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THE EFFECT OF AN APPLIED BIAS UPON THE REFLECTANCE AND ADHESION OF SILVER FILMS BEING SPUTTER-DEPOSITED ON POLYESTER SUBSTRATE

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Abstract

Thin reflective films are synthesized by using PVD methods with a bright metal of Al or Ag. For purposes of improving the reflectance and adhesion of such films particularly, substrate bias was applied during sputtering (namely, ion-plating) to enhance the deposition process with higher energy. And we succeeded in fabricating a quality silver film which possesses an adhesion of 85 Kg/cm^2 and a high reflectivity of more than 96 %. Both of reflectivity and adhesion are better in case of bias sputtering as controlled than non-bias sputtering, particularly the bias of 50-100 V showed most effective. The microstructures of sample films were examined by using various equipments and the XRD spectrum in particular showed that <111> direction is the preferred growth orientation.

Key words : *thin metallic film, reflective film, bias sputtering, ion-plating, polyester substrate*

1. Introductory Remarks

Ways of maximizing the illuminance by employing high reflectivity metallic thin films on the reflector surfaces for fluorescent lamps have been sought in order to improve the energy efficiency and to reduce the electricity consumption basically. The reflector of a fluorescence lamp has been mostly white-painted and its reflectivity is about 65 to 80 % only. Very recently some reflectors Al-anodized or coated with reflective thin films become popular with higher reflectivities up to 95 %[1], saving tremendous amount of overall electrical energy and contributing environmental preservation consequently is more feasible. The thin films are synthesized by using PVD methods with a lustrous metal of Al or Ag. Evaporation methods have been used for these purposes in Korea[2] and sputtering techniques have been developed mainly in U.S.A. to produce such reflective films. For purposes of improving the reflectance and adhesion of such films, we have studied various PVD techniques for a couple of years[2,3] For this investigation particularly, substrate bias was applied during sputtering[4,10] to enhance the deposition process with higher energy.

2. Specimen Preparation Conditions

As substrate, we used the same polyester film and deposition source as mentioned in reference 2. Then, reflective thin films were prepared by using R.F. mgnetron sputtering and bias sputtering. For R.F. magnetron sputter deposition, the experimental setup was the same as before[3]. Ag of 99.99 % purity was hired as the target of disc type with a dimensions of 2" dia. × 0.25" thickness. The base vacuum was kept down to 10^{-6} Torr by using a diffusion pump. Leaking Ar gas into the chamber, a glow discharge being generated and used in pre-cleaning the substrate to remove any contaminant on its surface, for 20 minutes as the target covered with its shutter. In case of bias sputtering, however, we applied substrate bias varying within a range of 0 to 300 V DC. It is normal practice to use RF in case of insulator substrates[11], but our polyester film was only 50 ㎛ thick, thin enough to use DC instead, for our RF sputtering system. As biasing the substrate, we minimized the current level to keep plasma away the polyester film, not to harm the surface. It is very important to circulate cooling water during the deposition process.

3. The Influence of Varying Parameters on Deposition Rates

In case of sputtering with bias of 0 to 300 V DC, deposition were carried out with various values in RF power, working pressure, and Ar flow rate. Overall, we found the deposition rates increased slightly as the bias increased. Fig. 1 shows the results of deposition rates for the samples prepared with the bias while RF power was fixed within a range of 25 to 100 W. Regardless of substrate bias, the deposition rates for film samples to have been prepared with various R.F. power show a tendency increasing monotonically as R.F. power increases. And the influence of bias is also positively monotonic, for most of the cases under experiments.

The experimental results of the samples deposited with varying the values of bias and process pressures are seen in Fig. 2. The values of RF power were fixed as 50 or 100 W for each run. While the influence of working pres-

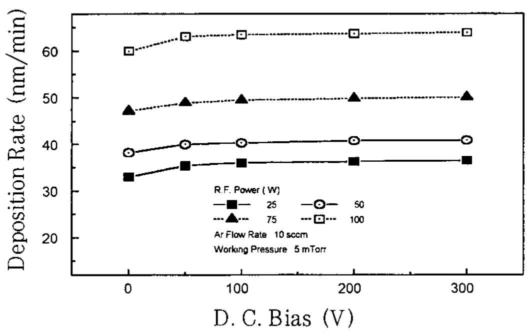


Fig. 1 Deposition rate as a function.of R.F. power and D.C. bias.

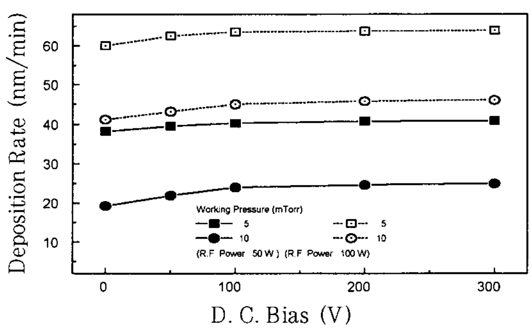


Fig. 2 Deposition rate as a function.of working pressure and D.C. bias. (Ar flow rate 10 sccm)

sure upon deposition rate shows inversely proportional in all the cases of sputtering, the additional influence of bias lessens that effect in general. Various Ar flow rates in a range of 5 to 20 sccm were applied during deposition on the substrate biased. As Ar flow rate is less than 10 sccm, this bias effect holds still. In case of Ar flow rate of 20 sccm, however, vacuum and depositant flux seem to be disturbed and irregular results depict. The deposition rates as a function of Ar flow rate reveal maxima at 10 sccm, regardless of bias values, consistent with the case as in ref. 3.

4. The Influence of Varying Parameters on Adhesion

The adhesion between the deposited film and the substrate was measured by employing a Sebastian Pull-Tester. The limit for pulling capacity was kept as 100 kg·force while the pulling rate was fixed as 2.5 kg/sec. Since the thin specimens are very flimsy as deposited on polyester film, we used epoxy with strong adhesive strength for the polyester side of each specimen to be adhered to a back plate. And also, we applied the same epoxy to a stud, making it to adhere to the silver side of the specimen. Then the testing unit was fixed with a spring mounting clamp for 12 hours before pull test.

To study the influence of Ar flow rates on the adhesion of resulted films, the flow rates were varied within a range of 5 to 20 sccm during deposition with various bias values to make samples for measuring the adhesivity. RF power was fixed as 50 or 100 W. The samples prepared with 10 sccm depicted excellent adhesion of 45 to 50 Kg/cm^2. These values surpasses more than double the cases of non-bias sputtering. On the other hand, the adhesion increased as the applied RF power increased during deposition, which is similar to the results discussed in ref. 3. It is concluded that the gas amount participating in reaction should be maintained as a proper level to obtain a high adhesivity for the resulting film, although the influence of flow rate is not as much as that of other process parameters. The influence of working pressure was also studied by keeping it within a range 5 to 10 mTorr during deposition with various bias values making specimens, while fixing RF power as 50 W or 100 W. The resulting adhesion values are seen in Fig. 3. The samples prepared in the working pressure of 5 mTorr revealed the best results with adhesion values as high as 50 Kg/cm^2. From this result, we deduce a fact that deposition process in higher vacuum produces higher adhesivity for the thin film. And it is reasoned as the higher the vacuum the less interference from the depositing particles being accelerated toward the substrate. This influence of working pressure is common, regard-

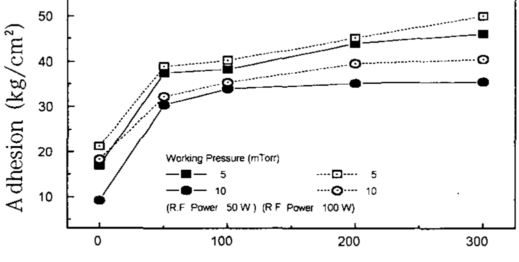


Fig. 3 The effect of D.C. bias with various working pressure values. (Ar flow rate : 10 sccm,.Radiated wave length : 700 nm)

less of DC bias.

Then, samples were fabricated by biasing the substrate during deposition with various values of RF power within a range of 25 to 100 W, and subjected to measuring their adhesivities. In case of non-bias sputtering, the specimens showed adhesion of 18.5 to 20.5 kg/cm^2. Compared to these, in case of bias sputtering, the adhesion more than doubled as high as 35 to 50 kg/cm^2. And under biased conditions, we ob served that the adhesion increased as the power increased. This is consistent to the positive influence of RF power in sputter deposition[3]. The results are demonstrated in Fig. 4. The reason being for the increasing adhesion under bias conditions, is that the depositing silver ions are more accelerated toward the substrate and reached there with higher dynamic energy as the bias value increases. As DC bias of 200 or 300 V is applied during deposition, we found that a minute current flowing through the substrate. This is explained as the plasma induced near the substrate as applying DC bias, which damages the substrate surface slightly but resulting in enhancing the adhesion.

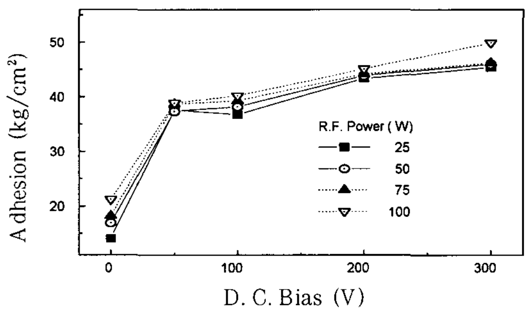


Fig. 4 The effect of D.C. bias with various R.F. power values. (Ar flow rate : 10 sccm, Working pressure : 5 mTorr)

5. The Influence of Varying Parameters on Reflectance

The reflectivity of thin films were measured by using a SpectroPhotometer. A light source with an intensity same as the solar surface at 6500℃ was irradiated within a visible light range of 400 to 700 nm. Reflectance of Ag films deposited by using sputtering has revealed above 96 %[3], so the influence of bias sputtering is not much expected. But anyways, with a bias of 100 V DC the reflectance shows some improvement by 0.5 % in average. This positive effect of bias on the reflectance and adhesion guarantees for quality reflective films.

The Influence of Ar flow rates were studied by fixing within a range of 5 to 20 sccm during making samples for measuring their reflectances. Collected results show that the faster the flow rate is, the less influence of DC bias. In case of 5 sccm, the ion-plated samples revealed higher reflectivity as much as 0.1 to 0.5 % than the ones prepared without bias. But in case of 10 sccm, there was no much difference among the samples whether the bias was applied or not. When the flow rate got increased to 20 sccm, the sputtered samples depicted higher reflectance as much as 0.1 to 0.8 % than the ones fabricated with bias. It seems that too fast Ar flow disturbs the vacuum condition causing irregular situation during deposition. So we decided to keep the flow rate below 10 sccm.

The working pressure was kept within a range 5 to 10 mTorr making more specimens, while fixing RF power as 50 or 100 W. The resulted reflectances are collected and arranged in Fig. 5. In case of non-bias sputtering with

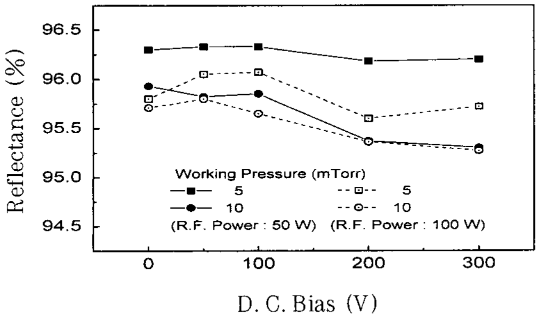


Fig. 5 The effect of D.C. bias with various working pressure values (Ar flow rate : 10 sccm, Radiated wave length : 700 nm)

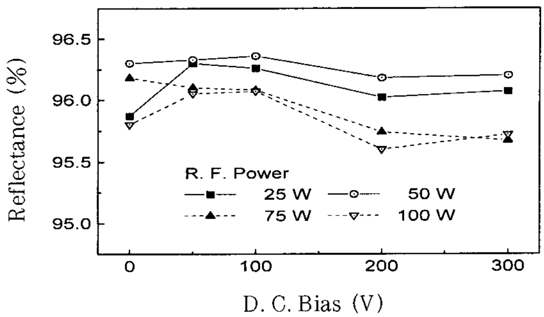


Fig. 6 The effect of D.C. bias with various R.F. power values. (Ar flow rate: 10 sccm, Working pressure : 5 mTorr, Radiated wave length :700 nm)

RF power 50 W, the highest reflectivity of 96.3% was obtained in a high vacuum of 5 mTorr. From the ion-plated samples, the superior reflectivity was obtained also in the case of 5 mTorr. In Particular, DC bias of 50 or 100 V yielded 96.4 % reflectivity, which is higher as much as 0.3 to 0.6 % than the case of DC bias of 200 or 300 V. This is due to surface damages done by plasma which was induced by too high DC bias applied to the substrate. In case of RF power of 100 W, the specimens fabricated at 5 mTorr also revealed higher reflectivities than those fabricated at 10 mTorr. It is concluded that higher vacuum renders more effectiveness for the better reflectivity.

Then RF power was varied with various values between 25 to 100 W, biasing the substrate during deposition. In case of DC biases of 50 and 100 V, the specimens revealed superior reflectance to the ones fabricated without bias. Fig. 6 shows the results obtained for each process condition, measured with a fixed wavelength of 700 nm. For non-bias sputtering cases, the best reflectivity of 96.3 % was obtained from the specimens that were deposited at RF power 50 W, while the specimens deposited at RF power 100 W showed 95.8 % reflectance similar to the case of RF power 25 W. It is noted that the power increased above a certain energy level may damage the surface of polyester film. Anyhow, overall reflectance was higher than 95.5 %, better than the upper limit of 95.0 % for the CPF product[1].

For bias sputtering cases, the specimens prepared at RF powers of 25 and 50 W depicted the reflectivity of 95.8 to 96.4 %, while the ones prepared at 75 and 100 W revealed lesser values of 95.5 to 96.0 %. This illustrates that the influence of RF power is stronger than the one of bias. In particular, the specimens fabricated with a bias of 50 or 100 V demonstrated superiority. As the bias increased to 200 or 300 V, the samples showed a tendency to less reflect. During these runs, we could observe that a minute current flowing through the substrate. Thus, it is concluded that plasma was induced by DC bias near the substrate and damaged slightly the substrate of polyester then resulted in a less reflectivity value, while this phenomenon affect the adhesion positively as discussed before.

6. Microstructural Differences Resulted

When film crystallinity and orientation were analyzed by using an XRD, we found out that the thin films grew on the planes of (111) and (200) with a preferred orientation of <111> for all the cases to have been prepared by using sputtering, regardless of bias values. We assume that crystallization occurred without additional heat-treatment during deposition because the melting point of silver is relatively low as 962 ℃ making the mobility high enough for it. Fig. 7 shows a typical spectrum of XRD analysis.

As cross-sections of sample films were analyzed, all the specimens showed columnar structures with small particulates formed near the interfacial area and columns grown perpendicular to the substrate. Columns get coarsened and less dense as RF power increased, but become thinner and denser as the applied bias increased. Thus, a proper combination of process parameters is very crucial for the best reflectivity. Fig. 8a shows a typical SEM photo of non-bias sputtering case, and Fig. 8b is for the case of bias sputtering. Looking carefully down on the cross-sections of polyester substrate, we found evidences of Ag metallic structure, which suggests that depositants penetrate the surface of polymer substrate during ion-plating. The reason behind this is that the sputtered particles as ions get high energy under the influence of electric field generated by the bias and collide with and penetrate the surface of polyester substrate. This phenomenon also is related with the

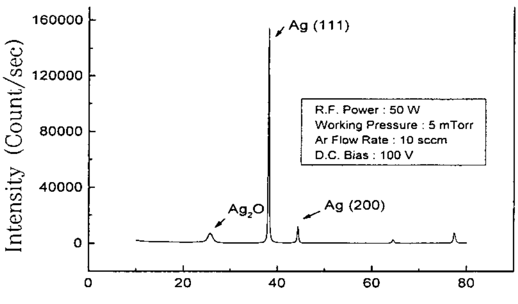


Fig. 7 A typical X-ray diffraction spectrum of Ag film, deposited by using bias sputtering.

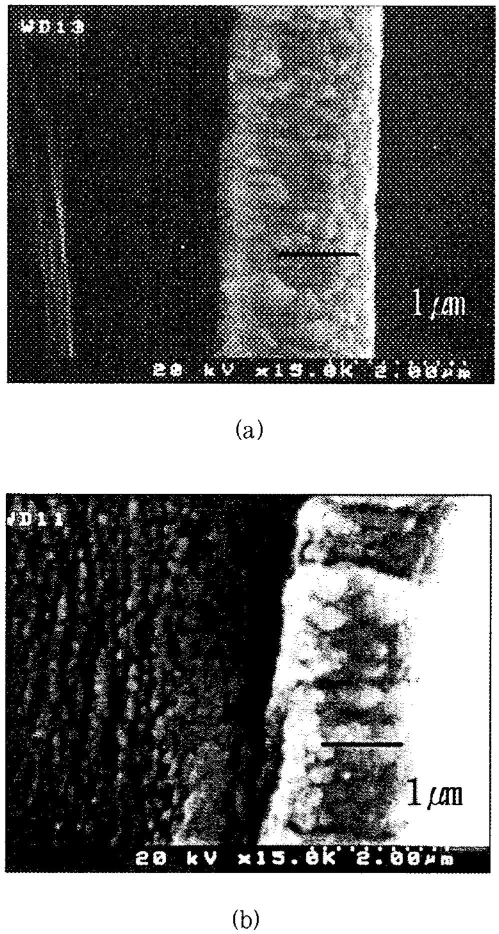
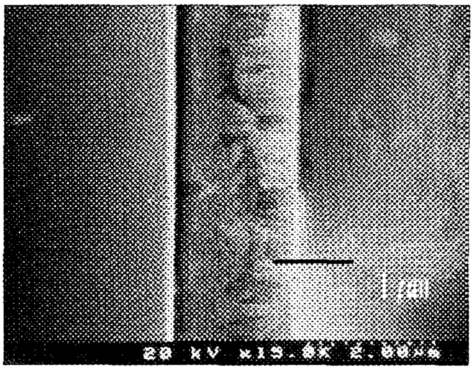


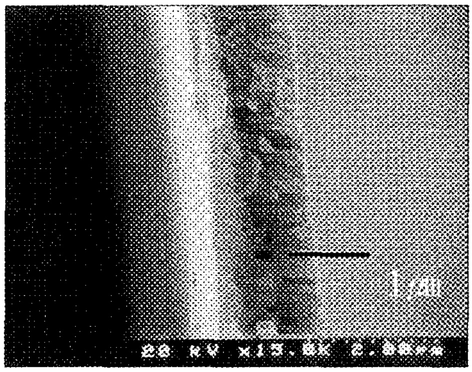
Fig. 8 Typical SEM micrographs of Ag films deposited on polyester (a) Non-bias, (b) 100 V D.C. bias. (R.F. power : 50 W, Ar flow rate 10 sccm, Working pressure : 5 mTorr)

increased adhesion between the thin film and the substrate.

Fig. 9 demonstrates typical cross-sectional micrographs taken from sample films deposited on glass substrate to observe the cross-sectional microstructure. They were prepared specially because of the difficulties with the specimens of polyester substrate rendering for SEM observation in general. RF sputtered samples showed a tendency that as RF power increases the thickness of columns increases, the space between columns get larger and the structure becomes less dense, as comparatively seen in Figs. 9a. and 9b. The influence of bias is clearly seen from Fig. 9c. While keeping RF power level the same, the specimen prepared with bias was resulted in thinner columns and denser structure than the case of non-bias. A typical morphology obtained with an AFM for the silver films shows the particle size getting larger as the applied power for the deposition increases, which is seen same as the above cross-sectional views. This is due to nucleation particles in early stage getting larger and columns growing thicker, resulting in decreasing the reflectivity of final structure.



(a)



(b)

Fig. 9 Typical SEM micrographs of Ag films deposited on the glass with (a) R.F. power : 100 W and non-bias, (b) R.F. power 50 W and D.C. bias : 100 V. (Ar flow rate: 10 sccm, Working pressure: 5 mTorr)

7. Conclusions

We succeeded in fabricating a quality silver film which possesses an adhesion of 85 Kg/cm^2 and a high reflectivity of more than 96 %. This reflectivity in particular reveals an excellent result, better than the product of CPF. The adhesion of ion-plated silver films resulted in 75 to 85 Kg/cm^2, which are more than twice the values RF sputtered ones of 30 to 40 Kg/cm^2. In cases of bias sputtering, the reflectivity enhanced as the Ar flow rate increased, which is more prone to than the case of non-bias. Both of reflectivity and adhesion are better in case of bias sputtering than non-bias sputtering, particularly 50-100 V showed most effective. The higher the vacuum is, both of the reflectivity and adhesion show higher values, in general.

XRD spectrum showed that <111> direction is the preferred growth orientation, and that the films contained crystals which were perhaps formed since the melting point of silver as 962 ℃ is low enough for high atomic mobility for diffusion. Cross-sections of thin films seen by using an SEM depicted a conical shape of microstructure and an evidence of silver atoms infiltrated the polyester substrate surface in case of bias sputtering. As the working pressure decreases, the structure grows elongate perpendicular to the substrate surface.

REFERENCES

1. CPF, "Sterling Silver Reflector," Engineering Manual.
2. *RI, EuiJae and HOANG, TaeSu*; "The Reflectance and Adhesion of Silver Films Prepared by Using E-Beam Evaporation on Polyester Substrate," Proceedings to Asian Finish '98, held in Seoul, Korea, 1998. 10.
3. *HOANG, TaeSu and RI, EuiJae*; "The Effect of Process Conditions on the Physical Properties of Silver Films Prepared by Using Sputtering on Polyester Substrate," Proceedings to Asian Finish '98, held in Seoul, Korea, 1998. 10.
4. D. M. Mattox, J. Vac. Sci. Tech., 10, 47 (1973).
5. L. J. Brillson, Thin Solid Films, 89, 461 (1982).
6. R. F. Hochman and D. M. Mattox, "Surface Cleaning, Finishing, and Coating," Metals Handbook, Ninth Ed., Vol. 5, p. 417, ASM (1982).
7. A. Erdemir, E. J. Lee and R. Hochman, " Tribological and Mechanical Properties of Ion Plated TiN Coatings," ASM Proceedings to the CAIPIM, Atlanta, GA (1985).
8. A. Matthews, D. G. Teer, Thin Solid Films, 80, 41-48 (1981).
9. S. Schiller, U. Heisig, K. Goddicke, Thin Solid Films, 64, 455-467 (1979).
10. W.R. Stowell, D. Chambers, J. Vac. Sci. Tech., 11, 653-656 (1974).
11. D. M. Mattox, J. Appl. Phys. 37, 3673 (1973).