Optical properties of titanium oxynitride thin films and application in selective solar absorber

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**NANYANG
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SINGAPORE

**OPTICAL PROPERTIES OF TITANIUM OXYNITRIDE THIN
FILMS AND APPLICATION IN SELECTIVE SOLAR ABSORBER**

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SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2018

**OPTICAL PROPERTIES OF TITANIUM OXYNITRIDE THIN
FILMS AND APPLICATION IN SELECTIVE SOLAR ABSORBER**

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School of Electrical & Electronic Engineering

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This thesis is dedicated to my parents and my wife.

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ABSTRACT

The selective solar absorber (SSA) is one of the key units in the concentrated solar power (CSP) system, which is promising for generating renewable and clean energy with solar energy. The titanium oxynitride (TiN_xO_y) thin film based SSA has drawn a lot of attention due to many advantages, such as environmental friendliness, low cost, and excellent optical property. In this thesis, the optical properties of TiN_xO_y thin films have been investigated and the SSA based on TiN_xO_y thin film has been designed and modeled.

The TiN_xO_y thin films were fabricated by radio frequency (RF) magnetron sputtering system and have been characterized systematically with various techniques: X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscope (AFM), transmission electron microscope (TEM), spectroscopic ellipsometry (SE), Hall effect measurement, spectrophotometer, etc. The localized surface plasmon resonance (LSPR) effect of the TiN nanoparticles, which were confirmed by high resolution TEM image, plays an important role in the optical properties of the TiN_xO_y thin films. Considering LSPR effect, free electron absorption and interband transitions, the dielectric function of the TiN_xO_y thin films was characterized by SE. It is found that the dielectric function of the TiN_xO_y layer is significantly affected by the N_2 flow rate during the sputtering deposition process as a result of the tuning of N/O ratio.

A single TiN_xO_y thin film based SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ has been designed. SiO_2 and TiO_2 thin films form a double-layer anti-reflection coating (ARC). A TiN_xO_y thin film serves as an absorbing layer. The optical properties of TiN_xO_y thin films can be easily adjusted by the N_2 flow rate, which is an effective way to optimize the performance of SSA. Due to the large free electron concentration, a Cu substrate is used as an infrared

reflector. The SSA based on the TiN_xO_y layer deposited with a N_2 flow rate of 2 sccm achieves a total solar absorptance of 94.44% and a total thermal emittance of 6.15% at the temperature of 400 °C.

A double TiN_xO_y thin films based SSA is also proposed in the thesis. In the SSA, a TiN_xO_y thin film with a low N/O ratio (TiNO_L) and a TiN_xO_y thin film with a high N/O ratio (TiNO_H) are utilized. At the same time, three absorption mechanisms in the TiN_xO_y thin films have been modeled: LSPR, free electron absorption and interband transitions. Because TiNO_H has a higher free electron concentration than that of TiNO_L, the absorption due to both the LSPR and free electron absorption in TiNO_H is found larger than that in TiNO_L. The absorption caused by the interband transitions in the TiNO_L and TiNO_H is close to each other. By using TiNO_L and TiNO_H, a double TiN_xO_y layer based SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiNO}_\text{L}\text{-TiNO}_\text{H}\text{-Cu}$ has been fabricated. It is found that the double TiN_xO_y layer based SSA has a wider low reflectance range than that of single TiN_xO_y layer based SSA.

A low cost and high thermal stable SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu}$ has been fabricated on glass substrate. In the SSA, to improve the thermal stability, W-Cu thin film structure is used to serve as an infrared reflector. Without W thin film, the reflectance in both visible and infrared ranges of the SSA increases due to the crystallization of the Cu layer at elevated temperatures. With a 15 nm W thin film, the increase of the reflectance in the visible range can be suppressed to maintain a high solar absorptance, while a high infrared reflectance can be maintained to achieve a low thermal emittance.

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LIST OF ABBREVIATIONS

ARC	anti-reflection coating
CSP	concentrated solar absorber
SSA	selective solar absorber
TES	thermal energy storage
HTF	heat transfer fluid
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
TEM	transmission electron microscope
AFM	atomic force microscope
SE	spectroscopic ellipsometry
LSPR	localized surface plasmon resonance
EMA	effective medium approximation
HRC	high-reflection coating
CVD	chemical vapor deposition
PECVD	plasma enhanced CVD
E-beam	electron beam
SEM	scanning electron microscope
TCO	transparent conductive oxide
FWHM	full width at half maximum
HRTEM	high-resolution TEM
SAD	selected area diffraction
MOSFET	metal oxide semiconductor field effect transistor
RF	radio frequency
UV	ultraviolet
IR	infrared
LCOE	levelized cost of electricity
MSE	mean square error
DNI	direct normal irradiance

LIST OF SYMBOLS

λ	wavelength of the light
ω	frequency of the light
q	electron charge
M	dipole moment
P	dielectric polarization
ε	dielectric constant
ε_1	real part of dielectric constant
ε_2	imaginary part of dielectric constant
D	electric displacement
ε_0	vacuum permittivity
ε_r	relative dielectric constant
N	complex refractive index
n	real part of the N
k	imaginary part of the N
α	absorption coefficient
E_g	bandgap
E_F	Fermi level
h	Planck constant
$h\nu$	photon energy
η	thermal conversion efficiency
α_{solar}	solar absorptance
α_{ts}	total solar absorptance
ε_T	thermal emittance
ε_{tt}	total thermal emittance
sccm	standard cubic centimeter per minute
$\tan(\Psi)$	amplitude ratio between p and s polarized light
$\exp(i\Delta)$	phase difference between p and s polarized light
ε_∞	high frequency dielectric constant

Chapter 1 INTRODUCTION

A thin film is a film in which one of the dimensions is much smaller than the other two dimensions and the thickness normally is less than 1 μm . Thin films include thin liquid films and thin solid films. In this thesis, thin solid films are simply called thin films. The deposition of thin films was pioneered in 1850 by M. Faraday, who used the electrodeposition technique [1]. With the help of vacuum technology, the development of thin films entered the modern era in 1950 [2]. Because the deposition of thin films can be well controlled under vacuum condition, thin films have been widely used in many applications, such as optical (e.g., anti-reflection coating (ARC) [3]), chemical (e.g., corrosion resistant coating [4]), electrical (e.g., thin film solar cells [5]), and mechanical (abrasion-resistant coating [6]) applications. In this chapter, some of the basic optical properties of thin film materials are introduced. Then, the application of thin films in the concentrated solar power (CSP) system is briefly described. In the motivation section, the reasons for investigating of the optical properties of TiN_xO_y thin films and the design of a TiN_xO_y layer based selective solar absorber (SSA) are given. Next, the objective, research scope, major contributions and organization of the thesis are presented.

1.1 Basic optical properties of thin film materials

When light shines on a thin film from free space, the physical phenomena of reflection, interaction and transmission occur, as shown in Figure 1.1 [7]. The magnitude of the reflection is represented by the reflectance, which is the ratio of the reflected optical power to the incident optical power. Then, light interacts with the atoms in the thin film. When the light reaches the back end of the thin film, some of the light transmits through the thin film,

which can be quantified by the transmittance, which is defined as the ratio of the transmitted optical power to the incident optical power. Due to the interaction between light and atoms, the optical processes occurring in the thin films are complicated and will be discussed in more details in the following section.

Figure 1.1 Occurrence of the physical phenomena of reflection, interaction and transmission when light shines on a thin film.

1.1.1 Interaction between light and thin films

When light propagates in a thin film, four major processes occur: refraction, absorption, scattering, and luminescence.

Refraction is caused by the different refractive indices between the film and the surrounding environment. For example, when light transmits from free space (i.e., the refractive index is 1) to a film with a refractive index of n , the velocity of light (v) in the thin film can be calculated with Eq. (1.1) [8]. Although the speed of light is changed in the thin film compared with the light speed in free space (c), the intensity of the light is not changed by refraction.

$$v = \frac{c}{n} \quad (1.1)$$

In the classical physical model, absorption is due to the resonant effect between the light and the transition frequencies of the atoms. Therefore, the intensity of light is reduced when

the light propagates in the thin film, and the attenuation process can be described by Beer's law, as shown in Eq. (1.2) [9].

$$I = I_0 e^{(-\alpha z)}, \quad (1.2)$$

where I is the intensity of light propagating a distance (z), I_0 is the initial intensity of light, and α is the absorption coefficient.

Scattering can be understood through the quantum theory of light (i.e., photons). With the presence of defects and impurities in the thin film, scattering effects occur and can be classified into elastic scattering (i.e., the frequency of the photons is unchanged) and inelastic scattering (i.e., the frequency is changed) [10]. Therefore, the intensity of the incident light is also attenuated because of scattering.

Luminescence is the opposite process of light absorption. Upon absorbing the energy of the incident light, the atoms in the thin film are excited. Some of the photons may possibly be spontaneously emitted when the atoms jump from the excited state to the ground state. Normally, the emitted photons have a lower frequency than the absorbed photons, which is known as Stokes shift [11].

1.1.2 Classification of optical materials

According to different standards, there are many kinds of optical materials. In this thesis, three types of optical materials will be described: dielectric, metal and semiconductor.

A dielectric thin film normally has a transparent window (i.e., no absorption) in the visible and near-infrared ranges, and the refractive index changes slightly in the transparent region. Table 1.1 lists some dielectric materials and the relevant transparent regions [12]. In the ultraviolet and far-infrared ranges, the absorptions are attributed to the interband transitions and the vibrational absorption, respectively.

Table 1.1 Dielectric materials and relevant transparent regions [12].

Dielectric	Transparent region (μm)
SiO ₂	0.2 – 3
TiO ₂	0.45 – 5
Al ₂ O ₃	0.2 – 6
NaCl	0.21 – 20
Diamond	0.25 – > 80

Due to a large number of free electrons, metal thin films usually have a very high reflectance in the infrared range [13]. Because of the existence of interband transitions, the reflectance of metal thin films decreases in the visible region and drops rapidly in the ultraviolet region. For example, Figure 1.2 shows the reflectance of Cu thin films with a thickness of $1\ \mu\text{m}$ and the reflectance is very close to 100% in the infrared range.

Figure 1.2 Reflectance spectrum of a Cu thin film with a thickness of $1\ \mu\text{m}$ in the wavelength range of $0.2 - 25\ \mu\text{m}$.

The optical properties of semiconductors are very similar to those of dielectric thin films. As shown in Table 1.2, there is also a transparent window for semiconductors [12, 14]. The difference is that both the low edge and high edge are shifted to larger values. The lower limit is determined by the fundamental band gap in the semiconductor, and the upper limit is caused by the lattice absorption and free carrier absorption.

Table 1.2 *Dielectric materials and relevant transparent regions [12].*

Semiconductor	Transparent region (μm)
Si	1.1 – 15
Ge	1.8 – 23
GaAs	1.0 – 20
CdTe	0.9 – 14

1.1.3 Optical physics in thin films

As stated in the above section, interband transitions, vibrational absorption, and free carrier absorption are responsible for absorption in thin films. To aid in understanding the physics behind the optical properties of thin films, some important physical theories are briefly presented here and will be discussed in more detail in Chapter 2.

The electronic bands in the thin film are formed due to the overlap and interaction among valence electrons. Interband transitions occur between the electronic bands when the photons satisfy at least two requirements [13, 15]. One is that the photon energy must be larger than the band gap. The other is that the transition must be abided by the rule of momentum conservation. Because the electronic bands are continuous in a certain range, the absorption spectra caused by interband transitions are also continuous and the threshold is determined by the upper and lower limits of the electronic bands.

Phonons describe the atomic vibrations in a thin film. The resonant frequencies of the phonons are in the infrared wavelength range, in contrast to interband transitions, which

occur in the visible and ultraviolet regions [16]. The electronic states of the atoms in a thin film can couple with the phonons, and the electron-phonon interaction broadens the discrete electronic states to form continuous vibronic bands.

Free carrier absorption means that the excited free carriers (i.e., electrons or holes) jump in the same excited state (i.e., intraband) after absorbing photons. Therefore, free carrier absorption does not generate electron-hole pair and occurs in the low photon energy range (visible or near infrared range) [17]. However, as shown in Figure 1.2, the reflectance of metals, which have a large number of free electrons, is close to 100% in the infrared range. There is a frequency ω_p , called the plasma frequency, that determines the starting point of high reflectance (i.e., $\sim 100\%$) [18]. As a result, free carrier absorption occurs when the light frequency is larger than ω_p .

1.1.4 An interesting materials: TiN_xO_y thin film

TiN_xO_y thin film possesses the properties of metallic TiN and dielectric TiO_2 [19]. TiN is well known because of low resistivity, high hardness and gold-like colour, and has been used in many applications, such as electrode in microelectronics, protective coating for tools and barrier layer in integrated circuit chip [20]. Because the Fermi energy level is in Ti 3d electrons' valence band, the TiN_x presents metallic behaviour. TiO_2 is a famous photocatalytic material [21]. However, because the bandgap of TiO_2 is 3.2 eV, only the high energy UV light can be used to activate the photocatalytic activity. As shown in Table 1.1, TiO_2 is a dielectric material and transparent in the wavelength range of 0.45 – 5 μm . To utilize the visible light, the bandgap of TiO_2 is narrowed by doping with nitrogen [22]. In the catalyst application of TiN_xO_y thin film, the ratio of N/O is very low. If the ratio of N/O increases, the TiN_xO_y thin film can be employed as energy efficient glazing [23]. With the increase of the ratio of N/O, the properties of TiN_xO_y thin film can be tuned to metallic TiN. Therefore, the ratio of N/O can be adjusted in a very wide range. As reported by Chen etc.

[24], the TiN_xO_y thin film is fabricated by sputtering TiN target with variable O_2 gas flow rates and the N/O ratio was tuned from 16.3 to 0.7.

The properties of TiN_xO_y are very sensitive to the ratio of N/O, including crystal structure, bandgap, resistivity and optical properties. For example, M.F. Hasaneen found that the crystal direction of TiN doped with oxygen changes from $\langle 111 \rangle$ to $\langle 002 \rangle$ while the oxygen content increases over 15% [25]. In the Ref. [24], the TiN_xO_y thin films are fabricated by sputtering TiN target with Ar/O_2 gases, and the resistivity of TiN_xO_y thin films can increase from $10^{-3} \Omega\cdot\text{cm}$ to $10^6 \Omega\cdot\text{cm}$ when the flow rate of O_2 increase from 2 sccm to 5 sccm. With the increasing of oxygen content in the TiN_xO_y thin film, the reflectance decreases in the infrared wavelength range [32]. Therefore, due to the wide tuning range of physical, chemical and optical properties, the TiN_xO_y thin films with different N/O ratios can be used in a lot of applications, such as selective solar absorber [26], transparent electrodes [27], plasmonic materials [28], thin film resistor [29] and biomaterial [30]. Besides sputtering, TiN_xO_y thin film can also be fabricated by many other techniques, such as plasma-enhanced atomic layer deposition [31], ion assisted deposition [32], and metal organic chemical vapor deposition (MOCVD) [33].

1.2 Thin films' application in concentrated solar power system

In the past century, a large amount of fossil energy has been consumed to meet the requirements of worldwide industrialization. However, the energy crisis and environmental problems have now become global challenges. Developing renewable and clean energy is the best way to solve these problems [34], and solar energy is a very promising candidate for a sustainable and clean energy source [35, 36, 37]. Due to its advantages of low cost, high efficiency and dispatch-ability with the help of thermal energy storage (TES) system, concentrated solar power (CSP) has undergone tremendous progress in the past decades [38,39]. In CSP system, solar energy is collected by a concentrated receiver, which heats a

heat transfer fluid (HTF). Then, the thermal energy in the HTF drives a turbine to generate electricity or is stored in the TES system. CSP systems can be classified into four main types according to the concentrated receiver: parabolic trough, solar tower, linear Fresnel reflector, and parabolic dish [40]. Among these types, CSP systems with parabolic trough receivers occupy 80% of the CSP market [41], and a diagram of a CSP system with parabolic trough receivers is shown in Figure 1.3. To utilize solar energy, the first important part in the CSP system is the solar energy receiver, which is composed of heat collecting tubes and parabolic trough mirrors. The parabolic trough mirrors concentrate the light onto the heat collecting tube, which transfers the solar energy to the HTF.

Figure 1.3 Diagram of a concentrated solar power system with parabolic trough mirrors as the solar energy receiver [42].

Because the solar spectrum on the earth's surface is in the range of $0.3 - 2.5 \mu\text{m}$, the heat collecting tube should have the capability to absorb all solar radiation energy in this wavelength range [43], which means that the heat collecting tube should have a very low reflectance over a very wide wavelength range. Due to the concentration effect of the parabolic trough, the temperature of the heat collecting tube may increase to a few hundred degrees [44], causing a large amount of black body radiation in the wavelength range of a few micrometers. Therefore, the other requirement for the heat collecting tube is to minimize the black body emittance, and thus, the heat collecting tube should also have a very high

reflectance in the wavelength range of black body radiation. To satisfy these two requirements, a functional thin film coating, called a selective solar absorber (SSA), is deposited on the surface of the heat collecting tube [43, 45]. Figure 1.4 shows the reflectance spectrum of an SSA, the solar radiation spectrum and the black body radiation spectrum at a temperature of 400 °C in the wavelength range of 0.3 – 25 μm [46]. As shown in Figure 1.4, the SSA has a very low reflectance in the wavelength range of solar radiation (i.e., absorbing the solar energy as much as possible), and a very high reflectance in the wavelength range of black body radiation (i.e., reducing the thermal emittance as much as possible) [47]. Obviously, the performance of the SSA plays a very important role in the conversion efficiency of the CSP system.

Figure 1.4 Reflectance spectra of a selective solar absorber, solar radiation (AM1.5) and black body radiation (400 °C) in the wavelength range of 0.3 – 25 μm [32].

To achieve the required performance, multilayer thin films are utilized in the SSA. Generally, the multilayer thin films in the SSA are composed of three major parts: an anti-reflection coating (ARC), absorbing layer and infrared reflector layer [46]. A general schematic structure of an SSA is shown in Figure 1.5 [46]. Single- or multi-layer dielectric thin films (e.g., SiO_2 , Si_3N_4 , Al_2O_3 , etc.) are utilized to form the ARC [3, 48, 49]. As the core

part of the SSA, most absorbing layer structures are the composites of dielectric embedded with conductive nanoparticles, such as Cr-Cr₂O₃, Mo-Al₂O₃, and TiN-TiO₂ (i.e., TiN_xO_y) [50, 51, 52]. The infrared reflector is usually formed by a metal layer with very large free electron concentration (i.e., very high reflectance in the infrared range, for example, the Cu thin film in Figure 1.2), such as Cu, Mo, and Al [45].

Figure 1.5 General schematic structure of an SSA with an ARC, absorbing layer and infrared reflector on a substrate [46].

1.3 Motivation of TiN_xO_y thin film based SSA

To absorb solar radiation energy, the absorbing layer should have a large absorption coefficient in the solar radiation range. Simultaneously, to achieve high reflectance by IR reflector in the wavelength range of black body radiation, the absorbing layer should also be transparent or have a small absorption coefficient in that range. Because TiN_xO_y can be used as transparent electrodes for IR window [32], the light can transmit the TiN_xO_y thin film in the infrared range. At the same time, the TiN_xO_y thin film with high nitrogen content also has a large absorption coefficient in the solar radiation range as the TiN_x is served as the absorbing center. Therefore, the TiN_xO_y thin film is a potential candidate of absorbers in the SSA application. Besides the excellent stable physical and chemical properties [53, 54], the TiN_xO_y thin film also has the following three important properties: low fabrication cost, environmental friendliness and intrinsic high diffusion barrier ability.

Firstly, because of good uniformity and high adhesion, sputtering technique has become the major fabrication method for the thin film deposition in SSA. The TiN_xO_y thin film can

be deposited by using only one sputtering Ti/TiN target with N_2/O_2 reactive gases. Therefore, the fabrication cost of TiN_xO_y thin film is lower than the cost of composites of metal-dielectric (e.g., $Mo-Al_2O_3$, $Ni-Al_2O_3$, $Ni-SiO_2$, etc.), which are usually fabricated by co-sputtering techniques. In any clean and renewable energy system, the cost determines the market share in future. Currently, compared with other renewable energy technologies (e.g., photovoltaic cells, wind, hydro, etc.), the levelized cost of electricity (LCOE) of CSP is still high, in the range of tens of US cents per kWh [55]. Therefore, reducing the cost of CSP system is a major target for researchers. Secondly, the TiN_xO_y thin film has a good environmentally friend property. Because TiN_xO_y thin films are widely used in biomedical applications [56, 57], its environmental friendliness has already been confirmed. This property provides TiN_xO_y thin films with the potential for special applications, such as water purification and desalination [58]. Thirdly, the TiN_xO_y thin film can be used as a good barrier layer for metals (e.g., Al) in an elevated temperature [59]. W. Sinke found that the diffusion performance between TiN and Al was improved significantly if the TiN was exposed to air before the Al deposition [60]. So the TiN doped with oxygen (i.e., TiN_xO_y) has a better diffusion barrier property for metals than that of TiN. Because metal thin films or substrates are used as an infrared reflector, good diffusion barrier property of absorbing layer plays an important role in the SSA. Therefore, TiN_xO_y thin film has attracted a lot of attentions in the SSA application [24, 32, 26].

In this thesis, design of an SSA based on TiN_xO_y thin film is the main motivation. However, very little research has been done on the optical properties of TiN_xO_y thin films, including the dielectric function and absorption mechanisms. To design a high-performance SSA, the optical properties of TiN_xO_y thin films must be well understood firstly.

1.4 Objective and research scope

The main objective of this work is to investigate the optical properties of TiN_xO_y thin film and to design a high-performance SSA based on TiN_xO_y thin films. The research works are listed as follows.

(1) A TiN_xO_y thin film based SSA is fabricated using radio frequency (RF) magnetron sputtering technique.

(2) X-ray photoelectron spectroscopy (XPS), X-ray power diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), and the Hall effect are used to characterize the chemical composition, crystal structure, material structure, surface morphology and free electron concentration of the TiN_xO_y thin film, respectively.

(3) The optical properties of the TiN_xO_y thin films are analyzed by spectrophotometer and spectroscopic ellipsometry (SE).

(4) The localized surface plasmon resonance (LSPR) effect in TiN_xO_y thin films is investigated.

(5) The effect of the N_2 flow rate in the deposition process of TiN_xO_y thin films is studied. Because the chemical composition of a TiN_xO_y thin film varies with the N_2 flow rate, the optical properties of the thin films are strongly affected by the N_2 flow rate.

(6) The performance of an SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ is optimized by tuning the optical properties of the TiN_xO_y thin films.

(7) To achieve high solar absorptance and low thermal emittance, a double-layer TiN_xO_y thin film structure based SSA is designed, and the absorption mechanisms in the TiN_xO_y thin films are investigated.

(8) By using a glass substrate, a low cost and thermal stable SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ is realized by optimizing the thickness of the W thin film.

1.5 Major contributions

This thesis focuses on the investigation of the optical properties of TiN_xO_y thin films and the design of a TiN_xO_y thin film based SSA. The major contributions are highlighted in the following.

- (1) The optical properties of TiN_xO_y thin film have been systematically investigated.
 - ❖ The absorption measurement showed two distinct absorption bands. One is in the low photon energy range ($\sim 0.5 - 2.5$ eV), which is due to the LSPR of TiN nanoparticles in the TiN_xO_y thin film; the other is in the high photon energy range ($\sim 3.5 - 5$ eV), which is due to the interband transitions of the TiN_xO_y thin film.
 - ❖ Considering the interband transitions, LSPR and free electron absorption, the Drude-Lorentz model was used to model the dielectric function of the TiN_xO_y thin film.
 - ❖ The effect of the N_2 flow rate in the sputtering deposition process was found to play an important role in the optical properties of the TiN_xO_y thin films.
- (2) A TiN_xO_y thin film based SSA has been designed for low- and middle-temperature applications.
 - ❖ An SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ was designed. By controlling the N_2 flow rate during the deposition of the TiN_xO_y thin film, the complex refractive indices of the TiN_xO_y thin film were optimized for obtaining a high performance SSA.
 - ❖ An SSA based on a structure with double TiN_xO_y thin films was proposed and fabricated. There are two absorbing layers: TiN_xO_y with a low N/O ratio (TiNO_L) and TiN_xO_y with a high N/O ratio (TiNO_H). In the absorption measurement, the absorbance of TiNO_L is much lower than that of TiNO_H.

The structure with double TiN_xO_y absorption layers allows the SSA to simultaneously achieve high solar absorptance and low thermal emittance.

- ❖ The absorption mechanisms in the TiN_xO_y thin film, including interband transitions, LSPR absorption, and free electron absorption, have been modeled.

(3) An infrared reflector with a tungsten and copper thin film was designed to obtain a high thermal stable SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$.

- ❖ Thermal annealing at the temperature of 400°C has a significant impact on the optical properties of the Cu thin film deposited by sputtering at room temperature. The changes in the optical properties of the Cu thin film seriously degrade the solar absorptance of the SSA without W thin film.
- ❖ A tungsten thin film with a thickness of 15 nm can effectively suppress the impact of the crystallization of the Cu thin film on the solar absorptance of the SSA.

1.6 Organization

There are 6 chapters in this thesis. A brief description of each chapter's content is presented as following.

Chapter 1: The basic optical properties of thin films and the application of thin films in the CSP system are briefly introduced. Follow by the motivation, the objective and research scope, and the major contributions.

Chapter 2: Some fundamental knowledge of thin film optical properties is presented, including dielectric function, effective medium approximation, interaction between light and thin film, and light absorption mechanisms in thin films. In addition, the fabrication techniques, characterization methods and applications of thin films are described in this chapter.

Chapter 3: The optical properties of the TiN_xO_y thin film have been investigated by spectrophotometer and SE. The chemical composition, surface morphology and material structure of TiN_xO_y thin film are characterized by XPS, AFM and TEM, respectively. At the same time, the effect of N_2 flow rate in the deposition process on the optical properties of TiN_xO_y thin film is discussed.

Chapter 4: Based on the TiN_xO_y thin film, two types of SSA have been proposed for low- and middle-temperature applications. The N_2 flow rate in the deposition process changes the chemical compositions of TiN_xO_y thin films, and the relationship between the complex refractive index and the N_2 flow rate has been investigated. Then, the performance of the TiN_xO_y thin film based SSA is optimized by changing the N_2 flow rate. In addition, the absorption mechanisms in the TiN_xO_y thin film are examined.

Chapter 5: A low cost SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ is developed. In the SSA, W-Cu thin films are used as the infrared reflector. TiN_xO_y thin film serves as the absorbing layer and SiO_2 is the anti-reflection layer. It is found that the W thin film plays an important role in the thermal stability of SSA. To optimize the SSA, the thickness effect of the W thin film on the optical properties is also investigated.

Chapter 6: The conclusions for the work in the thesis and recommendations for future work are presented in this chapter.

Chapter 2 LITERATURE REVIEW

This chapter focuses on the fundamental optical theories of thin films, including the dielectric function, the effective medium approximation (EMA) model, interference of light in the thin film, and light absorption mechanisms. Then, some important thin film fabrication techniques and characterization methods are reviewed briefly. Next, some optical applications of thin films are introduced, including ARC for Si solar cells, high-reflection coating (HRC) for mirrors, thin film solar cells, and SSA. A summary is given at the end of this chapter.

2.1 Fundamental optical theories of thin films

2.1.1 Dielectric function

The dielectric function, which depends on the wavelength (λ) of light, describes the interaction between a material and light [61]. Because light is electromagnetic waves, the positive part (i.e., atomic nuclei or positive ions) and the negative part (i.e., electrons or negative ions) of the material are separated in the presence of light. This effect is called dielectric polarization, which is classified into electric polarization, atomic polarization and orientation polarization [62]. As shown in Figure 2.1(a), although negative electrons are strongly bound to the positive nucleus, the spatial charge distribution of the atom can be changed with an applied electric field (E), and this effect is called electric polarization. In Figure 2.1(b), the material consists of positive ions and negative ions. The relative positions of the two kinds of ions are distorted by E , and this phenomenon is called atomic polarization. Orientation polarization means that the orientation of a molecule with atoms of different

electronegativities, that can move freely (e.g., H₂O), is tuned with the presence of E , as shown in Figure 2.1(c).

Figure 2.1 Diagrams of dielectric polarization with an applied electric field: (a) electric polarization, (b) atomic polarization, and (c) orientation polarization [62].

In all these polarizations, each pair of positive charge and negative charge is treated as an electric dipole with a dipole moment M , which is equal to $q \times x$ (where q is the electric charge and x is the distance between the positive charge and the negative charge.). The dielectric polarization (P) is the sum of all the dipole moments per unit volume, and the expression is given in Eq. (2.1) [62].

$$P = \sum_i M_i \quad (2.1)$$

The dielectric constant (ϵ) is defined as the magnitude of the polarization and is an indicator of the ability to store electrostatic energy. As shown in Figure 2.2, the structure of two parallel electrodes inserted with a thin film can be used to derive the relationship between ϵ and P . Note that the direction of P is defined from the negative charge to the positive charge, and the direction of E is from the positive electrode to the negative electrode. Therefore, P and E have the same direction, as shown in Figure 2.2.

Figure 2.2 The schematic structure of two electrodes inserted with a thin film. The directions of E and P are also indicated [62].

According to Gauss's law, the E within the two electrodes can be calculated with Eq. (2.2) [62].

$$E = D / \varepsilon, \quad (2.2)$$

where D is the electric displacement. Due to E , P is generated inside the dielectric. Therefore, within the dielectric, E can be expressed by Eq. (2.3).

$$E = (D - P) / \varepsilon_0, \quad (2.3)$$

where ε_0 is the free space dielectric constant with a value of 8.854×10^{-12} F/m. Combining Eqs. (2.2) and (2.3), the relative dielectric constant ε_r ($=\varepsilon/\varepsilon_0$) is obtained, as shown in Eq. (2.4).

$$\varepsilon_r = 1 + \frac{P}{\varepsilon_0 E} = 1 + \chi \quad (2.4)$$

Since P is induced by E , P can be expressed by the relationship $P = \varepsilon_0 \chi E$, and χ is called the dielectric susceptibility. Generally, ε_r is simply written as ε .

It is well known that because light is an electromagnetic wave, E is a time-periodic electric field, which has the expression of $E = E_0 \exp(-i\omega t)$. Therefore, the optical dispersion mode between light and the dielectric follows the harmonic oscillator model, which was given by H.A. Lorentz in 1985 [63]. The classical physical model is shown in Eq. (2.5).

$$\sum_j m_j \frac{\partial^2 x_j}{\partial t^2} + m_j \gamma_j \frac{\partial x_j}{\partial t} + m_j \omega_j^2 x_j = \sum_j q_j E(t), \quad (2.5)$$

where m_j is the mass of the dipoles, x_j is the displacement between the positive charge and negative charge, t is the time, γ is the damping constant, ω_j is the resonance frequency, and q_j is the electron charge. For the time-periodic $E(t)$, the solution of Eq. (2.5) is written as follows.

$$x_j = \frac{q_j E_0}{m_j (\omega_j^2 - \omega^2 - i \omega \gamma_j)} \quad (2.6)$$

Combining Eq. (2.1), (2.4) and (2.6), the dielectric function $\varepsilon(\omega)$ has the following expression.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = 1 + \sum_j \frac{N_j q_j^2}{\varepsilon_0 m_j (\omega_j^2 - \omega^2 - i \omega \gamma_j)}, \quad (2.7)$$

where N_j is the number of dipoles in a unit volume. If we define the plasma frequency ω_{pj} by Eq. (2.8), the equation of $\varepsilon(\omega)$ can be rewritten as Eq. (2.9).

$$\omega_{pj} = \sqrt{\frac{N_j q_j^2}{\varepsilon_0 m_j}} \quad (2.8)$$

$$\varepsilon(\omega) = 1 + \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i \omega \gamma_j} \quad (2.9)$$

In Eq. (2.9), if the numerator and the denominator of the second item on the right side are multiplied by $(\omega_j^2 - \omega^2 + i \omega \gamma_j)$, the real and imaginary parts of $\varepsilon(\omega)$ can be written as Eqs. (2.10) and (2.11).

$$\varepsilon_1(\omega) = 1 + \sum_j \frac{\omega_{pj}^2 (\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + (\omega \gamma_j)^2} \quad (2.10)$$

$$\varepsilon_2(\omega) = \sum_j \frac{\omega_{pj}^2 \omega \gamma_j}{(\omega_j^2 - \omega^2)^2 + (\omega \gamma_j)^2} \quad (2.11)$$

As mentioned above, the dielectric function $\varepsilon(\omega)$ is used to describe the interaction between light and the materials. To determine how light propagates in the material, the complex refractive index $N = n + ik$ is utilized. With the help of Maxwell's relation, ε and N have the following relationship [61].

$$\varepsilon = N^2 \quad (2.12)$$

Therefore, ε_1 and ε_2 can be calculated with n and k , as shown in Eqs. (2.13) and (2.14).

$$\varepsilon_1 = n^2 - k^2 \quad (2.13)$$

$$\varepsilon_2 = 2nk \quad (2.14)$$

2.1.2 Effective medium approximation model

The dielectric function of a single material was derived in the above section. However, there are some materials that are composed of two or more kinds of materials. Here, we consider a simple situation: a dielectric matrix (ε_m) embedded with well separated spherical inclusions (ε_i) [64]. Obviously, the dielectric function of the matrix-inclusion composite is determined by both the dielectric functions of the matrix and the inclusions. As a result, it is difficult to calculate the dielectric function with the method presented in the above section. To simplify the calculation of the composite dielectric function, a homogeneous material with the dielectric function ε_{eff} is established to replace the composite by using an effective medium approximation (EMA) model [65]. In the following, the relationship among ε_m , ε_i and ε_{eff} will be deduced.

As shown in Figure 2.3, a spherical inclusion is inserted in the dielectric matrix and is exposed to an external applied electric field (E) [62]. Due to the polarization effect, charges are distributed on the surface of the spherical inclusion. Inside the inclusion, the charges on the surface induce another electric field (E') and the value is given by Eq. (2.15) [66]. P has the same definition as in Eq. (2.4).

$$E' = \frac{4\pi}{3} P \quad (2.15)$$

Figure 2.3 The dielectric matrix (ϵ_m) with an inserted spherical inclusion (ϵ_i) in the presence of an external electric field (E) [62].

Therefore, the local electric field (E_L) inside the inclusion has the following expression [65].

$$E_L = E + E' = E + \frac{4\pi}{3} P \quad (2.16)$$

Assume that the number of spherical inclusions in the matrix is N_{inc} , and the polarizability is α_p . Then, the dielectric polarization P can be given with Eq. (2.17) [62].

$$P = N_{inc} \alpha_p E_L \quad (2.17)$$

Combining Eq. (2.16) and (2.17), we obtain Eq. (2.18).

$$P = \frac{N_{inc} \alpha_p E}{1 - \frac{4\pi}{3} N_{inc} \alpha_p} \quad (2.18)$$

The well-known Clausius-Mossotti relation is obtained by substituting Eq. (2.18) into Eq. (2.4) [62].

$$\frac{\epsilon_{eff} - \epsilon_m}{\epsilon_{eff} + 2\epsilon_m} = \frac{4\pi}{3} N_{inc} \alpha_p \quad (2.19)$$

For a spherical inclusion with a dielectric constant ϵ_i and radius r , α_p is written as Eq. (2.20) [65].

$$\alpha_p = \left(\frac{\epsilon_i - \epsilon_m}{\epsilon_i + 2\epsilon_m} \right) r^3 \quad (2.20)$$

By substituting Eq. (2.20) into Eq. (2.19), we obtain the famous Maxwell-Garnett model [67], as shown in Eq. (2.21).

$$\frac{\epsilon_{eff} - \epsilon_m}{\epsilon_{eff} + 2\epsilon_m} = f \left(\frac{\epsilon_i - \epsilon_m}{\epsilon_i + 2\epsilon_m} \right), \quad (2.21)$$

where $f (= N_{inc} \frac{4\pi}{3} r^3)$ is the volume fraction of inclusions in the matrix. Bruggeman gives us a more general form for ϵ_{eff} in Eq. (2.22) for n types of materials in the composite [68].

$$\sum_n f_n \frac{\epsilon_n - \epsilon_{eff}}{\epsilon_n + 2\epsilon_{eff}} = 0, \quad (2.22)$$

where f_n is the volume fraction of each material in the composite, and ϵ_n is the corresponding dielectric function.

2.1.3 Interference of light in thin films

Due to the different optical properties, when light travels from one medium to another medium, reflection and refraction occur at the interface. To explain how light interacts with a thin film, a simple optical model with only one thin film on a substrate is given in Figure 2.4 [62]. Assume that the thickness of the substrate is infinite. The complex refractive indices of the incident medium, thin film and substrate are N_0 , N_1 and N_2 , respectively. The thickness of the thin film is d , and the incident angle of light is θ_i . By using Snell's law, the transmission angle θ_t is equal to $\arcsin(N_0 \sin(\theta_i) / N_{thin})$. When light propagates at the interface between the incident medium and thin film, some of the incident beam I_0 is reflected to form beam B_0 and the rest of the I_0 transmits into the thin film. When the I_0 in the thin film encounters the interface between the thin film and substrate, a portion of it is bounced back into the thin film and transmits into the incident medium to form beam B_1 . As we can see, optical interference

occurs between beams B_0 and B_1 [62]. Of course, optical interference exists among the entire reflected beam (i.e., $B_0, B_1, B_2, \dots$) and transmitted beam (i.e., $T_0, T_1, T_2, \dots$).

Figure 2.4 A simple optical model with one thin film on a substrate [62].

As shown in Figure 2.4, all the reflected beams originate from point O, but have different travel paths. For example, if beam B_0 travels from point O to point W with the travel path $|OW|$, beam B_1 should have the travel path $|OM| + |MQ|$ to reach the same plane as beam B_0 . The phase difference (δ) between B_0 and B_1 , caused by the different travel paths, has the following expression [69].

$$\delta = K_{thin}(|OM| + |MQ|) - K_0|OW|, \quad (2.23)$$

where $K_{thin} (= 2\pi N_1 / \lambda)$ and $K_0 (= 2\pi N_0 / \lambda)$ are the propagation numbers in the thin film and incident medium, respectively. By using Snell's law, it is easy to obtain δ with Eq. (2.24).

$$\delta = \frac{4\pi d N_1}{\lambda} \cos(\theta_t) \quad (2.24)$$

Normally, we define the film phase thickness (β) as half of δ , and the expression of β is given in Eq. (2.25).

$$\beta = \frac{2\pi d N_1}{\lambda} \cos(\theta_t) \quad (2.25)$$

The amplitude reflection coefficient (r_{012}) is the sum of all the reflected beams ($B_0, B_1, B_2 \dots$) divided by the incident beam I_0 , and the amplitude transmission coefficient (t_{012}) is the sum of all the transmitted beams ($T_0, T_1, T_2 \dots$) divided by the incident beam I_0 . First, r_{jk} and t_{jk} are defined as the amplitude reflection coefficient and amplitude transmission coefficient from medium j to medium k , respectively. According to Figure 2.4, r_{012} and t_{012} are written as Eqs. (2.26) and (2.27).

$$r_{012} = B_0 + B_1 + B_2 + \dots = r_{01} + t_{01}r_{12}t_{10}e^{-i2\beta} + t_{01}r_{12}r_{10}r_{12}t_{10}e^{-i4\beta} + \dots \quad (2.26)$$

$$t_{012} = T_0 + T_1 + T_2 + \dots = t_{01}t_{12}e^{-i\beta} + t_{01}r_{12}r_{10}t_{12}e^{-i3\beta} + t_{01}r_{12}r_{10}r_{12}r_{10}t_{12}e^{-i5\beta} + \dots \quad (2.27)$$

It is well known that the limit of the infinite series $y = a + ax + ax^2 + ax^3 + \dots$ is $a/(1-x)$.

Therefore, Eq. (2.26) and Eq. (2.27) can be simplified to Eq. (2.28) and Eq. (2.29) [70].

$$r_{012} = r_{01} + \frac{t_{01}t_{10}r_{12}e^{-i2\beta}}{1 - r_{10}r_{12}e^{-i2\beta}}, \quad (2.28)$$

$$t_{012} = \frac{t_{01}t_{12}e^{-i\beta}}{1 - r_{10}r_{12}e^{-i2\beta}}, \quad (2.29)$$

where r_{jk} and t_{jk} can be calculated with the Fresnel equation according to different polarization states (i.e., p- or s-polarized), and the equations are given in Eqs. (2.30) – (2.33) [62].

$$r_{jk,p} = \frac{N_k \cos(\theta_j) - N_j \cos(\theta_k)}{N_k \cos(\theta_j) + N_j \cos(\theta_k)}, \quad (2.30)$$

$$r_{jk,s} = \frac{N_j \cos(\theta_j) - N_k \cos(\theta_k)}{N_j \cos(\theta_j) + N_k \cos(\theta_k)}, \quad (2.31)$$

$$t_{jk,p} = \frac{2N_j \cos(\theta_j)}{N_k \cos(\theta_j) + N_j \cos(\theta_k)}, \quad (2.32)$$

$$t_{jk,s} = \frac{2N_j \cos(\theta_j)}{N_j \cos(\theta_j) + N_k \cos(\theta_k)}, \quad (2.33)$$

where N_k and N_j are the complex refractive indices of media k and j , and θ_k and θ_j are the light angles in media k and j , respectively.

2.1.4 Light absorption mechanisms in thin films

As discussed above, the refractive index of a medium is normally given by the complex formula $N=n+ik$. The extinction coefficient k is used to describe the absorption phenomenon in the medium, and is related to the absorption coefficient α as shown in Eq. (2.34) [62].

$$\alpha = \frac{4\pi k}{\lambda} \quad (2.34)$$

In the following, some important light absorption mechanisms are discussed, including interband transitions, free electrons absorption, localized surface plasmon resonance.

2.1.4.1 Interband transitions

To understand the interband transitions, the quantum mechanics of the interaction between light and the medium are examined [71]. As shown in Figure 2.5, a simple energy diagram with an electron occupying lower band while upper band remaining empty, is given. The gap between the maximum of the lower band and the minimum of the upper band is called bandgap (E_g). For the interband transition to occur, the minimum required photon energy is E_g . The interband transition undergoes continuous absorption from the threshold energy E_g to the maximum value determined by the maximum of the upper energy band and the minimum of the lower energy band.

Figure 2.5 Simple energy diagram with an electron occupying lower band while upper band remaining empty. An electron excited by a photon jumps from the lower band to the upper band.

According to the band structure of the solid, there are two distinct bandgaps, called direct and indirect bandgaps, and their diagrams are shown in Figure 2.6 [71]. In the energy-wave vector (E - K) diagram, if the maximum of the lower band and the minimum of the upper band have the same K value, the band structure is called a direct bandgap; if the maximum of the lower band and the minimum of the upper band have different K values, the band structure is called an indirect bandgap. The two different band structures have significant effect on light absorption. In a medium with an indirect bandgap structure, the transition from the top of the lower band to the bottom of the upper band cannot occur if there is only a photon striking the electron. For electron excitation from the maximum point of the lower band to the minimum point of the upper band in the indirect gap medium, a phonon must be involved to maintain the momentum conservation [72].

Figure 2.6 Diagrams of the band structure: (a) direct bandgap and (b) indirect bandgap [71].

2.1.4.2 Free electron absorption

A dipole structure with bonded electrons is used to discuss the dielectric function. However, there are some materials with a large number of free electrons, such as metals or doped semiconductors [73]. For free electrons, there is no restoring force from the positive nuclei center when interacting with the electromagnetic wave (i.e., light) [71]. According to

Eq. (2.5), the physical model of Eq. (2.35) is utilized to describe the interaction between free electrons and light [71].

$$m_0 \frac{\partial^2 x}{\partial t^2} + m_0 \gamma_D \frac{\partial x}{\partial t} = qE(t) \quad (2.35)$$

Compared with Eq. (2.5), there are only two terms on the right side of Eq. (2.35). The first term represents the electron acceleration, and the second term is called the damping force of the material. Because there is no restoring force, the resonance frequency is zero. All the parameters in Eq. (2.35) have the same definitions as those in Eq. (2.5). According to the solving method discussed above, the dielectric function of the free electrons is shown in Eq. (2.36), which is known as the Drude model [74].

$$\epsilon_{Drude}(\omega) = 1 - \frac{\omega_{pD}^2}{\omega^2 + i\omega\gamma_D}, \quad (2.36)$$

where γ_D is the damping factor, ω_{pD} is the plasma frequency and the expression of ω_{pD} is shown in Eq. (2.37) [75].

$$\omega_{pD} = \sqrt{\frac{N_e q^2}{\epsilon_0 m_0}}, \quad (2.37)$$

where N_e is the free electron concentration, q is the electron charge, ϵ_0 is the vacuum permittivity, and m_0 is the electron mass.

To investigate the interaction between free electrons and light, a material with a large number of free electrons (i.e., metal) is considered first. In this case, γ_D is very small and is therefore negligible, and Eq. (2.36) can be written as Eq. (2.38).

$$\epsilon_{Drude}(\omega) = 1 - \frac{\omega_{pD}^2}{\omega^2} \quad (2.38)$$

From Eq. (2.38), it is easy to find that ϵ_{Drude} is negative when ω is smaller than ω_{pD} , and ϵ_{Drude} is positive when ω is larger than ω_{pD} . According to Eq. (2.12), the real part of the complex refractive index N is close to zero (i.e., The refractive index of metals with a large

number of free electrons, such as Ag, Au and Cu, is less than 1.0 in the infrared wavelength range.) for $\omega < \omega_{pD}$ and positive for $\omega > \omega_{pD}$. At normal incidence, the reflectance R can be calculated with Eq. (2.39) [76].

$$R = \left| \frac{N-1}{N+1} \right|^2 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2.39)$$

Therefore, the value of R is close to one when $\omega < \omega_{pD}$ (i.e., $n \approx 0$) and decreases when $\omega > \omega_{pD}$, as shown in Figure 2.7. This can be used to explain the reflectance spectrum of a copper thin film shown in Figure 1.2.

Figure 2.7 Reflectance spectrum of an ideal material with a large number of free electrons.

As a result, only when the light frequency ω is larger than ω_{pD} , there is a chance for the light to be absorbed by free electrons. The physical mechanism of free electron absorption is illustrated in Figure 2.8, which shows the conduction band of a doped semiconductor [71].

Figure 2.8 The physical mechanism of free electron absorption in the conduction band of a doped semiconductor [71].

Therefore, free electron absorption does not create an electron-hole pair, and the photon energy will disappear as thermal energy [73]. The Fermi level E_F is determined by the free electron concentration. Free electron absorption occurs when the electron from an occupied state below the E_F jumps to an unoccupied state above the E_F after absorbing a photon with energy $\hbar\omega$. As we can see from Figure 2.8, to stay in the conduction band, the excited electron still needs to have a displacement in the K axis. Therefore, a phonon (i.e., scattering event) is needed to conserve the momentum in the free electron absorption process [71].

2.1.4.3 Localized surface plasmon resonance

As mentioned in chapter 1, the absorbing layer in an SSA is normally formed with the composite of a dielectric matrix embedded with conductive particles (e.g., Au- Al_2O_3 , TiN- TiO_2 , etc.). The localized surface plasmon resonance (LSPR), which is caused by the conductive nanoparticles, plays an important role in the solar absorption of the SSA. Therefore, the LSPR effect of the conductive nanoparticles is briefly reviewed here.

LSPR occurs in conductive nanoparticles (e.g., Au-NP, CuS-NP, TiN-NP, etc.) dispersed in a dielectric matrix [77, 78, 79], so there are free electron clouds confined in the

nanoparticles. In certain cases, the free electron cloud resonates with the electromagnetic waves (i.e., light), as illustrated in Figure 2.9 [80].

Figure 2.9 Schematic of the free electron cloud of conductive nanoparticles resonating with the excitation of an electromagnetic wave [64].

The LSPR model and the EMA model have the same physical structure, i.e., a composite of a dielectric matrix embedded with nanoparticles. When the size of the nanoparticles is much smaller than the wavelength of the incident electromagnetic wave, the polarizability (α_p) of the spherical conductive nanoparticles in the dielectric matrix is the same as in Eq. (2.20). When the denominator of Eq. (2.20) is zero (i.e., the real part of conductive nanoparticles (ϵ_i) is equal to $-2\epsilon_m$), LSPR occurs in the conductive nanoparticles at a specific frequency. For metals, the dielectric function can be described with the Drude model, which is given in Eq. (2.36). Thus, the real part of the metal nanoparticles is shown in Eq. (2.40).

$$\epsilon_r(\omega) = 1 - \frac{\omega_{pD}^2}{\omega^2 + \gamma_D^2}, \quad (2.40)$$

where ω_{pD} is the plasma frequency and γ_D is the damping factor. Combining this with the relation $\epsilon_r = -2\epsilon_m$, the resonance frequency of LSPR can be obtained with Eq. (2.41).

$$\omega = \sqrt{\frac{\omega_{pD}^2}{1 + 2\varepsilon_m}} - \gamma_D^2 \quad (2.41)$$

The result of Eq. (2.41) is calculated based on the electric dipole induction mode. When the dimension of the nanoparticle grows such that the assumption that the dimension of the particles is much smaller than the incident light wavelength no longer holds, the multiple induction modes play important roles in the polarizability of the nanoparticles, which can no longer be described with Eq. (2.20). In the beginning of the 20th century, Mie developed a theory to solve the multiple induction modes for spherical nanoparticles [81, 82]. If the shape of the nanoparticles is not spherical, some numerical methods have been developed to calculate the absorption caused by LSPR, such as the discrete dipole approximation (DDA) [83], multiple multipole (MMP) method [84], and finite difference time domain (FDTD) method [75, 85].

From the above discussion, the resonance frequency of LSPR can be tuned by the free electron concentration of the nanoparticles, the nanoparticle shape and size, and the dielectric constant of the embedding matrix [86, 87]. Additionally, the free electron concentration has a significant impact on the LSPR frequency and determines the range of the resonance frequency, as shown in Figure 2.10. Due to the high free electron concentration in the range of $10^{22} - 10^{23} \text{ cm}^{-3}$, the LSPR frequencies of the Au-NP and Ag-NP are in the visible range [77, 88, 89].

Figure 2.10 The relationship between the resonance frequency of LSPR and the free electron concentration [78].

2.2 Thin film fabrication methods

Thin film deposition was pioneered by M. Faraday in 1850. With the development of various technologies, many techniques have been developed to deposit thin films. In Table 2.1, some important technologies are listed. The deposition rate, material type, advantages and limitations are also shown [90]. In the following, some widely used thin film fabrication methods will be briefly introduced, including sputtering, chemical vapor deposition (CVD), and evaporation.

Table 2.1 Techniques of depositing thin films [90].

Technique	Deposition rate(Å/S)	Material type	Advantages	Limitations
Electroplating	10 ² – 10 ⁴	Metals	Simple facilities	Metal substrate
Anodization	10	Insulator	Simple facilities, thin amorphous films	Metal substrate, limited number of metals, limited thickness
Sputtering	10	Metals, Insulators, Semiconductors	High adhesion, Large range of materials	Vacuum facilities, suitable targets
Chemical vapor deposition	1 – 10 ³	Metals, Insulators, Semiconductors	Single crystal	Vacuum facilities, high substrate temperature
Evaporation	10 – 10 ³	Metals, Insulators, Semiconductors	Large range of materials and substrates	Vacuum facilities

2.2.1 Sputtering

Because there are no limitations on the sputtering material and substrate, sputtering technology has been widely used for thin film deposition. The physical deposition process of sputtering includes three steps: bombarding the particles from the target by plasma ions (e.g., Ar^+ , O^+ , N^+ , etc.), transporting the particles to the substrate, and particle growth on the substrate. In the bombardment process, the particles are ejected from the target surface by bombardment with energetic ions. Normally, these ions are argon ions (Ar^+). As shown in Figure 2.11, the ions can penetrate the target with a few atomic radii and transfer the momentum energy to the particles [91].

Figure 2.11 Physical process of bombarding a material surface with energetic Ar^+ [91].

The simplest method to generate the bombarding ions is to use the plasma of a DC glow discharge. However, DC sputtering can only be utilized for depositing conductive materials. If an insulator target is sputtered with DC glow discharge, the positive surface charges will be quickly built up on the target surface, which prevents other ions from impinging the target. To sputter an insulator target, RF sputtering technology has been developed. Because a magnetic field has the capability of constraining the bombarding ions (e.g., Ar^+) in a certain area, which increases the possibility of ions bombarding the target, RF magnetron sputtering

technology has been widely utilized. A schematic diagram of a RF magnetron sputtering system is shown in Figure 2.12. Thin film deposition by sputtering requires a pump to achieve a low-pressure atmosphere, which maintains high ion energy and reduces collisions between the material particles and air molecules. The RF magnetron sputtering system has been used in a wide range of applications owing to many advantages, such as good uniformity of the thin film on a large area substrate, high adhesion, and high deposition rate [92].

Figure 2.12 Schematic structure of a RF magnetron sputtering system.

2.2.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a very important process in the Si industry. It is used to deposit materials such as polysilicon for the gate of a metal oxide semiconductor field effect transistor (MOSFET), thick oxides for isolation, and nitrides for passivation [93]. As illustrated in Figure 2.13, there are three general steps for thin film deposition in the CVD process. First, the precursor gases are introduced into the reaction chamber. Second, with the

help of an external energy source, the gases react, and the products are absorbed on the substrate. Finally, the thin film grows and the byproducts are pumped out of the chamber.

Figure 2.13 Steps of thin film growth by chemical vapor deposition.

According to the energy source, a CVD can be classified as a thermal CVD, plasma-enhanced CVD (PECVD), photon-assisted CVD, or laser-assisted CVD. With the advantages of low temperature operation, high film density and good step coverage, PECVD has already been widely used. Normally, a PECVD system contains two parallel electrodes and the substrate is placed on the bottom electrode. With the RF power and gases, a plasma is generated between the electrodes. The plasma ions transfer energy to the reactive gases and dissociate the atoms into ions. Finally, the thin film is absorbed and grows on the substrate. The schematic structure of PECVD is shown in Figure 2.14.

Figure 2.14 Schematic structure of a PECVD system.

2.2.3 Evaporation

Evaporation is a kind of physical vapor deposition process, which transfers the high-energy atoms from a heated material source to a substrate in a vacuum chamber. The steps of the process are illustrated in Figure 2.15. First, the liquid or solid source material in the container is heated to a high temperature at which the atoms evaporate effectively. Second, the atoms of the source material evaporate into the chamber to generate the vapor. Third, the atoms of the vapor are transported and impinge the surface of the substrate. Finally, the thin film grows on the substrate. To guarantee uniformity, the substrate is continually rotated when depositing the thin film.

Figure 2.15 Diagram of thin film deposition by evaporation.

According to the energy source type, the evaporation process can be categorized as thermal evaporation or electron-beam (E-beam) evaporation. Thermal evaporation involves heating the materials with a refractory metal boat (e.g., W, Ta, Mo, etc.). Although the material of the refractory metal boat may dissolve in the target material, the melting problem has little effect on the thin film, as the evaporation coefficients of refractory metals are very

small. Currently, a state-of-the-art evaporation method is E-beam evaporation, which utilizes an electron-gun to heat the source material. Normally, an E-beam evaporation system contains one electron-gun and multiple crucibles in one chamber. By switching the crucibles, multiple thin film layers can be deposited continuously and easily with the E-beam evaporation system.

2.3 Thin film characterization methods

With the development of various technologies, many thin film characterization methods have emerged. In this chapter, the thin film characterization methods utilized in this thesis are briefly introduced with the following four categories: optical property, morphology, structure and chemical composition characterization.

2.3.1 Optical property characterization

2.3.1.1 Spectroscopic ellipsometry

In 1887, the ellipsometry technique was discovered by Drude [62]. With the development of the computer, ellipsometry has become increasingly powerful. The essence of ellipsometry is that the sample under inspect induces different changes on the amplitude and phase of polarized light (i.e., p- and s- polarized light) upon reflection or transmission. Normally, ellipsometry measurements are conducted in reflection mode, and thus, the substrate should be opaque or the reflection from the back of the substrate should be minimized. The basic structure of an ellipsometer is shown in Figure 2.16. With the help of a polarizer, the light source is divided into p- and s- polarized light. Then, the polarized light shines on the sample. Utilizing the analyzer, the p- and s- polarized lights are separated, and are finally detected by the detector.

Figure 2.16 Basic structure of an ellipsometer with polarized lights [62].

Spectroscopic ellipsometry (SE) measures the amplitude ratio (i.e., $\tan(\Psi)$) and phase difference (i.e., $\exp(i\Delta)$) between p- and s-polarized lights in a certain wavelength range, and the equation of the complex ratio of p- to s-polarized light ($\rho(\lambda)$) is written as Eq. (2.42) [62].

$$\rho(\lambda) = \frac{r_p(\lambda)}{r_s(\lambda)} = \tan(\Psi) \cdot \exp(i\Delta), \quad (2.42)$$

where $r_p(\lambda)$ and $r_s(\lambda)$ are the reflection coefficients of p- and s-polarized lights, and are given by Eqs. (2.30) and (2.31), respectively. Therefore, $\rho(\lambda)$ is a function of the complex refractive indices of the incident medium, thin films and substrate, and the thicknesses of the thin films. According to Eq. (2.12), the complex refractive index has a relationship with the dielectric function. As a result, by fitting the experimental and calculated Ψ and Δ , the optical properties and thicknesses of the thin films can be obtained.

In a special case, the sample is an ideal bulk structure (i.e., smooth surface with no thin film coating). The dielectric function of the bulk material can be directly calculated with the experimental data by Eq. (2.43) [94].

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2(\theta_i)[1 + \tan^2(\theta_i)(\frac{1-\rho}{1+\rho})^2], \quad (2.43)$$

where θ_i is the incident angle of light. The above equation is called the pseudo-complex dielectric function.

Because SE measures the amplitude ratio and phase difference information simultaneously, the resolution is very high. Additionally, SE does not require a vacuum environment and is a non-destructive technique. In addition to evaluating the optical constants and thicknesses of thin films, the application area of SE has already been expanded widely, to areas such as roughness measurement, composition analysis, and crystallinity characterization. Of course, there are some disadvantages of SE, such as indirect characterization of the optical properties, low spatial resolution (i.e., the spot size of light is in the range of millimeters.), and complicated data analysis for some samples with multilayer thin films. In summary, SE is a very important technique for characterizing the optical properties of thin films.

2.3.1.2 Ultraviolet-visible-infrared spectrophotometry

The ultraviolet-visible-infrared (UV/Vis/IR) spectrophotometry is used to measure the reflectance and transmittance of a liquid or solid medium as a function of wavelength. Generally, there are four main parts in a spectrophotometer: a light source, a monochromater, a lens system and a detector. According to the characterization mechanism, there are two kinds of spectrophotometer: single beam system and double beam system. In the double beam system, the light source is divided into two halves by a half mirror. One half of the light goes through the reference side and the other half passes through the sample. With the help of a special double beams system design, the intensity change of the light source is eliminated automatically. Therefore, the spectrophotometer with the double beam system is more accurate. The schematic structure of the measurement chamber is shown in Figure 2.17 [95].

Figure 2.17 Diagram of the measurement chamber of spectrophotometer with a double beam system [95].

In the double beam system, the measurement of reflectance can be conducted by the following steps. The intensities of reflected light of a reference and a sample are measured, and the expressions are given by Eq. (2.44) and Eq. (2.45), respectively [61].

$$I_{ref}(\lambda) = R_{ref}(\lambda) \cdot S(\lambda) \cdot Sens(\lambda), \quad (2.44)$$

$$I(\lambda) = R_{sample}(\lambda) \cdot S(\lambda) \cdot Sens(\lambda), \quad (2.45)$$

where $I_{ref}(\lambda)$ and $I(\lambda)$ are the intensities of the reflected light of a reference and a sample, respectively. $R_{ref}(\lambda)$ and $R_{sample}(\lambda)$ are the reflectance. $S(\lambda)$ is the spectral distribution of the light source, and $Sens(\lambda)$ is the sensitivity of the detector. $R_{sample}(\lambda)$ can be calculated based on Eq. (2.44) and (2.45), as in Eq. (2.46). Therefore, system errors caused by $S(\lambda)$ and $Sens(\lambda)$ are eliminated.

$$R_{sample}(\lambda) = \frac{I(\lambda)}{I_{ref}(\lambda)} \cdot R_{ref}(\lambda) \quad (2.46)$$

2.3.2 Morphology characterization

2.3.2.1 Atomic force microscope

Atomic force microscope (AFM) was invented by Bining and Quate in 1986 to scan the surface morphology by measuring the force between a probe and a sample surface [96]. AFM has already become a very common tool in many fields of science, such as physics, chemistry,

and biology. The principle diagram of an AFM is shown in Figure 2.18 [97]. The surface morphology is obtained by measuring the vertical and lateral deflection of a cantilever with the utilization of an optical lever, which amplifies the distance movement of the cantilever by reflecting a laser beam off the cantilever to the detector. By analyzing the beam position on the detector with a computer, the image information is obtained. Of course, some feedback circuits are used to control the cantilever.

Figure 2.18 Schematic diagram of AFM [97].

The probe on the cantilever is usually made of Si nitride or Si, with a pyramid shape with an end radius of a few tens of nanometers. In some special applications, the probe is coated with thin film materials, such as Au and Pt. According to the distance between the probe and the sample in the measuring process, AFM can be divided into three major modes: contact mode, non-contact mode and tapping mode. The working areas of the three modes are illustrated in Figure 2.19. Contact mode and non-contact mode work in the repulsive and the attractive regimes, respectively. Tapping mode has a working area between these two regimes.

Figure 2.19 The working areas of contact mode, non-contact mode and tapping mode in AFM [98].

With the help of the atomic force between the probe and sample, AFM has a very high resolution. Additionally, AFM is a three-dimensional technique that can not only measure the X-Y plane morphology with a resolution of 1 nm, but also measure the height along the Z-axis with a resolution of up to 0.1 nm. However, the obvious limitation of AFM is that it does not show the true sample surface morphology but instead gives information about the interaction between the probe and the surface, which depends on the aspect ratio of the probe.

2.3.2.2 Scanning electron microscope

By using a focused high-energy electron beam, scanning electron microscope (SEM) can reveal a wealth of information, such as surface morphology and chemical composition, from the interaction between the electron beam and the sample surface. The basic components of SEM include the electron gun, electron lens, sample stage, detector, computer, pump and controlling circuits. The schematic diagram of an SEM is shown in Figure 2.20 [99].

Figure 2.20 Schematic diagram of an SEM [99].

Because the electron beam has a smaller wavelength than visible light, the resolution of SEM is higher than that of an optical microscope. At the same time, the interaction between the electrons and the sample can provide a lot of useful information regarding the materials' characteristics. Generally, there are three kinds of useful electron signals: secondary electron signals, back-scatter electron signals and X-rays. Secondary electron signals are used to observe the topography. Due to the low electron energy, the secondary electrons can only be detected close to the sample surface. Back-scatter electrons are caused by elastic collisions between electrons and nuclei, and can be used to analyze the material composition. X-rays are generated by the recombination of electrons and holes and are utilized to determine the elemental composition.

2.3.2.3 Transmission electron microscope

The major difference between transmission electron microscope (TEM) and SEM is that the electron beam of the TEM must transmit through the sample. Therefore, the thickness of

the sample should be less than 100 nm, or the sample should be suspended on a copper grid. With an accelerating voltage in the range of 100 ~ 300 keV, TEM is very powerful and can be used to precisely and directly determine the physical structure of a material, including the crystal lattice, dislocation, boundary, etc. Taking 200 keV electrons as an example, the wavelength of the electron beam goes down to 2.5×10^{-12} m. The schematic structure of a TEM is shown in Figure 2.21 [100].

An electron gun is located at the top of the TEM, which emits electrons into the vacuum. Then, the lenses concentrate the electron beam to the proper size and location. After passing through the sample, the image is shown on a fluorescent screen. To guarantee good performance, TEM has very high requirements on the vacuum system.

Figure 2.21 Schematic structure of a TEM [100].

2.3.3 Structure characterization

As discussed above, TEM can be used to identify the structural properties. However, TEM is a very expensive instrument. To characterize the structures of materials, the X-ray diffraction (XRD) technique is generally utilized in many applications. Because the lattice constant of a material is on the order of a few angstroms, the wavelength of the electromagnetic wave, which can be diffracted by the atomic plane of a crystal, should have the same order as the material lattice constant. Therefore, X-rays are chosen to characterize the structural properties. In Table 2.2, the wavelengths of the $K\alpha$ radiation of some materials used in XRD are given.

Table 2.2 Wavelengths of the $K\alpha$ radiation of some target materials in the XRD system [101].

Target material	Wavelength of $K\alpha$ radiation (Å)
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

The principle of XRD can be explained by Bragg's law. As shown in Figure 2.22, the incident X-ray shines on the surface of the material and is diffracted with the same angle θ . Assume that the atomic plane distance of the materials is d .

Figure 2.22 Schematic diagram of X-ray diffraction occurring in the lattice of a material [102].

When the path difference of the adjacent incident X-rays meets the requirement of Eq. (2.48), constructive interference between the X-rays occurs. By detecting the intensity of the diffracted X-rays, the angle θ of the constructive point can be measured. Then, the plane space d can be calculated with Eq. (2.47) [100].

$$2d \cdot \sin(\theta) = m \cdot \lambda, \quad (2.47)$$

where m is an integer. XRD is a non-invasive technique, and has been used in many applications, such as identifying the crystalline phase and orientation, measuring the grain size, and determining the atomic arrangement.

2.3.4 Chemical composition characterization

X-ray photoelectron spectroscopy (XPS) is a powerful technique to analyze the chemical composition of a material and is also called electron spectroscopy for chemical analysis (ESCA). The principle of XPS is illustrated in Figure 2.23. All processes take place under ultra-high vacuum conditions. Monochromatic X-rays are shined on the sample. The electrons inside the atoms escape from the atoms after absorbing the photons from the X-ray. Then, the photon detector measures the kinetic energy (E_k) of the escaping electrons.

Figure 2.23 Schematic diagram of the XPS working principle [103].

As a result, E_k has a relationship with the photon energy ($h\nu$) of the X-ray, as shown in Eq. (2.48) [103].

$$E_k = h\nu - E_{BE} - E_{WF}, \quad (2.48)$$

where $h\nu$ is the photon energy, h is Planck's constant, ν is the frequency of the X-ray, E_{BE} is the binding energy, and E_{WF} is the work function. From the spectrum of E_k , which depends on the photon energy, XPS can easily identify the elements and the oxidation states. Due to the advantages of monochromatic X-ray and a single electron transition from the core level to the vacuum, XPS has extraordinary resolution. By using a sputtering gun, XPS can also characterize the depth profiles of the elements in a sample, which is especially useful in multilayer thin film structures.

2.4 Optical applications of thin films

Thin film technology has been used in many applications, such as optical, electrical, chemical, and mechanical applications. Here, the optical applications of thin film technology will be described, including anti-reflection coating (ARC) for Si solar cells, high-reflection coating (HRC) for mirrors, thin film solar cells, and selective solar absorber (SSA) for concentrated solar power (CSP).

2.4.1 Anti-reflection coating for Si solar cells

Recently, Si solar cells still occupy a large market share with 90% in the commercial solar cells [104]. Due to the high refractive index of Si (e.g., $n=3.88$ @ 632 nm), the reflectance of Si solar cells without any ARC or surface treatments is over 30% in the wavelength range from 300 nm to 1100 nm. To reduce the reflectance, ARC is commonly deposited on the surface of Si solar cells. With the advantages of low cost, good performance and excellent surface passivation, a single layer of Si_3N_4 with the thickness of ~70 nm is widely deposited on the Si solar cells as the single layer ARC [105]. However, the single

layer of Si_3N_4 only reduces the reflectance to zero at only one specific wavelength. To reduce the reflectance in a wider wavelength range (i.e., 300 – 1100 nm), two layers or multi layers ARC have been proposed, including high refractive index materials and low refractive index materials [106]. As shown in Figure 2.24, a low-cost triple-layer ARC has been designed with a graded refractive index profile of high refractive index – medium refractive index – low refractive index [48]. The high refractive index thin film is completed with a Si_3N_4 layer dispersed with high concentration Si nanocrystals. The medium refractive index thin film is obtained with another Si_3N_4 layer embedded with low concentration Si nanocrystals. The low refractive index medium is SiO_2 thin film.

Figure 2.24 Structure of a triple layer ARC on Si solar cells. RI stands for refractive index [48].

The triple layer-ARC was easily deposited on a Si substrate with PECVD. The required material compositions and layer thicknesses of the triple layer-ARC are achieved by controlling the reactant gases, gas flow rates, pressure, RF power, temperature, and the deposition time in the PECVD process. The refractive index of Si_3N_4 layer embedded with Si nanocrystals can be calculated with the Maxwell-Garnett EMA model, which is discussed previously. In Figure 2.25, the reflectance spectra of the Si substrate with triple-layer ARC, the Si substrate with single layer ARC and the Si substrate without ARC are shown in the wavelength range of 300 – 1100 nm. The arithmetical average reflectance measured in the wavelength range of 300 nm to 1100 nm of the Si substrate with triple layer-ARC is 5.6%,

which is significantly lower than that of the Si substrate without ARC (38.8%) and the Si substrate with single Si_3N_4 layer ARC (16.3%) [48].

Figure 2.25 The reflectance spectra of the Si substrate with the triple-layer ARC, the Si substrate with the single Si_3N_4 layer ARC and bare polished Si substrate in the wavelength range of 300 – 1100 nm [48].

2.4.2 High reflection coating for mirrors

Normally, a HRC is deposited on top of a metal substrate or metal thin film to increase the reflectance in a certain wavelength range. D. Glöß utilized a $\text{SiO}_2\text{-TiO}_2$ layer stack on an Al substrate to increase the reflectivity in the visible wavelength range [107]. The detailed structure is shown in Figure 2.26 (a), and the reflectance spectra of the bare Al substrate and the Al with a $\text{SiO}_2\text{-TiO}_2$ layer stack are given in Figure 2.26 (b).

After depositing the $\text{SiO}_2\text{-TiO}_2$ layer stack, the reflectivity of the mirror increases from 92% to 98% in the visible wavelength range. Due to the photocatalytic and photo-induced hydrophilic properties of the top TiO_2 layer, aluminum with a $\text{SiO}_2\text{-TiO}_2$ layer stack also has the advantage of being easy to clean [107].

Figure 2.26 (a) Al substrate with a SiO₂-TiO₂ layer stack HRC, and (b) the reflectance spectra of Al with an HRC and bare Al in the wavelength range of 400 – 800 nm [107].

In addition to increasing the reflectivity in the visible wavelength range, a mirror with high reflectivity in the solar radiation range (including ultra-violet, visible and infrared wavelength range) is desired for the parabolic trough mirrors in the CSP system. With the properties of formability and light weight, increasing attention is being paid to Al-based mirrors with HRC. In Figure 2.27, an Al-based mirror for CSP is shown [108]. The 3 μm anodized Al₂O₃ layer is used to protect the Al substrate from corrosion. The reflectance of the mirror is enhanced by the TiO₂-SiO₂-Al structure. The top 3 μm SiO₂ is deposited by sol-gel to serve as the protecting layer.

Figure 2.27 Schematic structure of an Al-based mirror for concentrated solar power application [108].

2.4.3 Thin film solar cells

Compared with the traditional crystalline Si solar cells, thin film solar cells have many advantages, such as low cost, flexibility, and being composed of abundant materials [109]. However, most thin film solar cells have lower conversion efficiency than crystalline Si solar cells. In general, thin film solar cells can be divided into inorganic and organic thin film solar cells [110, 111]. Thin film solar cells are fabricated by depositing thin films layer by layer on the substrate (e.g., glass, plastic, Al, etc.). Generally, there are four types of widely used thin film solar cells: amorphous Si (a-Si) solar cells, cadmium telluride (CdTe) thin film solar cells, copper indium gallium diselenide (CIGS) thin film solar cells, and organic thin film solar cells [61]. The schematic structures of the four types of thin film solar cells are shown in Figure 2.28. The common property of thin film solar cells is that a transparent conductive oxide (TCO) thin film is utilized as the electrode. There are many kinds of TCO materials, such as tin-doped indium oxide ($\text{In}_2\text{O}_3:\text{SnO}_2$, ITO), aluminum-doped zinc oxide ($\text{ZnO}:\text{Al}$, AZO), fluorine-doped tin oxide ($\text{SnO}_2:\text{F}$, FTO), and antimony-doped tin oxide ($\text{SnO}_2:\text{Sb}$, ATO) [112, 113, 114]. Normally, TCO materials have a transmittance of approximately 80% in the visible and near-infrared wavelength ranges. Because the thicknesses of all the thin films in thin film solar cells are in the range of tens of nanometers to a few micrometers, the

material cost can be greatly reduced. By using a simple roll-to-roll process, organic thin film solar cells can achieve low cost and large-scale production.

Figure 2.28 Schematic structures of thin film solar cells: (a) a-Si solar cells, (b) CdTe solar cells, (c) CIGS solar cells, and (d) organic solar cells [61].

2.4.4 Selective solar absorber

The technique of converting solar energy into thermal energy is promising for producing clean and renewable energy. To achieve high thermal conversion efficiency (η), a selective solar absorber (SSA) has been widely proposed in many applications, such as solar heating, concentrated solar power, and solar thermos-photovoltaics [115, 116]. The conversion efficiency η of the SSA, which works at temperature T and has concentration factor C , can be calculated with Eq. (2.49) [117].

$$\eta = \alpha_{solar} - \frac{\varepsilon_T \cdot \sigma \cdot T^4}{C \cdot I_s}, \quad (2.49)$$

where α_{solar} is the solar radiation absorptivity, ε_T is the thermal emissivity, σ is the Stefan-Boltzmann constant ($5.6696 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$), and I_s is the solar radiation intensity. To achieve high η , the SSA requires not only high absorption of solar radiation, but also low

emission of the blackbody radiation. With the utilization of Kirchoff's law, $\alpha_{solar}(\lambda)$ and $\varepsilon_T(\lambda)$ in the thermal equilibrium state can be obtained from the reflectance $R(\lambda)$ with Eqs. (2.50) and (2.51) [118, 119].

$$\alpha_{solar}(\lambda) = 1 - R(\lambda) \quad (2.50)$$

$$\varepsilon_T(\lambda) = \alpha_{solar}(\lambda) \quad (2.51)$$

According to Eq. (2.50), η decreases with an increase of the working temperature T . Therefore, the working temperature T should be low to obtain high η . The maximum efficiency of converting thermal energy into electrical energy, which is called Carnot efficiency η_c , can be calculated with Eq. (2.52) [120, 121].

$$\eta_c = 1 - \frac{T_L}{T_H}, \quad (2.52)$$

where T_H is the high temperature of the heat transfer fluid before converting the thermal energy into electricity, and T_L is the low temperature of the heat transfer fluid after converting the thermal energy into electricity. Therefore, a high working temperature of the SSA can lead to a high Carnot efficiency. As a result, there is a balance between the thermal transfer efficiency and Carnot efficiency.

According to the working temperature, the applications of SSA can be divided into low temperature applications ($T < 100^\circ\text{C}$), middle temperature applications ($100 < T < 400^\circ\text{C}$), and high temperature applications ($T > 400^\circ\text{C}$) [122]. In terms of the structure and material properties, there are generally six types of SSA: composite with the structure of dielectric embedded with conductive nanoparticles, semiconductor-metal stacks, multilayer dielectric-metal tandems, intrinsic absorbers, textured surface absorbers, and photonic-crystal-based absorbers [118, 123, 124]. The schematic diagrams of the six types of absorbers are shown in Figure 2.29 [118].

Figure 2.29 Schematic diagrams of six types of SSA: (a) dielectric-conductive nanoparticles composites, (b) semiconductor-metal stack, (c) multilayer dielectric-metal tandems, (d) intrinsic absorber, (e) textured surface absorber, and (f) photonic-crystal-based absorber [118].

Among the different types, the SSAs based on the composites with dielectric-conductive nanoparticles are widely used since there are many advantages, such as a high degree of design flexibility, high $\alpha_{solar}/\epsilon_T$, and wide range of material choices [46, 121, 125]. For SSAs constructed with composites, the dielectric candidates are oxides (i.e., SiO_2 , Al_2O_3 , Cr_2O_3 , etc.) and nitrides (i.e., Si_3N_4 , AlN , etc.), and the conductive nanoparticles are usually refractory metals (i.e., W, Cr, Ni, etc.) or transition metal carbide or nitride (TiC , TiN , etc.) [46].

2.4.5 TiN_xO_y thin film based SSA

Due to the stable chemical and physical properties, low fabrication cost, and environmental friendliness, TiN_xO_y thin film is a good candidate to be used as an absorber in an SSA for middle temperature applications [24, 118]. The TiN_x is the conductive nanoparticle, serving as the absorbing center, and TiO_y is used as the dielectric matrix. In

1991, a single TiN_xO_y thin film has been fabricated by activated reactive evaporation (ARE) for the SSA application, and it was found that the thickness and the oxygen content in the TiN_xO_y thin film affected the solar absorbance and thermal emittance significantly [126]. When the ratio of N/O is low, the optical properties of TiN_xO_y thin film are close to the optical properties of TiO_2 , which is not suitable to be used as an absorber due to the transparent property in the solar radiation range. When the ratio of N/O is high, the optical properties of TiN_xO_y thin film are close to TiN, which cannot be used as an absorber since most of the solar radiation is reflected back by metallic TiN. Therefore, the ratio of N/O in the TiN_xO_y thin film plays an important role in the SSA application.

To improve the performance, a single SiO_2 thin film is deposited on the top of TiN_xO_y thin film to serve as an ARC layer, and the SSA with the structure of $\text{SiO}_2/\text{TiN}_x\text{O}_y/\text{Cu}$ achieves high $\alpha_{\text{solar}}/\varepsilon_T$ (0.94/0.044) and can be thermally stable up to the temperature of 400 °C in the vacuum environment as the passivation effect of SiO_2 thin film [127]. A SSA formed by ZrNO and TiNO with a graded composition has been reported by A Rizzo, etc. [128]. With the help of a more complicated ARC with the structure of $\text{SiO}_2\text{-Si}_3\text{N}_4\text{-TiO}_2$, a TiN_xO_y thin film based SSA has been deposited by sputtering on Cu substrate and achieves a high solar absorbance of 97.5% and a low thermal emittance of 4.3% at the temperature of 100 °C [24]. A German company has already successfully commercialized a TiN_xO_y -based SSA, which has a high $\alpha_{\text{solar}}/\varepsilon_T$ (0.95/0.04) and is thermally stable up to 400 °C [129].

However, the TiN_xO_y based SSA degrades when the TiN_xO_y thin film is exposed to air at an elevated temperature. This is because N is replaced by O in TiN_xO_y due to the high reactivity between Ti and O atoms. When the annealing temperature is larger than 450 °C, the TiN_xO_y thin film becomes unstable even in a low pressure atmosphere, and the detailed degradation process has been reported by H. Schellinger [130]. To reduce the convective loss, the heat collecting tube is normally encapsulated in a glass tube, and the chamber between the

two tubes is vacuumed [131]. As a passivation layer, the ARC can improve the thermal stability of TiN_xO_y thin film [127]. Therefore, TiN_xO_y based SSA is still a good candidate for middle temperature applications while encapsulating in a glass tube.

2.6 Summary

In this chapter, the fundamental optical theories, fabrication techniques, characterization methods, and optical applications of thin films are presented. First, based on the classical Lorentz model, the dielectric function of a thin film is deduced. Then, EMA is proposed as a good method to solve the dielectric function of composite thin films. Considering the interference effect, the equations for the reflection and transmission coefficients are also obtained. Three major absorption mechanisms are briefly described: interband transitions, free electron absorption, and LSPR absorption. The second part of this chapter introduces three kinds of important thin film deposition techniques: sputtering, CVD, and evaporation. Third, the techniques for characterizing the optical, morphological, structural, chemical properties of thin films are described. Finally, the optical applications of thin films used in the ARC, HRC, thin film solar cells and SSA are given.

Chapter 3 INVESTIGATION OF OPTICAL PROPERTIES OF TiN_xO_y THIN FILMS

To design a TiN_xO_y thin film based SSA, the optical properties of TiN_xO_y thin film are investigated first. The TiN_xO_y thin films are deposited by RF magnetron sputtering from a pure TiN target with Ar and N_2 gases. The oxygen in the TiN_xO_y thin film is introduced by the residual oxygen or moisture in the sputtering chamber. Then, various techniques have been utilized to characterize the TiN_xO_y thin films, such as XPS, TEM, and SE. The chemical composition of TiN_xO_y thin film is determined by the XPS. The TEM confirms the existence of TiN nanoparticles in the TiN_xO_y thin films. The optical properties are characterized by SE and spectrophotometer. It is found that, there are two distinct absorption bands in the absorption measurement: one in the low photon energies of $\sim 0.5 - 2.5$ eV and the other in the high photon energies of $\sim 3.5 - 5$ eV, which correspond to the LSPR of the TiN nanoparticles in the thin films and the interband transitions in the TiN_xO_y , respectively. At the same time, it is shown that the N_2 flow rate in the sputtering process plays a significant role in the optical properties of the TiN_xO_y thin film. The summary is given at the end of this chapter.

3.1 Introduction

Due to the extraordinary optical and electrical properties, and chemical stability, TiN_xO_y thin films have been intensively studied in the past decades [132, 133]. The physical properties of TiN_xO_y thin films are between metallic TiN and insulated TiO_2 , and can be tuned by changing the ratio of N to O [134, 135]. Therefore, TiN_xO_y films can be considered

as a composite film containing metallic component (TiN) and dielectric (TiO_2); and the optical properties of the TiN_xO_y films could be dominated by the metallic TiN component. The N-rich TiN_xO_y thin films have been widely developed in optical, biomedical, electrical applications [56, 136, 137]. With the unique optical properties, TiN_xO_y thin films have been used as an absorber layer in SSA, which has a low reflectance in the solar radiation range and a high reflectance in the black body radiation range [24, 138]. TiN_xO_y thin films are also exceptionally promising plasmonic materials with tunable optical properties as the TiN nanoparticles exist in the thin films [139, 140]. It has been reported that TiN_xO_y films can be deposited by RF magnetron sputtering from a TiN target with only one reactive gas of O_2 [24]. Due to the existence of residual oxygen in the deposition chamber, TiN_xO_y films with around 30% of oxygen content can be also formed by reactive sputtering of Ti target with Ar/N_2 without purposeful introduction of O_2 gas [141].

When a large number of free electrons are confined in nano-structured materials (e.g., transition metal nitrides, metals, doped semiconductors, conductive metal oxides, etc.), LSPR could be excited by the optical radiation, leading to a strong light absorption and scattering [80, 140, 142], and the LSPR depends on the size and shape of the structures and the dielectric environment [143, 144, 145]. It has been reported that the TiN nanodisks with the diameters of 60 – 180 nm and disk thickness of 30 nm formed by electron-beam lithography show the LSPR with the resonance wavelength in the range of ~ 800 – 1200 nm depending on the diameter of the nano-disks [79]. Semi-shell TiN nano-structures exhibit a tunable LSPR with light [146]. Due to the plasmonic resonance in visible light range and intrinsic loss, a TiN absorber achieves an average absorption of 95% in the wavelength range of 400 – 800 nm [147].

In the TiN_xO_y thin films, the size of the TiN nanoparticles affects the electrical and electronic properties of the thin films, as it determines the mean free path of conduction

electrons (i.e., electron scattering at the grain boundaries) and the free-electron concentration [20]. Additionally, as an intermetallic compound, the optical properties of TiN are very sensitive to the stoichiometry [20, 148]. With a high concentration of free electrons in the TiN nanoparticles, LSPR could be also excited in the TiN_xO_y thin films. In this work, TiN nanoparticles are formed in the TiN_xO_y thin films deposited by RF sputtering of TiN target with zero oxygen gas flow rate, and the ratio of the nitrogen to oxygen in the TiN_xO_y thin films are changed by varying the N_2 flow rate during the deposition process, which leads to the change in the free-electron concentration. Absorbance measurement of the TiN_xO_y thin films shows that there is an absorption band in the photon energy range of $\sim 0.5 - 2.5$ eV, which is attributed to the LSPR of the TiN nanoparticles in TiN_xO_y thin films. Information of the LSPR behaviors has been obtained from the SE study, and the influence of the LSPR on the complex dielectric function of the TiN_xO_y has been examined also.

3.2 Fabrication of TiN_xO_y thin films

First, a Si substrate and a double-side polished silica substrate were cleaned in deionized (DI) water, acetone, isopropyl alcohol (IPA), and DI water sequentially for 10 minutes, respectively. Then the Si and silica substrate were dried with N_2 gas gun. The TiN_xO_y thin film deposition was carried out by RF magnetron sputtering of a pure 2 inch TiN target ($>99.9\%$ purity) with a Denton desktop sputtering system at room temperature in Ar/ N_2 environment. The deposition chamber was pumped down to 9×10^{-6} torr before the deposition. During the deposition, the Ar flow rate was maintained at 10 sccm, while the N_2 flow rate was set at 0, 3, 6 and 9 sccm, respectively. The sputtering power was maintained at 100 W. TiN_xO_y thin films with the thickness of ~ 60 nm were deposited on the following substrates for different types of measurements: the Si substrate for the measurements of XPS, Hall effect, AFM and SE; the silica substrate for the absorbance measurement; and a double side polished sodium chloride (NaCl) substrate for the TEM characterization.

3.3 Characterization of TiN_xO_y thin film

3.3.1 Chemical composition analysis by XPS

The chemical compositions of the TiN_xO_y thin films were examined with XPS (ESCALAB 250). In the XPS experiment, the sample surface was cleaned with 4 keV Ar^+ beam for 90 seconds to remove any contaminants before analyzing the elements in the thin films. The XPS spectra were calibrated by using the C 1s peak (285 eV) as the reference [149]. Figure 3.1 shows the XPS analysis for the TiN_xO_y thin film deposited only with Ar flow rate of 10 sccm. The survey scan of the elements in the thin films is shown in the Figure 3.1 (a). There are 4 kinds of elements in the thin films, including Ti, O, N and C. The presence of C 1s is due to the CO_2 absorption [150]. However, the intensity of C 1s is very weak. So the effect of CO_2 is negligible. Figure 3.1 (b), (c) and (d) show the high resolution deconvolution spectra of Ti 2p, N 1s and O 1s, respectively. It can be concluded from the XPS analysis that the Ti-O, Ti-N-O, and Ti-N states exist in the TiN_xO_y thin films.

Figure 3.1 XPS measurement of the TiN_xO_y thin film deposited only with Ar flow rate of 10 sccm: (a) survey scan, (b) Ti 2p, (c) N 1s, and (d) O 1s.

Although the films are deposited by sputtering a pure TiN target only with Ar/ N_2 gases, oxygen is still present in the films, which is due to the existence of residual oxygen or moisture in the deposition chamber [141, 151]. From the results of XPS, the relative atomic percentages of Ti, N, and O in the TiN_xO_y thin films with different N_2 flow rates are presented in Table 3.1. The presence of large amounts of oxygen content in the TiN_xO_y thin films deposited by a sputtering process without purposeful introduction of O_2 gas was also reported in other works [141]. There are three possible reasons responsible for the large amount oxygen existing in the TiN_xO_y thin films. Firstly, oxygen has stronger reaction ability than that of nitrogen with Ti ions [24]; and this oxygen would react with Ti in the films to oxidize. Secondly, the high environmental humidity (~70%) of Singapore supplies enough moisture. Because the sputtering system is open to public, the moisture enters into the chamber when changing targets or loading samples. Thirdly, the maximum power of the sputtering system is 100 W. So the deposition rate is low, which provides a long time for the reaction between oxygen and Ti. In future, one direct method of controlling the O_2 in the chamber is adding an N_2 glove box in front of the sputter system.

With the increase of N_2 flow rate from 0 to 9 sccm, the ratio of N to O in TiN_xO_y thin films decreases from 0.52 to 0.19, indicating that TiN content in the films decreases with the increase of N_2 flow rate. This is attributed to the decrease of deposition rate as a result of the nitriding effect of the TiN target by N_2 [141, 152]. With the decrease of deposition rate (in the present work, the deposition rate decreases from 2.29 to 1.14 nm/min with the increase of N_2 flow rate from 0 to 9 sccm.), the residual oxygen has more time to react with the Ti atoms and thus more oxygen is presented in the TiN_xO_y thin films.

Table 3.1 Relative atomic percentages of Ti, N, and O in the TiN_xO_y thin films obtained from the XPS analysis, and the ratio of N/O when the N_2 flow rate increases from 0 to 9 sccm.

	Ti	N	O	N/O
$\text{N}_2=0$ sccm	37.0%	21.6%	41.4%	0.52
$\text{N}_2=3$ sccm	38.0%	20.1%	41.9%	0.48
$\text{N}_2=6$ sccm	35.4%	17.2%	47.4%	0.36
$\text{N}_2=9$ sccm	35.4%	10.4%	54.2%	0.19

3.3.2 Electron concentration measured by Hall Effect measurement system

The concentration of conduction electrons in the TiN_xO_y thin films was measured with a Hall Effect measurement system (HL5500). To measure the carrier concentration, the sample of TiN_xO_y thin film on Si substrate with the size of $1 \times 1 \text{ cm}^2$ was used, and the four electrodes for Hall effect measurement were arranged as the Van der Pauw configurations [153], as shown in Figure 3.2.

Figure 3.2 Sample for Hall Effect measurement with four electrodes arranged as the Van der Pauw configuration.

The concentration of conduction electrons as a function of N_2 flow rate is shown in Figure 3.3. When the N_2 flow rate increases from 0 to 9 sccm, the concentration of conduction electrons decreases from $1.31 \times 10^{19} \text{ cm}^{-3}$ to $1.19 \times 10^{18} \text{ cm}^{-3}$. It is obvious that the N_2 flow rate

in the sputtering deposition process significantly affects the concentration of conduction electrons in the TiN_xO_y thin films. The conduction electrons of TiN_xO_y are mostly contributed by the TiN component. As shown in Table 3.1, the ratio of N to O of the TiN_xO_y thin films decreases with increasing N_2 flow rate, indicating that the TiN content decreases with increasing N_2 flow rate. The results of Hall Effect measurement confirm the decrease of the conduction-electron concentration with the increase of N_2 flow rate in the sputtering process.

Figure 3.3 Conduction-electron concentrations of the TiN_xO_y thin films obtained from the Hall Effect measurement.

3.3.3 Surface morphology characterization by AFM

The surface morphology of the as-deposited TiN_xO_y thin films on Si substrate was characterized with AFM (Bruker, Dimension Icon) in the tapping mode using a Si probe. The scan range of the AFM image is $1 \times 1 \mu\text{m}^2$. The AFM images of the thin films on the Si substrate deposited with various N_2 flow rates are shown in Figure 3.4. The AFM images show the existence of TiN_xO_y grains [56], and the average grain size is in the range of 14 – 25 nm. With the increase of the N_2 flow rate, we can see that the average grain size of the

TiN_xO_y decreases. Due to the TiN_xO_y grain morphology, some electrons are confined within the grains. Therefore, this kind of grain morphology of TiN_xO_y thin films creates a good condition for the generation of LSPR of TiN nanoparticles, which is confirmed by the high resolution TEM (HRTEM) image in the following section. The detail investigation of the LSPR effect of TiN nanoparticles will be discussed later in this chapter.

Figure 3.4 AFM images of the TiN_xO_y thin films on Si substrate with various N_2 flow rates of (a) 0, (b) 3, (c) 6, and (d) 9 sccm.

3.3.4 TiN nanoparticles observed with TEM

To investigate the TiN nanoparticles in the TiN_xO_y thin films, a HRTEM was used to characterize the TiN_xO_y thin films and the selected area diffraction (SAD) was carried out to analyze the crystal structure (JEOL 2010). To obtain the HRTEM image of the TiN_xO_y thin film, a crystalline $\langle 100 \rangle$ NaCl substrate with the purity more than 99.9% was used in the thin film deposition process [154]. The NaCl substrate has a size of $10 \times 10 \times 2$ mm, and the surface roughness is smaller than $100 \text{ \AA}$. The TEM sample of TiN_xO_y thin film on NaCl

substrate was prepared with wet stripping method [155]. Figure 3.5 illustrates the TEM sample preparation process of the TiN_xO_y thin films.

Figure 3.5 TEM sample preparation process for TiN_xO_y thin films.

Firstly, the sample (i.e., NaCl substrate with TiN_xO_y thin film) was put into a beaker with DI water to defoliate the TiN_xO_y thin film. The NaCl substrate was dissolved in the DI water and TiN_xO_y thin film was left in the water. Because the diameter of the TEM copper mesh grid is 3 mm, the TiN_xO_y thin film with the size of 1 cm^2 was broke into small pieces by the ultrasonic process. Then the sample of TiN_xO_y thin film was transferred to the TEM copper mesh grid by a pipette. The TEM sample of TiN_xO_y thin film was dried out by leaving it in the air at room temperature for several hours.

As shown in Figure 3.6, the HRTEM image indicates the existence of nanocrystalline structures in the TiN_xO_y thin film. The red circle area in the HRTEM image clearly shows the lattice of the nanoparticles and the size of the nanoparticles is $\sim 5\text{ nm}$. At the same time, the

SAD pattern of the nanocrystalline structures is shown at the bottom of Figure 3.6. The TiN crystal orientations including (111), (200) and (220) can be identified in the SAD pattern (JCPDS 38-1420) [57], suggesting that the nanocrystalline structures are TiN nanocrystals.

Figure 3.6 HRTEM image of the TiN_xO_y thin film deposited only with Ar. The bottom is the corresponding SAD pattern.

3.4 Optical characterization of TiN_xO_y thin films

3.4.1 Spectroscopic absorption measurement

Absorbance spectra of the TiN_xO_y thin films deposited on silica substrate were measured with an ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer (PerkinElmer

Lambda 950) in the wavelength range of 250 – 2500 nm. The absorbance spectra for TiN_xO_y thin films deposited with the N_2 flow rates of 0, 3, 6, 9 sccm are shown in Figure 3.7. As can be observed in the figure, in the measured photon energy range of 0.5 – 5 eV (i.e., the wavelength range is 250 – 2500 nm), all the absorbance spectra exhibit two distinct absorption bands: one in the low photon energy range of $\sim 0.5 - 2.5$ eV (i.e., the wavelength range is $\sim 500 - 2500$ nm) and the other in the high photon energy range of $\sim 3.5 - 5$ eV (i.e., the wavelength range is $\sim 250 - 350$ nm).

Figure 3.7 Experimental absorbance spectra in the wavelength range of 250 – 2500 nm for the TiN_xO_y thin films deposited with various N_2 flow rates: (a) 0 sccm, (b) 3 sccm, (c) 6 sccm, and (d) 9 sccm.

To compare the absorbance strength, the absorbance spectra of the TiN_xO_y thin films were normalized, as shown together in Figure 3.8. With the increase of the N_2 flow rate, the absorption band in the low photon energy range becomes weaker and the peak position shows

a blue shift; while the absorption band in the high photon energy range does not show very significant change.

Figure 3.8 Normalized absorbance spectra of the TiN_xO_y thin films in the photon energy range of 0.5 – 5 eV. The insert is a schematic illustration of electron cloud oscillating in the TiN nanoparticles under the influence of changing electric field of light.

The absorbance band in the low photon energy range is caused by the LSPR effect in the TiN_xO_y thin films and the reason can be explained with the above experimental results. First, as shown in the Hall Effect measurement results, there is a high concentration of free electrons in the TiN_xO_y thin films. Second, the AFM images show the TiN_xO_y thin films have a grain structure, which has the capability of constraining the free electrons within the grains. Additionally, the HRTEM image and SAD pattern confirm the existence of TiN nanoparticles in the TiN_xO_y thin films. The mean free path of conduction electrons is determined by the nanoparticle size. Therefore, with such high concentration of free electrons in the TiN nanoparticles, LSPR can be excited with the presence of light at the resonance energy. The schematic diagram of the free electrons oscillation is illustrated in the insert of Figure 3.8. At

the same time, it has been reported that for 30 nm thick 400 °C-grown TiN nanodisk arrays formed by electron-beam lithography, the LSPR resonance wavelength is in the range of ~ 800 – 1200 nm depending on the diameter of the nanodisks [79].

Therefore, the absorption band in the low photon energy range shown in Figure 3.8 is attributed to the LSPR in the TiN nanoparticles with the resonance wavelength in the range of ~ 960 – 1100 nm (photon energy of ~ 1.12 – 1.29 eV), which has a relationship with the N_2 flow rate in the sputtering deposition. With the increase of N_2 flow rates, the concentration of free electrons in the TiN_xO_y thin films decrease and plays an important role in the LSPR as discussed in Chapter 2. As expected, it is observed that a higher concentration of free electrons leads to a higher LSPR peak intensity. This is consistent with the observation that LSPR in quantum dots of semiconductor copper (i) sulphide is largely affected by the free carriers' concentration in the quantum dots (i.e., the LSPR absorbance intensity increases with the free-carrier concentration) [144]. As discussed later, the large absorbance in the high photon energy range is due to the interband transitions in the TiN_xO_y thin films.

3.4.2 Dielectric function modeling with SE

As introduced in Chapter 2, SE is a powerful technique with very high precision for optical property characterization [62]. To investigate the dielectric function, the SE measurements on the TiN_xO_y thin films deposited on Si substrate with various N_2 flow rates were conducted with an ellipsometer (J.A. Woollam VB-250) in the wavelength range of 350 – 1500 nm at the angle of incidence of 75°, and the experimental ellipsometric angles Ψ and Δ spectra with the N_2 flow rates of 0, 3, 6, and 9 sccm are shown in Figure 3.9. The Ψ and Δ have the same definitions with those in the Eq. 2.43.

Figure 3.9 Experimental and calculated ellipsometric angles (Ψ and Δ) for various N_2 flow rates: (a) 0 sccm, (b) 3 sccm, (c) 6 sccm, and (d) 9 sccm, respectively. The insert in (a) shows the three-phase model (i.e., air/ TiN_xO_y layer (grains + air voids)/Si substrate) used in the ellipsometric modeling.

Because the experimental Ψ and Δ are not directly related to the dielectric function or thickness of the thin film, it is necessary to create a model for the sample and the general solution procedure of SE is illustrated in Figure 3.10 [156].

Figure 3.10 General procedure of obtaining the dielectric function or thickness of thin film with SE [156].

Because the TiN_xO_y thin film can be considered as the composite of TiN and TiO₂, the optical model of TiN_xO_y thin film depends both on the TiN and TiO₂. First, a Drude-Lorentz model is usually used to describe the optical dispersion of TiN, where the Drude term and the Lorentz oscillators represent the intraband (i.e., free electron absorption) and interband transitions, respectively [20, 157]. There are various possible interband transitions in TiN, such as the transitions at the $\Gamma_{15} - \Gamma_{12}$, $X_5 - X_2$, $L_3 - L_3'$ points of the Brillouin zone which correspond to strong interband absorption at $\sim 2.3, 3.9, 5.6$ eV, respectively [20]. For TiN_xO_y thin film, the interband transitions may be dependent of the chemical composition and the nanocrystalline structures of the thin film.

In this work, the large absorbance in the high photon energy range (3.5 – 5 eV) shown in Figure 3.8 can be attributed to the interband transitions in the TiN_xO_y thin films. Here one Lorentz oscillator is used to represent the interband transitions. As discussed below, the modeling involving the Lorentz oscillator agrees well with the experimental results of ellipsometric spectra in the high photon energy range where the interband transitions occur. This indicates that one Lorentz oscillator can adequately represent the interband transitions in the photon energy of 3.5 – 5 eV. As the TiN_xO_y thin films exhibit a high concentration of conduction electrons, the Drude term is used to characterize the optical response of the free electrons in the thin films. Taking the contributions of the free electrons, LSPR and interband transitions in the TiN_xO_y thin films into account, the complex dielectric function ($\varepsilon = \varepsilon_r + i\varepsilon_m$, where ε_r and ε_m are the real and imaginary parts of the complex dielectric function ε , respectively) of the TiN_xO_y thin film is given with Eq. (3.1).

$$\varepsilon(E) = \varepsilon_{\infty} + \varepsilon_{Drude} + \varepsilon_{LSPR} + \varepsilon_{interbands} , \quad (3.1)$$

where ε_{∞} is the high frequency dielectric constant. The contribution of the free electrons is described by the Drude term and the expression is shown in Eq. (3.2).

$$\epsilon_{Drude}(E) = -\frac{E_p^2}{E^2 + i\Gamma_D E}, \quad (3.2)$$

where E_p is the plasma energy; E is the photon energy; Γ_D is the Drude damping factor. The contributions of the LSPR and interband transitions are represented by the following two Lorentz oscillators, respectively,

$$\epsilon_{LSPR}(E) = \frac{f_{LSPR} E_{LSPR}^2}{E_{LSPR}^2 - E^2 - i\Gamma_{LSPR} E}, \quad (3.3)$$

$$\epsilon_{interbands}(E) = \frac{f_i E_i^2}{E_i^2 - E^2 - i\Gamma_i E}, \quad (3.4)$$

where f_{LSPR} , E_{LSPR} and Γ_{LSPR} are the strength, resonance energy and damping (broadening) factor of the oscillator for the LSPR, respectively; and f_i , E_i and Γ_i are the strength, resonance energy and damping (broadening) factor of the oscillator for the interband transitions, respectively. As a result, the real part (ϵ_r) and imaginary part (ϵ_m) of the complex dielectric function of TiN_xO_y thin film can be calculated with Eqs. (3.1) – (3.4).

An ellipsometric modeling is carried out to fit the ellipsometric data (ellipsometric angles Ψ and Δ) shown in Figure 3.9. In the ellipsometric modeling, the TiN_xO_y thin film is treated as an effective medium layer consisting of TiN_xO_y grains and air voids as there may be some nano-gaps between the grains in the TiN_xO_y thin film; and the three-phase model (i.e., air/TiN_xO_y grains with air voids/Si substrate) is used, as illustrated in the insert of Figure 3.9(a). The effective complex dielectric function of the TiN_xO_y layer can be calculated with the Bruggeman effective medium approximation (B-EMA) [158]

$$\frac{\epsilon_{TiN_xO_y} - \epsilon_i}{\epsilon_{TiN_xO_y} + 2\epsilon_i} f = \frac{\epsilon_{air} - \epsilon_i}{\epsilon_{air} + 2\epsilon_i} (f - 1), \quad (3.5)$$

where ϵ_i is the effective complex dielectric function of the TiN_xO_y layer (i.e., TiN_xO_y grains + air voids); $\epsilon_{TiN_xO_y}$ is the complex dielectric function of the TiN_xO_y grains; ϵ_{air} is the dielectric

function of air; f is the volume fraction of TiN_xO_y grains in the TiN_xO_y thin film. By using Eqs. (3.1) – (3.4), the complex dielectric function $\epsilon_{TiN_xO_y}$ of the TiN_xO_y grains is calculated with the contributions of the intraband transition (the conduction electrons), interband transitions (the bound electrons) and the LSPR (the surface-bound charge density oscillations of the TiN nanoparticles) taken into account. The model parameters for the Drude term and Lorentz oscillators for the LSPR and interband transitions, layer thickness and air volume fraction are the fitting parameters in the fitting to the experimental ellipsometric angles (Ψ and Δ) in a wide wavelength range (in this work, 350 – 1500 nm). A procedure for ellipsometric fitting can also be found in other studies [158, 159]. The ellipsometric fittings for the TiN_xO_y thin films deposited with the N₂ flow rates of 0, 3, 6 and 9 sccm are shown in Figure 3.9 (a) – (d), respectively. Excellent agreement between the modeling and experiment has been achieved for all the TiN_xO_y thin film samples.

3.5 N₂ flow rate effect on the TiN_xO_y thin films

3.5.1 LSPR energy position shift

The LSPR energies (E_{LSPR}) obtained from the ellipsometric fittings for various N₂ flow rates are shown in Figure 3.11. As can be observed in the figure, E_{LSPR} increases with the N₂ flow rate, which could be due to the changes in the structural properties and dielectric environment (which could be affected by the non-conductive composition, e.g., TiO₂ in the TiN_xO_y thin films) of the TiN nanoparticles. It is well known that LSPR strongly depends on particle size, shape, and inter-particle spacing, which directly influence the restoring forces of oscillating electrons inside the particle [160, 161]. Numerical simulations show a strong dependence of the resonant energy on the morphology of noble metal particles [162, 163].

Figure 3.11 LSPR energy position as a function of N_2 flow rate.

The size effect on the LSPR energy position was experimentally demonstrated in the study reported in [79], where the well-defined TiN nanodisk arrays were formed by electron-beam lithography. Blue-shift of the LSPR peak with the decreasing particle size was observed in the study, e.g., for the TiN nanodisks grown at 400 °C, the LSPR peak absorption occurs at the wavelengths of ~ 800 nm (~ 1.55 eV) and ~ 1200 nm (~ 1.03 eV) for the smallest particles (60 nm) and the largest particles (200 nm), respectively [79].

In this work, the average grain size obtained from the AFM measurement decreases from ~ 25 nm to ~ 14 nm as the N_2 flow rate increases from 0 to 9 sccm. The grain size measurement suggests that the size of the particles is responsible for the LSPR decreases with increasing N_2 flow rate, which is also supported by the results shown in Table 3.1 that TiN content in the films decreases with increasing N_2 flow rate. As a result, the LSPR position increases from 1.03 eV to 1.27 eV as the N_2 flow rate increases from 0 to 9 sccm. This is consistent with the general observation of blue-shift of LSPR position when decreasing the size of conductive nanoparticles.

3.5.2 N_2 flow rate effect on LSPR strength

The strength of the LSPR oscillator (f_{LSPR}) obtained from the ellipsometric fittings for various N_2 flow rates are shown in Figure 3.12. The dependence of the normalized absorbance peak intensity in the low photon energy range on the N_2 flow rate is also shown in the figure. It can be observed from the figure that the strength of the LSPR oscillator decreases with the increase of N_2 flow rate, which is consistent with the dependence of the normalized absorbance peak intensity on the N_2 flow rate. This actually reflects the fact that the free-electron concentration of the TiN_xO_y thin films decreases with the increase of N_2 flow rate. As the concentration of the free electrons in the TiN_xO_y is lower, the LSPR absorbance intensity is lower and the strength of the LSPR oscillator is smaller.

Figure 3.12 LSPR strength (f_{LSPR}) and the normalized absorbance peak intensity as a function of the N_2 flow rate.

3.5.3 Evolution of plasma energy in the Drude term

Plasma energy (E_p) as one important parameter in the Drude term is directly related to the free-electron concentration. The relationship between E_p and the free electron concentration (N_v) is given by the Eq. (3.6).

$$E_p = \sqrt{\frac{N_v q^2}{\epsilon_0 m^*}}, \quad (3.6)$$

where q is the electronic charge; ϵ_0 is the free space permittivity; and m^* is the electron effective mass. The values of E_p obtained from the ellipsometric fittings for the TiN_xO_y thin films deposited with various N₂ flow rates are shown in Figure 3.13. For comparison, the conduction-electron concentration obtained from the Hall Effect measurement is also shown in the figure. As shown in Figure 3.13, both E_p and the conduction-electron concentration decrease with the increase of N₂ flow rate. Thus the decrease of E_p with the increase of N₂ flow rate can be attributed to the fact that there are less free electrons in the TiN_xO_y thin film deposited with a higher N₂ flow rate.

Figure 3.13 E_p as a function of the N₂ flow rate. The conduction-electron concentrations (N_c) obtained from the Hall Effect measurement are also included for comparison.

Assume that the free electron concentration (N_v) and the conduction-electron concentration (N_c) has the following relationship.

$$N_v = N_0 + N_c, \quad (3.7)$$

where N_0 is the concentration of those free electrons that do not contribute in the Hall Effect measurement. According to Eq. (3.6), the relationship between E_p^2 and N_c can be expressed by

$$E_p^2 = A(N_0 + N_c), \quad (3.8)$$

where $A=q^2/(\epsilon_0 m^*)$. The above assumption is reasonable as explained in the following. The free electrons in the metallic nanoparticles respond to the optical excitation; however, not all of the free electrons contribute in the Hall Effect measurement because some of the free electrons are confined in the nanoparticles (note that the metallic nanoparticles are embedded in the dielectric) and are not able to contribute in the current conduction. Therefore, the conduction-electron concentration (N_c) yielded from the Hall effect measurement should be smaller than the free electron concentration that is determined from the plasma energy E_p . The linear relationship between E_p^2 and N_c is observed in Figure 3.14. The value of N_0 obtained from the linear fittings is $2.93 \times 10^{18} \text{ cm}^{-3}$.

Figure 3.14 The relationship between E_p^2 and N_c .

3.5.4 Complex dielectric function in the low photon energy range

The LSPR of the free electrons in the TiN nanoparticles has a significant influence on the complex dielectric function of the TiN_xO_y thin films in the low photon energy range of 0.5 –

2.5 eV. Figure 3.15(a) shows the real part of the complex dielectric function due to the contribution of LSPR for various N_2 flow rates.

Figure 3.15 Real part of complex dielectric function in the low energy range of 0.5 – 2.5 eV: (a) the contribution of LSPR for various N_2 flow rates; and (b) individual contributions of the LSPR and Drude term for 0 sccm N_2 flow rate. The ϵ_r of the TiN_xO_y thin films deposited with 0 sccm N_2 flow rate and ϵ_r of bulk TiN are included in Figure 3.15(b) for comparison.

As can be observed in the figure, the real part of the complex dielectric function increases when photon energy decreases in the photon energy range of 0.5 – 1.5 eV (wavelength range of ~ 800 – 2500 nm); and such LSPR effect is reduced for a higher N_2 flow rate as a result of the decrease in the free electron concentration. For bulk TiN in the photon energy range, the experimental real part of complex dielectric function is negative [157]. However, as shown in Figure 3.15(b), the real part of the complex dielectric function of the TiN_xO_y thin films deposited with 0 sccm N_2 flow rate obtained from the above ellipsometric study is positive, which is partially due to the contribution of LSPR of the TiN nanoparticles (the oxide composition may play an important role also), as demonstrated in Figure 3.15(b).

On the other hand, as shown in Figure 3.16(a), the imaginary part of the complex dielectric function due to the LSPR contribution decreases with the increase of N_2 flow rate, which is the result of the decrease in the free electron concentration, being consistent with the effect of N_2 flow rate on the LSPR absorbance (Figure 3.8). Figure 3.16(b) shows that the imaginary part of the complex dielectric function of the TiN_xO_y thin films in the low energy range (0.5 – 1.5 eV) is indeed significantly affected by the LSPR contribution.

Figure 3.16 Imaginary part of complex dielectric function in the low energy range of 0.5 – 2.5 eV: (a) the contribution of LSPR for various N_2 flow rates; and (b) individual contributions of the LSPR and Drude term for 0 sccm N_2 flow rate. The ϵ_m of the TiN_xO_y thin films deposited with 0 sccm N_2 flow rate and ϵ_m of bulk TiN are included in Figure 3.16(b) for comparison.

3.6 Summary

In conclusion, TiN_xO_y thin films have been deposited by RF magnetron sputtering of TiN target with various N_2 flow rates. The XPS characterization confirms that the Ti-N, Ti-O, and Ti-N-O chemical states present in the thin films; the Hall effect measurement shows that the

conduction electron concentration of the TiN_xO_y thin films decreases with the increasing of N_2 flow rate; the AFM measurement suggests that TiN_xO_y thin films are formed by TiN_xO_y grains; and the TEM characterization shows the existence of TiN nanocrystals in the TiN_xO_y thin films. The absorbance spectra measured in the photon energy range of 0.5 – 5 eV (wavelength range of 250 – 2500 nm), exhibit two distinct absorption bands: one in the low photon energy range of $\sim 0.5 - 2.5$ eV (wavelength range of $\sim 500 - 2500$ nm) and the other in the high photon energy range of $\sim 3.5 - 5$ eV (wavelength range of 250 – 350 nm).

With the increase of the N_2 flow rate, the absorption band in the low photon energy range becomes weaker and shows a blue shift; while the absorption band in the high photon energy range does not show very significant change. The absorption band in the low photon energy range is attributed to the LSPR of the TiN nanoparticles in the TiN_xO_y thin films; while the large absorbance in the high photon energy range is due to the interband transitions of TiN_xO_y . By taking the contributions of the free electrons, LSPR and interband transitions into account, a model with a Drude term and two Lorentz oscillators is able to well fit the ellipsometric spectra in the photon energy range of $\sim 0.8 - 3.5$ eV for the TiN_xO_y thin films with various N_2 flow rates. The resonance energy and strength of the LSPR oscillator are accurately determined from the ellipsometric modeling. The resonance energy of LSPR is in the range of $\sim 1 - 1.3$ eV and blue-shifts with the increase of the N_2 flow rate; and the strength decreases significantly with increasing N_2 flow rate. The plasma energy yielded from the ellipsometric modeling shows a correlation with the conduction electron concentration obtained from the Hall Effect measurement. In the photon energy of 0.5 – 1.5 eV (wavelength range of $\sim 800 - 2500$ nm), the LSPR plays a significant role in the complex dielectric function of the TiN_xO_y thin films.

Chapter 4 DESIGN AND MODELING OF TiN_xO_y THIN FILM BASED SELECTIVE SOLAR ABSORBER

4.1 Introduction

As a clean and renewable energy technique, concentrated solar power (CSP) offers some unique advantages such as high energy-conversion efficiency, excellent thermal energy storage capability, and the potential to retrofit current coal power plants [164, 165]. In a CSP system, the selective solar absorber (SSA) plays an important role by absorbing solar energy as much as possible and reducing the black body emission energy as much as possible [46,166]. As introduced in chapter 2, different types of SSA have been reported [45].

A high-performance SSA is generally structured with three functional coatings: anti-reflection coating (ARC), absorbing layer, and infrared reflector [167, 168, 169]. With high mechanical, chemical and thermal stability, oxides and nitrides (e.g., SiO_2 , TiO_2 , Si_3N_4 , etc.) are usually selected to serve as an ARC [24]. Due to high thermal conductivity and high infrared reflectance, Cu or Al is utilized as an infrared reflector in the low and middle temperature SSA applications [24]. Stainless steel substrate with W or Mo thin film as an infrared reflector is applied in the high temperature applications [51, 170]. As the critical part in SSA, absorbing layer materials (e.g., metal-oxides composites (e.g. $\text{Cr-Cr}_2\text{O}_3$ [51], $\text{W-Al}_2\text{O}_3$ [171], Ni-NiO [172]), transition metal nitrides (e.g. TiN [173], TiAlN [174], HfN_x [175]), and transition metal oxynitrides (e.g. TiN_xO_y [24], NbTiON [176])) have been widely studied.

As the absorbing layer in the SSA, TiN_xO_y thin film has a lot of advantages, such as extraordinary optical properties, high hardness, good chemical and thermal stability, and environmental friendliness [130, 126, 24]. Furthermore, the absorption property of TiN_xO_y can be tuned by changing the N/O atomic ratio [134, 177]; for example, it was reported that the optical properties of the TiN_xO_y films fabricated by reactive mid-frequency magnetron sputtering from TiN target can be controlled in terms of the reactive gas flow rate [24]. This adds the flexibility to optimize the performance of SSA. However, because O_2 is much easier to react with metallic Ti as compared to N_2 , it is hard to vary N/O ratio in the TiN_xO_y by reactive sputtering of Ti target with the conventional mixed gases of N_2 and O_2 [178]. In this work, by utilizing the residual oxygen or moisture in the sputtering chamber, the TiN_xO_y thin film is deposited by sputtering TiN target with Ar and N_2 gases.

Because the TiN_xO_y thin film can be treated as the composite of TiN and TiO_2 [179], the conductive TiN serves as the absorption center while the TiO_2 is used as the dielectric matrix. This is similar to the metal-oxides composites, in which the metal nanoparticles are dispersed in the dielectric matrix. Recently, a composite absorbing layer with the structure of TiN- SiO_2 has already been reported for SSA in high temperature applications (700 °C) [121], and the TiN nanoparticles are used as the absorption center in the composite since they are able to induce absorptions caused by interband transitions, LSPR, and scatterings [180]. At the same time, the volume fraction of TiN nanoparticles in the composite has a significant effect on the optical properties of the TiN_xO_y absorbing layer. With a larger volume fraction of TiN nanoparticles in the TiN_xO_y thin film, the solar absorptance of SSA increases, but the thermal emittance increases also; and vice versa [181]. To achieve high solar absorptance and low thermal emittance at the same time, SSA with double absorbing layers (including a low absorbing layer and a high absorbing layer) has been reported [182, 183, 184]. In Section 4.3,

a double TiN_xO_y layer based SSA will be designed and the absorption mechanisms will also be analyzed carefully.

4.2 Design of a single TiN_xO_y layer based SSA

In this work, a high performance SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ has been developed. The TiN_xO_y absorbing layer is fabricated by RF magnetron sputtering of a pure TiN target with Ar and N_2 gases. The introduction of oxygen in the TiN_xO_y is realized by using the residual oxygen or moisture in the deposition chamber. It is found that the optical properties of the TiN_xO_y layer in a wide spectral region from ultra-violet (UV) to infrared can be significantly changed by changing the N_2 flow rate as a result of the change in the chemical stoichiometry of the TiN_xO_y thin films. Therefore, the performance of TiN_xO_y based SSA can be easily optimized by varying the N_2 flow rate. This provides a simple but effective way for the design of a high performance SSA. With the TiN_xO_y absorbing layer deposited with the N_2 flow rate of 2 sccm, the SSA achieves a high solar thermal conversion efficiency.

4.2.1 Experimental details

The schematic diagram of SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ is shown in Figure 4.1. In this structure, Cu substrate with high thermal conductivity is utilized as an infrared reflector; TiN_xO_y film serves as an absorbing layer; and SiO_2 and TiO_2 thin films form a double-layer ARC. The SiO_2 , TiO_2 , and TiN_xO_y thin films were deposited by RF magnetron sputtering of 2 inch SiO_2 , TiO_2 and TiN targets (all the targets have a purity > 99.9%), respectively, with a RF magnetron sputtering system (Denton Desktop Pro.). The chamber was pumped down to 9×10^{-6} torr for all the deposition processes. The sputtering was carried out at room temperature, and the sputtering power was maintained at 100 W. The Ar/ O_2 gases were used to deposit SiO_2 and TiO_2 thin films with an O_2 flow rate of 1.5 sccm.

The TiN_xO_y thin films used in the SSA were deposited by Ar/ N_2 gases with the N_2 flow rate at 2, 5, 8 sccm, respectively. The flow rate of Ar was kept at a constant value of 10 sccm, and the deposition pressure was maintained at around 3×10^{-3} torr.

Figure 4.1 Schematic diagram of SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$.

Figure 4.2 shows the Ti 2p core level of two situations of TiN_xO_y thin films, one deposited with 0 sccm N_2 flow rate and another deposited with 9 sccm N_2 flow rate (Ar flow rate was maintained at 10 sccm).

Figure 4.2 XPS analyses of the Ti 2p core level of the two situations of TiN_xO_y thin films on Si substrate: (a) deposited with 0 sccm N_2 ; and (b) deposited with 9 sccm N_2 . In both situations, the Ar flow rate was maintained at 10 sccm.

Compared to the TiN_xO_y thin film with 0 sccm N_2 , the TiN_xO_y thin film with 9 sccm N_2 has more Ti-O but less Ti-N. The presence of oxygen in the TiN_xO_y thin films deposited by a sputtering process without purposeful introduction of O_2 gas was also reported previously [141, 142], and the reason has been discussed in chapter 3.

4.2.2 Tuning optical constants of TiN_xO_y thin film

The optical properties of TiN_xO_y thin films deposited on Si substrate were analyzed with SE, and the measurements were conducted in the wavelength range of 0.3 – 1.5 μm at the angle of incidence of 75° . In this work, the complex dielectric function ($\varepsilon = \varepsilon_r + i\varepsilon_m$, where ε_r and ε_m are the real and imaginary parts of the complex dielectric function (ε), respectively) of the TiN_xO_y thin film is obtained from the SE analysis based on the Drude-Lorentz dispersion model [185, 186]. The SE analysis process of TiN_xO_y thin film has been discussed in chapter 3. In the fittings, the mean square error (MSE) was utilized as a criteria [187]. The MSE is smaller than 30 for all the SE fittings. The experimental and calculated ellipsometric angles (Ψ and Δ) of TiN_xO_y thin films with the N_2 flow rates of 2, 5, and 8 sccm are shown in Figure 4.3, respectively, in the wavelength range of 0.3 – 1.5 μm .

Figure 4.3 Experimental and calculated ellipsometric angles (Ψ and Δ) of TiN_xO_y thin films with the N_2 flow rates of 2, 5 and 8 sccm, respectively, in the wavelength range of 0.3 – 1.5 μm .

From the complex dielectric functions, the refractive index (n) and extinction coefficient (k) of the TiN_xO_y thin films are calculated with the Eqs. (2.12) – (2.14). Figure 4.4 shows the refractive index and extinction coefficient of the TiN_xO_y thin films deposited with the N_2 flow rate of 2, 5, 8 sccm, respectively, in the wavelength range of 0.3 – 1.5 μm . As shown in Figure 4.4, with the increasing of N_2 flow rate, the refractive index of TiN_xO_y increases in the wavelength range of 0.3 – 0.9 μm and decreases in the wavelength range of 0.9 – 1.5 μm . The extinction coefficient decreases significantly as the flow rate of N_2 increases, especially in the infrared range. The evolution of the complex refractive indices of TiN_xO_y thin film is attributed to the change of the volume fraction of TiN nanoparticles, and the effect has already been discussed in the literature [121]. The large dependence of both the refractive index and extinction coefficient of the TiN_xO_y layer on the N_2 flow rate provides an opportunity to optimize the performance of SSA.

Figure 4.4 Refractive indices and extinction coefficients in the wavelength range of 0.3 – 1.5 μm of the TiN_xO_y thin films deposited with the N_2 flow rates of 2, 5, and 8 sccm, respectively.

4.2.3 Optimizing the performance of the TiN_xO_y based SSA

To achieve a low reflectance in a wide wavelength range (i.e. $0.3 - 1.5 \mu\text{m}$), a graded refractive index profile is usually utilized in a multilayer ARC, which includes low refractive index material (e.g. MgF_2 , SiO_2 , etc.) and high refractive index material (e.g. TiO_2 , Si_3N_4 , etc.) [48]. In this work, SiO_2 and TiO_2 are chosen to form a double-layer ARC on the TiN_xO_y layer due to their match in the refractive index profile. As shown in Figure 4.5, a graded refractive index profile, i.e., low refractive index (SiO_2) – medium refractive index (TiO_2) – high refractive index (TiN_xO_y) is indeed achieved in the wide spectrum range of $0.34 - 1.5 \mu\text{m}$.

Figure 4.5 Refractive indices of SiO_2 , TiO_2 and TiN_xO_y thin films in the wavelength range of $0.3 - 1.5 \mu\text{m}$. The TiN_xO_y thin films were deposited with the N_2 flow rates of 2, 5 and 8 sccm, respectively.

The refractive indices and extinction coefficients of TiN_xO_y , TiO_2 and SiO_2 thin films in the infrared range beyond the wavelength of $1.5 \mu\text{m}$, which cannot be determined experimentally, can be obtained by the extension of the results shown in Figure 4.5 using an appropriate optical dispersion model [188, 189]. With the knowledge of the optical constants in the spectrum range of $0.3 - 25 \mu\text{m}$, a simulation of the reflectance ($R(\lambda)$) of the SiO_2 - TiO_2 -

TiN_xO_y-Cu SSA structure is carried out by using MATLAB. Because the optical constants of all the thin films and the structure of the SSA are known, only the thicknesses of the thin films need to be optimized. Here, an original optimization method has been taken. Firstly, the thickness of all the thin films in the SSA increases from 10 nm to 100 nm with 1 nm step. Take note that the minimum thickness starts from 10 nm as the consideration of fabrication feasibility. Secondly, based on the theory described in chapter 2, the reflectance of the SSA with all the different thicknesses combinations can be calculated by using MATLAB. Finally, to minimize the reflectance in the solar radiation range and maximize the reflectance in the black body radiation range, the optimized thicknesses of the SiO₂, TiO₂ and TiN_xO_y thin films can be found out by minimizing the following function of merit (FOM).

$$FOM = \left(\frac{1}{N} \sum_{j=1}^N \left(\frac{Rcal_low_j - Rtar_low_j}{Tol_low} \right)^2 \right)^{1/2} + \left(\frac{1}{M} \sum_{j=1}^M \left(\frac{Rcal_high_j - Rtar_high_j}{Tol_high} \right)^2 \right)^{1/2}, \quad (4.1)$$

where Rcal_low and Rcal_high are the calculated reflectance in the solar radiation range and black body radiation range, respectively. Rtar_low and Rtar_high are the targeted reflectance in the solar radiation range and black body radiation range, respectively. Tol_low and Tol_high are the tolerance between calculated reflectance and targeted reflectance in the solar radiation range and black body radiation range, respectively. The N and M is the number of reflectance in the solar radiation range and black body radiation range, respectively.

The optimized thicknesses of the three layers for the N₂ flow rates of 2, 5 and 8 sccm are shown in Figure 4.6. The total thickness of the three layers is around 180 nm for the N₂ flow rates of 2, 5 and 8 sccm. With the increase of N₂ flow rate from 2 to 8 sccm, the thickness of the absorbing layer (i.e. the TiN_xO_y layer) increases from 57 to 75 nm due to the decrease of the absorption coefficient of TiN_xO_y with increasing N₂ flow rate.

Figure 4.6 Optimized thicknesses of the SiO_2 , TiO_2 and TiN_xO_y thin films used in the SSA for the N_2 flow rates of 2, 5 and 8 sccm, respectively.

4.2.4 Performance of the TiN_xO_y based SSA

As the SSA layers are deposited on Cu substrate, the transmittance is zero; thus the solar absorptance (α_{solar}) at a specific wavelength (λ) in the solar radiation range can be calculated with Eq. (2.51). Under the thermal equilibrium condition, the absorptance is equal to the emittance. Therefore the thermal emittance (ε_T) at a specific wavelength in the infrared radiation range can be obtained with Eq. (2.52). The total solar absorptance (α_{ts}) and total thermal emittance (ε_{tt}) are given by Eqs. (4.2) and (4.3), respectively [190, 191].

$$\alpha_{\text{ts}} = \frac{\int_{\lambda=0.3\mu\text{m}}^{\lambda=25\mu\text{m}} P_{\text{solar}}(\lambda) \times \alpha_{\text{solar}}(\lambda) d\lambda}{\int_{\lambda=0.3\mu\text{m}}^{\lambda=25\mu\text{m}} P_{\text{solar}}(\lambda) d\lambda}, \quad (4.2)$$

$$\varepsilon_{\text{tt}} = \frac{\int_{\lambda=0.3\mu\text{m}}^{\lambda=25\mu\text{m}} P_{\text{bb}}(\lambda) \times \varepsilon_T(\lambda) d\lambda}{\int_{\lambda=0.3\mu\text{m}}^{\lambda=25\mu\text{m}} P_{\text{bb}}(\lambda) d\lambda}, \quad (4.3)$$

where $P_{\text{solar}}(\lambda)$ is the intensity of the solar radiation (AM 1.5), $P_{\text{bb}}(\lambda)$ is the intensity of black body radiation.

To realize high solar absorptance and low thermal emittance, the reflectance should be low in the solar radiation range and high in the infrared range. The transition point between those two regions is at the cross point of the solar radiation spectrum and the blackbody radiation spectrum. In the mid-temperature SSA application (e.g., 400 °C), the blackbody radiation exceeds to the solar radiation at the wavelength of 1.5 μm , as shown in Figure 4.8. On the other hand, around 90% of solar energy is in the wavelength range of 0.3 – 1.5 μm [192]. Therefore, the transition point (λ_c) in this work is set at the wavelength of 1.5 μm .

With the optimized layer thicknesses shown in Figure 4.6, the total solar absorptance (α_{ts}) and total thermal emittance (ε_{tt}) of the SSA are calculated with Eqs. (4.2) and (4.3), respectively, for the N_2 flow rates of 2, 5 and 8 sccm, and the results are shown in Table 4.1. It is found from the table that, with the increase of the N_2 flow rate from 2 to 8 sccm, the α_{ts} decreases from 95.11% to 90.16%, and the ε_{tt} also decreases from 7.30% to 6.60%. The change of α_{ts} with the N_2 flow rate can be explained by the change of the chemical stoichiometry of the TiN_xO_y thin films. The XPS analysis shows that the ratio of N to O in the TiN_xO_y layers decreases from 0.49 to 0.21 with the increase of N_2 from 2 to 8 sccm. This means that the amount of the TiN component in the TiN_xO_y layers decreases with the increase of the N_2 flow rate. The TiN component serves as the absorption center in the TiN_xO_y absorbing layers. Therefore, when the N_2 flow rate increases, α_{ts} decreases with the decrease of the amount of the TiN component. The SSA of the N_2 flow rate of 2 sccm has the largest α_{ts} (95.11%) due to the largest absorption in the TiN_xO_y layer deposited with the N_2 flow rate of 2 sccm. For the TiN_xO_y thin film deposited with the N_2 flow rate of 8 sccm, the SSA has the smallest ε_{tt} (6.60%) at the temperature of 400 °C.

Table 4.1 α_{ts} and ε_{tt} calculated with Eq. (4.1) and Eq. (4.2), respectively for the optimized layer thicknesses shown in Figure 4.6.

	SSA ($\text{N}_2=2$ sccm)	SSA ($\text{N}_2=5$ sccm)	SSA ($\text{N}_2=8$ sccm)
α_{ts}	95.11%	94.48%	90.16%
ε_{tt}	7.30%	7.13%	6.60%

To evaluate the performance of the SSA, the solar thermal conversion efficiency (η) is calculated with Eq. (2.50). The η depends on the concentration factor (χ). The solar thermal conversion efficiency at the temperature of 400°C as a function of the concentration factor is calculated with Eq. (2.50) for the N_2 flow rates of 2, 5 and 8 sccm, respectively, and the result is shown in Figure 4.7.

Figure 4.7 Solar thermal conversion efficiency (η) at the temperature of 400°C as a function of the concentration factor (χ) for the N_2 flow rates of 2, 5 and 8 sccm.

When the χ is one, η is 10.20%, 11.55%, and 13.40%, for the N_2 flow rates of 2, 5 and 8 sccm, respectively, showing a very low η . When χ is 5, there is a large increase in η , i.e., η is 78.13%, 77.89% and 74.81% for the N_2 flow rates of 2, 5 and 8 sccm, respectively. It can be observed from Figure 4.7 that the N_2 flow rate of 2 sccm provides the highest η for χ equal to or larger than 5. In the mid-high temperature SSA applications, the solar energy usually is

concentrated on the absorber with parabolic trough with the χ of ≥ 10 [193, 194]. Therefore, the N_2 flow rate of 2 sccm has been chosen to deposit the TiN_xO_y absorbing layer in the fabrication of the mid-high temperature (i.e. 400 °C) SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$ in this work.

The reflectance of the fabricated SSA with the N_2 flow rate of 2 sccm has been measured with an UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950) and a FT-NIR/MIR spectrometer (PerkinElmer Frontier) in the wavelength ranges of 0.3 – 2.5 μm and 2.5 – 25 μm , respectively. Compared with the simulation results in Figure 4.8, the experimental measurements agree well with the simulated results in the wavelength range of 0.3 – 25 μm . The SSA has a low reflectance (<0.1) in the wavelength range of 0.3 – 1.5 μm (i.e. the solar radiation range) and high reflectance in the wavelength range of 1.5 – 25 μm (i.e. the black body radiation range at 400 °C). The measured solar absorptance and thermal emittance at the temperature of 400 °C of the fabricated SSA are 94.44% and 6.15%, respectively, which agree well with the calculation discussed early (the calculated solar absorptance and thermal emittance at the temperature of 400 °C are 95.11% and 7.30%, respectively).

Figure 4.8 Spectra of solar radiation (AM 1.5) intensity, black body radiation at 400 °C, and the simulated and experimental reflectance of the SSA with the TiN_xO_y thin film deposited with the N_2 flow rate of 2 sccm.

4.3 Modeling of a double TiN_xO_y layers based SSA

With the utilization of a double TiN_xO_y absorbing layers: a TiN_xO_y layer with low N/O ratio (TiNO_L) and a TiN_xO_y layer with high N/O ratio (TiNO_H), a SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiNO_L-TiNO_H-Cu}$ has been proposed. Optical properties of the TiNO_L and TiNO_H layers were investigated with SE in the wavelength range of $0.3 - 2.5 \mu\text{m}$. In the optical properties modeling process, the absorption mechanisms in TiN_xO_y thin films, including LSPR, free electron absorption and interband transitions, were taken into account. Because TiNO_H has a higher free electron concentration than that of TiNO_L , the absorption strengths due to both the LSPR and free electron absorption in the TiNO_H are larger than those in the TiNO_L . After obtaining the optical constants of TiN_xO_y thin films from the SE modeling, the reflectance of the SSA in the wide wavelength range of $0.3 - 25 \mu\text{m}$ covering both the solar radiation and black body radiation has been optimized; and the simulated results agree well with the experimental results.

4.3.1 Experimental details

In this work, based on the combination of the double absorbing layers (i.e., TiNO_L thin film and the TiNO_H thin film), the diagram of the SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiNO_L-TiNO_H-Cu}$ is shown in Figure 4.9.

Figure 4.9 Schematic structure of the SSA with $\text{SiO}_2\text{-TiO}_2\text{-TiNO_L-TiNO_H}$ on Cu

Because the TiN serves as the absorbing centers, the absorbing strength of the TiN_xO_y thin film can be tuned by changing the N/O ratio. In the double TiN_xO_y thin film based SSA, the SiO₂ and TiO₂ thin films form a double-layer ARC while the Cu substrate serves as the infrared reflector. The SiO₂, TiO₂ and TiN_xO_y (both TiNO_L and TiNO_H) thin films were deposited by RF magnetron sputtering of SiO, TiO₂, and TiN targets (all targets have a purity > 99.9%), respectively, with a Denton desktop sputtering system at room temperature. For all the deposition processes, the chamber was pumped down to 9×10^{-6} torr. The SiO₂ and TiO₂ thin films were deposited in the gas ambient of Ar (10 sccm) and O₂ (1.5 sccm) flow. The gases of Ar (10 sccm) and N₂ (6 sccm) were utilized to deposit TiNO_L thin film. The TiNO_H thin film was deposited with Ar gas (10 sccm) only. The sputtering power was maintained at 100 W. Both the TiNO_L and TiNO_H thin films with the thickness of 60 nm were deposited on a silica substrate for the absorbance measurements and a Si substrate for the XPS and SE measurements.

The transmittance (T) and reflectance (R) spectra of the TiNO_L and TiNO_H thin films on silica substrate were measured in the wavelength range of 300 – 2500 nm with an UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950). Based on the measured T and R , the absorbance (A_α) was calculated with Eq. (4.4) [195].

$$A_\alpha = \log_{10}\left(\frac{1-R}{T}\right) \quad (4.4)$$

As can be observed in the Figure 4.10, the absorbance of TiNO_H is apparently larger than that of TiNO_L in the wavelength range of 300 – 2500 nm. The absorption at the wavelengths shorter than ~600 nm (i.e. photon energy larger than 2 eV) is attributed to the interband transitions in the TiN_xO_y thin films; while the absorbance peak near the wavelength of 1000 nm (i.e. photon energy of ~1.2 eV) for both TiNO_L and TiNO_H thin films is believed to be due to the LSPR effect of the conductive TiN nanoparticles in the TiN_xO_y thin films [140].

Figure 4.10 Absorbance spectra of TiNO_L and TiNO_H thin films on silica substrate in the wavelength range of 300 – 2500 nm.

The chemical compositions of TiNO_L and TiNO_H thin films were analyzed with a XPS instrument (ESCALAB 250 Xi). To eliminate the effect of sample's surface contamination, the surface was pre-cleaned with 4 keV Ar ion beam for 90 seconds firstly. The XPS spectra were calibrated by using the C 1s peak (285 eV) as the reference. The high resolution spectra of Ti 2p, N 1s, O 1s and the deconvolution results of the TiNO_L and TiNO_H thin films are shown in Figure 4.11.

The Ti 2p spectra were deconvoluted into three pairs of spin-orbit-split doublets assigned as Ti-O ($2p_{3/2}$: ~458.7 eV), Ti-N-O ($2p_{3/2}$: ~456.7 eV), Ti-N ($2p_{3/2}$: ~455.6 eV) states, respectively [196]; the N 1s spectra were deconvoluted into the Ti-N-O and Ti-N states at the binding energies of ~398 eV and ~397 eV, respectively [132]; and the O 1s spectra were deconvoluted into the Ti-N-O (1s: ~531.5 eV) and Ti-O (1s: ~530.7 eV) states [197]. Based on the N 1s and O 1s spectra, the N/O ratio is 0.36 and 0.52 in the TiNO_L and TiNO_H thin films, respectively. In the deposition process of the TiNO_H thin film, there is no N_2 gas; thus the deposition process is faster and there is less time for the oxygen to react with Ti

atoms. In contrast, in the deposition process of the TiNO_L thin film, the N_2 has a nitriding effect on the TiN target, leading to a slow deposition. Therefore, the N/O ratio of the TiNO_H thin film is higher than that of the TiNO_L thin film.

Figure 4.11 Deconvolution of the spectra of (a) $\text{Ti } 2p$, (b) $\text{N } 1s$ and (c) $\text{O } 1s$ of the TiNO_L thin film; and (d) $\text{Ti } 2p$, (e) $\text{N } 1s$ and (f) $\text{O } 1s$ of the TiNO_H thin film.

4.3.2 Optical dispersion modeling

The optical dispersion modeling for the TiN_xO_y thin films on the Si substrates were carried out with an ellipsometer (J.A. Woollam) in the wavelength range of 300 – 2500 nm at the angle of incidence of 75° . The measured ellipsometric angles (Ψ and Δ) for the TiNO_L

and TiNO_H thin films are shown in Figure 4.12 (a) and (b), respectively. The detail information of the SE fitting procedure has been given in Chapter 3. A ellipsometric fitting can be carried out in a wide wavelength range by freely varying the parameters in Eq. (3.1) and the film thickness as well to minimize the root mean squared error (RMSE) of the comparison between the calculated and measured Ψ and Δ . The RMSE is given by [198, 199]

$$RMSE = \sqrt{\frac{1}{2N-M} \sum_{i=1}^N \left[\left(\frac{\Psi_i^{cal} - \Psi_i^{exp}}{\sigma_{\Psi,i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{cal} - \Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}} \right)^2 \right]}, \quad (4.5)$$

where N is the number of experimental data points; M is the total number of fitting parameters; Ψ_i^{cal} and Δ_i^{cal} are the calculated Ψ and Δ , respectively; Ψ_i^{exp} and Δ_i^{exp} are the experimental Ψ and Δ , respectively; $\sigma_{\Psi,i}^{exp}$ and $\sigma_{\Delta,i}^{exp}$ are the standard deviations of experimental Ψ and Δ , respectively. The ellipsometric fitting results of the TiNO_L and TiNO_H thin films are shown in Figure 4.12 (a) and (b), respectively.

Excellent agreement between the modeling and experiment has been achieved in the wavelength range of 300 – 2500 nm. The values of some important parameters of Eq. (3.1) yielded from the ellipsometric fittings for the TiNO_L and TiNO_H thin films are shown in Table 4.2, including plasma energy (E_p), LSPR strength (f_{LSPR}), LSPR position (E_{LSPR}), interband transition strength (f_{int}) and interband transition energy position (E_{int}). The E_{LSPR} yielded from the modeling is 1.37 and 0.97 eV for the TiNO_L and TiNO_H thin films, respectively, which are consistent with the absorbance measurements shown in the Figure 4.10.

Figure 4.12 Experimental and calculated ellipsometric angles (Ψ and Δ) of (a) TiNO_L and (b) TiNO_H thin films in the wavelength range of 300 – 2500 nm.

Table 4.2 Values of some important parameters of Eq. (3.1) yielded from the ellipsometric fittings for the TiNO_L and TiNO_H thin films.

	E_p (eV)	f_{LSPR}	E_{LSPR} (eV)	f_{int}	E_{int} (eV)
TiNO_L	0.94	3.75	1.37	3.73	4.74
TiNO_H	1.49	14.08	0.97	3.40	4.62

With the model parameters obtained from the ellipsometric fittings, the dielectric functions of the TiNO_L and TiNO_H thin films are calculated with Eq. (3.1) at each wavelength. The refractive index and extinction coefficient of the TiNO_L and TiNO_H thin films are obtained with Eqs. (2.12) – (2.14). As shown in Figure 4.13, the refractive indices of both the TiNO_L and TiNO_H thin films are high with a value of around 3. The refractive indices of the TiNO_H are lower in the wavelength range of 300 – 1400 nm and higher in the wavelength range of 1400 – 2500 nm than those of the TiNO_L, respectively. On the other hand, the extinction coefficients of the TiNO_H are always larger than those of the TiNO_L in the whole wavelength range of 300 – 2500 nm; in particular, a very large difference of extinction coefficients between the TiNO_H and the TiNO_L appears in the infrared region of ~1200 – 2500 nm. This highlights the influence of the N/O ratio in the TiN_xO_y thin films on the optical properties [200]. The difference of the extinction coefficients explains the results shown in the Figure 4.10 that the absorbance of TiNO_H is significantly larger than that of TiNO_L in the wavelength range of 300 – 2500 nm.

Figure 4.13 Refractive indices and extinction coefficients of the TiNO_L and TiNO_H thin films in the wavelength range of 300 – 2500 nm.

4.3.3 Absorption mechanisms analysis in the TiN_xO_y thin films

Combining the Eq. (2.14) and Eq. (2.35), the relationship between the imaginary part (ϵ_m) of the dielectric function and the absorption coefficient (α) can be expressed with Eq. (4.6).

$$\epsilon_m = \frac{n\lambda}{2\pi} \alpha, \quad (4.6)$$

where n is the refractive index and λ is the wavelength. Therefore, the absorption mechanism can be qualitatively analyzed by the imaginary part of the dielectric function. As shown in Figure 4.14, the imaginary parts of the dielectric function of the TiNO_L and TiNO_H thin films in the photon energy range of 0.5 to 4.1 eV are composed by the imaginary parts of Drude term, LSPR oscillator (E_{LSPR}) and interband transitions (E_{int}).

Figure 4.14 Imaginary part of the dielectric function and the imaginary parts of Drude term, LSPR (E_{LSPR}), and interband transitions (E_{int}) of (a) TiNO_L thin film and (b) TiNO_H thin film in the photon energy of 0.5 to 4.1 eV.

In the following, the LSPR effect, free electron absorption and interband transitions are modeled as three main absorption mechanisms in the TiN_xO_y thin films.

4.3.3.1 Localized surface plasmon resonance effect

In the infrared range, the LSPR effect of the TiN nanoparticles plays an important role in the absorption process of the TiN_xO_y thin films [201]. In the Figure 3.6, the HRTEM image with the corresponding TiN selected area diffraction (SAD) pattern confirms the existing of the TiN nanoparticles in the TiN_xO_y thin films [185]. As shown in Figure 4.15, the imaginary part of the LSPR oscillator of the TiNO_H is much larger than that of the TiNO_L in the low photon energy range of 0.5 – 1.5 eV, indicating that the strength of the LSPR in the TiNO_H is stronger than that in the TiNO_L. According to the XPS results, the N/O ratio in TiNO_H is larger than that in TiNO_L. So the volume fraction of TiN nanoparticles in the TiNO_H is higher than that in the TiNO_L. Therefore, the absorption strength caused by LSPR in TiNO_H is stronger than that in TiNO_L, which is one of the important factors responsible for the difference in absorbance in the infrared range between the TiNO_H and TiNO_L thin films.

Figure 4.15 Imaginary part of the LSPR oscillator for TiNO_H and TiNO_L thin films in the photon energy of 0.5 – 4.1 eV.

4.3.3.2 Free electron absorption

The free electron absorption causes the different absorbance in the infrared wavelength range between the TiNO_L and TiNO_H thin films. As discussed in the Chapter 2, the optical properties of the free electrons can be modeled by the Drude term. Figure 4.16 shows the imaginary parts of the Drude term of the dielectric function of the TiNO_H and TiNO_L in the photon energy range of 0.5 – 4.1 eV. Due to the higher free electron concentration in the TiNO_H thin film, the imaginary part of the Drude term of the TiNO_H is obviously larger than that of the TiNO_L in the low photon energy range of 0.5 – 1.5 eV.

Figure 4.16 Imaginary part of the Drude term of the TiNO_H and TiNO_L thin films in the photon energy of 0.5 – 4.1 eV. The insert shows the plasma energy (E_p) and resistivity (R_s) of the TiNO_H and TiNO_L thin films.

As shown in the insert of Figure 4.16, the plasma energy (E_p), which is obtained from the ellipsometric fitting, is 1.49 eV for the TiNO_H and 0.94 eV for the TiNO_L. The relationship between the E_p and the free electron concentration (N_v) is given by [141]

$$E_p = \sqrt{\frac{N_v q^2}{\epsilon_0 m^*}}, \quad (4.7)$$

where q is the electron charge, ε_0 is the free space permittivity, and m^* is the effective mass of the electron. Therefore, the E_p and N_v has a proportional relationship. The fact that the N_v in the TiNO_H is higher than that in the TiNO_L has been confirmed by the resistivity measurements with a four-point probe. As shown in the insert of Figure 4.16, the resistivity (R_s) of the TiNO_H thin film is much lower than that of the TiNO_L thin film.

4.3.3.3 Interband transitions

The absorbance of the TiNO_L and TiNO_H in the high photon energy range of 2 – 4.1 eV is mainly due to the interband transitions in TiN_xO_y thin films. This argument is reasonable if the TiN_xO_y thin films can be considered as a nano-composite film of TiN and TiO_2 to certain extent. Note that TiN has several interband transition points at the $\Gamma_{15} - \Gamma_{12}$ (~2.3 eV), $X_5 - X_2$ (3.9 eV), $L_3 - L_3'$ (5.6 eV) points of the Brillouin zone [20] and TiO_2 has a bandgap of around 3.2 eV [202]. In the Figure 4.10, it is obvious that there is no large difference of the absorbance in the high photon energy range between the TiNO_H and the TiNO_L. The results of absorbance measurements agree with the results of modeling. As shown in Figure 4.17, the imaginary part of the interband transitions of the TiNO_H thin film is close to that of the TiNO_L thin film in the photon energy range of 2 – 4.1 eV.

Figure 4.17 Imaginary part of the interband transitions of the TiNO_H and the TiNO_L thin films in the photon energy of 0.5 – 4.1 eV.

4.3.4 Performance of the double TiN_xO_y layer based SSA

To obtain low reflectance in the solar radiation range and high reflectance in the black body radiation range, a simulation was carried out to optimize the thicknesses of the layers in the SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiNO}_\text{L}\text{-TiNO}_\text{H}\text{-Cu}$. The optimized thicknesses of the SiO_2 , TiO_2 , TiNO_L , and TiNO_H layers are 81, 28, 42, and 40 nm, respectively. A SSA sample with the optimized layer thicknesses was fabricated. The simulated and experimental reflectance spectra in the wavelength range of 0.3 – 25 μm of the SSA are shown in Figure 4.18. It can be observed from the figure that the simulation agrees well with the actual measurement.

Figure 4.18 Experimental and simulated reflectance spectra of the SSA, solar radiation spectrum (AM 1.5), and black body radiation spectrum at the temperature of 200, 300, and 400 °C in the wavelength range of 0.3 – 25 μm .

The total solar absorptance (α_{ts}) and total thermal emittance (ε_{tt}) can be calculated with Eq. (4.1) and Eq. (4.2), respectively. The solar radiation spectrum (AM 1.5) and the black body radiation spectra at the temperatures of 200, 300, and 400 °C are also shown in Figure 4.18. The SSA sample achieves a solar absorptance of 95.6%, and a thermal emittance of 6.0%,

7.4%, and 9.5% at the temperatures of 200, 300, and 400 °C, respectively. With the increase of temperature, the peak of the black body radiation blue-shifts and the thermal emittance increases. Therefore, the SSA in this work is suitable for the middle/low temperature applications.

4.3.5 Comparison of the single and double TiN_xO_y layer based SSA

As shown in Figure 4.19 (a), the experimental reflectance of the double TiN_xO_y based SSA (double-SSA) shows a good agreement with that of simulated reflectance in the wavelength range of 300 – 2500 nm. For the sake of comparison of our previous single TiN_xO_y absorption layer based SSA (single-SSA) with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$, the simulated and experimental reflectance spectra are shown in Figure 4.19 (b) in the wavelength range of 300 – 2500 nm.

Figure 4.19 Simulated and experimental reflectance spectra in the wavelength range of 300 – 2500 nm of (a) double-SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiNO}_L\text{-TiNO}_H\text{-Cu}$ and (b) single-SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y\text{-Cu}$.

If we define that the low reflectance range is less than 10%, the transition point from low reflectance to high reflectance in the infrared range red-shifts from $\sim 1.5 \mu\text{m}$ in the single-SSA to $\sim 1.8 \mu\text{m}$ in the double-SSA. Therefore, the double-SSA has a wider low reflectance range than that of the single-SSA. At the same time, the reflectance values of both the single-SSA and the double-SSA are around 60% at the wavelength of 2500 nm. As a result, the double-SSA achieves a steeper reflectance transition from low to high than that of the single-SSA. The total solar absorptance of the double-SSA is 95.6%, which is larger than that of the single-SSA with the total solar absorptance of 94.4%. However, the single-SSA has a higher reflectance in the wavelength range of $2.5 - 25 \mu\text{m}$ than that of the double-SSA, as shown in Figure 4.20. Therefore, the total thermal emittance of the single-SSA is lower than that of the double-SSA.

Figure 4.20 Reflectance spectra of the single-SSA and the double-SSA in the wavelength range of $2.5 - 25 \mu\text{m}$.

4.4 Summary

By using TiN_xO_y as the absorbing layer, a high performance SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y$ on Cu substrate has been designed. SiO_2 and TiO_2 layers form a double-

layer ARC while Cu substrate serves as an infrared reflector. TiN_xO_y layer was deposited by sputtering of a pure TiN target with Ar and N_2 . Introducing of oxygen in the TiN_xO_y layer was realized by utilizing the residual oxygen or moisture in the deposition chamber. The N_2 flow rate has a large effect on the optical properties of the TiN_xO_y layer; and with the increase of the N_2 flow rate, the extinction coefficient of the TiN_xO_y layer decreases significantly. Based on the optical properties of the TiN_xO_y layer obtained from the SE analysis, the thicknesses of the SiO_2 , TiO_2 and TiN_xO_y layers are optimized to achieve the highest total solar absorptance and the lowest total thermal emittance for a given N_2 flow rate. The N_2 flow rate of 2 sccm provides the highest solar thermal conversion efficiency for the concentration factor ≥ 5 . The SSA fabricated with the N_2 flow rate of 2 sccm shows a high solar absorptance of 94.44% and a low thermal emittance of 6.15% at the temperature of 400 °C.

Comparing with the single TiN_xO_y absorber layer based SSA, the double TiN_xO_y absorber layer based SSA provides another opportunity to optimize the performance of SSA. In the double TiN_xO_y based SSA, there are two absorber layers: TiN_xO_y with low N/O ratio (TiNO_L) layer and TiN_xO_y with high N/O ratio (TiNO_H) layer. The optical properties of the TiNO_L and TiNO_H thin films have been characterized by SE. To investigate the different absorption properties of the two TiN_xO_y thin films, the absorption mechanisms have been modeled. In the analysis of SE, three absorption mechanisms in TiN_xO_y thin film have been studied, including LSPR effect, free electron absorption and interband transitions. In the low photon energy range, the absorption is caused by the LSPR and the free electron absorption. In the high photon energy range, the absorption is induced by the interband transitions.

Chapter 5 THERMAL STABILITY OF TiN_xO_y

THIN FILM BASED SELECTIVE SOLAR

ABSORBER ON GLASS SUBSTRATE

To reduce the cost, a SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu}$ has been fabricated on glass substrate by RF magnetron sputtering for the low- ($<100^\circ\text{C}$) and middle-temperature ($100^\circ\text{C} < T < 400^\circ\text{C}$) applications. Structural, chemical and optical properties of the SSA experienced thermal annealing at different temperatures for various durations have been investigated with the characterization techniques: XPS, XRD, AFM, SE and spectrophotometry. In the SSA, W-Cu thin film structure is used as the infrared reflector. If there is no W thin film in the infrared reflector, the reflectance of the SSA in both visible and infrared ranges increases due to the crystallization of the Cu layer at elevated temperatures. After adding the W thin film with an appropriate film thickness, the increase of the reflectance in the visible range is suppressed, while a high reflectance in the infrared range is maintained to achieve a low thermal emittance. In this work, a low cost SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ achieves a total solar absorptance of 92.2% after annealing at 400°C for 6 hours and a total thermal emittance of 4.4% at the temperature of 400°C .

5.1 Introduction

In the solar thermal energy systems, the SSA is one of the key units [203]. To reduce the cost, a glass substrate is widely used [204, 205], and a metallic thin film (e.g., Cu, Al, Mo,

etc.) is deposited on the glass substrate to serve as an infrared reflector [46]. Due to its good chemical and physical properties, TiN_xO_y has been commercially used as a solar energy absorber [206]. What's more, the cost of the TiN_xO_y thin film is lower than those cermet thin film (metal nanoparticles-dielectric composites, e.g., $\text{Ni-Al}_2\text{O}_3$, W-AlN , Mo-SiO_2 , etc. [46]) since the TiN_xO_y thin film can be deposited by sputtering one target (Ti or TiN). However, because the nitrogen can be replaced by oxygen in the TiN_xO_y thin film at high temperatures due to oxidation, the TiN_xO_y based SSA usually is suitable for low or mid-temperature (i.e., $<400^\circ\text{C}$) applications [129,207]. With the advantage of low electrical resistivity ($\sim 1.7\ \mu\Omega\cdot\text{cm}$) and large thermal conductivity, Cu is a good infrared reflector to reduce the infrared emittance. However, Cu has a large atomic diffusion coefficient, particularly when the temperature is higher than 200°C [201, 208]. In some commercial products, titanium carbide (TiC) thin film is deposited on the top of Cu as a barrier layer because of its high thermal and chemical stability [209, 210]. TiC thin film can be deposited by atomic layer deposition (ALD) [211], PECVD [212], physical vapor deposition (PVD) [213], etc. However, there are some disadvantages by using these methods, such as low productivity, high temperature process, and hard control of the process parameters to obtain desirable stoichiometric TiC_x [214]. In addition, the electrical resistivity of TiC is relatively high ($\sim 42\ \mu\Omega\cdot\text{cm}$) [215]. Therefore, the infrared reflectance of TiC barrier layer is much lower than that of Cu, leading to a higher thermal emittance than that of Cu.

With their high thermal stability, refractory metals, such as tungsten (W), tantalum (Ta), and titanium (Ti), are also widely utilized as Cu barrier layer [201, 216, 217]. Particularly, with the low electrical resistivity ($\sim 5.6\ \mu\Omega\cdot\text{cm}$), W thin film is very suitable as an infrared reflector [201], but it still has a higher resistivity than Cu. Therefore, the reflectance of W thin film is lower than that of Cu in the infrared range. In the case of Cu thin film being used as infrared reflector, the Cu thin film may undergo structural changes such as crystallization

at elevated temperatures during the operation, leading to changes in its optical properties. The introduction of a more thermally stable W layer can suppress such changes. In this work, with the combination of highly thermal stable W and highly conductive Cu, it is possible to realize a high-performance infrared reflector, which has the high reflectance in the infrared range and high thermal stability simultaneously. In the W-Cu infrared reflector, the W layer must be thick enough to guarantee the barrier capability of the W layer but thin enough to achieve high infrared transmittance so that the Cu can play a dominant role in the infrared reflection of the structure. Therefore, the thickness effect of W thin film should be investigated.

5.2 Structure and experimental details

The schematic structure of the TiN_xO_y based low cost SSA is shown in Figure 5.1. In the SSA, the SiO_2 layer is used as a single-layer ARC, the TiN_xO_y film serves as the absorbing layer, the W-Cu thin film structure is utilized as the infrared reflector, and the glass is used as the substrate.

Figure 5.1 Schematic structure of the SSA with the SiO_2 - TiN_xO_y -W-Cu thin film structure on glass substrate.

The SiO_2 - TiN_xO_y -W-Cu thin film structure was deposited on glass substrate by RF magnetron sputtering (Denton Desktop Pro. Sputtering system) of 2-inch SiO_2 , TiN, W, and Cu targets (all the targets have a purity > 99.9%), respectively. The chamber was pumped down to 9×10^{-6} torr for all the deposition processes. The sputtering was carried out at room temperature, the sputtering power was maintained at 100 W, and the Ar gas flow rate was fixed at 10 sccm.

Because there are four thin films in our proposed thermal stable SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu}$ on glass substrate, it is better to investigate the thermal stability of each thin film separately. Therefore, we are going to investigate the TiN_xO_y based SSA without W thin film in next section first.

5.3 Thermal stability of SSA without W thin film

5.3.1 Design the SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$

The optical properties of the TiN_xO_y thin film deposited on Si substrate were characterized by using SE (J.A. Woollam, VB-250) with the incidence angle of 75° in the wavelength range of 300 – 1500 nm with the Drude-Lorentz model [20]. The optical constants including refractive index and extinction coefficient of the TiN_xO_y thin film in the wavelength range of 300 – 1500 nm were thus obtained from the SE analysis. The detailed methodology for the SE analysis has been discussed in Chapter 3. The optical constants of both SiO_2 and Cu can be obtained from the literature [218, 219]. With the known optical constants of SiO_2 , TiN_xO_y and Cu, the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ for given thicknesses of the SiO_2 , TiN_xO_y and Cu thin films can be calculated in a wide wavelength range. To achieve the best performance of the SSA, the thicknesses of the SiO_2 and TiN_xO_y layers were optimized to obtain the lowest reflectance in the solar radiation range and highest reflectance in the black body radiation range. The optimized thicknesses of the SiO_2 and TiN_xO_y layers are 73 and 92 nm, respectively (the thickness of the Cu layer was maintained at 1 μm). The calculated reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ in the wavelength range of 250 – 2500 nm is shown in Figure 5.2, and the insert shows the SSA structure with each layer's detailed thickness. Note that the refractive indices and extinction coefficients of TiN_xO_y in the wavelength ranges of 250 – 300 nm and 1500 – 2500 nm were

calculated using the Drude-Lorentz optical dispersion model with the model parameters yielded from the SE fitting in the wavelength range of 300 – 1500 nm.

Figure 5.2 Calculated reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA with the optimized layer thicknesses and solar radiation intensity (AM1.5) in the wavelength range of 250 – 2500 nm. The inset shows the structure of the SSA with each layer's detailed thickness.

5.3.2 Thermal annealing effect on the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$

The SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ was fabricated by RF magnetron sputtering. Then, the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ sample was annealed in a quartz tube furnace (Thermo Scientific tube furnace) with Ar gas flowing for one hour at the temperatures of 200, 300, and 400 °C, respectively. Due to the temperature limitation of the glass substrate, the annealing temperature is limited to less than 400 °C. To examine the long-term thermal stability, the above-mentioned sample was further annealed for 6 hours at the temperature of 400 °C with the same conditions. The reflectance spectra were recorded each time after annealing process. The reflectance spectra of the as-deposited and thermally-annealed SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ were measured in the wavelength range of 250 – 2500 nm with an UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 950), as shown in Figure 5.3. With the increase of

annealing temperature from 200 to 400 °C, the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ increases largely in the wavelength ranges of 300 – 800 nm and 1200 – 2500 nm but has a small decrease in the wavelength range of 800 – 1200 nm, which can be attributed to the crystallization of the Cu layer caused by the annealing process as discussed later. Because around 50% of the solar energy is in the wavelength range of 300 – 800 nm [220], the large increase of reflectance in that wavelength range severely reduces the absorption of solar energy.

Figure 5.3 Experimental reflectance spectra of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ for different annealing temperatures/annealing durations.

Table 5.1 shows the arithmetical average reflectance in the wavelength range of 300 – 800 nm of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ for different annealing temperatures and annealing durations. The average reflectance significantly increases from 5.2% for the as-deposited sample to 14.8% for the sample annealed at 400 °C for 6 hours. The total solar absorptance (α_{ts}) can be calculated with Eq. (4.1) and the results are also listed in Table 5.1. The α_{ts} significantly decreases with annealing temperature/annealing duration, which is

mainly due to the increase in the reflectance in the wavelength range of 300 – 800 nm as a result of annealing process.

Table 5.1 *Arithmetical average reflectance of SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ in the wavelength range of 300 – 800 nm and total solar absorptance (α_{ts}) of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ for different annealing temperatures/annealing durations.*

	As deposited	200°C for 1 hour	300°C for 1 hour	400°C for 1 hour	400°C for 6 hour
Average reflectance (300 – 800 nm)	5.2%	6.3%	7.6%	10.9%	14.8%
Total solar absorptance (α_{ts})	92.2%	90.9%	89.9%	87.5%	84.1%

To understand the increase in the reflectance and decrease of the α_{ts} of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA, the SiO_2 and TiN_xO_y thin films were deposited on a Si substrate. Then the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ was carried out the same annealing processes with the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$. The reflectance spectra of the as-deposited and annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ structures were measured after each annealing process, and the results are shown in Figure 5.4. As can be observed in the figure, there is almost no change in the reflectance of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ structure even after 400°C annealing for 6 hours, showing that the annealing does not cause significant changes in the SiO_2 and TiN_xO_y thin films. Therefore, it can be concluded that the changes in the reflectance and α_{ts} of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ is caused by the Cu thin film. There are two possible reasons for the changes: crystallization of the Cu thin film, which leads to changes in the optical properties of the Cu thin film; and or diffusion of the Cu atoms as Cu has a very large diffusion coefficient [221].

Figure 5.4 Experimental reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Si}$ structure for different annealing temperatures/annealing durations.

5.3.3 Characterization of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$

5.3.3.1 XPS depth profile of the SSA

The XPS measurement with the Ar ion beam as the etching tool was used to characterize the atomic depth profiles of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ samples (ESCALAB 250Xi). The depth profiles of O, Si, Ti, N and Cu elements are shown in Figure 5.5 (a) and (b), respectively. It is observed that the annealing did not produce significant changes in the atomic depth profiles. As reported in [222], the TiN_xO_y thin film can be used as a barrier layer in semiconductor device. Therefore, Cu diffusion is prevented by the TiN_xO_y thin film and should not be the major factor responsible for the changes in the reflectance and α_{ts} of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA in Table 5.1.

Figure 5.5 Depth profiles of O, Si, Ti, N and Cu in the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass SSA}$ obtained from the XPS analysis with the Ar ion beam as the etching tool. The annealing was conducted at 400 °C for 1 hour.

5.3.3.2 Structure characterization of the SSA

The microstructures were analyzed by using a XRD (Bruker, D8 Discover) with the grazing angle of 1° . The surface morphologies were characterized with an AFM (Bruker, Dimension Icon) in the tapping mode using a Si probe. Figure 5.6 shows the XRD patterns of

the as-deposited and 400 °C-annealed SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$, and the insets are the corresponding AFM images. The AFM images reveal that there is no significant change in the surface morphologies. However, the XRD patterns shown in Figure 5.6 indicate that there was crystallization in the Cu film during the annealing as the full width at half maximum (FWHM) of Cu (111) peak decreases from 1.39° to 1.00° after the annealing process. The calculation of the Cu crystalline grain size with the Scherrer's equation [223] shows that the grain size increases from 6.14 nm to 8.52 nm after the 400 °C annealing. The crystallization would lead to a lower electrical resistivity of the Cu layer. This argument is supported by the observation that the sheet resistance of the Cu thin film decreases from 115.6 m Ω /square to 42.9 m Ω /square after the annealing at 400 °C for one hour. It has been shown that a material with low electrical resistivity exhibits a high reflectivity [224].

Figure 5.6 XRD measurements of the as-deposited and 400 °C annealed $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ SSA. The insets show the corresponding AFM images with the image size of 500 × 500 nm². The annealing was conducted at 400 °C for 1 hour.

5.3.3.3 Thermal annealing effect on the Cu thin film

To examine the influence of annealing on the optical properties of Cu thin film, SE was used to measure the refractive index and extinction coefficient in the wavelength range of 300 – 1500 nm of the Cu thin film deposited on glass substrate without and with 400 °C-annealing for one hour, and the results are shown in Figure 5.7. It is obvious that the annealing process has a large impact on the optical properties of the Cu thin film. After the 400 °C annealing, the refractive index of the Cu thin film increases in the wavelength range of 300 – 350 nm but largely decreases in the wavelength range of 350 – 1500 nm. The extinction coefficient of the Cu thin film increases in the wavelength range of 300 – 1500 nm, especially in the infrared wavelength range, which could be attributed to the increase in the free electron mobility concentration after the annealing. Therefore, the 400 °C-annealing process changes the optical properties of the Cu thin film significantly.

Figure 5.7 Refractive indices and extinction coefficients in the wavelength range of 300 – 1500 nm of the as-deposited and 400 °C-annealed Cu thin films.

By using the refractive index and extinction coefficient of the Cu thin films with/without 400 °C-annealing, the reflectance spectra of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ with the as-

deposited and 400 °C-annealed Cu thin films were calculated in the wavelength range of 250 – 2500 nm, and the results are shown in Figure 5.8. It can be observed from the figure that the annealing of the Cu thin film leads to an increase in the reflectance in the wavelength ranges of 350 – 750 nm and 1350 – 2500 nm but a decrease in the wavelength range of 750 – 1350 nm. The changes are consistent with the experimental observation of the annealing effect on the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ as shown in Figure 5.3.

Figure 5.8 Reflectance spectra of the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ in the wavelength range of 250 – 2500 nm calculated by using the optical constants of the as-deposited and the 400 °C-annealed Cu thin films.

Therefore, the annealing effect on the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ can be attributed to the annealing-caused change in the optical properties of the Cu thin film. Note that there is a difference between the calculated reflectance data shown in Figure 5.8 and the experimental reflectance data shown in Figure 5.3. There are two possible reasons for the difference. Firstly, the samples used in the two figures are not identical in terms of annealing treatment. In Figure 5.8, the Cu/Si sample was annealed at 400 °C for one hour and

there was no further annealing. In Figure 5.3, the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ sample was annealed at 200 °C, 300 °C, 400 °C for one hour, respectively, and 400 °C for another 6 hours. The second reason is that the optical data of Cu in the wavelength ranges of 250 – 300 nm and 1500 – 2500 nm may be not very accurate because they were obtained from the calculation using the optical dispersion model with the model parameters for the Cu layer yielded from the ellipsometric analysis in the wavelength range of 300 – 1500 nm (note that the working wavelength range of our ellipsometer is only in the range of 300 -1500 nm). However, the difference does not affect the conclusions in this work.

5.4 Thermal stability of the SSA with W thin film

5.4.1 Thickness effect on the optical properties of W thin films

As shown in Figure 5.7, the optical properties of Cu changes largely after annealing. To solve the problem, a W thin film with high thermal stability is inserted between the TiN_xO_y layer and Cu layer. However, one major disadvantage is that W has a larger electrical resistivity than that of Cu. Therefore, to utilize the high reflectance of Cu thin film in the infrared range, it is important to find out a suitable thickness of the W thin film such that both high thermal stability and high infrared reflectance can be achieved for a SSA by using the combination of W and Cu layers. Figure 5.9 shows the measured reflectance spectra in the wavelength range of 250 – 2500 nm of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-W-Cu-Glass}$ structures with the W layer thicknesses of 0, 15, 30 and 60 nm, respectively. A 73 nm SiO_2 layer is used in the structure to protect the W thin film from oxidation. Without W thin film (i.e., the thickness of W thin film is zero), there is a large difference in the reflectance in the wavelength range of 250 – 1500 nm between the as-deposited and 400 °C-annealed samples. With increase of the W film thickness, the difference in the reflectance is reduced rapidly, and when the W film thickness increases to 60 nm, the difference almost disappears.

Therefore, the optical properties of W thin film are much thermally stable than that of Cu thin film.

Figure 5.9 Reflectance spectra of the as-deposited and 400 °C-annealed $\text{SiO}_2\text{-W-Cu-Glass}$ structure with the W thin film thicknesses of 0, 15, 30 and 60 nm, respectively.

It can be also observed from Figure 5.9 that with the increase of W film thickness from 0 to 60 nm, the reflectance of the $\text{SiO}_2\text{-W-Cu-Glass}$ structure in the wavelength range of 1500 – 2500 nm decreases significantly. For examples, for the annealed samples, the reflectance at the wavelength of 2500 nm is 96.9% for the case of without W thin film, the reflectance slightly decreases to 93.6% for the case of 15 nm W thin film, and it largely decreases to 61.7% for the case of 60 nm W thin film. The decrease of the infrared reflectance is due to the decrease of the infrared transmittance of the W thin film with the increase of W film thickness.

To characterize the thickness effect of W thin film on the optical properties, the W thin films with the thickness of 15, 20, 30, 60 nm were deposited on Si substrate by sputtering of a pure W target. The complex refractive indices of W thin films can be obtained by using SE in

the wavelength range of 300 – 1500 nm [225]. As shown in Figure 5.10, the refractive index and extinction coefficient of W thin films do not have much difference with the thickness increasing from 15 – 30 nm. When the thickness reaches to 60 nm, the refractive indices of W are slight smaller than those of other W thin films, and the extinction coefficients are a little smaller in the wavelength range of 300 – 1200 nm and a little larger in the wavelength range of 1200 – 1500 nm than those of other W thin films.

Figure 5.10 Refractive indices and extinction coefficients of W thin films with the thickness of 15, 20, 30, 60 nm in the wavelength range of 300 – 1500 nm, respectively.

By observing the results of Figure 5.9, the light almost cannot reach the interface between W thin film and Si substrate when the thickness of W increases to 60 nm. Therefore, the

complex refractive indices of W thin film with the thickness of 60 nm are a little inaccurate if taking the same optical model in the SE fitting process. As a result, it is concluded from Figure 5.10 that the thickness of W thin film does not have significant effect on the complex refractive indices.

The transmittance in the wavelength range of 250 – 2500 nm of W thin films with the thicknesses of 15, 20, 30 and 60 nm on glass has been measured, as shown in Figure 5.11. With the unitization of the complex refractive indices in the Figure 5.10, the transmittance spectra of W thin films are calculated in the wavelength range of 300 – 1500 nm. It is shown that the experimental results are consistent with those of calculated results in the wavelength range of 300 – 1500 nm.

Figure 5.11 Experimental transmittance spectra in the wavelength range of 250 – 2500 nm of W thin films with the thickness of 15, 20, 30 and 60 nm on glass, and the calculated transmittance spectra in the wavelength range of 300 – 1500 nm.

The average experimental transmittance over the wavelength range of 1500 – 2500 nm of W thin film is 22.8%, 18.1%, 9.8% and 4.5% for the W film thickness of 15, 20, 30, and 60

nm, respectively. The 60 nm W thin film blocks almost all the infrared light, and thus the infrared reflectance of the structure is determined by the W thin film. As the W thin film has a much lower infrared reflectance due to its higher electrical resistivity than that of the Cu thin film, the SiO_2 -W-Cu-Glass structure has a much lower infrared reflectance as compared to the structure without W thin film. In contrast, the much higher infrared transmittance of the 15 nm W thin film allows the Cu layer play an important role in the infrared reflectance of the SiO_2 -W-Cu-Glass structure, and thus the infrared reflectance of the structure is not largely reduced due to the introduction of the W thin film. Therefore, to achieve high thermal stability, high thermal absorption and low infrared emittance, 15 nm W thin film is utilized in the W-Cu infrared reflector in this work.

5.4.2 Thermal annealing effect on the SSA with SiO_2 - TiN_xO_y -W-Cu-Glass

To illustrate the effect of the W thin film, the thicknesses of SiO_2 , TiN_xO_y and Cu thin films in the SSA with SiO_2 - TiN_xO_y -W-Cu-Glass have the same values with those in the SSA with SiO_2 - TiN_xO_y -Cu-Glass. The same fabrication method and annealing process were conducted on the SSA with SiO_2 - TiN_xO_y -W-Cu-Glass. The reflectance spectra of the as-deposited and thermally-annealed SiO_2 - TiN_xO_y -W-Cu-Glass SSA are shown in Figure 5.12. An annealing, even the annealing at 400 °C for 6 hours, does not cause a significant change in the reflectance in the wavelength range of 250 – 900 nm. It leads to a small decrease and a large increase in the reflectance in the wavelength ranges of 900 – 1600 nm and 1600 – 2500 nm, respectively, which increases the solar absorptance and decreases the thermal emittance simultaneously.

Figure 5.12 Reflectance spectra of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ in the wavelength range of 250 – 2500 nm under different annealing conditions.

The average reflectance over the wavelength range of 300 – 800 nm and the total solar absorptance (α_{ts}) of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ under the different annealing conditions have been calculated, and the results are shown in Table 5.2. Compared to the as-deposited sample, the sample annealed at 400 °C for 6 hours causes only a slight increase (1.6%) in the average reflectance and no significant change in the α_{ts} (α_{ts} remains above 92%). The situation of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ is much better than that of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$. As shown in Table 5.1, the average reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ significantly increases from 5.2% for the as-deposited condition to 14.8% for the annealing at 400 °C for 6 hours, while the α_{ts} decreases largely from 92.2% for the as-deposited condition to 84.1% for the annealing at 400 °C for 6 hours. Obviously, the thermal stability of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ is better than that of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$.

Table 5.2 *Arithmetical average reflectance in the wavelength range of 300 – 800 nm and total solar absorptance (α_{ts}) of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ under different annealing conditions.*

	As-deposited	200 °C for 1 hour	300 °C for 1 hour	400 °C for 1 hour	400 °C for 6 hour
Average reflectance (300 – 800 nm)	4.1%	4.3%	4.4%	5.0%	5.7%
Total solar absorptance (α_{ts})	92.7%	92.5%	92.6%	92.5%	92.2%

5.4.3 Structure characterization of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$

In Figure 5.12, the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ has a large increase after thermal annealing in the wavelength range of 1600 – 2500 nm, and the change is very similar with that of SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ in Figure 5.3. So the reflectance changes in the infrared range are due to the change of the optical constants of the Cu film as a result of crystallization in the Cu film caused by thermal annealing. To illustrate the crystallization phenomenon, the comparison of the XRD patterns of the Cu phase between the as-deposited and 400 °C-annealed SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ suggests that there is crystallization in the Cu film caused by the annealing, as shown in Figure 5.13. At the same time, the W thin film also becomes more crystalline after thermal annealing, but the peak intensity of W thin film only increases a little. The AFM images in the insets of Figure 5.13 show that the surface morphologies of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ are stable after the 400 °C-annealing for 1 hour.

Figure 5.13 XRD patterns of the as-deposited and 400 °C-annealed SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$. The insets are the AFM images of (a) as-deposited, and (b) 400 °C annealed SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ for 1 hour. The AFM image size is $500 \times 500 \text{ nm}^2$.

5.5 Thermal annealing effect on the thermal emittance

Figure 5.14 shows the reflectance spectra in the wavelength range of 2.5 – 25 μm of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ and SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ of both as-deposited and annealed at 400 °C for 6 hours. Except the as-deposited SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$, the reflectance of all other samples is more than 90% in the wavelength range of 4 – 25 μm . It should be pointed out that the reflectance at the wavelength of 2500 nm in Figure 5.12 is lower than that in Figure 5.14. The discrepancy is due to the fact that the reflectance measurements in the wavelength range of 0.25 – 2.5 μm and 2.5 – 25 μm were conducted with two different systems, respectively. It is found that the system used for the measurement in the wavelength ranges of 0.25 – 2.5 μm has a lower accuracy. However, the discrepancy does not affect the conclusions of this study. Because the W thin film has a

higher electrical resistivity than that of Cu, the as-deposited SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ has a low reflectance. However, after 400°C -annealing for 6 hours, the reflectance of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ has a comparable reflectance with that of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ in the wavelength range of $2.5 - 25\ \mu\text{m}$. The total thermal emittance (ε_t) can be calculated with Eq. (4.2). The black body radiation spectrum at the temperature of 400°C is also shown in Figure 5.14.

Figure 5.14 Reflectance spectra in the wavelength range of $2.5 - 25\ \mu\text{m}$ of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ and the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ of both as-deposited and annealed at 400°C for 6 hours. The black body radiation spectrum in the wavelength range of $1.5 - 25\ \mu\text{m}$ at the temperature of 400°C is shown in this figure also.

The ε_t is calculated for the working temperature of 400°C . After the annealing at 400°C for 6 hours, the ε_t at the working temperature of 400°C of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-Cu-Glass}$ decreases from 7.7% to 2.9%, and the ε_t at the working temperature of 400°C of the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ decreases from 17.2% to 4.4%. Therefore, for the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$, an annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% for the annealing at 400°C for 6 hours) while it is still able to

maintain the solar absorptance at a high value (e.g., 92.2% for the annealing at 400 °C for 6 hours).

5.6 Summary

Taking the advantages of high thermal stability of W and high infrared light reflectance of Cu, a W-Cu thin film structure infrared reflector has been utilized in the SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$, which is deposited by RF magnetron sputtering. When there is no W layer in the SSA, the reflectance in the wavelength range of 300 – 800 nm and 1500 – 2500 nm increases largely due to the crystallization of Cu after thermal annealing. To reduce the effect of low thermal stability of Cu, a W thin film with high thermal stability is inserted between the TiN_xO_y layer and Cu layer. Additionally, the thickness of W thin film has been optimized to achieve high thermal stability and high infrared reflectance. It is shown that for the SSA with $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$, an annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% for the annealing at 400 °C for 6 hours) while it is still able to maintain the solar absorptance at a high value (e.g., 92.2% for the annealing at 400 °C for 6 hours).

Chapter 6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

To realize a low cost and environmentally friendly SSA for the CSP system, a TiN_xO_y based SSA was designed and fabricated. The optical properties of TiN_xO_y thin films were investigated by using various characterization techniques. A single TiN_xO_y layer based SSA was optimized by tuning the chemical composition of the TiN_xO_y thin film. To achieve high solar absorptance and low thermal emittance simultaneously, a double-layer TiN_xO_y structure based SSA was also designed and optimized. The absorption mechanisms in the TiN_xO_y absorbing layers were studied both theoretically and experimentally. The thermal stability of the low cost TiN_xO_y thin film based SSA was characterized. With the utilization of a W-Cu infrared reflector, the SSA achieved high thermal stability up to 400 °C.

6.1.1 Investigation of the optical properties of TiN_xO_y thin film

In this work, TiN_xO_y thin films were deposited with various N_2 flow rates (i.e., 0, 3, 6 and 9 sccm) by the RF magnetron sputtering technique. In the absorbance spectra of all the TiN_xO_y thin films, there are two distinct absorption bands: one in the low photon energy range, which is attributed to the LSPR of the TiN nanoparticles in the TiN_xO_y thin films, and the other in the high photon energy range, which is due to interband transitions in the TiN_xO_y thin films. With an increase of the N_2 flow rate, the absorption band in the low photon energy range weakens and shows a blue shift; while the absorption band in the high photon energy range does not show a very significant change. By considering the features in the absorbance

spectra, the optical properties of the TiN_xO_y thin films are modeled with a Drude term and two Lorentz oscillators in the ellipsometry analysis. The parameters extracted from the SE fitting are consistent with the results obtained from the absorbance experiments.

6.1.2 Single-layer TiN_xO_y structure based SSA

A high performance SSA with the structure of $\text{SiO}_2\text{-TiO}_2\text{-TiN}_x\text{O}_y$ on a Cu substrate was designed. SiO_2 and TiO_2 layers were used to form a double-layer ARC. A TiN_xO_y thin film was utilized as the absorbing layer and the Cu substrate served as the infrared reflector. The optical properties of TiN_xO_y were significantly changed by the N_2 flow rate, which allowed us to optimize the performance of the TiN_xO_y based SSA. The N_2 flow rate of 2 sccm provides the highest solar thermal conversion efficiency when the concentration factor is equal to or larger than 5. The SSA fabricated with a N_2 flow rate of 2 sccm shows a high total solar absorptance of 94.44% and a low total thermal emittance of 6.15% at a temperature of 400 °C.

6.1.3 Double-layer TiN_xO_y structure based SSA

Compared with the single-layer TiN_xO_y structure based SSA, the double-layer TiN_xO_y structure based SSA provides another opportunity to optimize the performance of SSA. In the double-layer TiN_xO_y structure based SSA, there are two absorbing layers: the TiN_xO_y layer with low N/O ratio (TiNO_L) and the TiN_xO_y layer with high N/O ratio (TiNO_H). It was found that the double-layer TiN_xO_y structure based SSA has a wider low reflectance range than the single-layer TiN_xO_y structure based SSA, and the transition point (i.e., 10%) from low reflectance to high reflectance in the infrared range redshifts from $\sim 1.5 \mu\text{m}$ in the single-layer TiN_xO_y SSA to $\sim 1.8 \mu\text{m}$ in the double-layer TiN_xO_y SSA. The optical properties of the TiNO_L and TiNO_H thin films were characterized by SE. To investigate the different absorption properties of the two TiN_xO_y thin films, the absorption mechanisms were

modeled. By SE analysis, we studied the three absorption mechanisms in the TiN_xO_y thin films: LSPR effect, free electron absorption and interband transitions. Absorption in the lower photon energy range, which is caused by the LSPR and free electron absorption, is stronger in the TiNO_H thin film than in the TiNO_L thin film. In the higher photon energy range, the absorption caused by the interband transitions in the TiNO_H thin film is close to that in the TiNO_L thin film.

6.1.4 A low cost SSA with high thermal stability

Due to the advantages of the high thermal stability of W and low electrical resistivity of Cu, a W-Cu thin film infrared reflector was utilized in the SSA with the structure of $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$. When there is no W layer in the SSA, the reflectance in the wavelength ranges of 300 – 800 nm and 1500 – 2500 nm increases largely due to the crystallization of Cu after thermal annealing. To reduce the effect of the low thermal stability of Cu, a W thin film with high thermal stability is inserted between the TiN_xO_y layer and Cu layer. It was shown that for the $\text{SiO}_2\text{-TiN}_x\text{O}_y\text{-W-Cu-Glass}$ SSA with a 15 nm W thin film, annealing can significantly reduce the thermal emittance to a low value (e.g., 4.4% after annealing at 400 °C for 6 hours) while maintaining a high solar absorptance (e.g., 92.2% after annealing at 400 °C for 6 hours).

6.2 Recommendations for future work

6.2.1 Synthetizing transition metal oxynitride thin films

Due to their high hardness, chemical inertness and excellent thermal stability, transition metal nitrides and transition metal oxides are used in a wide range of applications, such as hard coatings on tools, barrier layers in microelectronics, and heat absorbing layers in CSP. By combining transition metal nitrides and oxides, oxynitrides not only can inherit many advantages from the nitrides and oxides, but also have the capability of tuning the properties

by changing the N/O ratio. In addition to TiN_xO_y , there are many other kinds of transition metal oxynitride thin films, such as WN_xO_y , CrON , and TaN_xO_y [217, 226]. As discussed in this thesis, TiN_xO_y thin film can only be used in SSAs for low- and middle-temperature applications as N can be easily replaced by O at high temperature (over 400°C). Therefore, it is necessary to synthesize transition metal oxynitrides, which are thermally stable at very high temperatures.

6.2.2 Embedding metal nanoparticles in TiN_xO_y thin films

In SSAs, composites of metal particles and ceramics (i.e., cermet) have been widely used for low- or high- temperature applications, such as $\text{Pt-Al}_2\text{O}_3$, $\text{Mo-Si}_3\text{N}_4$, and $\text{W-Al}_2\text{O}_3$ [227, 228]. In cermet, the metal nanoparticles serve as the absorbing center. As discussed in this thesis, the TiN_xO_y thin film can be viewed as a composite of titanium nitrides and titanium oxides, in which the titanium nitrides are the absorbing center. In the TiN_xO_y thin film, the optical properties can be further tuned by embedding metal nanoparticles, such as Ti, W, Au, and Cu. Notably, the LSPR positions of Au and Cu nanoparticles are in the visible wavelength range, which comprises a large portion of the solar spectrum. Therefore, the optical properties of TiN_xO_y thin films embedded with Au or Cu nanoparticles will be interesting for the application in SSAs.

6.2.3 Combining solar thermal systems and photovoltaic cells

A system that combines solar thermal systems and photovoltaic cells is called a photovoltaics-thermal hybrid solar system (PVT) [229]. In the solar thermal system, the concentrator is used to increase the temperature of the heat transfer fluid (HTF) to a few hundred degrees. However, the concentrator can only concentrate the direct normal irradiance (DNI) solar radiation. Thus, diffused solar radiation is wasted in the solar thermal system. For photovoltaic cells, both the direct normal incident light and diffused light can be utilized. As

a result, PVT integrates the advantages of solar thermal systems and photovoltaic cells. At the same time, PVT can generate thermal energy and electricity simultaneously [230]. Additionally, photovoltaic cells have been commercialized for a long time. Therefore, the relatively new solar thermal system can be rapidly commercialized by combining photovoltaic cells.

LIST OF PUBLICATIONS

JOURNAL PAPERS

- [1] **J. Zhang**, T. P. Chen, Y. C. Liu, Z. Liu, and H. Y. Yang, “Modeling of a selective solar absorber thin film structure based on double TiN_xO_y layers for concentrated solar power applications,” *Solar Energy*, vol. 142, pp. 33 – 38, 2017.
- [2] **J. Zhang**, T. P. Chen, Y. C. Liu, Z. Liu, and H. Y. Yang, “W/Cu thin film infrared reflector for TiN_xO_y based selective solar absorber with high thermal stability,” *Journal of Applied Physics*, vol. 121, pp. 203101, 2017.
- [3] **J. Zhang**, T. P. Chen, X. D. Li, Y. C. Liu, Y. Liu, and H. Y. Yang, “Investigation of localized surface plasmon resonance of TiN nanoparticles in TiN_xO_y thin films,” *Optical Materials Express*, vol. 6, No, 7, pp. 2422 – 2433, 2016.
- [4] **J. Zhang**, T. P. Chen, Y. C. Liu, Z. Liu, and H. Y. Yang, “Design of a High Performance Selective Solar Absorber with the Structure of SiO_2 - TiO_2 - TiN_xO_y -Cu,” *ECS J. Solid State Sci. Technol.*, vol. 5, no. 7, pp. N43 – N47, 2016.
- [5] **J. Zhang**, T. P. Chen, Y. Liu, and J. I. Wong, “Si nanocrystal-based triple-layer anti-reflection coating for Si solar cells,” *Journal of Applied Physics*, vol. 114, pp. 053109, 2013.

INTERNATIONAL CONFERENCES

- [1] **J. Zhang**, T. P. Chen, X. D. Li, H. K. Li, “SiO₂-TiO₂-TiN_x Triple Layer based Selective Solar Absorber,” *the International Conference on Materials for Advanced Technologies*, June 2015, Singapore.

PATENTS

- [1] T. P. Chen, **J. Zhang** and J. I. Wong, “Anti-Reflection Coating with Variable Graded Refractive Index Profile and Capability of Down-Converting UV Light,” US Provisional Application No.: 61/788,540, 2013.

BIBLIOGRAPHY

- [1] Alfred Wagendristel and Youming Wang, “An introduction to physics and technology of thin films,” River Edge, NJ: World Scientific, Singapore, 1994.
- [2] J. E. Greene, “Transitioning from the art to the science of thin films: 1964 to 2003,” *J. Vac. Sci. Technol. A*, vol. 21, no. 5, pp. S71–S73, 2003.
- [3] S.-H. Jeong, J.-K. Kim, B.-S. Kim, S.-H. Shim, and B.-T. Lee, “Characterization of SiO₂ and TiO₂ films prepared using RF magnetron sputtering and their application to anti-reflection coating,” *Vacuum*, vol. 76, no. 4, pp. 507–515, 2004.
- [4] B. Matthes, E. Broszeit, J. Aromaa, H. Ronkainen, S. P. Hannula, A. Leyland, and A. Matthews, “Corrosion performance of some titanium-based hard coatings,” *Surf. Coatings Technol.*, vol. 49, no. 1–3, pp. 489–495, 1991.
- [5] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, and M. Grätzel, “Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%,” *Thin Solid Films*, vol. 516, no. 14, pp. 4613–4619, 2008.
- [6] M. Lekka, N. Kouloumbi, M. Gajo, and P. L. Bonora, “Corrosion and wear resistant electrodeposited composite coatings,” *Electrochim. Acta*, vol. 50, no. 23, pp. 4551–4556, 2005.
- [7] Angela Piegari and Francois Flory, “Optical thin films and coatings: from materials to applications,” Cambridge: Woodhead Publishing Ltd, 2013.

- [8] See <http://physics.info/thin-films/summary.shtml> for the information about the light speed in the thin films.
- [9] G. F. Lothian, “Beer’s law and its use in analysis,” *Analyst*, vol. 88, no. 678, pp. 678–685, 1852.
- [10] H. Le Gall and J. P. Jamet, “Theory of the elastic and inelastic scattering of light by magnetic crystals,” *Phys. Stat. Sol.*, vol. 46, p. 467, 1971.
- [11] F. K. Shan, G. X. Liu, W. J. Lee, and B. C. Shin, “Stokes shift, blue shift and red shift of ZnO-based thin films deposited by pulsed-laser deposition,” *J. Cryst. Growth*, vol. 291, no. 2, pp. 328–333, 2006.
- [12] Driscoll Walter G. and Vaughan William, “Handbook of optics,” New York: McGraw-Hill, 1978.
- [13] A. D. Rakić, A. B. Djurišić, J. M. Elazar, and M. L. Majewski, “Optical properties of metallic films for vertical-cavity optoelectronic devices,” *Appl. Opt.*, vol. 37, no. 22, pp. 5213–5271, 1998.
- [14] Madelung Otfried, “Semiconductors — Basic Data, 2nd revised Edition,” Berlin, Heidelberg: Springer Berlin Heidelberg, 1996.
- [15] F. Bassani and G. Pastori Parravicini, “Electronic states and optical transitions in solids,” Oxford: Pergamon Press, 1975.
- [16] William W. Parson, “Modern optical spectroscopy: with exercises and examples from biophysics and biochemistry, 2nd edition,” Berlin, Heidelberg: Springer Berlin Heidelberg : Imprint: Springer, 2015.
- [17] D. A Clugston and P. A. Basore, “Modelling free-carrier absorption in solar cells,” *Prog. Photovoltaics Res. Appl.*, vol. 5, no. 4, pp. 229–236, 1997.

- [18] Peter Y. Yu and Manuel Cardona, “Fundamentals of semiconductors: physics and materials properties,” Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg, 2010.
- [19] S. Venkataraj, D. Severin, S. H. Mohamed, J. Ngaruiya, O. Kappertz, and M. Wuttig, “Towards understanding the superior properties of transition metal oxynitrides prepared by reactive DC magnetron sputtering,” *Thin Solid Films*, vol. 502, no. 1–2, pp. 228–234, 2006.
- [20] P. Patsalas and S. Logothetidis, “Optical, electronic, and transport properties of nanocrystalline titanium nitride thin films,” *J. Appl. Phys.*, vol. 90, No. 9, pp. 4725–4734, 2001.
- [21] Amy L. Linsebigler, Guangquan Lu, and John T. Yates, Jr., “Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results,” *Chem. Rev.*, vol. 95, pp. 735–758, 1995.
- [22] D. Heřman, J. Šícha, and J. Musil, “Magnetron sputtering of TiO_xN_y films,” *Vacuum*, vol. 81, no. 3, pp. 285–290, 2006.
- [23] M. E. A. Warwick, G. Hyett, I. Ridley, F. R. Laffir, C. Olivero, P. Chapon, and R. Binions, “Synthesis and energy modelling studies of titanium oxy-nitride films as energy efficient glazing,” *Sol. Energy Mater. Sol. Cells*, vol. 118, pp. 149–156, 2013.
- [24] F. Chen, S. W. Wang, L. Yu, X. Chen, and W. Lu, “Control of optical properties of TiN_xO_y films and application for high performance solar selective absorbing coatings,” *Opt. Mater. Express*, vol. 4, No. 9, pp. 1833, 2014.
- [25] M. F. Hasaneen, D. Biro, L. Székely, P. Nemes-Incze, and P. B. Barna, “Substructure in the columnar crystals of the Ti_{0.45}O_{0.20}N_{0.35} oxynitride thin film,” *Vacuum*, vol. 86, no. 12, pp. 2105–2108, 2012.

- [26] C. Nunes, V. Teixeira, M. L. Prates, N. P. Barradas, and A. D. Sequeira, “Graded selective coatings based on chromium and titanium oxynitride,” *Thin Solid Films*, vol. 442, no. 1–2, pp. 173–178, 2003.
- [27] H. G. Chun et al., “Effects of Ag interlayer on the optoelectrical properties of TiON films,” *Vacuum*, vol. 84, no. 11, pp. 1255–1257, 2010.
- [28] G. V. Naik, J. Kim, A. Boltasseva, “Oxides and nitrides as alternative plasmonic materials in the optical range,” *Opt. Mater. Express*, vol. 1, No. 6, pp. 1090–1099, 2011.
- [29] N. D. Cuong, D. J. Kim, B. D. Kang, C. S. Kim, and S. G. Yoon, “Characterizations of high resistivity TiN_xO_y thin films for applications in thin film resistors,” *Microelectron. Reliab.*, vol. 47, no. 4–5 SPEC. ISS., pp. 752–754, 2007.
- [30] R. J. Koerner, L. A. Butterworth, I. V. Mayer, R. Dasbach, and H. J. Busscher, “Bacterial adhesion to titanium-oxy-nitride (TiNOX) coatings with different resistivities: A novel approach for the development of biomaterials,” *Biomaterials*, vol. 23, no. 14, pp. 2835–2840, 2002.
- [31] M. Sowińska et al., “Plasma-enhanced atomic layer deposition of titanium oxynitrides films: A comparative spectroscopic and electrical study,” *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 34, no. 1, pp. 01A127, 2016.
- [32] A. Bittar, “Study of TiO_xN_y thin film selective surfaces produced by ion assisted deposition,” *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 15, no. 2, pp. 223, 1997.
- [33] S. K. Pradhan and P. J. Reucroft, “A study of growth and morphological features of TiO_xN_y thin films prepared by MOCVD,” *J. Cryst. Growth*, vol. 250, no. 3–4, pp. 588–594, 2003.

- [34] A. Alper and O. Oguz, "The role of renewable energy consumption in economic growth: evidence from asymmetric causality," *Renew. Sustain. Energy Rev.*, vol. 60, pp. 953–959, 2016.
- [35] S. A. Kalogirou, S. Karellas, K. Braimakis, C. Stanciu, and V. Badescu, "Exergy analysis of solar thermal collectors and processes," *Prog. Energy Combust. Sci.*, vol. 56, pp. 106–137, 2016.
- [36] V. Devabhaktuni, M. Alam, S. Shekara Sreenadh Reddy Depuru, R. C. Green, D. Nims, and C. Near, "Solar energy: trends and enabling technologies," *Renew. Sustain. Energy Rev.*, vol. 19, pp. 555–564, 2013.
- [37] P. V. Kamat, "Meeting the clean energy demand: nanostructure architectures for solar energy conversion," *Phys. Chem.*, vol. 392, pp. 2834–2860, 2007.
- [38] J. Khan and M. H. Arsalan, "Solar power technologies for sustainable electricity generation – A review," *Renew. Sustain. Energy Rev.*, vol. 55, pp. 414–425, 2016.
- [39] C. Prieto, P. Cooper, A. I. Fernández, and L. F. Cabeza, "Review of technology: thermochemical energy storage for concentrated solar power plants," *Renew. Sustain. Energy Rev.*, vol. 60, pp. 909–929, 2016.
- [40] N. Jelley and T. Smith, "Concentrated solar power: Recent developments and future challenges," *Proc. Inst. Mech. Eng. Part A J. Power Energy*, vol. 229, no. 7, pp. 693–713, 2015.
- [41] M. Liu, N. H. Steven Tay, S. Bell, M. Belusko, R. Jacob, G. Will, W. Saman, and F. Bruno, "Review on concentrating solar power plants and new developments in high temperature thermal energy storage technologies," *Renew. Sustain. Energy Rev.*, vol. 53, pp. 1411–1432, 2016.

[42] See

<http://www.engineering.com/DesignerEdge/DesignerEdgeArticles/ArticleID/9286/A-Review-of-Concentrated-Solar-Power-in-2014.aspx> for the information about CSP with parabolic trough.

[43] C. Atkinson, C. L. Sansom, H. J. Almond, and C. P. Shaw, “Coatings for concentrating solar systems – A review,” *Renew. Sustain. Energy Rev.*, vol. 45, pp. 113–122, 2015.

[44] V. K. Jebasingh and G. M. J. Herbert, “A review of solar parabolic trough collector,” *Renew. Sustain. Energy Rev.*, vol. 54, pp. 1085–1091, 2016.

[45] N. Selvakumar and H. C. Barshilia, “Review of physical vapor deposited (PVD) spectrally selective coatings for mid- and high-temperature solar thermal applications,” *Sol. Energy Mater. Sol. Cells*, vol. 98, pp. 1–23, 2012.

[46] F. Cao, K. McEnaney, G. Chen, and Z. Ren, “A review of cermet-based spectrally selective solar absorbers,” *Energy Environ. Sci.*, vol. 7, no. 5, p. 1615, 2014.

[47] J. Zhang, T. P. Chen, Y. C. Liu, Z. Liu, and H. Y. Yang, “Design of a High Performance Selective Solar Absorber with the Structure of SiO_2 - TiO_2 - TiN_xO_y -Cu,” *ECS J. Solid State Sci. Technol.*, vol. 5, no. 7, pp. N43–N47, 2016.

[48] J. Zhang, T. P. Chen, Y. Liu, and J. I. Wong, “Si nanocrystal-based triple-layer anti-reflection coating for Si solar cells,” *J. Appl. Phys.*, vol. 114, no. 5, 053109, 2013.

[49] Q.C. Zhang, “Optimizing analysis of W-AlN cermet solar absorbing coatings,” *J. Phys. D: Appl. Phys.*, vol. 34, no. 21, pp. 3113 – 3120, 2001.

[50] M. F. M. Costa and V. Teixeira, “Microtopographic characterization of graded Cr-Cr₂O₃ cermet solar coatings,” *Proceedings of the society of photo-optical instrumentation engineers (SPIE)*, vol. 4419, pp. 744–747, 2001.

- [51] V. Teixeira, E. Sousa, M. F. Costa, C. Nunes, L. Rosa, M. J. Carvalho, M. Collares-Pereira, E. Roman, and J. Gago, "Spectrally selective composite coatings of Cr-Cr₂O₃ and Mo-Al₂O₃ for solar energy applications," *Thin Solid Films*, vol. 392, no. 2, pp. 320–326, 2001.
- [52] C. Nunes, V. Teixeira, M. L. Prates, N. P. Barradas, and a. D. Sequeira, "Graded selective coatings based on chromium and titanium oxynitride," *Thin Solid Films*, vol. 442, no. 1–2, pp. 173–178, 2003.
- [53] M. Q. Hovish and R. H. Dauskardt, "Optical properties of metal oxynitride thin films grown with atmospheric plasma deposition," *J. Phys. D. Appl. Phys.*, vol. 49, no. 39, p. 395302, 2016.
- [54] L. A. Leonova, E. L. Boytsova, and A. A. Pustovalova, "The study of titanium oxynitride coatings solubility deposited by reactive magnetron sputtering," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 135, no. 1, pp. 12026, 2016.
- [55] L. E. Vieira de Souza and A. M. Gilmanova Cavalcante, "Concentrated solar power deployment in emerging economies: The cases of China and Brazil," *Renew. Sustain. Energy Rev.*, vol. 72, pp. 1094–1103, 2017.
- [56] B. Subramanian, C. V. Muraleedharan, R. Ananthakumar, and M. Jayachandran, "A comparative study of titanium nitride (TiN), titanium oxy nitride (TiON) and titanium aluminum nitride (TiAlN), as surface coatings for bio implants," *Surf. Coatings Technol.*, vol. 205, No. 21–22, pp. 5014–5020, 2011.
- [57] J. Probst, U. Gbureck, and R. Thull, "Binary nitride and oxynitride PVD coatings on titanium for biomedical applications," *Surf. Coatings Technol.*, vol. 148, No. 2–3, pp. 226–233, 2001.

- [58] G. Ni, G. Li, S. V. Boriskina, H. Li, W. Yang, T. Zhang, and G. Chen, “Steam generation under one sun enabled by a floating structure with thermal concentration,” *Nat. Energy*, vol. 1, No. 9, p. 16126, 2016.
- [59] N. Kumar, M. G. Fissel, K. Pourrezaei, B. Lee, and E. C. Douglas, “Growth and properties of TiN and TiOxNy diffusion barriers in silicon on sapphire integrated circuits,” *Thin Solid Films*, vol. 153, no. 1–3, pp. 287–301, 1987.
- [60] W. Sinke, G. P. A. Frijlink, F. W. Saris, G. P. A. Frijlink, and F. W. Saris, “Oxygen in titanium nitride diffusion barriers Oxygen in titanium nitride diffusion barriers,” *Appl. Phys. Lett.*, vol. 47, pp. 471, 1985.
- [61] Michael Quinten, “A practical guide to optical metrology for thin films,” Weinheim: Wiley-VCH; Chichester: John Wiley, pp. 35 – 49, 2012.
- [62] Hiroyuki Fujiwara, “Spectroscopic ellipsometry: principles and applications,” Hoboken: John Wiley & Sons, Ltd., pp. 24 – 31, 2007
- [63] H.A. Lorentz, “Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern,” Leipzig: B.G. Teubner, 1906.
- [64] D. Stroud, “The effective medium approximations: Some recent developments,” *Superlattices Microstruct.*, vol. 23, no. 3, pp. 567–573, 1998.
- [65] Tuck C. Choy, “Effective medium theory: principles and applications,” Oxford [England]: Clarendon Press; New York: Oxford University Press, 1999.
- [66] C. Kittel, “Introduction to Solid State Physics, 6th edition,” John Wiley & Sons, Inc., New York, 1986.
- [67] J.C.M. Garnett, “Colours in metal glasses and in metallic films,” *Philosophical Transactions of the Royal Society of London Series A-Containing Papers of a Mathematical or physical Character*, vol. 203, pp. 385 – 420, 1904.

- [68] D.A.G. Bruggeman, "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen," *Annalen der Physik*, vol. 24, pp. 636 – 679, 1935.
- [69] Eugene Hecht, "Optics, 4th edition," Addison-Wesley, 2002.
- [70] R. M. A. Azzam and N. M. Bashara, "Ellipsometry and polarized light," Amsterdam; New York: North-Holland Pub. Co.; New York: sole distributors for the U.S.A. and Canada, Elsevier North-Holland, 1977.
- [71] Mark Fox, "Optical properties of solids," Oxford; New York: Oxford University Press, 2010.
- [72] See <https://www.doitpoms.ac.uk/tlplib/semiconductors/direct.php> for the information about momentum conversation.
- [73] M. Rudiger, J. Greulich, A. Richter, and M. Hermle, "Parameterization of free carrier absorption in highly doped silicon for solar cells," *Electron Devices, IEEE Trans.*, vol. 60, No. 7, pp. 2156–2163, 2013.
- [74] M. Veszeli, K. Andersson, C. G. Ribbing, K. Järrendahl, and H. Arwin, "Optical constants and Drude analysis of sputtered zirconium nitride films.," *Appl. Opt.*, vol. 33, No. 10, pp. 1993–2001, 1994.
- [75] Y. Zhong-Cai and S. Jia-Ming, "Collisional, nonuniform plasma sphere scattering calculation by FDTD employing a drude model," *Int. J. Infrared Millimeter Waves*, vol. 28, No. 11, pp. 987–992, 2007.
- [76] A. D. Rakić, A. B. Djurišić, J. M. Elazar, and M. L. Majewski, "Optical properties of metallic films for vertical-cavity optoelectronic devices," *Appl. Opt.*, vol. 37, No. 22, pp. 5213–5271, 1998.

- [77] S. Zhu, T. P. Chen, Y. C. Liu, S. F. Yu, and Y. Liu, “Tunable surface plasmon resonance of gold nanoparticles self-assembled on fused silica substrate,” *Electrochem. Solid-State Lett.*, vol. 13, No. 12, pp. K96, 2010.
- [78] J. M. Luther, P. K. Jain, T. Ewers, and a P. Alivisatos, “Localized surface plasmon resonances arising from free carriers in doped quantum dots,” *Nat. Mater.*, vol. 10, No. 5, pp. 361–366, 2011.
- [79] U. Guler, J. C. Ndukaife, G. V. Naik, a. G. A. Nnanna, A. Kildishev, V. M. Shalae, and A. Boltasseva, “Local heating with lithographically fabricated plasmonic titanium nitride nanoparticles,” *Nano Letters*, vol. 13, No. 12, pp. 6078 – 6083, 2013.
- [80] E. Hutter and J. H. Fendler, “Exploitation of localized surface plasmon resonance,” *Adv. Mater.*, vol. 16, No. 19, pp. 1685–1706, 2004.
- [81] Gustav Mie, “Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen,” *Annalen der Physik*, vol. 330, No. 3, pp. 377 – 445, 1908.
- [82] Q. Fu and W. Sun, “Mie theory for light scattering by a spherical particle in an absorbing medium,” *Appl. Opt.*, vol. 40, pp. 1354–1361, 2001.
- [83] B. T. Draine and P. J. Flatau, “Discrete-dipole approximation for scattering calculations,” *J. Opt. Soc. Am. A*, vol. 11, No. 4, pp. 1491–1499, 1994.
- [84] Takumi Sannomiya and Christian Hafner, “Multiple multipole program modelling for nano plasmonic sensors,” *J. Comput. Theor. Nanosci.*, vol. 7, No. 8, pp. 1578 – 1595, 2010.
- [85] S. Liu, S. Zhong, and S. Liu, “Finite-difference time-domain algorithm for dispersive media based on runge-kutta exponential time differencing method,” *Int. J. Infrared Millimeter Waves*, vol. 29, No. 3, pp. 323–328, 2008.

- [86] S. Link, M. B. Mohamed, and M. A. El-Sayed, "Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant," *J. Phys. Chem. B*, vol. 103, No. 16, pp. 3073–3077, 1999.
- [87] M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafigullin, I. Vezmar, and R. L. Whetten, "Optical absorption spectra of nanocrystal gold molecules," *J. Phys. Chem. B*, vol. 101, No. 19, pp. 3706–3712, 1997.
- [88] A. Bansal, J. S. Sekhon, and S. S. Verma, "Scattering efficiency and LSPR tunability of bimetallic Ag, Au, and Cu nanoparticles," *Plasmonics*, vol. 9, No. 1, pp. 143–150, 2014.
- [89] Y. W. Ma, L. H. Zhang, Z. W. Wu, M. F. Yi, J. Zhang, and G. S. Jian, "The study of tunable local surface plasmon resonances on Au-Ag and Ag-Au Core-Shell alloy nanostructure particles with DDA method," *Plasmonics*, vol. 10, No. 6, pp. 1791–1800, 2015.
- [90] Alfred Wagendristel and Yuming Wang, "An introduction to physics and technology of thin films," River Edge, NJ: World Scientific, Singapore, 1994.
- [91] P. Sigmund, "Theory of sputtering .I. sputtering yield of amorphous and polycrystalline targets," *Phys. Rev.*, vol. 184, No. 2, pp. 383–416, 1969.
- [92] S. Swann, "Magnetron sputtering," *Phys. Technol.*, vol. 19, no. 6, pp. 67–75, 1988.
- [93] Chue San Yoo, "Semiconductor manufacturing technology," Hackensack, N.J.; London: World Scientific, 2008.
- [94] D. E. Aspnes and A. A. Studna, "Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV," *Phys. Rev. B*, vol. 27, No. 2, pp. 985–1009, 1983.

- [95] See http://www.perkinelmer.co.uk/lab-solutions/resources/docs/APP_LAMBDA650IntegratingSpheres.pdf for the information about spectrophotometer with double beam system.
- [96] G. Binnig and C. F. Quate, “Atomic Force Microscope,” *Phys. Rev. Lett.*, vol. 56, No. 9, pp. 930–933, 1986.
- [97] See <http://www.nanoscience.gatech.edu/ziwang/research/afm.html> for the information about the principle of AFM.
- [98] See <http://www.nanoscience.com/technology/afm-technology/how-afm-works/> for the information about the working areas of the AFM.
- [99] See <http://vip.wartburg.edu/biology/SEMweb/SEMworking.html> for the information about the structure of SEM.
- [100] Brent Fultz and James Howe, “Transmission Electron Microscopy and Diffractometry of Materials, 4th edition,” Berlin, Heidelberg : Springer Berlin Heidelberg : Imprint: Springer, 2013.
- [101] See <http://pd.chem.ucl.ac.uk/pdmn/inst1/anode.htm> for the information about the $K\alpha$ wavelength of targets materials.
- [102] See <http://www.geo.umass.edu/courses/geo311/lecture%2019%20-%20diffraction%201.pdf> for the information about the principle of XRD.
- [103] See https://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy for the information about the working principle of XPS.
- [104] T. D. Lee and A. U. Ebong, “A review of thin film solar cell technologies and challenges,” *Renew. Sustain. Energy Rev.*, vol. 70, pp. 1286–1297, 2016.

- [105] J. Ko, D. Gong, K. Pillai, K. S. Lee, M. Ju, P. Choi, K. R. Kim, J. Yi, and B. Choi, "Double layer $\text{SiN}_x\text{:H}$ films for passivation and anti-reflection coating of c-Si solar cells," *Thin Solid Films*, vol. 519, No. 20, pp. 6887–6891, 2011.
- [106] S. Lien, D. Wu, W. Yeh, and J. Liu, "Tri-layer antireflection coatings ($\text{SiO}_2/\text{SiO}_2\text{--TiO}_2/\text{TiO}_2$) for silicon solar cells using a sol–gel technique," *Sol. Energy Mater. Sol. Cells*, vol. 90, No. 16, pp. 2710–2719, 2006.
- [107] D. Glöß, P. Frach, C. Gottfried, S. Klinkenberg, J. S. Liebig, W. Hentsch, H. Liepack, and M. Krug, "Multifunctional high-reflective and antireflective layer systems with easy-to-clean properties," *Thin Solid Films*, vol. 516, No. 14, pp. 4487–4489, 2008.
- [108] F. Sutter, S. Ziegler, M. Schmücker, P. Heller, and R. Pitz-Paal, "Modelling of optical durability of enhanced aluminum solar reflectors," *Sol. Energy Mater. Sol. Cells*, vol. 107, pp. 37–45, 2012.
- [109] K. L. Chopra, P. D. Paulson, and V. Dutta, "Thin-film solar cells: an overview," *Prog. photovoltaics*, vol. 12, No. 23, pp. 69–92, 2004.
- [110] A. G. Aberle, "Thin-film solar cells," *Thin Solid Films*, vol. 517, No. 17, pp. 4706–4710, 2009.
- [111] Hoppea and Sariciftci, "Organic solar cells: An overview," *J. Mater. Res*, vol. 19, No. 7, pp. 1925, 2004.
- [112] H. Hosono, "Recent progress in transparent oxide semiconductors: Materials and device application," *Thin Solid Films*, vol. 515, No. 15 SPEC. ISS., pp. 6000–6014, 2007.
- [113] K. Ravichandran, N. Jabena Begum, S. Snega, and B. Sakthivel, "Properties of sprayed aluminum-doped zinc oxide films—A Review," *Mater. Manuf. Process.*, vol. 6914, No. January, pp. 1–13, 2014.

- [114] T. Minami, “Transparent conducting oxide semiconductors for transparent electrodes,” *Semicond. Sci. Technol.*, vol. 20, No. 4, pp. S35–S44, 2005.
- [115] M. Joly, Y. Antonetti, M. Python, M. A. G. Lazo, T. Gascou, A. Hessler-Wyser, J.-L. Scartezzini, and A. Schüler, “Selective solar absorber coatings on receiver tubes for CSP – energy-efficient production process by sol-gel dip-coating and subsequent induction heating,” *Energy Procedia*, vol. 57, pp. 487–496, 2014.
- [116] C. Atkinson, C. L. Sansom, H. J. Almond, and C. P. Shaw, “Coatings for concentrating solar systems – A review,” *Renew. Sustain. Energy Rev.*, vol. 45, pp. 113–122, 2015.
- [117] P. Bermel, M. Ghebrebrhan, W. R. Chan, Y. X. Yeng, M. Araghchini, R. Hamam, C. H. Marton, K. F. Jensen, M. Soljacic, J. D. Joannopoulos, S. G. Johnson, I. Celanovic, M. Soljačić, J. D. Joannopoulos, S. G. Johnson, and I. Celanovic, “Design and global optimization of high-efficiency thermophotovoltaic systems.,” *Opt. Express*, vol. 18 Suppl 3, No. 103, pp. A314–A334, 2010.
- [118] C. E. Kennedy, “Review of mid- to high- temperature solar selective absorber materials,” *Technical Rep. NREL*, pp. 1–53, 2002.
<http://www.nrel.gov/docs/fy02osti/31267.pdf>
- [119] T. Yokoyama, T. D. Dao, K. Chen, S. Ishii, R. P. Sugavaneshwar, M. Kitajima, and T. Nagao, “Spectrally selective mid-infrared thermal emission from molybdenum plasmonic metamaterial operated up to 1000 °C,” *Adv. Opt. Mater.*, vol. 4, no. 12, pp. 1987–1992, 2016.
- [120] See <http://www.oberlin.edu/physics/dstyer/P111/Carnot.pdf> for the information about Carnot efficiency.
- [121] F. Cao, L. Tang, Y. Li, A. P. Litvinchuk, J. Bao, and Z. Ren, “A high-temperature stable spectrally-selective solar absorber based on cermet of titanium nitride in SiO₂

- deposited on lanthanum aluminate,” *Sol. Energ. Mat. Sol. Cells*, vol. 160, pp. 12–17, 2017.
- [122] Y. Ning, W. Wang, Y. Sun, Y. Wu, H. Man, C. Wang, S. Zhao, E. Tomasella, A. Bousquet, and Y. Zhang, “Tuning of reflectance transition position of Al-AlN cermet solar selective absorbing coating by simulating,” *Infrared Phys. Technol.*, vol. 80, pp. 65–70, 2017.
- [123] J. Moon, D. Lu, B. VanSaders, T. K. Kim, S. D. Kong, S. Jin, R. Chen, and Z. Liu, “High performance multi-scaled nanostructured spectrally selective coating for concentrating solar power,” *Nano Energy*, vol. 8, pp. 238–246, 2014.
- [124] T. K. Kim, B. VanSaders, J. Moon, T. Kim, C. H. Liu, J. Khamwannah, D. Chun, D. Choi, A. Kargar, R. Chen, Z. Liu, and S. Jin, “Tandem structured spectrally selective coating layer of copper oxide nanowires combined with cobalt oxide nanoparticles,” *Nano Energy*, vol. 11, pp. 247–259, 2015.
- [125] H. C. Barshilia, N. Selvakumar, K. S. Rajam, D. V. Sridhara Rao, K. Muraleedharan, and A. Biswas, “TiAlN/TiAlON/Si₃N₄ tandem absorber for high temperature solar selective applications,” *Appl. Phys. Lett.*, vol. 89, no. 19, pp. 1–4, 2006.
- [126] M. Lazarov, B. Röhle, T. Eisenhammer, and R. Sizmann, “TiN_xO_y-Cu-coatings for low emissive solar selective absorbers,” *Proceedings of the Soc. Photo. Opt. Instrumentat. Engineers (SPIE)*, vol. 1536, pp. 183–191, 1991.
- [127] M. Lazarov, R. Sizmann, and U. Frei, “Optimization of SiO₂-TiN_xO_y-Cu interference absorbers: numerical and experimental results,” *Proc. of SPIE, Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XII*, vol. 2017, pp. 345 – 356, 1993.

- [128] C. Nunes, V. Teixeira, M. L. Prates, N. P. Barradas, and A. D. Sequeira, “Graded selective coatings based on chromium and titanium oxynitride,” *Thin Solid Films*, vol. 442, no. 1–2, pp. 173–178, 2003.
- [129] See http://www.almecogroup.com/uploads/1172-ALMECO_TinoxEnergy_ENG_S402_07_2014_mail.pdf for the information about the parameters of commercial TiN_xO_y based SSA.
- [130] H. Schellinger, M. P. Lazarov, H. Klank, and R. Sizmann, “Thermal and chemical metallic - dielectric transitions of TiN_xO_y -Cu absorber tandems,” *SPIE's 1993 Int. Symp. Opt. Imaging, Instrum.*, vol. 2077, No. 19, pp. 366–376, 1993.
- [131] G. Espinosa-rueda, J. Luis, N. Hermoso, N. Martínez-sanz, and M. Gallas-torreira, “Vacuum evaluation of parabolic trough receiver tubes in a 50 MW concentrated solar power plant,” *Sol. Energy*, vol. 139, pp. 36–46, 2016.
- [132] M. H. Chan and F. H. Lu, “Preparation of titanium oxynitride thin films by reactive sputtering using air/Ar mixtures,” *Surf. Coat. Tech.*, vol. 203, No. 5-7, pp. 614–618, 2008.
- [133] J. Graciani, S. Hamad, and J. F. Sanz, “Changing the physical and chemical properties of titanium oxynitrides $\text{TiN}_{1-x}\text{O}_x$ by changing the composition,” *Phys. Rev. B*, vol. 80, No. 18, pp. 184112, 2009.
- [134] S. J. Cho, C. K. Jung, and J. H. Boo, “A study on the characteristics of TiO_xN_y thin films with various nitrogen flow rate by PECVD method,” *Curr. Appl. Phys.*, Vol. 12, pp. S29–S34, 2012.
- [135] J. M. Chappé, N. Martin, J. Lintymer, F. Sthal, G. Terwagne, and J. Takadoum, “Titanium oxynitride thin films sputter deposited by the reactive gas pulsing process,” *Appl. Surf. Sci.*, vol. 253, No. 12, pp. 5312–5316, 2007.

- [136] F. Maury and F. D. Duminica, "TiO_xN_y coatings grown by atmospheric pressure metal organic chemical vapor deposition," *Surf. Coatings Technol.*, vol. 205, No. 5, pp. 1287–1293, 2010.
- [137] N. D. Cuong, D. J. Kim, B. D. Kang, C. S. Kim, and S. G. Yoon, "Characterizations of high resistivity TiN_xO_y thin films for applications in thin film resistors," *Microelectron. Reliab.*, vol. 47, No. 4–5, pp. 752–754, 2007.
- [138] J. C. Francois and M. Sigrist, "The optical properties of titanium nitrides and carbides: spectral selectivity and photothermal conversion of solar energy," *Sol. Energ. Mater.*, vol. 7, No. 3, pp. 299–312, 1982.
- [139] G. V. Naik, J. L. Schroeder, X. J. Ni, A. V. Kildishev, T. D. Sands, and A. Boltasseva, "Titanium nitride as a plasmonic material for visible and near infrared wavelengths," *Opt. Mater. Express*, vol. 2, No. 4, pp. 478–489, 2012.
- [140] U. Guler, G. V. Naik, A. Boltasseva, V. M. Shalaev, and A. V. Kildishev, "Performance analysis of nitride alternative plasmonic materials for localized surface plasmon applications," *Appl. Phys. B-Lasers Opt.*, vol. 107, No. 2, pp. 285–291, 2012.
- [141] N. White, A. L. Campbell, J. T. Grant, R. Pachter, K. Eyink, R. Jakubiak, G. Martinez, and C. V. Ramana, "Surface/interface analysis and optical properties of RF sputter-deposited nanocrystalline titanium nitride thin films," *Appl. Surf. Sci.*, vol. 292, pp. 74–85, 2014.
- [142] C. M. Zgrabik and E. L. Hu, "Optimization of sputtered titanium nitride as a tunable metal for plasmonic applications," *Opt. Mater. Express*, vol. 5, No. 12, pp. 478–489, 2015.

- [143] S. Zhu, T. P. Chen, Y. C. Liu, Y. Liu, and S. Fung, "A quantitative modeling of the contributions of localized surface plasmon resonance and interband transitions to absorbance of gold nanoparticles," *J. Nanopart. Res.*, vol. 14, No. 5, pp. 856, 2012.
- [144] J. M. Luther, P. K. Jain, T. Ewers, and A. P. Alivisatos, "Localized surface plasmon resonances arising from free carriers in doped quantum dots," *Nat. Mater.*, vol. 10, No. 5, pp. 361–366, 2011.
- [145] J. Kim, G. V. Naik, N. K. Emani, U. Guler, and A. Boltasseva, "Plasmonic resonances in nanostructured transparent conducting oxide films," *IEEE J. Sel. Top. Quant.*, vol. 19, No. 3, pp. 1–7, 2013.
- [146] M. B. Cortie, J. Giddings, and A. Dowd, "Optical properties and plasmon resonances of titanium nitride nanostructures," *Nanotechnology*, vol. 21, No. 11, pp. 115201, 2010.
- [147] W. Li, U. Guler, N. Kinsey, G. V. Naik, A. Boltasseva, J. Guan, V. M. Shalaev, and A. V. Kildishev, "Refractory plasmonics with titanium nitride: broadband metamaterial absorber," *Adv. Mater.*, vol. 26, No. 47, pp. 7959–7965, 2014.
- [148] J. H. Kang and K. J. Kim, "Structural, optical, and electronic properties of cubic TiN_x compounds," *J. Appl. Phys.*, vol. 86, No. 1, pp. 346-350, 1999.
- [149] M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson, and R. S. C. Smart, "X-ray photoelectron spectroscopic chemical state Quantification of mixed nickel metal, oxide and hydroxide systems," *Surf. Interface Anal.*, vol. 41, No. 4, pp. 324–332, 2009.
- [150] D. Arias, A. Devia, and J. Velez, "Study of TiN/ZrN/TiN/ZrN multilayers coatings grown by cathodic arc technique," *Surf. Coatings Technol.*, vol. 204, No. 18–19, pp. 2999–3003, 2010.

- [151] N. K. Ponon, D. J. R. Appleby, E. Arac, P. J. King, S. Ganti, K. S. K. Kwa, and A. O'Neill, "Effect of deposition conditions and post deposition anneal on reactively sputtered titanium nitride thin films," *Thin Solid Films*, vol. 578, pp. 31–37, 2015.
- [152] S. Wrehde, M. Quaas, R. Bogdanowicz, H. Steffen, H. Wulff, and R. Hippler, "Optical and chemical characterization of thin TiN_x films deposited by DC-magnetron sputtering," *Vacuum*, vol. 82, No. 10, pp. 1115–1119, 2008.
- [153] See <https://en.wikipedia.org/wiki/File:VanderPauwContactPlacement.jpg> for the information about Van der Pauw configurations.
- [154] S. J. Henley, M. N. R. Ashfold, and D. Cherns, "The growth of transparent conducting ZnO films by pulsed laser ablation," *Surf. Coatings Technol.*, vol. 177–178, pp. 271–276, 2004.
- [155] G. Safran and P. Panine, "A novel method for the cross-sectional TEM preparation of thin films deposited onto water-soluble substrates," *Microsc. Res. Tech.*, vol. 25, pp. 346–349, 1993.
- [156] J.A. Woollam Co., Inc., "Guide to using WVASE spectroscopic ellipsometry data acquisition and analysis software".
- [157] S. T. Sundari, R. Ramaseshan, F. Jose, S. Dash, and A. K. Tyagi, "Investigation of temperature dependent dielectric constant of a sputtered TiN thin film by spectroscopic ellipsometry," *J. Appl. Phys.*, vol. 115, No. 3, pp. 033516, 2014.
- [158] X. D. Li, T. P. Chen, P. Liu, Y. Liu, Z. Liu, and K. C. Leong, "A study on the evolution of dielectric function of ZnO thin films with decreasing film thickness," *J. Appl. Phys.*, vol. 115, No. 10, pp. 1 – 5, 2014.

- [159] T. P. Chen, Y. Liu, M. S. Tse, P. F. Ho, G. Dong, and S. Fung, "Depth profiling of Si nanocrystals in Si-implanted SiO₂ films by spectroscopic ellipsometry," *Appl. Phys. Lett.*, vol. 81, No. 25, pp. 4724, 2002.
- [160] X. D. Li, T. P. Chen, Y. Liu, and K. C. Leong, "Influence of localized surface plasmon resonance and free electrons on the optical properties of ultrathin Au films: a study of the aggregation effect," *Opt. Express*, vol. 22, No. 5, pp. 5124, 2014.
- [161] S. Link and M. A. El-Sayed, "Optical properties and ultrafast dynamics of metallic nanocrystals," *Annu. Rev. Phys. Chem.*, vol. 54, pp. 331–366, 2003.
- [162] H. Kuwata, H. Tamaru, K. Esumi, and K. Miyano, "Resonant light scattering from metal nanoparticles: Practical analysis beyond rayleigh approximation," *Appl. Phys. Lett.*, vol. 83, No. 22, pp. 4625 – 4627, 2003.
- [163] S. W. Prescott and P. Mulvaney, "Gold nanorod extinction spectra," *J. Appl. Phys.*, vol. 99, No. 12, pp. 123504, 2006.
- [164] J. Moon, D. Lu, B. VanSaders, T. K. Kim, S. D. Kong, S. Jin, R. Chen, and Z. Liu, "High performance multi-scaled nanostructured spectrally selective coating for concentrating solar power," *Nano Energy*, vol. 8, pp. 238–246, 2014.
- [165] A. W. Dowling, T. Zheng, and V. M. Zavala, "Economic assessment of concentrated solar power technologies: A review," *Renew. Sustain. Energy Rev.*, vol. 72, pp. 1019–1032, 2017.
- [166] H. C. Barshilia, P. Kumar, K. S. Rajam, and a. Biswas, "Structure and optical properties of Ag-Al₂O₃ nanocermet solar selective coatings prepared using unbalanced magnetron sputtering," *Sol. Energy Mater. Sol. Cells*, vol. 95, pp. 1707–1715, 2011.

- [167] Q. Zhang, Y. Yin, and D. R. Mills, “High efficiency Mo-Al₂O₃ cermet selective surfaces for high-temperature application,” *Sol. Energy Mater. Sol. Cells*, vol. 40, pp. 43–53, 1996.
- [168] C. Nunes, V. Teixeira, M. L. Prates, N. P. Barradas, and a. D. Sequeira, “Graded selective coatings based on chromium and titanium oxynitride,” *Thin Solid Films*, vol. 442, pp. 173–178, 2003.
- [169] E. Wäckelgård, A. Mattsson, R. Bartali, R. Gerosa, G. Gottardi, F. Gustavsson, N. Laidani, V. Micheli, D. Primetzhofer, and B. Rivolta, “Development of W–SiO₂ and Nb–TiO₂ solar absorber coatings for combined heat and power systems at intermediate operation temperatures,” *Sol. Energy Mater. Sol. Cells*, vol. 133, pp. 180–193, 2015.
- [170] F. Cao, L. Tang, Y. Li, A. P. Litvinchuk, J. Bao, and Z. Ren, “A high-temperature stable spectrally-selective solar absorber based on cermet of titanium nitride in SiO₂ deposited on lanthanum aluminate,” *Sol. Energy Mater. Sol. Cells*, vol. 160, pp. 12 – 17, 2017.
- [171] A. Antonaia, A. Castaldo, M. L. Addonizio, and S. Esposito, “Stability of W-Al₂O₃ cermet based solar coating for receiver tube operating at high temperature,” *Sol. Energy Mater. Sol. Cells*, vol. 94, pp. 1604–1611, 2010.
- [172] S. Zhao, C. Ribbing, and E. Wackelgard, “Optical constants of sputtered Ni/NiO solar absorber film-depth-profiled characterization,” *Sol. Energy Mater. Sol. Cells*, vol. 84, pp. 193–203, 2004.
- [173] X. H. Gao, Z. M. Guo, Q. F. Geng, P. J. Ma, A. Q. Wang, and G. Liu, “Enhanced optical properties of TiN-based spectrally selective solar absorbers deposited at a high substrate temperature,” *Sol. Energy Mater. Sol. Cells*, vol. 163, pp. 91–97, 2017.

- [174] A. Biswas, D. Bhattacharyya, H. C. Barshilia, N. Selvakumar, and K. S. Rajam, "Spectroscopic ellipsometric characterization of TiAlN/TiAlON/Si₃N₄ tandem absorber for solar selective applications," *Appl. Surf. Sci.*, vol. 254, pp. 1694–1699, 2008.
- [175] C.-G. Ribbing and A. Roos, "Transition metal nitride films for optical applications," *Soc. photo-optical Instrum. Eng.*, vol. 3133, pp. 148–162, 1997.
- [176] Y. Liu, C. Wang, and Y. Xue, "The spectral properties and thermal stability of NbTiON solar selective absorbing coating," *Sol. Energy Mater. Sol. Cells*, vol. 96, pp. 131–136, 2012.
- [177] S. H. Mohamed, O. Kappertz, J. M. Ngaruiya, T. Niemeier, R. Drese, R. Detemple, M. M. Wakkad, and M. Wuttig, "Influence of nitrogen content on properties of direct current sputtered TiO_xN_y films," *Phys. Status Solidi Appl. Res.*, vol. 201, pp. 90–102, 2004.
- [178] C. Rousselot and N. Martin, "Influence of two reactive gases on the instabilities of the reactive sputtering process," *Surf. Coatings Technol.*, vol. 142–144, pp. 206–210, 2001.
- [179] D. A. Duarte, J. C. Sagás, A. S. Da Silva Sobrinho, and M. Massi, "Modeling the reactive sputter deposition of N-doped TiO₂ for application in dye-sensitized solar cells: Effect of the O₂ flow rate on the substitutional N concentration," *Appl. Surf. Sci.*, vol. 269, pp. 55–59, 2013.
- [180] F. Cao, D. Kraemer, T. Sun, Y. Lan, G. Chen, and Z. Ren, "Enhanced thermal stability of W-Ni-Al₂O₃ cermet-based spectrally selective solar absorbers with tungsten infrared reflectors," *Adv. Energy Mater.*, vol. 5, pp. 1401042, 2015.
- [181] Qi-Chu Zhang and David R. Mills, "High solar performance selective surface using bi sublayer cermet film structures," *Sol. Energy Mater. Sol. Cells*, vol. 27, pp. 273–290, 1992.

- [182] Q. C. Zhang, "Recent progress in high-temperature solar selective coatings," *Sol. Energy Mater. Sol. Cells*, vol. 62, pp. 63–74, 2000.
- [183] S. Esposito, a. Antonaia, M. L. Addonizio, and S. Aprea, "Fabrication and optimisation of highly efficient cermet-based spectrally selective coatings for high operating temperature," *Thin Solid Films*, vol. 517, pp. 6000–6006, 2009.
- [184] L. Zheng, F. Zhou, Z. Zhou, X. Song, G. Dong, M. Wang, and X. Diao, "Angular solar absorptance and thermal stability of Mo–SiO₂ double cermet solar selective absorber coating," *Sol. Energy*, vol. 115, pp. 341–346, 2015.
- [185] J. Zhang, T.P. Chen, X.D. Li, Y.C. Liu, Y. Liu, and H.Y. Yang, "Investigation of localized surface plasmon resonance of TiN nanoparticles in TiN_xO_y thin films", *Optical materials express*, vol. 6, No. 7, pp. 2422 – 2433, 2016.
- [186] N. Deegan, R. Daghrir, P. Drogui, and M. A. El Khakani, "Bandgap tailoring of in-situ nitrogen-doped TiO₂ sputtered films intended for electrophotocatalytic applications under solar light," *J. Appl. Phys.*, vol. 116, pp. 153510, 2014.
- [187] V. Stranak, M. Quaas, R. Bogdanowicz, H. Steffen, H. Wulff, Z. Hubicka, M. Tichy, and R. Hippler, "Effect of nitrogen doping on TiO_xN_y thin film formation at reactive high-power pulsed magnetron sputtering," *J. Phys. D. Appl. Phys.*, vol. 43, pp. 285203, 2010.
- [188] G. Droulers, a. Beaumont, J. Beauvais, and D. Drouin, "Spectroscopic ellipsometry on thin titanium oxide layers grown on titanium by plasma oxidation," *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 29, pp. 021010, 2011.
- [189] M. Jerman, Z. Qiao, and D. Mergel, "Refractive index of thin films of SiO₂, ZrO₂, and HfO₂ as a function of the films' mass density," *Appl. Opt.*, vol. 44, pp. 3006 – 3012, 2005.

- [190] N. Selvakumar, S. B. Krupanidhi, and H. C. Barshilia, "Carbon nanotube-based tandem absorber with tunable spectral selectivity: Transition from near-perfect blackbody absorber to solar selective absorber," *Adv. Mater.*, pp. 2552–2557, 2014.
- [191] K. Valleti, D. Murali Krishna, and S. V. Joshi, "Functional multi-layer nitride coatings for high temperature solar selective applications," *Sol. Energy Mater. Sol. Cells*, vol. 121, pp. 14 – 21, 2014.
- [192] Louis Spanoudis, "Solar energy collector having solar selective coating of low reflectance", United States Patent, No. 4334523, 1982.
- [193] H. L. Zhang, J. Baeyens, J. Degève, and G. Cacères, "Concentrated solar power plants: Review and design methodology," *Renew. Sustain. Energy Rev.*, vol. 22, pp. 466 – 481, 2013.
- [194] O. Behar, A. Khellaf, and K. Mohammadi, "A review of studies on central receiver solar thermal power plants," *Renew. Sustain. Energy Rev.*, vol. 23, pp. 12 – 39, 2013.
- [195] J. Zhang, T. P. Chen, Y. C. Liu, Z. Liu, and H. Y. Yang, "Modeling of a selective solar absorber thin film structure based on double TiN_xO_y layers for concentrated solar power applications," *Sol. Energy*, vol. 142, pp. 33–38, 2017.
- [196] M.-H. Chan and F.-H. Lu, "X-ray photoelectron spectroscopy analyses of titanium oxynitride films prepared by magnetron sputtering using air/Ar mixtures," *Thin Solid Films*, vol. 517, pp. 5006 – 5009, 2009.
- [197] I. M. Ismail, B. Abdallah, M. Abou-Kharroub, and O. Mrad, "XPS and RBS investigation of TiN_xO_y films prepared by vacuum arc discharge," *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 271, pp. 102 – 106, 2012.

- [198] F. K. Urban and D. Barton, “Numerical ellipsometry: High accuracy modeling of thin absorbing films in the n-k plane,” *Thin Solid Films*, vol. 562, pp. 49 – 55, 2014.
- [199] W. Rzodkiewicz, A. Kudla, A. Misiuk, and S. Lasisz, “Spectroscopic ellipsometry investigation of influence of high pressure-high temperature process on optical properties of SiO₂-Si structures,” *Proceedings of SPIE*, vol. 4517, pp. 134 – 139, 2001.
- [200] D. Zhu, F. Mao, and S. Zhao, “The influence of oxygen in TiAlO_xN_y on the optical properties of colored solar-absorbing coatings,” *Sol. Energy Mater. Sol. Cells*, vol. 98, pp. 179 – 184, 2012.
- [201] F. Cao, D. Kraemer, T. Sun, Y. Lan, G. Chen, and Z. Ren, “Enhanced thermal stability of W-Ni-Al₂O₃ cermet-based spectrally selective solar absorbers with tungsten infrared reflectors,” *Adv. Energy Mater.*, vol. 5, pp. 1401042, 2015.
- [202] A. Amtout and R. Leonelli, “Optical properties of rutile near its fundamental band gap,” *Phys. Rev. B*, vol. 51, pp. 6842 – 6851, 1995.
- [203] S. Pratesi, M. De Lucia, M. Meucci, and E. Sani, “Structural and optical properties of copper-coated substrates for solar thermal absorbers,” *Superlattices Microstruct.*, vol. 98, pp. 342–350, 2016.
- [204] Q. C. Zhang and Y. G. Shen, “High performance W-AlN cermet solar coatings designed by modelling calculations and deposited by DC magnetron sputtering,” *Sol. Energy Mater. Sol. Cells*, vol. 81, pp. 25–37, 2004.
- [205] R. C. Juang, Y. C. Yeh, B. H. Chang, W. C. Chen, and T. W. Chung, “Preparation of solar selective absorbing coatings by magnetron sputtering from a single stainless steel target,” *Thin Solid Films*, vol. 518, pp. 5501–5504, 2010.

- [206] R. A. Taylor, T. P. . Otanicar, Y. L. Hewakuruppu, and D. DeJarnette, “Comparison of selective transmitters for solar thermal applications,” *Appl. Opt.*, vol. 55, pp. 3829–3839, 2016.
- [207] Y. Yin, L. Hang, S. Zhang, and X. L. Bui, “Thermal oxidation properties of titanium nitride and titanium-aluminum nitride materials - A perspective for high temperature air-stable solar selective absorber applications,” *Thin Solid Films*, vol. 515, pp. 2829–2832, 2007.
- [208] M. Kotilainen, M. Honkanen, K. Mizohata, and P. Vuoristo, “Influence of temperature-induced copper diffusion on degradation of selective chromium oxy-nitride solar absorber coatings,” *Sol. Energy Mater. Sol. Cells*, vol. 145, pp. 323–332, 2016.
- [209] See http://www.kyprossolar.com/files/Tinox_Productinformation_EN.pdf for the information about TiC thin film as a barrier layer in the TiN_xO_y based SSA.
- [210] X.-H. Gao, Z.-M. Guo, Q.-F. Geng, P.-J. Ma, and G. Liu, “Structure, optical properties and thermal stability of TiC-based tandem spectrally selective solar absorber coating,” *Sol. Energy Mater. Sol. Cells*, vol. 157, pp. 543–549, 2016.
- [211] S.-K. Choi, H. Kim, J. Kim, T. Cheon, J. H. Seo, and S.-H. Kim, “Properties of plasma-enhanced atomic layer deposited TiC_x films as a diffusion barrier for Cu metallization,” *Thin Solid Films*, vol. 590, pp. 311–317, 2015.
- [212] J. Nguyen, C. Jaoul, N. Glandut, and P. Lefort, “Hydrogen insertion in titanium carbide based thin films (nc- TiC_x /a-C:H) - comparison with bulk TiC_x ,” *Thin Solid Films*, vol. 612, pp. 172–178, 2016.
- [213] N. Oláh, Z. Fogarassy, A. Sulyok, M. Veres, G. Kaptay, and K. Balázs, “TiC crystallite formation and the role of interfacial energies on the composition during the

- deposition process of TiC/a:C thin films,” *Surf. Coatings Technol.*, vol. 302, pp. 410–419, 2016.
- [214] A. A. Adjaottor, E. I. Meletis, S. Logothetidis, I. Alexandrou, and S. Kokkou, “Effect of substrate bias on sputter-deposited TiC_x, TiN_y and TiC_xN_y thin films,” *Surf. Coatings Technol.*, vol. 76–77, pp. 142–148, 1995.
- [215] S. J. Wang, H. Y. Tsai, S. C. Sun, and M. H. Shiao, “Characterization of sputtered titanium carbide film as diffusion barrier for copper metallization,” *J. Electrochem. Soc.*, vol. 148, pp. G500, 2001.
- [216] H. C. Chang, C. S. Lee, S. H. Chen, E. Y. Chang, and J. Z. He, “Study of Ti/W/Cu, Ti/Co/Cu, and Ti/Mo/Cu Multilayer structures as schottky metals for GaAs diodes,” *J. Electron. Mater.*, vol. 33, pp. 15–17, 2004.
- [217] A. Dan, J. Jyothi, K. Chattopadhyay, H. C. Barshilia, and B. Basu, “Spectrally selective absorber coating of WAlN/WAlON/Al₂O₃ for solar thermal applications,” *Sol. Energy Mater. Sol. Cells*, vol. 157, pp. 716–726, 2016.
- [218] I. H. Malitson, “Interspecimen comparison of the refractive index of fused silica,” *J. Opt. Soc. Am.*, vol. 55, pp. 1205, 1965.
- [219] H.-J. Hagemann, W. Gudat, and C. Kunz, “Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al₂O₃,” *J. Opt. Soc. Am.*, vol. 65, pp. 742, 1975.
- [220] Z. Wang, Y. Liu, B. Huang, Y. Dai, Z. Lou, G. Wang, X. Zhang, and X. Qin, “Progress on extending the light absorption spectra of photocatalysts,” *Phys. Chem. Chem. Phys.*, vol. 16, pp. 2758–74, 2014.
- [221] M. Kotilainen and P. Vuoristo, “Aluminium and tantalum nitride barriers against copper diffusion in solar absorbers,” *Surf. Eng.*, vol. 32, pp. 615–623, 2016.

- [222] N. Kumar, M. G. Fissel, and K. Pourrezaei, "Growth and properties of TiN and TiO_xN_y diffusion barriers in silicon on sapphire integrated circuits," *Thin Solid Films*, vol. 153, No. 1 – 3, pp. 287–301, 1987.
- [223] R. Bavadi and S. Valedbagi, "Physical properties of titanium nitride thin film prepared by DC magnetron sputtering," *Mater. Phys. Mech.*, vol. 15, pp. 167–172, 2012.
- [224] T. T. Hu, J. H. Hsu, J. C. Huang, S. Y. Kuan, C. J. Lee, and T. G. Nieh, "Correlation between reflectivity and resistivity in multi-component metallic systems," *Appl. Phys. Lett.*, vol. 101, pp. 011902, 2012.
- [225] I. Valyukh, S. V. Green, C. G. Granqvist, G. A. Niklasson, S. Valyukh, and H. Arwin, "Optical properties of thin films of mixed Ni-W oxide made by reactive DC magnetron sputtering," *Thin Solid Films*, vol. 519, no. 9, pp. 2914–2918, 2011.
- [226] T. K. Tsai, Y. H. Li, and J. S. Fang, "Spectral properties and thermal stability of CrN/CrON/Al₂O₃ spectrally selective coating," *Thin Solid Films*, vol. 615, pp. 91–96, 2016.
- [227] HY Cheng, Y. Tzeng, and JM Ting, "Characteristics of sputter deposited Pt/Al₂O₃ thin films," *Ceramics international*, vol. 42, no.16, pp. 19393–19396, 2016.
- [228] X. H. Gao, Z. M. Guo, Q. F. Geng, P. J. Ma, and G. Liu, "Microstructure and Optical Properties of SS/Mo/Al₂O₃ Spectrally Selective Solar Absorber Coating," *J. Mater. Eng. Perform.*, vol. 26, no. 1, pp. 161–167, 2017.
- [229] T. T. Chow, "A review on photovoltaic/thermal hybrid solar technology," *Appl. Energy*, vol. 87, no. 2, pp. 365–379, 2010.
- [230] V. V. Tyagi, S. C. Kaushik, and S. K. Tyagi, "Advancement in solar photovoltaic/thermal (PV/T) hybrid collector technology," *Renew. Sustain. Energy Rev.*, vol. 16, no. 3, pp. 1383–1398, 2012.