EFFECTS OF DIFFERENT WETTING LAYERS ON THE GROWTH OF SMOOTH
ULTRA-THIN SILVER THIN FILMS

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ABSTRACT

EFFECTS OF DIFFERENT WETTING LAYERS ON THE GROWTH OF SMOOTH ULTRA-THIN SILVER THIN FILMS

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Ultra-thin silver films (thickness below 10 nm) are of great interest as optical coatings in low emissive windows and plasmonic devices. However, producing these films has been a continuing challenge because of their tendency to form clusters rather than smooth contiguous thin films.

In this work we have studied the effects of Cu, Ge and ZnS as wetting layers to achieve ultra-smooth ultra-thin silver films. The silver films (5 nm) were grown by RF sputter deposition on silicon and glass substrates using a few monolayers of the different wetting materials. SEM imaging was used to characterize the surface properties such as island formation and roughness of the films. And the optical properties, such as reflection and transmission, were measured to identify the optical impact of the different wetting layers.

Then, a multi-layer silver based structure, low emissive coating was designed. The low emissive coating combines high transmittance over most visible spectrum and high reflectance over infrared spectrum. Such kind of coating is utilized as highly transparent in the visible and heat-reflective coating for the purpose of energy saving. The designed coatings were fabricated and their performances were evaluated. The comparison between the samples with different wetting layers shows that the designs with Cu wetting layer which has similar optical properties to silver produces the best overall performance. In the absence of a wetting layer, the measured optical spectra shows a significant departure from the model prediction, which we attribute primarily to the formation of silver film clusters.

Dedicated to my parents

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LIST OF ABBREVIATIONS AND NOTATIONS

IR	Infrared
SEM	Scanning Electron Microscope
RF	Radio-Frequency
CVD	Chemical Vapor Deposition
ALD	Atomic Layer Deposition
PLD	Pulsed Laser Deposition
DC	Direct Current
Low-E	Low Emissive

CHAPTER I.

INTRODUCTION

1.1 Ultra-thin Silver Films

Silver (Ag) is a noble metal which is being explored for applications in many nanoelectronic devices, optical modulators, plasmonics, optical metamaterials, low emissive coatings, and many other applications in nanophotonic [1-4]. Some novel properties, such as artificial plasmonic response, negative refractive index, have also been observed with Ag films [4]. This is basically due to Ag's low real refractive index and low loss in the visible spectrum to near IR optical frequencies [5] and high electrical conductivity.

The qualities of the silver film, such as film roughness and thickness, are vital to achieve high optical quality, repeatability, and reliability. Silver films are generally deposited by physical deposition techniques, such as resistive evaporation, electron beam evaporation, and RF/DC sputter deposition, although chemical vapor deposition is also sometimes used. However, Ag films growing on dielectric surfaces typically exhibit in islands (Volmer-Weber growth mode) [6-9] and consistently reveal a rough surface morphology with larger grain sizes than what is desired in nano-scale building blocks and electrical interfaces [10]. Therefore, it is of great importance to develop techniques and

methods to fabricate ultra-thin, ultra-smooth noble metal films with sub-nanometer scale roughness, low resistivity and a high degree of thickness.

1.2 Silver-based Low Emissive Coating

Low emissive coatings are multilayer coatings composed of dielectric layer sandwiched between metal layers. These coatings combine high transmittance over most of visible spectrum and high reflectance over the IR (infrared) spectrum. They are utilized as highly transparent heat-reflective coatings for the purpose of saving energy in homes and commercial buildings.

Metal-based coatings have to be thin enough to give a high visible transmittance, but at the same time smooth enough to give a high IR reflectance. To achieve this goal, the metal layers must be formed by a continuous film, without island growth, to avoid anomalous scattering and absorption. Metals, such as Ag, Cu, Au and Al all have the character of high IR reflectance [11]. But silver is probably the best choice for the metal layer because of its comparatively low absorption in the visible range [5, 12].

1.3 Thesis Outline

In this thesis we explore effective methods to fabricate ultra-thin, ultra-smooth Ag film with just a few nanometers thickness by applying different wetting layers. SEM imaging is used to characterize the surface properties such as island formation and roughness. The optical properties of these films were also measured to identify the optical impact and effectiveness of the different wetting layers. Then we design the silver based low emissive multilayer structure with different wetting layers. Also, we fabricate these coatings by RF (radio-frequency) magnetron sputtering and evaluate the optical performance of the fabricated coatings by the spectrometer.

This thesis is composed of four chapters. In chapter II, we discuss how to fabricate ultra-thin, ultra-smooth Ag layer with Cu, Ge and ZnS as the wetting layer by RF magnetron sputtering system. The surface qualities of the Ag films are evaluated by SEM imaging. We also measure the optical properties of these films.

Chapter III shows the design and fabrication samples of low emissive coatings with different wetting layers. We also make a sample without any wetting layer as the comparison reference. Then we measure the spectra for all the samples and for comparison. Finally, chapter IV provides a summary of our conclusion and the points for the future work that needs to be done.

CHAPTER II.

FABRICATION AND CHARACTERIZATION OF ULTRA-THIN, ULTRA-SMOOTH
SILVER LAYER USING DIFFERENT WETTING LAYERS

2.1 Introduction of Thin Film Growth

As modern microelectronics and optoelectronics industry is developing towards greater integration and miniaturization, the electronic and optical devices have been trending towards nanometer dimension. These structures are fabricated by a combination of lithography for lateral dimensional control, and thin film growth for vertical dimensional control. In this work, we only focus on the thin film growth aspects. First we will describe the theories of thin film growth mechanism and explore the commonly used methods to control the film growth.

There are three possible modes of thin film growth on surfaces: Frank-van der Merwe or layer by layer growth, Volmer-Weber growth and Stranski Krastanov growth.

- (1) Frank-Van der Merwe (also called two dimensional layer growth mode): when the deposited atom falls on the substrate, it tends to be bound to the substrate atoms because of the greater wetting effect between the deposited atom and the substrate atoms. So at the initial nucleation stage, the film takes the two-dimension character. As the result, it forms a complete monolayer on the surface. Subsequently atoms form uniform distribution of atoms, allowing the film to growth uniformly.
- (2) Volmer-Weber (also called three dimensional island growth mode): this mode occurs

when the deposited atoms have greater tendency to bind to each other than to the substrate atoms. This arises due to the poor wetting effect between the deposited atom and the substrate atoms. As a result, it forms a comparatively rough surface with significant topographic features. This mode is displayed by many soft metals such as gold, silver and copper grown on insulators [10].

(3) Stranski-Krastanov growth (also called layer plus island growth mode): this mode is an intermediate case. During the initial nucleation and growth stage it takes the layer growth mode within the first several monolayers. But during subsequent growth, it converts to island growth mode.

To achieve an atomically smooth film, which is preferred for the optical devices, we need to find effective fabrication methods to maintain the thin film growth in the layer-by-layer growth mode.

2.2 Metal-Dielectric Structures

One type of band-pass thin film filter is based on the Fabry-Perot interferometer. The Fabry-Perot interferometer consists of two parallel reflecting surfaces separated by a distance. Its transmission spectrum exhibits peaks of high transmission at specific wavelengths corresponding to the resonance of the two separated reflecting surface [13]. The Fabry-Perot interferometer structure can be applied in thin film stacks by depositing two ultra-thin metallic reflecting layers separated by a dielectric spacer with a specific thickness. This metal-dielectric thin film structure provides us with an effective prototype for a band-pass filter.

There is another common type of band-pass filter which is composed with all dielectric layers. The principle is also the Fabry-Perot interferometer consisting of a spacer layer

bounded by two high reflecting thin film stacks. But considering the low reflection from a single dielectric interface, this kind of filter usually needs dozens of layers to achieve the high reflection requirement on the both sides of the cavity. As the result, the film stack will be of the order of several micro-meters thick. Although this is done in dielectric filters, metal provides an alternative for realizing similar spectral transmission with just a few layers.

By comparing these two kind of optical thin film filters, the advantages of metal-dielectric structure is obvious. It needs much less layers. In other words, the total thickness is much thinner than the all dielectric filter. This makes friendlier for large scale manufacturing. But metal-dielectric structures also have their disadvantages compared to the all dielectric structures. The metal layers will produce some absorption as a consequence of the transmission through these metals. Even at the nanometer scale, there is still some absorption from the metal layers. This can be reduced by design but cannot be eliminated. For the high energy applications, such as high power lasers, the metal-dielectric filter is unsuitable because even a small portion of the absorbed energy might be enough to damage the metal films. For low emissive applications the source is solar radiation. Therefore, metal-dielectric structure is more appealing than the all-dielectric structure considering the simplicity of the thin film stack.

There are many kinds of highly reflective metals which could be considered for low emissive coating applications, such like Al, Cu, Au, Cr and Ag. Au is unfavorable because it is one of the most expensive metals. The transmission, absorption and reflection spectra of all the other four metals for a thickness of 5nm are shown in Figure 2-1, Figure 2-2 and Figure 2-3.

Figure 2-1. 5nm Al, Cu, Ag and Cr transmission spectra

Figure 2-2. 5nm Al, Cu, Ag and Cr absorption spectra

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Figure 2-3. 5nm Al, Cu, Ag and Cr reflection spectra

From the above plots, silver and copper has higher transmission in the visible wavelength range while chromium and aluminum have low transmissions. Chromium also exhibits very high absorption. Comparing copper with silver in absorption spectrum, it is obvious that silver is much lower in absorption at less than 5% in the entire visible wavelength range. In addition, the reflection of silver in the IR wavelength range shows a continuous increase. This satisfies the longer wavelength reflection requirement well. Thus, we can conclude that silver is one of the most suitable metals for the low emissive coating applications.

2.3 Fabrication and Characterization of Ag Ultra-thin Films

There are several different deposition methods such as chemical vapor deposition (CVD), atomic layer deposition (ALD), sputter deposition, evaporation and pulsed laser deposition (PLD) for thin film structures fabrication. Different methods can also be applied

of combination in a fabrication process, depending on the desired materials in the design. CVD and ALD are based on chemical reaction of volatile precursors. Sputter deposition, evaporation and PLD are physical deposition which uses mechanical, electromechanical or thermodynamics to produce thin film from a solid material in a low pressure environment. In this study, we use radio frequency (RF) sputter deposition. This is one of the most widely used process in large scale coating applications in industry.

2.3.1 Sputter Deposition

Low pressure sputter deposition is one of the most promising techniques for the fabrication of thin film devices. A wide variety of thin films can be made with high purity and a relatively high deposition rates [14]. Sputter deposition is a thin film deposition technique which uses inert heavy atom (usually Argon) bombarding the bulk solid target to remove the target atoms one atom or molecule at a time. Ionization due to the strong electric and magnetic fields near the cathode ions and electrons (plasma) from the neutral gas, which will then be accelerated towards the cathode surface (target). If the incidence energy is greater than the bonding energy of the target atoms, some of the atoms can be ejected from the target. This is known as sputtering. The ejected atoms and particles will then deposit on the substrate surface forming an amorphous thin film. The ratio of the number of Argon ions to the number of ejected atoms is now as the sputtering yield, which plays a large role in the deposition rate.

Generally, there are two kinds of power sources for sputter deposition: RF power and DC (direct current) power. The RF power supply is applied when the target is an insulator because the alternating polarity can neutralize the charge accumulation to sustain the glow discharge with an insulator target. DC or RF power supply can be used if the target is a

conductor. DC power provides a comparatively higher deposition rate, so it is preferred in metal deposition systems.

Figure 2-4. Denton Explorer 14 RF magnetron sputtering system

The sputter deposition equipment we used is the Denton Vacuum Explorer 14 RF magnetron sputtering system, which is shown in Figure 2-4. The Denton Vacuum Explorer 14 RF magnetron sputter deposition system is equipped with the Angstrom Sciences Onyx-3 magnetron sputtering cathode, supplied by a 13.56MHz radio frequency power supply or direct current power supply. A high vacuum in the main chamber is achieved by a Pfeiffer TMH 261 turbo molecular drag pump. The film deposition rate is controlled by Inficon XTM/2 deposition monitor using a quartz piezo crystal sensor.

There are two cathodes, and both of them can be supplied by DC or RF power. The front face of the cathode is covered with a target material and the back side is water cooled. The substrate is placed on the center stage which is kept rotating during the deposition

process to equalize the deposition rate from all directions. Generally, the main chamber is pumped down to about 1 μ Torr to remove moisture and absorbed gases. This is known as the base pressure. The working pressure is normally in the mTorr level, which is achieved filling the chamber with Argon.

2.3.2 Sputtered Ag Thin Films without a Wetting Layer

It is well documented that silver has a tendency to grow in Volmer-Weber (island) mode on oxide substrates [15]. This is particularly prevalent in sputtering because the Ag atoms arrive with significant energy due to the recoil from the target, equivalent to several hundred eV. As a result, the silver atoms migrate on the substrate surface even at room temperature until they find an energetically favorable nucleation sites. As more and more Ag atoms are supplied to the substrate, silver islands will grow and coalesce to form a contiguous but not yet continuous film [16]. This has significant implications for optical performance of thin films. The optical constants of a 100Å silver is vastly different from that of bulk silver. The islands and voids of the Ag film will cause scattering and absorption, and thus the reflection will be lower.

Experiment Detail

A 3 inch diameter Ag target was mounted on cathode #2 which is supplied by RF power. Two pieces of substrates (Si and silica glass) which both were cleaned by acetone, methanol, IPA, dried by compressed dry nitrogen were then placed on the stage in the chamber. The main chamber was evacuated for about 10 hours down to a base pressure below 1.5×10^{-6} Torr. A 3 minute pre-sputtering process was applied with the shutter closed before each deposition in order to clean the oxides on the surface of the target. The deposition was performed under a pure Argon working pressure 4×10^{-3} Torr (4mT). The RF power was

maintained at 50W. Then we deposited the Ag film for 54 second maintaining a deposition rate of 0.9A/s. The nominal thickness of Ag was found to be 5nm, which was verified by physical stylus profile measurements. The depositions were performed at room temperature (22°C).

Then we examined the surface morphology by using the JSM-5800LV Scanning Electron Microscopy (SEM). Here we use the Si substrate sample because the SEM requires a conductive substrate for high resolution imaging at the nanoscale. Then we evaluated the optical performance of the samples by measuring their optical performances. This was done by a normal incidence reflection/transmission tool by Filmetrics which has the capability to measure the reflection and transmission spectrum from 380nm to 1050nm. We used the glass substrate sample for optical performance evaluation because we could then measure both the transmission and reflection simultaneously. Furthermore, silica glass is the commonly used substrate for optical devices.

The SEM images are shown in Figure 2-5. There are four different magnifications shown. We can see clearly that there are many separated islands distributed on the Si substrate which correspond to the Volmer-Weber growth mode mentioned above. The average grain sizes are about 38.8nm.

Figure 2-5. 5nm silver on Si substrate with different magnifications

Then we explore the optical performance of these samples by measuring the reflection optical spectrum, shown in Figure 2-6. The prediction from the optical model was based on the bulk silver properties using the transfer matrix method in the OpenFilters software. The reflectance measurement were the measurement results taken from the Filmetrics tool. From the comparison, we can observe that the reflection decreases as wavelengths gets longer. This is the opposite behavior one would expect from bulk silver. This is caused by the separated Ag clusters on the silica glass substrate. At short wavelengths the behavior is similar to bulk metal. At longer wavelengths, the clusters appear increasingly small and disconnected compared to the wavelengths, hence the film starts to behave more like a dielectric. This has profound implications on the optical filter design, and will generally

result in a degraded performance in the infrared. So we are trying to find some effective methods to fabricate ultrathin silver films with a smooth surface morphology to allow closer match to the bulk.

Figure 2-6. Reflection spectrum measurement of 5nm Ag on glass substrate

2.3.3 Sputtered Ag Thin Films with a Cu Wetting Layer

Copper is a relatively inexpensive material with excellent electrical and optical properties and is widely used in the microelectronics industry [17]. Because of its higher surface energy in comparison with Ag, it can act as a good wetting layer for the growth of Ag films.

The 3 inch diameter Cu target was mounted on cathode #1 supplied by a DC power. We did the same pumping down sequence, pre-sputtering process as mentioned in the previous section. The first layer is Cu (cathode #1) wetting layer with a 20W DC power. We did 15 seconds of deposition with the deposition rate of 0.66Å/s and the nominal thickness of 1nm of Cu. Then without breaking the vacuum, we subsequently deposited the Ag (cathode #2)

film for 54 seconds with the deposition rate of 0.9A/s. The nominal thickness of Ag was 5nm. The thin film sequence is shown in Figure 2-7.

Figure 2-7. Thin film sequence with a wetting layer

The SEM images of Ag with Cu wetting layer on Si substrate are shown in Figure 2-8 with the SEM images of Ag without a wetting layer as a comparison reference. There are some scratches shown in Figure 2-9. on the sample which were put there intentionally as a focus reference. With a smooth and continuous thin film without any defects under the SEM, it becomes impossible to distinguish an out-of-focus image from a smooth continuous film. In that case, we cannot tell whether it's the problem of focusing or it's really a perfect thin film. So by placing some scratches on the sample, we are able to focus on the edges of a scratch. If we can see a sharp edge on the screen, we know that the microscope has been well focused. And then we observe the rest area of the thin film to see the surface morphology.

Figure 2-8. (a) Sample with Cu (scale bar: 500nm) (b) Sample with Cu (scale bar: 200nm)
 (c) Sample without Cu (scale bar: 500nm) (d) Sample without Cu (scale bar: 200nm)

Figure 2-9. Scratch on the sample

Comparing the topology of the above images, without the layer of Cu, the deposited Ag formed distinct polycrystalline granular clusters with irregular shape (incomplete coalescence). This makes the film discontinuous which provides anomalous optical and electrical properties compared to bulk Ag. This indicates that the initial stage of Ag growth on a Si substrate began by nucleation of isolated Ag clusters, and then the islands grew by accumulation of Ag atoms into larger three dimensional islands (Volmer-Weber growth mode). This resulted in the Ag film with a rough surface, characterized by a low reflection in the infrared range which will be shown in the later optical performance measurement results.

The sputtered 1 nm thick Cu seed layer is shown as an effective method to fabricate the ultra-thin, smooth Ag films with better surface morphology in comparison to straight Ag films. The representative bond dissociation energies of Ag-Ag is $162.9 \pm 2.9 \text{ kJ mol}^{-1}$ and the bond dissociation energies of Ag-Cu is 176 kJ mol^{-1} [17]. The higher Ag-Cu bond energy makes the Ag atoms tend to be more tightly bound to the Cu surface, rather than bound to their neighboring Ag atoms. This enables the growth mode from three-dimensional mode (island growth mode) to two-dimensional mode (layer by layer growth mode). Hence Ag islands on a Cu layer tend to be smoother than Ag films on Si, giving a much smoother Ag film at a smaller thickness.

The optical spectra of the measurement and simulation model are shown in Figure 2-10 below, with the reflection spectrum of 50Å Ag on glass substrate there as the comparison. From the reflection spectrum, the reflection of the sample with Cu wetting layer is significantly improved in the longer wavelength range. The reflection can be seen to increase in the near infrared range, which qualitatively agrees with the simulation results.

The discrepancy between the measurement and the model could be attributed to film thickness deviations and some granularities in the film even with the Cu seed layer. The point is that by applying Cu as the wetting layer for Ag ultrathin film growth, the tendency of reflection in the longer wavelength is increasing, which is consistent with conductive metal films. This is also a strong evidence that the Ag film is now nearly continuous due to the addition of the Cu wetting layer between the substrate and Ag film.

Figure 2-10. Reflection comparison of Ag on glass with Cu and without Cu wetting layer

2.3.4 Sputtered Ag Thin Films with a Ge Wetting Layer

An effective method to create ultra-smooth Ag films by electron beam evaporation of a germanium (Ge) seed layer has been reported in 2008. [10] With a thin Ge seed layer, a dramatic improvement of the Ag surface roughness was achieved. Although deposition of Ge on Si substrate also occurs via Volmer-Weber growth mode, the density of Ge nuclei is much larger and the islands were significantly smaller than those for Ag deposited directly

on the substrate, resulting in an effectively smooth and planar surface similar in smoothness to a layer-by-layer growth mode (Frank-Van der Merwe) [10]. In our case, we tried Ge as wetting layer for the silver thin film growth by sputter deposition instead of evaporation. The Ge target was installed on cathode #1. The power was 100W (RF). Deposition time was 14s to achieve a 1nm Ge wetting layer. Then a 54s silver deposition was performed.

The SEM images for the sample with Ge wetting layer are shown in Figure 2-11. below. In comparison with the images with no wetting layers, it can be seen that Ge has a pretty good wetting effect for Ag film. It also provides a much smoother and more uniform silver thin film layer. As before, we used a tweezer scratch to allow focusing on the film surface.

Figure 2-11. (a) Sample with Ge (scale bar: 500nm) (b) Sample with Ge (scale bar: 100nm)
 (c) Sample without Ge (scale bar: 500nm) (d) Sample without Ge (scale bar: 100nm)

Figure 2-12. Scratch on the sample

The measured reflection spectra results are shown in Figure 2-13, along with the reflection spectrum of 50Å Ag on glass substrate as a comparison. We have known that Ge has a good wetting effect for Ag growth. The measured reflectance spectrum also shows that the sample with Ge wetting layer has higher reflection in the near IR spectrum, while the reflectance of the sample without wetting layer decline in the longer wavelengths.

Figure 2-13. Reflection comparison of Ag on glass with Ge and without Ge wetting layer

2.3.5 Sputtered Ag Thin Films with a ZnS Wetting Layer

ZnS is a dielectric material which has good optical property and commonly used for optical filter coating. The sulfur in the ZnS can also react chemically with Ag to improve binding, although at the expense of altered optical properties. So sulfur will provide a greater binding energy for Ag than the binding energy between Ag and Ag atom themselves. When the Ag atoms fall on the ZnS wetting layer, it will react with S and will stick onto the wetting layer instead of migrating towards another Ag atom on the substrate. As a result,

the Ag growth mode converts to a two-dimensional growth mode and form a smoother thin film. We installed the ZnS target onto cathode #1. The deposition power was kept at 100W (RF). The first layer is ZnS. The deposition time was 14 seconds for a nominal 1nm ZnS wetting layer. After that, we applied a 54 second Ag thin film deposition.

The SEM images are shown in Fig.2-14. It can be seen that ZnS also has a very good wetting effect for Ag thin film growth.

Figure 2-14. (a) Sample with ZnS (scale bar: 500nm) (b) Sample with ZnS (scale bar: 100nm) (c) Sample without ZnS (scale bar: 500nm) (d) Sample without ZnS (scale bar: 100nm)

The reflection spectrum measurement for the glass substrate sample is shown in Figure 2-15. It works very well for single layer of Ag. The improvement in reflection in the longer wavelength range is clearly noticeable.

Figure 2-15. Reflection comparison of Ag on glass with ZnS and without ZnS wetting layer

CHAPTER III.

FABRICATION AND TEST OF LOW EMISSIVE STRUCTURES

3.1 Introduction

The next step is to apply these ultra-thin silver films in some real applications and test how they work. Low emissive (Low-E) coating, also called solar control coating is a kind of coating which provides a high visible transmittance and high infrared reflectance. This kind of coating can be applied on the architectural glass and automotive glass to transmit the visible light, but reflect back infrared light (solar heat). Thus Low-E coating will help to save energy cost in heated or air conditioned buildings [18].

The low emissive coatings that are most commonly used are made by metal based multilayer coatings. Silver is the best choice for the metal layer because of its high IR reflectivity and comparatively low absorption in the visible range which we have demonstrated in the previous chapter [11]. The Figure 3-1 shows the reflectance spectra with different thickness of Ag simulated by OpenFilters. For the low emissive coatings applied on the glass, this kind of coating should provide a good transparency property in the visible range (390nm-700nm). That means the metal layer has to be thin enough (below 100Å) to make high visible transmittance and also should be continuous and smooth to avoid anomalous absorption and give a high reflection in the IR range simultaneously. That is one of the motivations for us to fabricate ultra-thin silver film.

Figure 3-1. Transmission spectra of different thickness Ag films on glass substrates

One approach to increase the transmission in the visible and the reflection in the IR is to use resonator structure. The thin metal layers need to sandwich one dielectric film on both sides and work as high reflecting layers to achieve resonance and high transmission at specific wavelengths. If we keep the total silver thin film thickness same, but make one single layer with dielectric layer for the structure, it will work as a reflector instead of a transmission filter. We did a comparison between these two structures in OpenFilters. The substrates for both are silica glass. One is metal-dielectric-metal structure with 10nm silver for each metal layer. The other one is metal-dielectric structure with 20nm silver for the single metal layer. The comparison result is shown below in Figure 3-2. As a result, even though the total thickness of silver in both structures are the same, we have to split one metal layer to two separate layers, and each of them has thinner thickness, to achieve a resonance effect. This is another motivation for us to look for methods to fabricate ultra-

thin smooth silver films.

Figure 3-2. Reflection spectra comparison between the metal-dielectric-metal structure and metal-dielectric structure on glass substrates

In this study, we choose SiO₂ to be the dielectric material because of its high solar transmittance, long-term stability and low cost.

3.2 Fabrication of Low Emissive Structures

3.2.1 Design and Fabrication without a Wetting Layer

First we fabricated the low emissive structures without any wetting layers, but kept all the other factors the same, such as the thickness of silver layer and the SiO₂ layer, the thin film growth environment (pressure, temperature). We used this structure as the reference sample.

We first mounted the silver and SiO₂ targets on to the two cathodes for determining the deposition rate. Then we prepared the glass substrate slides by cleaning in solvents and dry nitrogen gas. Then we put the cleaned substrate on the rotation stage in the vacuum

chamber, and evacuated the main chamber for about 10 hours until the pressure dropped down to 1 μ Torr. The first layer is 5nm silver, the second layer is 82nm SiO₂, the third layer is 5nm silver and the fourth layer is 23nm SiO₂. The deposition rate of silver were found to be 0.926A/s, and the deposition rate of SiO₂ was 0.35A/s. The thickness of each layer was controlled by time. Then we measured the reflection and transmission spectra by a spectrometer. The fabricated sample is shown in Figure 3-3. The measured reflection, transmission and absorption spectra are shown in Figure 3-4, Figure 3-5 and Figure 3-6 with the OpenFilters simulation results as reference.

Figure 3-3. The low emissive coating without any wetting layer

Figure 3-4. Reflection spectrum measurement of the low emissive coating without any wetting layer

Figure 3-5. Transmission spectrum measurement of the low emissive coating without any wetting layer

Figure 3-6. Absorption spectrum measurement of the low emissive coating without any wetting layer

We can see that the measured reflection shows a declining trend in the longer wavelengths range, while the simulation predicts that the reflection is supposed to be increasing. The transmission in the visible spectrum is low due to the high absorption and/or scattering in the visible range and IR range. The spectral measurements are strictly specular. These differences are caused by the granularity of the two 5nm silver films. As we have seen in 2.2.2, without any wetting layer, the silver film grows in many separated clusters rather than a smooth continuous thin film. The formation of silver film causes abnormal absorption and scattering. These results will be used as a reference to compare against the other samples with wetting layers.

3.2.2 With Cu Wetting Layers

In the next sample, we demonstrate the design with Cu as the wetting layer. Since there are three materials involved in the design, and the third magnetron cathode in our chamber had been removed, we were unable to perform all of the depositions with just one pump down process.

The substrates were the same microscope slides as before. Prior to the pump down process, the substrates were cleaned using standard solvent cleaning and dry nitrogen. The first layer is a 1nm wetting layer Cu. So we first mounted the Cu target on cathode #1 and connected the cathode to the DC power supply. Then the sample was placed on the center of the rotation stage in the vacuum chamber and then pumped down. When the pressure was down to 1×10^{-6} Torr, we did the first layer deposition which is a 14 second DC power deposition. After the deposition, we vented the chamber with dry nitrogen, dismantled the Cu target, mounted SiO₂ target on cathode #1, mounted silver target on cathode #2 and both of them were connected to the RF power supply. Then we repeated the pump down process. When the pressure was ready, first deposited the 5nm silver and then the 82nm SiO₂, both of them were controlled by time. This was the first period of the design. We changed the target after the Cu deposition, but not after the silver deposition, because Cu was believed to be optically less significant in this design than silver, so it was better to reduce the time of silver exposed to the air during the fabrication process. Then we needed another period of the structure so we vent the chamber again and repeated the previous process. All the other metal and dielectric layers were kept at the same thicknesses and sequence we have discussed in the previous section except the addition of the two Cu wetting layers. The structure is shown in Figure 3-7.

Figure 3-7. The thin film sequence of low emissive coating with Cu wetting layers

The photograph of the fabricated sample is shown below with the sample without any wetting layers as the comparison in Figure 3-8.

Figure 3-8. The low emissive coating with Cu wetting layers

From the comparison of the samples, we can see that the sample with the Cu wetting layers is more transparent in the visible than the original sample. The measured reflection, transmission and absorption spectra are shown in Figure 3-9, Figure 3-10 and Figure 3-11.

Figure 3-9. Reflection spectrum measurement of the low emissive coating with Cu wetting layers

Figure 3-10. Transmission spectrum measurement of the low emissive coating with Cu wetting layers

Figure 3-11. Absorption and scattering spectrum measurement of the low emissive coating with Cu wetting layers

We have plotted spectra of the sample without any wetting layer in the same chart as a reference. From the comparison, we can see that the 1 nm Cu wetting layer significantly improves the reflection spectrum in the longer wavelength range, making the reflection increase to 30% at a wavelength of 1000nm. At the same time, Cu wetting layer also improves the visible transmission of the sample. The transmission is not as high as predicted by the model because the model assumes that every layer is perfectly flat and the interface are distinctly separated. This is impossible due to the tiny thickness of silver layer and copper layer, and this makes the relatively high absorption and scattering, but we can figure out that the Cu wetting layer highly improves the low emissivity coating performance. These fabrication samples also demonstrate that the Cu layer we used as the wetting layer promotes the silver to grow in layer growth mode.

3.2.3 With Ge Wetting Layers

Next, Ge was selected because Ge has been demonstrate as a promising material as wetting layer for silver thin film growth, and has been applied and demonstrated in the literature [10]. Our preliminary samples showed smooth silver films with Ge which was discussed in chapter 2. So a complete optical thin film coating structure with Ge wetting layer was fabricated to test the optical performance and quality.

There still were three materials involved for deposition, while we just had two sputtering cathodes. So we first did the Ge wetting layer deposition on cathode #1. The RF power was 100W, working pressure was 4 mTorr, the deposition time was 15 seconds and the nominal thickness was 10Å. Then we vented the chamber and changed the target, mounting SiO₂ target on cathode #1 and silver target on cathode #2. After pump down, when the pressure was ready, we performed the deposition, which was same as what we

did for previous samples. We chose to vent the chamber and change the target after the Ge deposition to protect the silver layer from being exposed to air. After that, we did the other period of layers, keeping the Ge and silver thicknesses same, but the second SiO₂ layer's thickness was 230Å.

The thin film sequence of low emissivity coating the structure is shown in Figure 3-12.

Figure 3-12. The thin film sequence of low emissive coating with Ge wetting layers

The fabrication sample is shown in the photograph below in Figure 3-13. The fabrication sample without any wetting layer is also shown in Figure 3-14 for comparison.

Figure 3-13. The low emissive coating with Ge wetting layers

The measured reflection, transmission and absorption spectra are shown in Figure 3-14, Figure 3-15 and Figure 3-16.

Figure 3-14. Reflection spectrum measurement of the low emissive coating with Ge wetting layers

Figure 3-15. Transmission spectrum measurement of the low emissive coating with Ge wetting layers

Figure 3-16. Absorption and scattering spectrum measurement of the low emissive coating with Ge wetting layers

From the comparison, the Ge also greatly improved the quality of the ultra-thin silver films, making the transmission in the visible wavelength range higher and the reflection also higher by 25% at 1000nm wavelength. At the same time, the scattering and absorption were also decreased.

3.2.4 With ZnS Wetting Layers

Then we tried ZnS because sulfur has a good binding effect with silver which can help silver form a high quality ultra-thin film. The fabrication process was similar to the previous samples except the wetting material is ZnS. The structure is shown below in Figure 3-17.

Figure 3-17. The thin film sequence of low emissive coating with ZnS wetting layers

The fabrication sample is shown in Figure 3-18.

Figure 3-18. The low emissive coating with ZnS wetting layers

The measured reflection spectrum is shown in Figure 3-19, Figure 3-20 and Figure 3-21.

Figure 3-19. Reflection spectrum measurement of the low emissive coating with ZnS wetting layers

Figure 3-20. Transmission spectrum measurement of the low emissive coating with ZnS wetting layers

Figure 3-21. Absorption and scattering spectrum measurement of the low emissive coating with ZnS wetting layers

From the spectra above, we can see that in the near infrared wavelength, below 900nm, the sample with ZnS as wetting layer has a lower reflection than the sample without any wetting layer. Despite this lower reflection, we can clearly see that the trend of the reflection for the sample with ZnS wetting layer shows an increase. So it will also have a relatively better heat isolation effect than the sample without any wetting layer. The transmission and absorption were also improved by the ZnS wetting layer. So we can conclude that the sample showed the correct trend but did not work as well as we had expected when compared to the OpenFilters model. Some of this could be due to the reaction of Ag with S. Although sulfur provides silver a better binding energy which helps silver form smooth ultra-thin film which we have seen in the SEM image, the chemical reaction between sulfur and silver could change the optical property of the silver, especially

at the interfaces, resulting in the deterioration of the performance.

3.2.5 Comparison of Structures with Different Wetting Layers

From the comparison we have made between each sample with different wetting layers and the sample without wetting layer, we can conclude that all the three wetting layers assist the ultra-thin silver form a continuous and smooth film and also improve the low emissivity coatings optical performance by increasing the visible transmission and at the same time enhancing the infrared reflection. In this section, we compare the optical performance directly between these three samples with different wetting layers to find out which wetting layer has the best assistance for the low emissivity coating quality enhancement.

The three fabricated low emissivity coating samples with different wetting layers are shown below in Figure 3-22.

Figure 3-22. The three low emissive coatings with different wetting layers

From the comparison, we can figure out that the sample with Cu wetting layer has the highest visible transmission, while ZnS has the lowest visible transmission. The reflection comparison is shown in Figure 3-23 which is more evident.

Figure 3-23. Reflection spectra comparison of the samples with different wetting layers

The sample with the Cu wetting layer provides the highest reflection in the long wavelengths range. This is because Cu is also a metal with high reflection which is similar to silver. So Cu not only works as a good wetting layer, but also improves the whole reflectivity of the layers in the infrared range. The Ge wetting layer is also a good wetting layer which we have seen in chapter 2. But Ge has a very high refractive index and it is not as reflective as compared to Cu. So film structure has a lower reflection than the sample with the Cu wetting layer. The sample with ZnS wetting layer showed the worst optical performance. We have seen in the previous chapter that ZnS helps silver to form a smooth and uniform thin film due to the reaction between the silver and sulfur in ZnS. But this reaction also deteriorates the optical performance of the silver. We see that silver will tarnishes if we keep it exposed in sulfur containing environment for some time, and that is because of the reaction with atmospheric sulfur. So this explains why the coating

containing ZnS wetting layer has the worst optical performance.

The transmission comparison is shown in Figure 3-24. The transmission spectra of three samples are similar. All three samples have the almost same transmission spectrum, about 50% transmission in the visible. The sample with Cu wetting layer has a lower transmission in the near infrared range due to the higher reflection of the Cu.

Figure 3-24. Transmission spectra comparison of the samples with different wetting layers

The absorption and scattering comparison is shown in Figure 3-25. The sample with Cu wetting layer has a larger absorption and scattering due to the large imaginary refractive index of Cu. The sample with ZnS wetting layer also has a large absorption and scattering because the chemical reaction between silver and sulfur changes the optical property of the silver layer.

Figure 3-25. Absorption and scattering spectra comparison of the samples with different wetting layers

CHAPTER IV.

CONCLUSION AND FUTURE WORK

Ultra-thin silver film plays an important role in optical thin film filters and plasmonic devices due to their excellent optical properties. The quality of silver films is vital to the performance of these devices. However, fabricating these silver films has been a continuing challenge because of their tendency to form clusters rather than smooth continuous thin film which will have profound implications on the optical devices. In this work, we have proved that Cu, Ge and ZnS all have good wetting effects for ultra-thin silver film growth. The SEM images exhibit that the fabricated silver layers with wetting layers have very low surface roughness with no island formation. The optical spectra measurements for the samples deposited on glass substrates show that the samples with Cu and ZnS wetting layers have higher reflection and less absorption loss compared with the samples without a wetting layer. These differences are attributed to the good wetting effect of the seed layer, resulting in a highly uniform silver surface.

To explore the feasibility of these methods for ultra-thin silver film growth, we also applied them to realistic coating designs. The heat isolation coatings, also known as low emissive coatings, were designed based on the Fabry-Perot interferometer, which consists of two ultra-thin metallic reflecting layers separated by a dielectric spacer. This metal-dielectric structure combine high transmission over most of the visible spectrum and high reflectance over the IR spectrum. Then the designed structures were fabricated by sputter

deposition and the reflectance and transmittance were measured with a white light spectrometer. All three samples with wetting layers provide much better optical performance compared with the samples without a wetting layer. They have higher transmission in the visible spectrum which means these structure have better resonance effects due to the higher qualities of the two reflecting metal layers. The reflectance spectra of the samples with different wetting layers all show an increasing reflection trend in the longer wavelengths, while the sample without any wetting layer shows a declining reflection trend in near IR spectrum. These spectra also demonstrate that all three wetting layers assist the ultra-thin silver to form a continuous and smooth film. By the comparison of three samples with different wetting layers, we conclude that the low emissive coating with Cu wetting layers has the best optical performance. Cu is a metal which is similar to silver. It not only works as a good wetting layer, but also improves the whole reflectivity of the layers in the infrared spectrum.

Future work may include two aspects. First of all, some other materials can be attempted as wetting layers. Chromium is a metal with high surface energy which makes it have excellent adhesion to many surfaces. So it might be a good wetting material for ultra-thin silver growth. The impact of Chromium wetting layer on the optical performance of the coatings remains to be further investigated. Secondly, an ultra-thin silver film can be fabricated by depositing a thick film and then etching it back using plasma etching with active laser monitoring of the reflection. Conventional thin film growth starts from the substrate, while this method is from the top of the surface layer. We first want to deposit 1000Å silver on the substrate. Then use a high density plasma such as the inductively coupled plasma to etch the thin film down to the desired thickness. This work is currently

in progress within our group.

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