Durability of Ultra-Thin Silver Films and Silver–Gold Alloy Films under UV Irradiation *

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Silver films (Ag) and silver–gold films (Ag–Au) with thickness ∼15 nm are coated on Bk7 glasses through thermal evaporation. After doping gold of 5.2%, the grain size of the Ag film reduces from 13.6 nm to 9.1 nm, also the surface roughness decreases from 1.45 nm to 0.94 nm. A UV lamp is used as the irradiation light source to accelerate the corrosion process in the atmosphere. After 17 h irradiation, the pure silver film surface turns dark, and the transmittances reduce from 350 nm to 500 nm, while the Ag–Au film degrades much less, almost negligibly after UV radiation. Additional x-ray photoelectron spectroscopy and atomic force micrographs data are provided to show atomic content of films and their surface morphologies. It is suggested that small grain size and high packing density of alloy film prevent reaction of silver with oxygen in the atmosphere, which leads to high stability of the Ag–Au film.

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Silver films are widely used in beam splitters,[1] reflection mirror,[2] absorbed film[3] and photodetector devices.[4–6] However, when silver films contact with clean air, the film surface easily undergoes a chemical reaction with oxygen or sulfur,[7] and the tarnishing process will reduce the lifetime of an optical device containing a silver film. Dielectric multilayers are used to protect silver mirrors,[2] such as Ta_2O_5/SiO_2 multilayers, and thin copper film is deposited under the silver film to enhance the environmental durability of the silver film.[2] Alumina/titania monolayers deposited by atomic layer deposition (ALD)[8] and plasmapolymer coatings[7] are also considered as the tarnish protection layers. Silver alloying is another way to maintain the luster of silver.[9–17] The Ag–Al alloy film with thickness ∼95 nm has been considered to improve thermal stability,[9] and the surface of Ag–Al films shows no change after annealing at 600℃. Silver jewelry contains low percentages of copper and zinc,[13] and doping metals such as Pt, Pd and Au[14–17] have been reported in previous works. Previous durability investigations have covered thick silver films ($d > 50$ nm) and silverware, while there is less research on ultra-thin silver films ($d < 20$ nm). Ultra-thin silver films have special optical properties, and they have been widely used in beam splitters or surface plasmon resonance devices.[18] A thin silver film is easier to corrosode than a thick silver film or silver jewelry, and its optical properties would change more, thus it is important to improve the service life of thin silver film.

In this Letter, we compare the durability for pure Ag films and Au-doped thin Ag films under UV irradiation. Co-evaporation technology is used to fabricate Au-doped thin Ag film with thickness less than 20 nm. A UV lamp is used to accelerate the corrosion process. The durabilities of Ag and Ag–Au film are characterized by visual observation and spectrum analysis, and the physical mechanism of surface degradation is discussed from element analysis and surface morphologies.

Ultra-thin Ag and Ag–Au films were deposited on Bk7 glasses by using thermal evaporation. A tungsten boat was used as evaporation source, and the deposition process was performed at room temperature (∼25℃) and high vacuum ($\sim 1.5 \times 10^{-3}$ Pa). Ag films were deposited by a tungsten boat using silver powder, and deposited rate was controlled at ∼1.0 nm/s. Ag–Au films were coated by using two different tungsten boats, and the deposition ratio of two materials is controlled by evaporation current. A small amount of Au is considered in the Ag–Au alloy film, due to the fact that a large percentage of Au would change much of the optical properties for the silver film. Since the evaporation temperature of gold (∼1400℃) is much higher than that of silver (∼1030℃), the deposited current of Au is slightly higher than Ag as the two materials are evaporating simultaneously.

The variable angle spectroscopic ellipsometer (VASE) was used to obtain Δ and Ψ, a spectrophotometer (Lambda 900) was used to measure transmittance T, and the testing wavelengths are changed from 300 nm to 800 nm. The angles of ellipsometry measurement are 55° and 65°, while the angle of transmittance is 0°. The optical constant of the thin silver film depends on its thickness, meanwhile the silver film has

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large extinction coefficient.[6,19] It is difficult to use the ellipsometer data only to calculate optical constant of the ultra-thin silver film, thus adding transmittance T into the simulation process is helpful to obtain the reliable optical constant.

It is well known that silver films are not stable when they contact hydrogen sulfide (H_2S) and oxygen (O_2) in atmosphere,[20] moreover the photoelectric device containing a silver film usually works under light irradiation.[4,18] In that case, we built a UV irradiation setup to simulate the environmental conditions. A 300-W UV lamp (OSRAM) is used as light source, and samples were placed below the lamp around 15 cm in the atmosphere. After 17 h, the color of the silver film surface changes, and then we analyze optical constant, elemental contents and surface morphologies of samples. The surface element is measured by a Philips x-ray photoelectron spectrometer (Phi 5300), Al-kα is used as excitation source, and the excitation power is 150 W. AFM data is measured by the instrument produced by Bruker Corporation.

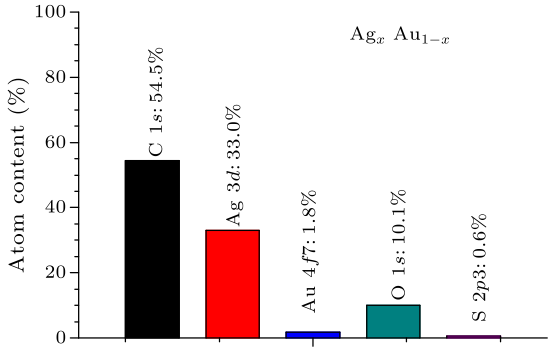

Fig. 1. The atom content of the as-deposited alloy film characterized by XPS.

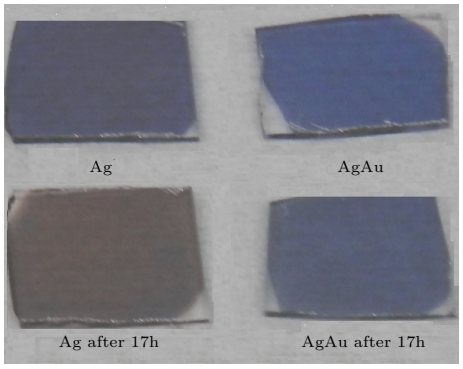

Fig. 2. Photos of the as-deposited samples and samples after irradiation.

The elemental content of the as-deposited Ag–Au film is checked by XPS, as shown in Fig. 1. Elements of C, Ag, Au, O and S can be found in the XPS spectrum, the percentage of Ag is 33.0%, and the percentage of Au is 1.8%. If we ignore elements C, O and S, the ratio of silver and gold is Ag:Au=18.3:1, and the percentage of Au can be calculated to be 5.2%. The result indicates that co-evaporation method can obtain the Ag–Au film with proper ratio of Au. Figure 2 shows the photo of as-deposited samples and samples after irradiation obtained by camera. It clearly shows that the Ag film surface turns dark for 17 h irradiation, while the colors of Ag–Au film are almost unchanged.

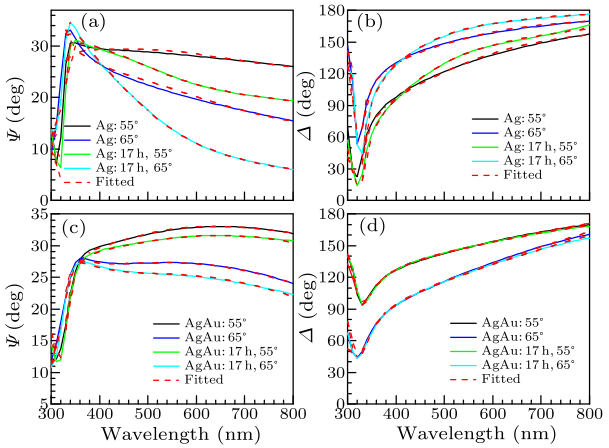

Fig. 3. Measured and simulated Δ and Ψ of samples, and red dashed lines are the simulated data.

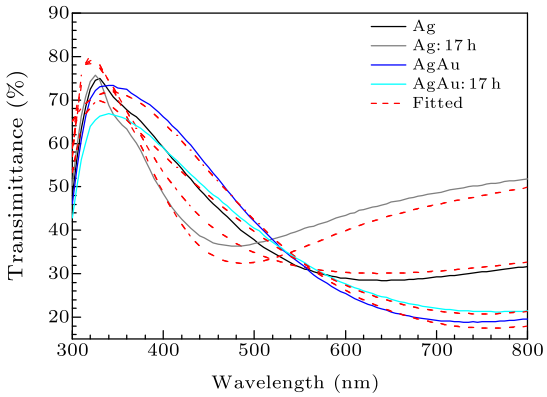

Fig. 4. Transmittances measured by Lambda 900, where the red dashed lines are the simulated data.

Previous reports provide many methods to investigate the optical properties of alloy films.[11,12,21] Yang *et al.* used a three-layer model consisting of the effect medium theory (EMA) with a Ag–Cu alloy layer to describe the silver–copper films deposited by magnetron sputtering.[11] Ovidio Peña-Rodríguez *et al.* built a three-phase multilayer model (Ambient/Ag–Au or voids/Ag–Au) to analyze the ellipsometric spectra,[21] and the second and third layers represent the surface roughness. However, as the film thickness is very small, it is difficult for multilayer models to describe optical constant for the mixture of silver with oxides or silver–gold with oxides. In that case, we use one equivalent layer to represent the optical constants of the mixture material. Measured Δ, Ψ and transmittance T are shown in Figs. 3 and 4, and three independent parameters (Δ, Ψ and T) are used to cal-

culate the variables of n, k and d. Different oscillators are used to describe the equivalent layer. The Drude–Lorentz model is used to describe optical constants for Ag (14.3 nm), Ag–Au (12.3 nm), and Ag–Au after irradiation,[22] while the Tauc–Lorentz mode combining Gaussian oscillators is used to describe optical constant for Ag after irradiation.[23]

Figures 3(a) and 3(b) give Ψ and Δ for the Ag film before and after irradiation, and the red dashed lines show the simulated result. Both Ψ and Δ of the Ag film decrease significantly after irradiation. Figures 3(c) and 3(d) show Ψ and Δ of the Ag–Au film before and after irradiation, Ψ decreases slightly, and Δ shows no changes. Moreover, transmittance of the Ag film reduces from wavelength 350 nm to 500 nm, and it increases much for longer wavelength, while transmittances of the Ag–Au film are almost unchanged after irradiation.

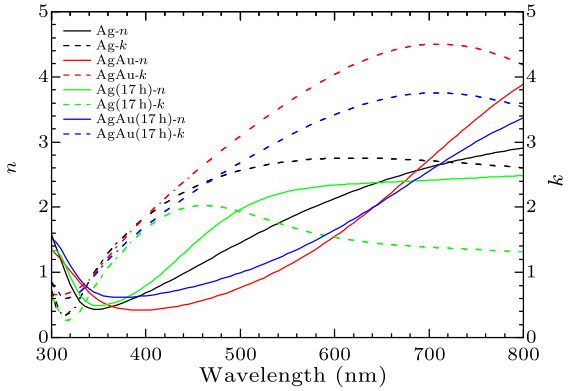

Fig. 5. Optical constants of samples before and after irradiation.

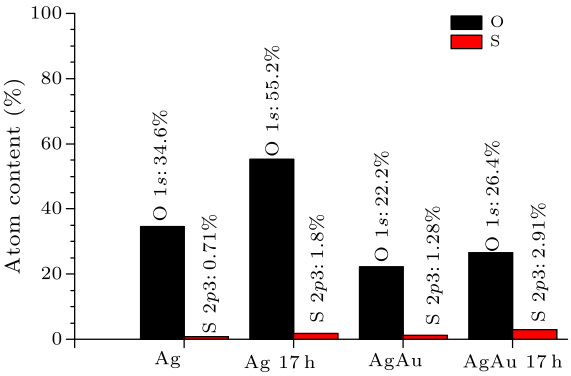

Fig. 6. Atom contents of O and S for samples measured by XPS.

Additionally, Fig. 5 gives optical constant of samples derived from Figs. 3 and 4. Here N and k curves represent the optical constant of the equivalent layer, and the fitting method with the equivalent layer has shown good results in optical constant investigation for different thicknesses of ultra-thin silver films.[6] The work[21] shows that the optical constants of thicker silver film do not change after adding a small amount of gold. However, ultra-thin silver film is not the same case, both refractive index and extinction coefficient change slightly, and the reason is that the optical constants of the ultra-thin silver film is more sensitive to the film thickness. Also, it is found that n and k of the Ag–Au film change less after UV irradiation, while optical constant of the Ag film changes much.

It is worth noting the change of oxygen and sulfur element in the Ag film corrosion process. Thus we take percentages of O and S from XPS data, as shown in Fig. 6. In the as-deposited sample, oxygen contents are 34.6% and 22.2% for Ag and Ag–Au films separately, while sulfur content is low. There are many sources for oxygen element, such as adsorption oxygen, trace water and oxygen oxidation, while absorption oxygen and water are also called the substrate oxygen in previous research.[24] After UV irradiation, percentages of elements O and S increase for both the Ag and Ag–Au films. Oxygen content in the Ag film shows an increase of 20.6%, and it is suggested that the increase of oxygen causes the change of optical constant for the pure Ag film.

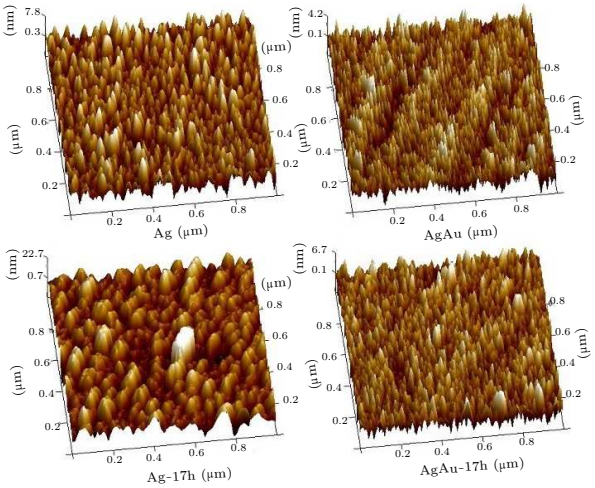

Fig. 7. Surface morphologies of films before and after UV irradiation.

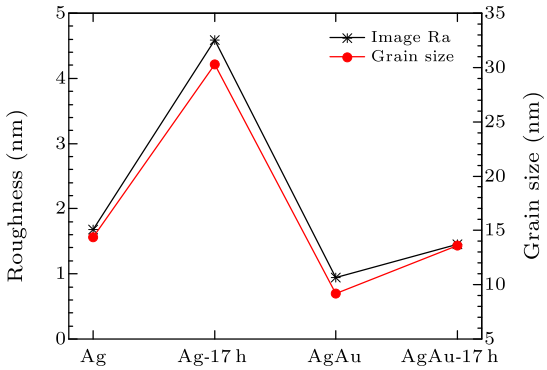

Fig. 8. Grain size and average surface roughness of samples.

The surface morphologies of samples measured by

AFM are also shown in Fig. 7. We calculate the average surface roughness for each sample, and the roughness data of samples are 1.68 nm (Ag), 4.59 nm (Ag after 17 h), 0.941 nm (Ag–Au), and 1.45 nm (Ag–Au after 17 h), respectively. Moreover, we choose a certain area from AFM pictures to calculate the grain size, and the grain sizes are 14.4 nm, 30.3 nm, 9.2 nm and 13.6 nm, respectively. The data of grain sizes and average surface roughness are shown in Fig. 8. The Ag film shows larger surface roughness and larger grain size than the Ag–Au alloy film, and both surface roughness and grain size of the Ag film grow much after UV irradiation.

When thin silver films are irradiated by UV light, electrons of silver can be excited from 4*d* band to 5 *sp* state band,[25] and numerous photo-generated electrons are kept in high energy level, thus oxygen molecules can seize them. In that case, UV irradiation increases the chemical reaction of silver with absorbed oxygen.[26] Thus just after 17 h, the color of Ag film changes obviously. However, the Ag–Au film has smaller surface roughness and larger number of grain particles. The grain boundary is small, and the grains become closer. The porosity of the Ag–Au film is higher than the Ag film, and the film surface absorbs less oxygen molecules or chemisorbed water. It reduces the reaction of the alloy film with oxygen in the atmosphere, which leads to high durability.

In conclusion, the alloying method can prolong the service life of thick silver film and silver jewelry, and it also improves the stability for ultra-thin Ag–Au alloy film under UV irradiation. The main features are such that the color and transmittance of alloy film almost do not change after 17 h UV irradiation. The Au-doped Ag thin film shows higher film density and smaller grain size, and the surface structure enhances the stability of optical properties when it is exposed to UV irradiation in long hours. The reason why the Ag–Au film is more durable than the silver film is that high packing density of the alloy film prevents the surface to absorb hydroxyl species or chemisorbed water, and that reduces the reaction of silver with oxygen in the atmosphere. This result will be useful for the ultra-thin silver coated film device to be used with a longer life time in wide applications, such as beam splitters, photoelectric detection and plasma devices.

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