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Optical reflectivity improvement by upgrading metallic glass film quality

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The effects of atomic-defect and free-volume amounts of metallic glassy film on the optical reflectivity and mechanical properties of the sputtered metallic glass thin films are explored. With a lower Ar working pressure and the proper post-annealing at temperatures slightly lower than the glass-transition temperature T_g, film free volumes and defects would reduce, resulting in better atomic bonding and higher film hardness/modulus, which in turn leads to lower electric resistivity and higher optical reflectivity. Annealing above T_g would induce crystalline structure which would lead to competition with the optical transition of the Drude free electrons and hinder the optical reflectivity in the visible range. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4825361]

Metallic coating on various substrates could provide high reflectivity over a broad spectral range, including common lighting and more sophisticated solar energy applications. For the latter case, there are primarily two approaches to harvest solar energy. One approach is to convert solar energy into electricity, e.g., solar cells, and another is to directly convert solar energy into thermal energy. The former draws energy from electromagnetic wave with wavelength typically around 400–1000 nm, and the latter uses wavelength in the visible and infrared (IR) spectral ranges around 400–2000 nm. On the other hand, if it is for ultraviolet (UV) LED applications, the reflection in the wavelength region of 200–400 nm would be of concern.

In the case of solar to thermal energy conversion, solar energy is collected through a reflector made of monolithic metals or with additional coatings. For example, enhancement in light reflection can be made by applying high reflective metallic coating (such as pure Ag, Au, Cu, or Al) or with additional dielectric overcoats (such as SiO_2 or TiO_2). Metallic-coated reflectors have already been widely used. However, when a reflector is in use, there are still some associated aging problems such as oxidation, corrosion/erosion, thermal stability, and thermal fatigue. These aging problems gradually alter the surface characters and degrade the performance of the reflector.

The free electron model of metals provides simple explanation of the optical properties of metals. The optical reflectivity (R) can be related to electric resistivity (ρ) as R = 1 − C × \(\sqrt{\rho}\) where C is a proportional constant. The high reflectivity in the infrared spectral region, metallic films typically have a reflection minimum in the visible/UV region, which is not predicted by the simple model. The reflection minimum is explained by the optical transitions from the filled electronic bands to the empty bands. For Al, the strong absorption at \(\sim 800\) nm is absent in the liquid state or in the vapor-quenched films, suggesting that this absorption should be due to the well-defined band structure of aluminum crystal. In contrast, for the transition metals such as Ag, Au, and Cu, the reflectivity dip is due to the d-band electrons and occurs in the visible/UV region. Due to the localization of the d-band electrons, the reflectivity properties of the transition metals are scarcely changed by the destruction of crystalline structure. Nevertheless, the d-orbital electrons in these transition metals can be modified to sp-orbital electrons by alloying with non-transition elements. It is thus motivated to reduce the reflection dip due to the electronic transitions by applying thin film metallic glasses (TFMGs).

TFMGs are another category of metallic coating. Previous efforts in research and development of the metallic glasses or amorphous alloys are mostly focused on the bulk metallic glasses (BMGs). But due to the relatively brittle characteristics, BMGs have not been widely applied so far. Recently, TFMGs are of interest in new areas related to micro-electro-mechanical systems (MEMS), optical, or biomedical device.

In our previous study, multi-component sputtered Ag-Mg-Al coating has been demonstrated to exhibit reasonable light reflectivity for the visible light without the minimum in the visible/UV region. The reflection of the as-sputtered (AS) Ag-Mg-Al TFMGs was measured to be \(\sim 40\%\)–75\% over 200 to 1000 nm. There is still room for improvement. In this study, the film quality upgrade is aimed via modifying the sputtering and annealing conditions so as to improve the light reflection performance of TFMGs.

The multi-component AgMgAl alloys used for this study were synthesized by magnetron co-sputtering on glass substrate, using an Ag_{45}Mg_{30}Al_{25} alloy target (DC at 100 W) and pure Al target (also DC at 70 W), 50.8 mm in diameter. By adjusting the relative powers, the optimum resulting films have the nominal compositions in at. \% of Ag_{40}Mg_{18}Al_{42}. The chamber was initially evacuated to a pressure of \(1 \times 10^{-7}\) Torr before being backfilled with high-purity argon (Ar) gas to various Ar pressures from \(1 \times 10^{-3}\) to \(6 \times 10^{-3}\) Torr in order to examine the sputter back pressure effect on the light reflection. Then, the targets were placed on DC and RF guns and pre-sputtered for 5 min. The working distance between the target and sample was 120 mm during sputtering process. The applied voltage and sputtering time were adjusted based on the calibrated coating rates of each targets and the final film thickness varied from 100 to 1000 nm, with the optimum thickness

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of about 200 nm. To obtain uniform thickness, the samples were rotated with an average speed of 16 rpm.

The AS AgMgAl TFMGs were subject to post-sputtering thermal annealing in vacuum for 10 min at temperatures below the grass transition temperature, $T_g$ (~142 °C), termed as the sub-$T_g$ annealing, including the TFMGs annealed at 110, 130, 140 °C by rapid thermal annealing (RTA). Annealing was also conducted to temperatures above $T_g$ at 150 and 170 °C. $T_g$ was measured by differential scanning calorimetry (DSC).

The coated specimens were characterized by X-ray diffraction (XRD), scanning or transmission electron microscopy (SEM or TEM), energy dispersive spectrometry (EDS). The film thickness was measured by 3D alpha-step profilometer, the film resistance ($R_s$) was measured by four-point probe, and the electrical resistivity was subsequently calculated by the multiplication of $R_s$ and thin film thickness $d$.

The light reflection of the coated samples was measured using n&K Analyzer 1280, which was calibrated using a standard silicon wafer. Data were collected by the reflection (IR regime) wavelength (Figure 2(a)).

Metallic coating of pure metals are generally using thermal evaporation or e-gun evaporation under high vacuum. But it is not easy to deposit multicomponent metallic films due to the distinct evaporation rate for various elements. In contrast, the sputtering rates of various elements in an alloy target are more comparable. However, in the sputtering process, the energetic particles (i.e., Ar ions) are used to bombard the target and to eject the atoms for the deposition. The vacuum level is lower than that of the thermal evaporation or e-gun evaporation, despite it is evacuated to $10^{-7}$ Torr before sputtering process. The working Ar gas pressure becomes one of the key issues for the film quality. We thus first study the effect of Ar pressure on the quality of deposited films.

The films were first deposited to various thicknesses from 100 to 1000 nm. The XRD pattern of the AS film is presented in Figure 1 (the bottom curve), exhibiting the diffuse hump typical for the amorphous structure in TFMGs. With increasing film thickness, the surface roughness $R_a$ was measured to increase from 0.6 nm up to 2.0 nm (not shown). In order to form a stable continuous solid film, 200 nm film thickness is considered to be optimum. Thus, in what follows, all films for this study have the fixed thickness of 200 nm. The basic properties of this AS 200 nm Ag$_{40}$Mg$_{18}$Al$_{42}$ film using the Ar pressure of $3 \times 10^{-3}$ Torr (as the starting reference film) are about 0.6 nm for surface roughness $R_a$, 107 GPa for modulus $E$, 4 GPa for hardness $H$, 1200 n2m for electric resistivity $\rho$ (Table I), and 35%, 62%, 71%, 73%, 73%, respectively, for light reflection $R$ at 200, 300 (UV regime), 400, 550, 700 (visible regime), and 1000 nm (IR regime) wavelength (Figure 2(a)).

In order to examine the Ar working pressure effect during magnetron sputtering, five Ar pressure levels were selected, namely, $1 \times 10^{-3}$, $2 \times 10^{-3}$, $3 \times 10^{-3}$, $4 \times 10^{-3}, 6 \times 10^{-3}$ Torr, for a film thickness of ~200 nm. For Ar pressure lower than $1 \times 10^{-3}$ Torr, plasma plume may become unstable. When the Ar pressure is low (e.g., $1 \times 10^{-3}$ Torr), the sputtering can proceed in a more stable manner and the resulting films tend to have a lower degree of defects and thus a higher film quality, with the sacrifice of lower lower

![FIG. 1. XRD scans of the 200 nm thick Ag$_{40}$Mg$_{18}$Al$_{42}$ films, prepared using the Ar pressure of $2 \times 10^{-3}$ Torr, under the AS and annealed conditions (at 130, 140, and 170 °C). The major precipitated phases are the Ag and Al-rich phases, with their face-centered cubic (111) plane diffraction peaks closely at 2θ = 38°-39°.]

<table>
<thead>
<tr>
<th>(Under the AS condition)</th>
<th>$1 \times 10^{-3}$ Torr</th>
<th>$2 \times 10^{-3}$ Torr</th>
<th>$3 \times 10^{-3}$ Torr</th>
<th>$4 \times 10^{-3}$ Torr</th>
<th>$6 \times 10^{-3}$ Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (nm)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.6</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>$\rho$ (n2m)</td>
<td>1000</td>
<td>1100</td>
<td>1200</td>
<td>1300</td>
<td>1700</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td>111</td>
<td>100</td>
</tr>
<tr>
<td>$H$ (GPa)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(Using Ar $2 \times 10^{-3}$ Torr)</th>
<th>AS</th>
<th>110 °C</th>
<th>130 °C</th>
<th>140 °C</th>
<th>150 °C</th>
<th>170 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (nm)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>$\rho$ (n2m)</td>
<td>1100</td>
<td>1100</td>
<td>1050</td>
<td>1000</td>
<td>1000</td>
<td>530</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>107</td>
<td>109</td>
<td>110</td>
<td>116</td>
<td>116</td>
<td>124</td>
</tr>
<tr>
<td>$H$ (GPa)</td>
<td>4.0</td>
<td>4.4</td>
<td>4.3</td>
<td>4.4</td>
<td>4.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>
sputtering yield. In contrast, when the Ar pressure is higher (e.g., $6 \times 10^{-3}$ Torr), the sputtering process tends to be more energetic and the resulting films could possess more defects (including free volumes and impurities) and a lower film quality.\(^{21}\) With a higher amount of light scattering defect species in the film, the reflection would be appreciably degraded.

As compared in Table I, at the low Ar pressure level, $R_a$ of the AS films remains low at about 0.2 nm and electric resistivity remains low at about 1000–1100 n$\Omega$m, directly suggesting the higher film quality with fewer atomic defects. The light reflection is also slightly higher, reaching 50%, 72%, 74%, 75%, 75%, and 76%, respectively, for light reflection $R$ at 200, 300, 400, 550, 700, and 1000 nm wavelength (Figure 2(a)), consistent with the predicted rule in our previous paper.\(^{12}\) Note that the reflection improvement over the starting reference film in the UV regime is more pronounced (upgraded from $R = 35\%$–$62\%$ to $R = 50\%$–$72\%$). On the contrary, at high Ar pressure, $R_a$ inclines to 0.9 nm and electric resistivity increases to 1700 n$\Omega$m, resulting in the much degraded reflection of 25%, 40%, 50%, 55%, 60%, and 65% at 200, 300, 400, 550, 700, and 1000 nm wavelength (Figure 2(a)), since the sputtering yield rate for the Ar pressure of $1 \times 10^{-3}$ Torr might be too low for practical application, it is considered that $2 \times 10^{-3}$ Torr might be the optimum condition.

In our previous study on post-sputtering thermal annealing of the TFMGs,\(^{22}\) it was found that sub-$T_g$ short-term annealing could reduce the atomic defects and free volumes. It follows that proper post-sputtering annealing might further upgrade the film quality and thus optical reflection. Based on DSC scans (not shown), $T_g$ of the current AgMgAl films is $\approx 142^\circ$C. When the annealing temperature was set to 110, 130, 140, 150, and 160°C (slightly above $T_g$), the film structure seems to be relaxed during the 10 min annealing. However, these annealed films are still basically amorphous in nature, as evidenced by their XRD scans shown in Figure 1. In contrast, the films annealed at 170°C ($\approx 30^\circ$C above $T_g$) exhibit crystalline second particle phases (mostly Ag and Al), as evidenced from the XRD patterns (Figure 1), the $R_a$ readings (Table I), and the TEM measurements (below).

As compared with the starting reference film, all the film properties move to the upgraded direction on sub-$T_g$ annealing, as shown in Table I. For the optimum annealing at 140°C, electric resistivity decreases to about 1000 n$\Omega$m (from 1100 n$\Omega$m), modulus increases to 116 GPa (from 107 GPa), and hardness increases to 4.4 GPa (from 4.0 GPa). The lower electric resistivity implies the higher film quality and the higher modulus and hardness reflect the higher atomic bonding with lower atomic defects and lower free volumes. In our previous paper,\(^{22}\) it has been demonstrated that the strength or hardness would increase with decreasing free volume. All of these improvements of film quality would lead to a higher light reflection, as compared in Figure 3. For the films annealed at the optimum 140°C, reflection $R$ becomes 50%, 77%, 78%, 79%, 79%, and 80% at 200, 300, 400, 550, 700, and 1000 nm wavelength (Figure 2(b)). Note that the films annealed at 170°C, with precipitated Ag/Al phases, show a lower reflection over 400 to 800 nm wavelength, similar to typical for pure Al reflection coatings.\(^{22}\) The reflection $R$ for this film is 50%, 77%, 76%, 70%, 68%, and 85% at 200, 300, 400, 550, 700, and 1000 nm wavelength (Figure 2(b)).

![FIG. 2. Light reflection curves for the 200 nm thick Ag$_{40}$Mg$_{18}$Al$_{42}$ films, (a) prepared using Ar pressures from $1 \times 10^{-3}$ to $6 \times 10^{-3}$ Torr, under the AS condition without annealing, and (b) prepared using the reference Ar pressure of $2 \times 10^{-3}$ Torr, under the AS and annealed conditions (at 140 and 170°C).](image1)

![FIG. 3. TEM micrographs of (a) bright-field image, (b) dark-field image (with the inserted diffraction pattern), and (c) HAADF Z-contrast image. By TEM/nano-beam-EDS, the bright particles in (c) are measured to be pure Ag, and the darker surrounding regions are Al-rich phase with the average composition of Al$_{50}$Ag$_{35}$Mg$_{15}$ (in at. %).](image2)
Through detailed TEM characterization, coupled with nano-beam TEM/EDS and high-angle annular dark field (HAADF) technique, the microstructures of the films are identified. For the as-sputtered AgMgAl films, it is basically featureless characteristic of the amorphous nature. On annealing at temperatures above \( T_g \), the nanocrystalline phase is crystallized out of the amorphous matrix. Figures 3(a) and 3(b) show that bright and dark field (BF and DF) images (with the inserted diffraction pattern DP) of the AgMgAl film, sputtered using an Ar pressure of \( 2 \times 10^{-3} \) Torr and post-annealing at \( 170 \) °C for 10 min. Nano-crystalline Ag particles nearly spherical in shape are seen from the BF or DF images, measuring around 15 nm. The HAADF image can reveal the Z-contrast imaging, as shown in Fig. 3(c), illustrating the spherical Ag particles in bright contrast and the Al-rich background in darker contrast. By TEM/nano-beam-EDS, the local composition of the bright spherical regions is indeed basically Ag, and the darker region surrounding the Ag particles is Al-rich, with the rough composition of about \( \text{Al}_{50}\text{Ag}_{35}\text{Mg}_{15} \) (in at. %). The fine Ag particles would cause the d-orbital absorption or the lower reflection around 200–250 nm wavelength. And the Al-rich surrounding regions would cause the slight reflection drop over 400–800 nm wavelength. The observed reflection curves in Figure 2(b) are in perfect agreement with the TEM observations and measurements, and consistent with physical predictions.13,14

In summary, the light reflection of the AgMgAl TFMG films is demonstrated to be improved via the reduction of film surface roughness, film quality in terms of a lower degree of atomic defects and free volumes, and electric resistivity. This can be achieved by proper control of film thickness, Ar working pressure, and post-sputtering sub-\( T_g \) annealing. The interrelationship between film surface morphology, microstructure, local composition, and orbital absorption is well established in this study. It is demonstrated that with a higher film quality and lower film resistivity, the light reflection can be improved. To make further efforts along this line, e-beam evaporation, which usually result in even greater film quality, might be another route for future research.

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