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Morphology-induced plasmonic resonances in silver-aluminum alloy thin films

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We have investigated the optical properties of sputter-deposited silver-aluminum alloy thin films on silicon substrates at room temperature. In addition to the primary feature that corresponds to the bulk plasma resonance, a secondary dip appears in the optical reflectance spectra, which shifts and diminishes with thermal annealing. Careful structural characterization of both the as-deposited and annealed films suggests that the resonant feature originates from the surface plasmon resonances, which are localized in the dielectric gap between grains. This result indicates that the morphology of metal alloys could have a significant effect on their optical properties. © *2011 American Institute of Physics*. [doi:10.1063/1.3619840]

In recent years, nanoplasmonics and metamaterials have seen a significant growth, due mainly to the sheer diversity of applications, from surface enhanced Raman spectroscopy, scanning microscopy with nanometer resolution, and solar energy harvesting to high-speed nanophotonic circuits, transformation optics, and optical cloaking.[1,2] However, a common drawback of all metal-based plasmonic materials and metamaterials is the high optical loss of metals at optical frequencies, which has become a bottleneck for many applications. In widely used noble metals such as silver (Ag) and gold (Au), the loss is a combination of free electron dissipation described by the Drude model and the absorption due to electronic transitions between occupied, bound *d* states and unoccupied hybridized *sp* states above the Fermi level.[3] A number of studies have been performed that compare the plasmonic merit of different metals.[4]

The use of metal alloys and intermetallics to improve optical qualities, by reducing the loss and chemical reactivity, seems an obvious approach as the number of free electron metals in the periodic table is limited.[5] It has been shown that alloying a noble metal with a second metal that contributes two or three electrons per atom to the free electron gas can modify the metal's reflection and absorption spectra.[6] However, the alloying process may also induce a spatial inhomogeneity of composition as well as additional change of morphology, through surface roughness and grain boundaries, especially in deposited films. Their effects on the optical properties have not been well studied and warrant examination. This paper aims to examine the role of alloying as well as microstructure on optical properties of noble metal thin films.

In this letter, we investigate the optical properties of silver-aluminum (Ag-Al) alloy thin films deposited on silicon substrates by sputtering. In addition to a slight blue-shift of the bulk plasma frequency with increasing Al composition, we observe a secondary resonance dip in the optical reflection spectra, which shifts and diminishes after thermal annealing. Careful structural characterization of both as-deposited and annealed films is carried out with scanning and transmission electron microscopy, x-ray scattering, and atomic force microscopy (AFM). Our studies suggest that this resonance feature of optical reflectance originates from the localized surface plasmon (SP) modes in the gap between grains (or grain boundaries). This result shows that the morphology of metal alloys could have a significant effect on their optical properties.

The Ag-Al alloy thin films are sputter-deposited onto (100) silicon wafers by dc magnetron sputtering with an Argon gas at ambient temperature. The Argon gas pressure is 3 mTorr, and the base pressure of the deposition chamber is about 2×10^{-7} Torr. The substrate holder is rotated at 30 rpm during deposition to obtain films of uniform composition. Two 75-mm diameter targets of pure Ag and Al are co-sputtered to create a thin film of thickness nominally 500 nm. Controlling the sources' sputtering power individually can vary the composition of the alloy films. Afterwards, we determine the Ag and Al compositions using a calibrated JEOL JXA-8530F electron microprobe. Some of the deposited films are annealed at 300 °C for 1 h in vacuum (1×10^{-5} Torr).

Fig. 1(a) shows the optical reflectance spectra of Ag-Al alloy films with Al compositions varying from 0 to 8.7 at. %. The measurements are done with a spectrophotometer in a

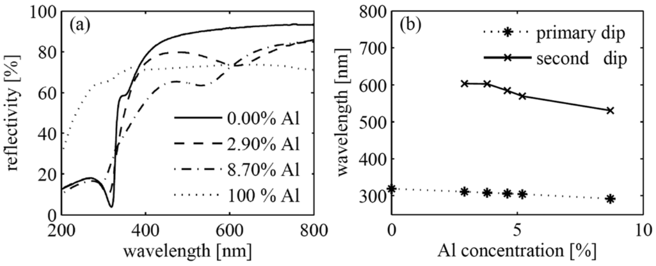

FIG. 1. (a) Measured optical reflectance spectra of Ag-Al alloy films with Al content between 0 and 8.7 at. %. There are two minima: one around 300 nm, the other ∼500–600 nm. (b) Wavelengths of the primary reflection dip and the second dip as a function of Al content.

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normal incidence configuration. Within the wavelength range of 200 nm to 800 nm, there are two reflectance minima: one around 300 nm, the other near 600 nm. The first one is associated with the bulk plasma resonance of the metal. For Ag, the plasma resonant frequency is about 3.8 eV.[6] Resonant excitation of bulk plasma in the pure Ag sample results in the reflectance dip at wavelength of about 320 nm. Since the bulk plasma frequency of Al is significantly larger than that of Ag (Refs. 6 and 7), alloying Al with Ag would blue-shift the bulk plasma resonance. The corresponding reflection dip moves gradually to shorter wavelengths with increasing Al concentration. In addition to the frequency shift, the dip also becomes broader and shallower. This indicates an increase in electron dissipation that is caused mainly by electron scattering on impurity-induced defects. Interestingly, we find an unexpected second reflectance dip that appears between 500 nm and 600 nm for the Ag-Al alloys. It shifts to shorter wavelength as the Al concentration increases, as shown in Fig. 1(b).

The appearance of an additional reflectance dip suggests the existence of a resonance in the Ag-Al alloy films. To explore its origin, we conducted a detailed structural characterization. The deposited films consist of small crystallites or grains that are randomly oriented. The average grain size d is computed from the x-ray diffraction (XRD) spectra generated from a Shimadzu x-ray diffractometer. It has been shown that the width of the x-ray diffraction peak is inversely proportional to d.[7] The grain size was also confirmed using a standard plan-view transmission electron microscope (TEM). The surface roughness of the metal films was probed by the AFM in tapping mode. The surface structures were characterized using a scanning electron microscope (SEM).

The resulting surface roughness and grain size for several samples before and after annealing are presented in Table I. Previous studies show that protuberances of the surface produce electromagnetic resonance of Ag films.[8,9] Those films were deposited at low temperature which creates significant surface roughness of around 20 nm to 30 nm. Our films are deposited at room temperature. The larger mobility of surface atoms produces smoother films.[10] The root mean square (RMS) surface roughness in our films is between 3 nm and 5 nm. SEM images do not reveal any systematic change of surface morphology with increasing Al concentration. After annealing, the surface roughness does not change significantly, yet the second reflectance dip changes dramatically (Fig. 2). Therefore, this reflectance feature cannot be related to surface roughness.

Another possibility for this behavior is the resonant excitation of SP resonances of the metallic grains in the alloy films, which can reduce optical reflection.[11] Since the reflectance dip of our samples shifts to shorter wavelengths with increasing Al composition, the corresponding metallic grains should become smaller. However, the measured grain size of all the films is nearly identical (Table I). After thermal annealing, the grain size is almost double and the SP resonances are expected to move to a lower frequency. On the contrary, we observe a blue shift of the reflectance dip (Fig. 2). Hence, the origin of the second dip behavior based on SP resonances localized in metallic grain is ruled out.

TABLE I. Structural parameters of Ag-Al alloy thin films.

Al concentration (at. %)	Surface roughness before annealing (RMS) (nm)	Mean grain size before annealing (nm)	Mean grain size after annealing (nm)
8.7	5.78 ± 0.78	20.75	51.81
5.2	3.71 ± 0.33	23.58	48.04
4.6	5.39 ± 0.39	20.97	43.12
3.8	3.59 ± 0.45	23.76	46.86
2.9	3.13 ± 0.13	21.44	46.02

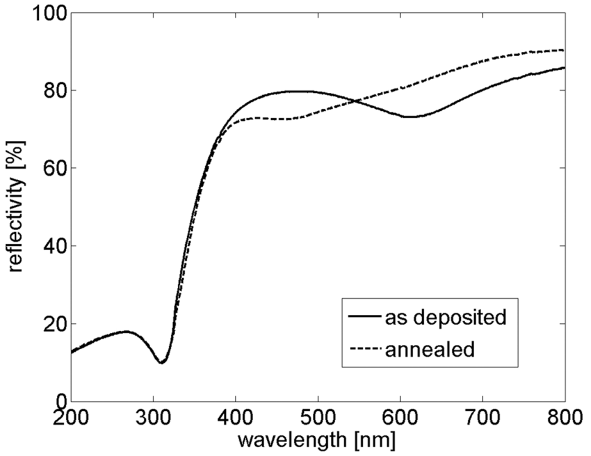

FIG. 2. Comparison of optical reflectance spectra of an Ag-Al alloy film with Al concentration 3.8 at. % before and after thermal annealing. The primary dip at 320 nm does not change, and the secondary dip around 600 nm blue shifts.

Finally, we consider the possible resonances associated with grain boundaries in the Ag-Al alloy films. Between adjacent crystallites of different orientation, there are atom dislocations, lattice vacancies, and other defects along the grain boundaries (as illustrated in Figure 3). Thus the density of free electrons is dramatically reduced in this region, and the grain boundaries might behave like dielectric rather than metal.[12] Such metal-dielectric-metal structures could give rise to surface plasmon resonances.[1] Although it is difficult to determine the exact dimension of the grain boundaries, the width will be significantly smaller than its length. The associated resonance can be regarded as the gap SP. Moreover, the grain boundary (or gap) width is much smaller than the optical wavelength. As such, the resonant

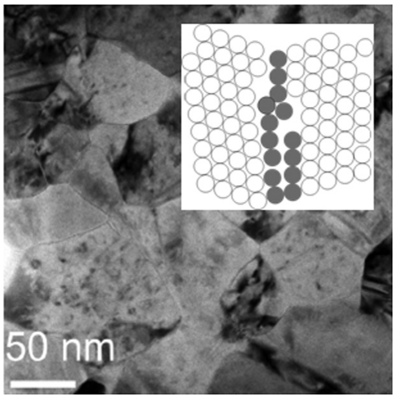

FIG. 3. A plan-view TEM image of an Ag-Al alloy thin film showing the randomly oriented crystallites. The inset is a schematic of the grain boundary.

frequency can be estimated in the quasi-static limit:[13] $\omega_g = \omega_p/1 + \sqrt{1+\varepsilon_f}$, where ω_p is the bulk plasma frequency of metal and ε_f is the effective dielectric constant of the gap. Thus, the grain boundary (or gap) SP frequency ω_g scales with the bulk plasma frequency ω_p. This is consistent with the experimental observation that as the primary reflectance dip at ω_p blue shifts with Al concentration, the secondary dip follows (Fig. 1). Moreover, thermal annealing of the alloy samples reduces the defects in the grain boundaries and the value of ε_f decreases and ω_g increases. This agrees with the observed blue-shift of the secondary reflectance dip after thermal annealing (Fig. 2). The primary reflectance dip does not shift after annealing as ω_p is not affected. Hence, the secondary reflectance dip is attributed to the excitation of SP resonance in the grain boundaries.

In conclusion, we have performed optical and microstructural characterization of Ag-Al alloy films deposited by sputtering on silicon substrates at room temperature. In addition to the primary feature that corresponds to the bulk plasma resonance, a secondary dip appears in the optical reflectance spectra. The role of surface roughness, grain size, and grain boundaries was considered. With AFM, TEM, and x-ray diffraction measurements, we ruled out the resonances related to surface roughness and metal grain size as possible causes for the secondary dip. However, we found surface plasmon resonances at the grain boundaries to be consisted with our observations. The influence of grain boundaries on optical properties has significant implications for the design of metal-based nanoplasmonic materials.

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