filter [277] or ensuring the entire system is visible transparent [278]. Both approaches are applicable to this film system. The simplest method to enhance visible reflectivity involves covering the film with an organic reflective coating, although careful consideration is required to avoid compromising selective IR performance by introducing broad-spectrum absorption characteristics. Additionally, integrating a DBR composed of IR-transparent inorganic material is a viable solution. The DBR would not significantly add the overall thickness due to the short target wavelength, but precise fabrication is necessary to prevent shifts in the photonic band gap. Besides, the insertion of a nanometer-level DBR adds structural complexity to the film system.

Moreover, solar absorption can be directly minimized by replacing the Si matrix with a visibly transparent material. This alteration would render the entire system low-loss across a wide range of short wavelengths, with minimal visible light absorbed due to destructive interference on the surface of the Al NWs in the longitudinal direction. Notably, the low-intensity absorption caused by interference contributes to structural color formation, offering aesthetic benefits without compromising cooling performance for specific applications.

#### 6.6 Summary

In this study, an ultrathin selective inorganic radiative cooler comprising a lossy SiAlON layer positioned atop a Si-Al NWs spacer is designed, achieving an average emission of 0.806 within the atmospheric transparent window. The development of these two novel materials (i.e., SiAlON and Si-Al NWs structure) breaks the restriction of nature-existent materials, enabling enhanced optical performance in a simplified, ultra-thin double-layer film. The film system establishes an F-P cavity in the spacer layer to attain near-perfect absorption at approximately 10.8 µm, with a second-order resonance occurring within the secondary window at 3~5 µm. The resonance-induced absorption extends into the visible range, contributing to a colorful appearance of the sample. However, the corresponding absorption of solar energy limits its cooling performance. Additionally, the top SiAlON layer serves as both the absorber and the multiple reflector, thereby broadening the bandwidth and enhancing absorption. Furthermore, the strength and bandwidth of the main absorption peak are highly dependent on the strength of the F-P resonance and its proximity to the SiAlON intrinsic absorption peak, which can be finely controlled through adjustments in structural parameters such as layer thickness and aluminum filling fraction. Finally, the cooling performance of the film system was assessed through IR photography and thermal measurements under varying weather conditions. The results indicate that the double-layer radiative cooling film achieves a

temperature reduction of 3.9°C at a relative humidity of 40% under conditions with no direct sunlight. The cooling effect diminishes progressively as humidity increases, with a nighttime temperature reduction of 2°C observed at a relative humidity of 90%. Although the film system exhibits significant shortwavelength absorption, which limits its daytime cooling performance, this study represents a significant advancement in simplifying and miniaturizing inorganic radiative cooling systems.

## **Chapter 7 Conclusions**

This thesis investigated the microstructure and optical performance of a SiAlON/Si-Al NWs double-layer film system, aiming at fulfilling the dual-band regulatory requisites of RC, namely, minimal absorption within the solar radiation band and heightened emission within the atmosphere transparent window. To address this challenge, a selective absorbent material SiAlON was developed, achieving a wideband absorption from 8 to 16 µm. The optical performance of the SiAlON composite can be flexibly tuned by varying the depositing conditions, since the intrinsic absorbing property is highly dependent on the material composition. Besides, Si-Al NWs composite with high RI values was deposited, acting as a low-loss spacer material. Exceptional electromagnetic properties were achieved by incorporating aluminum nanowires into silicon, as evidenced by the metallic behaviors in the short-wavelength regime and dielectric properties in the IR spectrum range. Moreover, the adjustment towards the Al volume fraction directly determines the NWs structure, thereby realizing the optical property control of the Si-Al composite. After the development of the IR absorbing material and the spacer, these two novel materials were combined and constructed an ultrathin RC system. The contribution of each layer was detailly studied, followed by the investigation of the full-band performance modulation based upon the layer thicknesses and Al filling fraction variation.

Both the IR photography and 24-h outdoor thermal measurement were applied to get the temperature drop of the film system. The conclusions were drawn as follows:

- SiAlON exhibits wideband extinction features from 8 to 16 µm due to the combination of vibration modes of multiple chemical bonds, including N-Si-O, Si-Al-ON, and Al-O. A single-layer SiAlON film achieves a maximum absorption of approximately 27% with a thickness of only 490 nm. Furthermore, the performance of the composite can be tailored to the 8~13 μm range, with its absorption peak centered at 12 μm, through compositional modifications achieved by enhancing the oxidation effect of sputtered fragments via the introduction of reactive nitrogen gas N<sub>2</sub>. Besides, the dissociation energies of the relevant bonds must be carefully evaluated during ion-assisted sputtering, as they determine bonding preferences and influence the stoichiometric ratio and molecular structure of the resulting material, thereby directly affecting the influences the optical response of the composite. This phenomenon occurs because weaker bonds (i.e., nitrogen bonds) are more likely to break as ion impact energy increases, facilitating elemental substitution and the formation of more stable bonds (i.e., oxygen bonds).
- In consideration of the emphasis on selective absorption in  $8 \sim 13 \mu m$ , the Si<sub>3</sub>N<sub>4</sub> target is replaced with the SiO<sub>2</sub> target to enhance extinction capability

at ~8  $\mu$ m. The resultant product demonstrates strong absorption with multiple peaks at 8  $\mu$ m, 10  $\mu$ m, and 13  $\mu$ m, aligning precisely with the AW and fulfilling the requirements for absorbing materials outlined in **Objective 1**. From the above, the chemical intermixing method proves to be an effective approach for flexibly controlling the intrinsic absorption band of materials, including the peak position and bandwidth. The development of selective absorbent materials offers significant potential for simplifying the design of optical absorbers with tailored absorption selectivity, thereby enabling their broader application.

- The formation of Al NWs is attributed to the spontaneous phase separation between silicon and aluminum, which is strongly dependent on the filling fraction and surface diffusion length of the aluminum during the cosputtering process. The forming window of the NWs can be further broadened by manipulating adatom diffusion and reevaporation through ion bombardment, thereby modifying the microstructure and broadband optical properties of the composite.
- The insertion of the Al NWs enhances capacitance coupling, with its intensity directly proportional to the volume fraction of Al. The Si-Al NW system achieves a maximum Al volume fraction of 64%, corresponding to an effective RI value of 8. This RI value, exceeding twice the refractive index of silicon (3.4), satisfies the requirement for refractive index

enlargement as outlined in **Objective 2**. However, high Al% sample with strengthened coupling manifests correspondingly high Ohmic losses, leading to relatively large k value. Considering the requirement for low loss, the suitable Al filling fraction for constructing light confinement is approximately 50%, yielding an RI value of 6.2. Additionally, the composite exhibits typical dielectric properties in the mid-IR with an F-P resonance peak, which positively enhances the absorption of the upper absorbing layer.

- The double-layer film system is constructed using cost-effective materials, including Si<sub>3</sub>N<sub>4</sub>, AlN, Si, Al, and Al foil substrate, significantly enhancing its potential for mass production and widespread application. Furthermore, as outlined in Section 3.4, the deposition time for this 682 nm-thick RC film is only 400 minutes in the laboratory, which is 48 minutes shorter than the 770 nm-thick film reported in the literature (referenced in Section 1.3). Additionally, sputtering speeds can be further increased in industrial, where the upper power supply limits exceed those typically available in laboratory.
- Broadly, selective emission within the AW arises from the combined effects of F-P resonance in Si-Al spacer and intrinsic absorption of the SiAlON composite. Consequently, careful consideration of the peak locations is essential to achieve bandwidth broadening without compromising average absorption intensity. Compared to the Si<sub>3</sub>N<sub>4</sub>/Si system, this 682 nm-thick film system demonstrates effective selective absorption over a broader

bandwidth of approximately 5  $\mu$ m, attributed to the incorporation of the wideband absorbent SiAION composite, along with an enhanced average AW emissivity of 0.806. Furthermore, as Si approaches the RI limits of naturally existing IR transparent materials, this work successfully addresses the challenge of further thickness reduction (88 nm thinner than the Si<sub>3</sub>N<sub>4</sub>/Si system) through material innovation, while maintaining high levels of IR selectivity and emissivity. However, while the SiAION/Si-Al film system exhibits improved solar reflectivity compared to previously reported systems, the resonance-induced solar absorption remains substantial, exceeding the target of <10%. Consequently, future research should focus on optimizing performance in the short-wavelength region.

• IR photography demonstrates that the film system achieves a temperature reduction of approximately 3.9°C under winter daytime conditions with a relative humidity of 40%. The 24-hour temperature tests indicate nighttime cooling effect of the double-layer RC film sample, with a temperature reduction of around 3°C in low-humidity (50~60%) conditions and approximately 2°C in high-humidity (80~90%) environments. Thus, the temperature drop can be further increased in the dry environment, as high humidity level significantly compresses the cooling performance of the RC film. However, due to its notable solar absorption, the temperature of the RC film sample exceeds the ambient temperature during the daytime. The

temperature difference between the sample and the atmosphere is greater on sunny days compared to cloudy days, and this result also emphasizes the need for further improvements in short-wavelength reflectivity. Conversely, the film system exhibits selective IR emission and comparatively lower solar absorption compared to a copper plate, resulting in a slower temperature increase, with a maximum variation of 20°C observed during the daytime. This performance suggests that the RC film is suitable for application on highly solar-absorbent surfaces or systems, effectively reducing the rate of temperature rise.

# **Chapter 8 Future work**

Despite the satisfactory performance of this simple ultrathin film system in the IR regime, efforts must be made to minimize its solar absorption introduced by Si matrix in the Si-Al spacer. Meanwhile, the IR selective absorbing feature cannot be sacrificed. Consequently, three directions for further short-wavelength reflectivity optimization are proposed:

- The simplest approach involves introducing a commercial solar filter with low IR absorption. In this context, considerations must be given to the cohesion between the coating and the SiAION surface. Moreover, **Chapter 5** mentioned a method of fabricating ultrahigh porous Si by selectively etching the Al phase from the Si-Al nano-network sample, enabling the formation of an inorganic reflective coating. The nanoporous structure has the potential to achieve high scattering-induced reflectivity once shifting the matrix into a visible transparent material. This approach ensures better cohesion between the reflective coating and the film system, with minimal influence on IR performance. However, the increase in thickness, ranging from tens to hundreds of micrometers, poses a limitation on further integration.
- Design a DBR to block solar radiation from entering the film system. Similar to the radiative cooling system design, the optimization of the DBR

structure can be efficiently achieved using TMM and PSO algorithms in MATLAB. By focusing on the concentration of solar radiation within the visible light range (400~760 nm), the DBR structure can be simplified. This relatively short target wavelength range ensures that the designed DBR remains compact, significantly benefiting system miniaturization. However, the manufacturing process must be performed with nanometer-scale precision, as the reflective performance of the DBR is highly sensitive to thickness variations. This level of accuracy is crucial to achieving the desired light blocking effect and ensuring the overall effectiveness of the system.

Shifting the Si matrix to a wideband transparent material represents another viable method to reduce overall solar absorption, given the predominant role of Si in visible absorption. This requires the selection of an appropriate dielectric-metal system characterized by low solubility and high metal filling fraction. Additionally, careful consideration of sputtering parameters controlling the vertical growth of NWs is essential. It is noteworthy that a decrease in the spacer RI occurs as Si approaches the RI value bound of the transparent material. Consequently, this adjustment may lead to a corresponding increase in the overall fill metal fill metal to maintain optimal performance.

Furthermore, a broader range of manipulation of the optical constants of spacers

is essential for optimizing the performance of optical regulation devices across various applications. This involves extending the work on RI modulation through the incorporation of metal nanostructures to a wider material system, including altering the dielectric matrix and varying the types of inserted metals. Herein, employing dielectric materials with distinct intrinsic properties, such as lower loss or higher thermal stability, as the matrix enhances the overall performance and durability of optical devices. Similarly, varying the types of metals used for constructing nanostructures optimizes properties, such as controlling plasmonic resonance, allowing devices to be tailored for specific target wavelengths. By providing a versatile framework for the selection and integration of materials, this research demonstrates a comprehensive range of materials for specific applications and facilitates the development of highly efficient optical regulation devices. Dielectric-metal metamaterial-based devices can thus be customized for a wide range of applications, from enhanced RC systems to advanced photonic circuits and sensors. Moreover, the ability to tune optical constants across various materials and configurations within the dielectric-metal system highlights their potential for innovation and adaptation in optical engineering, addressing both current and future technological challenges.

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## Appendix A

| No. | Authers (year) | Materials                         | E <sub>AW</sub> | R <sub>solar</sub> | ΔT (°C) | Ref.  |
|-----|----------------|-----------------------------------|-----------------|--------------------|---------|-------|
| 1   | Hsu, P.C et    | Nano-PE                           | 90%             | /                  | 6.5     | [279] |
|     | al. (2017)     |                                   |                 |                    |         |       |
| 2   | Zhai, Y. et    | Ag/SiO <sub>2</sub>               | 93%             | 96%                | /       | [280] |
|     | al. (2017)     | particle in TPX                   |                 |                    |         |       |
| 3   | Li, T. et al.  | Wood                              | 90%             | 96%                | > 5     | [31]  |
|     | (2019)         |                                   |                 | 0.70/ /0           |         |       |
| 4   | Aili, A et al. | PVDF/PMMA,                        | 87%/            | 97%/9              | 6/4     | [165] |
|     | (2019)         | Ag                                | 82%             | 5%                 |         |       |
| _   | Gao, M. et     | PDM5,                             | 04%             | /                  | 77      | [24]  |
| 5   | al. (2019)     | adhesive. PET                     | 94%             | 7                  | 1.1     | [2+]  |
|     | Chen V et      | Si $\Omega_2$ sphere in           |                 |                    |         |       |
| 6   | al (2020)      | biomass fiber                     | 80%             | 95.5%              | 6       | [64]  |
|     | Li. D. et al.  | PEO fiber &                       |                 |                    |         |       |
| 7   | (2020)         | matrix                            | 78%             | 96.3%              | 5       | [172] |
| 8   | Zhu, R. et     | In <sub>2</sub> O <sub>3</sub> in |                 | /                  | > 7     | [181] |
|     | al. (2020)     | PMMA                              | 50%             |                    |         |       |
|     | Yang, Z. et    | Cr <sub>2</sub> O <sub>3</sub> in |                 |                    |         |       |
| 9   | al. (2020)     | HDPE                              | 86%             | 50%                | -3.3    | [187] |

 Table A.1 Summary of the published organic radiative coolers.

| 10 | Zhang, H.                         | Al <sub>2</sub> O <sub>3</sub> particles  | 060/ | 05%   | 51   | [211] |
|----|-----------------------------------|---|------|-------|------|-------|
| 10 | et al. (2020)                     | in PDMS   | 90%  | 93%   | 5.1  | [211] |
| 11 | Wu, W. et<br>al. (2020)           | PDMS  | 96%  | 92%   | 5.6  | [212] |
| 12 | Song, J et<br>al. (2020)          | PDMS with<br>morphology,<br>Ag  | 99%  | /     | /    | [213] |
| 13 | Zhao, X. et<br>al. (2020)         | VO <sub>2</sub> particles in PMMA   | 90%  | 5%    | ~5   | [214] |
| 14 | Xue, X. et<br>al. (2020)          | TiO <sub>2</sub> , glass,<br>fluorescent<br>particles in<br>polystyrene-<br>acrylates | 90%  | 93.4% | 6    | [216] |
| 15 | Wang, X. et<br>al. (2020)         | PVDF/TEOS framework   | 96%  | 97%   | 6    | [281] |
| 16 | Zhong, H.<br>et al. (2021)        | PVA,PVDF<br>fibric  | 94%  | 94%   | 9    | [208] |
| 17 | Zhang, Y.<br>and Yu, J.<br>(2022) | SiO <sub>2</sub> particles<br>in PVDF-HFP<br>fabric                                   | 94%  | 97%   | 15.9 | [282] |
| 18 | Li, M. et al.<br>(2023)           | TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub><br>nanoparticles<br>in PES          | 92%  | 97%   | 3~5  | [217] |

| 19 | Jeon, H. et<br>al. (2023) | Glass bubbles/<br>BaSO4 particle<br>in PDMS                       | 76.6%/<br>75% | 80.6%/<br>88.3% | 1~2    | [283] |
|----|---------------------------|---|---------------|-----------------|--------|-------|
| 20 | Ni, J. et al.<br>(2023)   | Al <sub>2</sub> O <sub>3</sub> particles<br>in nanoporous<br>PVDF | 94.3%         | 91.8%           | 8.3    | [284] |
| 21 | Zhou, K. et<br>al. (2023) | SiO <sub>2</sub> and ZnO in porous PE                             | /             | 92.1%           | 4.4    | [285] |
| 22 | Liu, S et al.<br>(2023)   | TiO2-PDMS,<br>Al2O3-PDMS,<br>rough PDMS<br>surface                | 97%           | 96%             | 5.2    | [286] |
| 23 | Li, X. et al.<br>(2024)   | BST nanorods in TPU fibric  | 93.2%         | 97.2%           | 10.3   | [218] |
| 24 | Lin, Y. et                | TiO <sub>2</sub> particles  | 85% to        | 90% to          | 6.5 to | [287] |
|    | al. (2024)                | in PVC  | 90%           | 93%             | 7.4    | [207] |
| 25 | Xin, Y. et<br>al. (2024)  | SiO <sub>2</sub> particle in catkin fiber                         | 84.4 %        | 94.5 %          | 6.2    | [288] |

| No.      | Authers (year) | Materials                               | E <sub>AW</sub> | R <sub>solar</sub> | ΔT (°C) | Ref.  |
|----------|----------------|---|-----------------|--------------------|---------|-------|
|          |                | α-quartz                                |                 |                    |         |       |
| 1        | Rephaeli, E.   | grating, SiC,                           | >50%            | <95%               | <8      | [29]  |
| 1        | et al. (2013)  | MgF <sub>2</sub> , TiO <sub>2</sub> ,   |                 |                    |         |       |
|          |                | Ag                                      |                 |                    |         |       |
|          | Raman, A.P.    | SiO <sub>2</sub> , HfO <sub>2</sub> ,   | -               | . –                | 4.9     | [225] |
| 2        | et al. (2014)  | Ag, Ti                                  | 70%             | 97%                |         |       |
|          | Hussain,       |   |                 |                    |         |       |
| 3        | M.M. et al.    | Alternate Al,                           | 87%             | 97%*               | 12.2    | [82]  |
|          | (2015)         | Ge layers                               |                 |                    |         |       |
| 4        | Zhu et al.     | Silica photonic                         | 88%             | 96.2%              | 13      | [158] |
|          | (2015)         | crystal                                 |                 |                    |         |       |
| ~        | Chen, Z. et    | Si <sub>3</sub> N <sub>4</sub> , Si, Al | 90%             | ,                  | 12      | [20]  |
| 5        | al. (2016)     |   | (max)           | /                  | 42      | [38]  |
| <i>.</i> | Zou C. et al.  | Doped Si                                | 77%             | 90%                | 10      | [99]  |
| 6        | (2017)         | arrays, Ag                              |                 |                    |         |       |
| _        | Kou, J. et al. | PDMS, SiO <sub>2</sub> ,                | 65%             | 97%                | 8.2     | [221] |
| 7        | (2017)         | Ag                                      |                 |                    |         |       |
| 8        | Alketbi, A.S.  | Si, porous                              | 80%             | 75%                | /       | [22]  |
|          | et al.(2018)   | SiO <sub>2</sub> , SiC, Ag              |                 |                    |         |       |
| 6        | Chen, D. et    | SiC                                     | 0.50 /          | ,                  | /       | [160] |
| 9        | al. (2018)     | metasurface                             | 97%             | /                  |         |       |

**Table A.2** Summary of the published inorganic radiative coolers.

| 10 | Lee, G.J.                 | SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> ,  | 70%         | 80%         | 3.9         | [227] |
|----|---------------------------|--|-------------|-------------|-------------|-------|
|    | et al.(2018)              | (Ag-SiO <sub>2</sub> )-Ag  |             |             |             |       |
| 11 | Ao, X.<br>et al.(2019)    | Ultra white<br>glass/<br>NaZnPO4 Ag  | 90%/<br>70% | 94%/<br>93% | 2.5/<br>1.5 | [220] |
| 12 | Yao, K. et al.<br>(2019)  | SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> ,  | 80%         | ~100%       | 11          | [224] |
| 13 | Liu, Q. et al.<br>(2019)  | Alternated Al,<br>MgF <sub>2</sub> , Ge<br>layers  | 80%         | /           | /           | [226] |
| 14 | Li, S. et<br>al.(2020)    | ZnS, Ge,<br>Nichrome   | 95%         | 25%         | /           | [162] |
| 15 | Chen, D. et<br>al. (2020) | SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> ,<br>Al <sub>2</sub> O <sub>3</sub> , Ag | 87%         | 94.8%       | 5.7         | [184] |
| 16 | Fan, X. et al.<br>(2020)  | Si <sub>3</sub> N <sub>4</sub> , SiC,<br>SiO <sub>2</sub> , BaSO <sub>4</sub>              | /           | /           | 12          | [196] |
| 17 | Xia, Z. et al.<br>(2020)  | SiO <sub>2</sub> particles,<br>PP, Ag, Cu  | /           | 99%         | 8           | [228] |
| 18 | Ma, H. et al.<br>(2020)   | Si <sub>3</sub> N <sub>4</sub> , SiO <sub>2</sub> ,<br>Ag                                  | 75%         | >98%        | 8           | [236] |
| 19 | Zhou, Y. et<br>al. (2021) | Ti, Ge,<br>(Si3N4), Ti   | 78%         | /           | /           | [161] |
| 20 | Lin, C. et al.<br>(2022)  | SiO <sub>2</sub> particles,<br>SiO <sub>x</sub> N <sub>y</sub>                             | 94.6%       | 96.4%       | 2.5         | [198] |

| 21 | Loke, S. et al. | NeXolv LaRC-                                       | 55.4% | 89.6% | /  | [239] |
|----|-----------------|--|-------|-------|----|-------|
|    | (2022)          | CP1  |       |       | /  |       |
|    |                 | polyimide, Ag                                      |       |       |    |       |
|    | Li Tatal        | Silica-alumina                                     |       |       |    |       |
| 22 | (2022)          | nanofibrous  | 93%   | 95%   | 5  | [229] |
|    | (2023)          | aerogels   |       |       |    |       |
| 23 | Liu, M. et al.  | Al <sub>2</sub> O <sub>3</sub> , VO <sub>2</sub> , | 21%/  | 88%/  | 5/ | [286] |
| 23 | (2023)          | SiO <sub>2</sub> , Al                              | 75%   | 85%   | /  | [200] |

SiO<sub>2</sub>, ITO,

\*The reflectivity is given by an additional reflector.

## **Appendix B**

## The physical reason for absorption difference between simulated and experimental results

The fitting error is the main reason of the intensity mismatching between the simulated and experimental results because the former is highly dependent to the input optical constants. The calculated intrinsic absorption of the single-layer absorber meets the curve of extinction coefficient, while the first-order resonant peak appears at  $\lambda = 4nd$ .

Herein, the optical constants of a 190 nm thick sample (the sample is deposited under the same conditions as the 490 nm case) is taken into calculation. The relatively low film thickness results in a slight reduction in the magnitude of both n and k, hence affect the simulated value. Besides, although the mean square error (MSE) in fitting procedures remains at a very low level (approximately 1), there are still some assumptions followed by ellipsometric analysis that result in the fitting inaccuracies:

- All the interfaces are abrupt and perfectly flat.
- All films and the substrate are uniform along the direction normal to the sample surface.
- The optical constants used for any layer in the model or the substrate are held fixed, which exactly describe the corresponding material in the sample.

The tested reflection of the sample is overestimated due to the calibration procedure, which results in the reduction of absorption.

## **Appendix C**

The innovation patents from this thesis are listed as the following:

- Junhua Gao, Yuxin Jiang, Zhilin Chen, Hongtao Cao, Hao Chen, An infrared selective absorption composite film with adjustable refractive index and its preparation method (一种折射率可调的红外选择性吸收复合膜及 其制备方法). CN114941129A (Innovation patent, Temporary approved).
- Hongtao Cao, Yuxin Jiang; Junhua Gao, Hao Chen, Zhilin Chen, Hui Xiong, A method for refractive index regulation of silicon-based material with low dispersion band. (一种低色散波段的硅基材料薄膜的折射率大幅调控方 法). CN117802465A (Innovation patent, Temporary approved).