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# Growth of Ag thin films on glass substrates with a 3-mercaptopropyltrimethoxysilane (MPTMS) interlayer

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**Abstract.** We report that very thin Ag films on glass substrates with a 3-mercaptopropyl trimethoxysilane (MPTMS) interlayer grow relatively flatter and become electrically continuous with a smaller thickness due to an interaction between Ag atoms and the molecule. Because optical transmittance of Ag films with and without the MPTMS layer is almost the same, it is found out that the Ag film with the interlayer is more suitable for the use as a semi-transparent electrode for display devices.

## 1. Introduction

Thin metal films with high transmittance and low resistivity can be used as transparent electrodes in various electronic devices such as solar cells or organic light-emitting diodes [1-3]. Though a thinner film shows a higher transmittance, it becomes discontinuous and has a high electrical resistance. Therefore, it is preferable to develop a process for thinner continuous films. It is well known that film growth is affected by various deposition parameters, such as deposition rate, temperature, substrate surface condition and so on. For Cu sputtered film, reports have been made that organic silane molecule layers, such as 3-mercaptopropyltrimethoxy silane (MPTMS) or 3-aminopropyltrimethoxysilane (APTMS) gave influences on nucleation of Cu films due to a chemical interaction between Cu atoms and the molecules[4, 5].

Previously, we have investigated properties of Ag thin films with an MPTMS interlayer on SiO<sub>2</sub>/Si substrates. It was found that Ag thin films with the interlayer were electrically continuous compared to those without the interlayer [6]. For the use as transparent electrode, optical property of the films is an important factor. In the present paper, we prepare the Ag thin films on glass substrates with and without an MPTMS interlayer and investigate their electrical and optical properties.

## 2. Experiment

A Corning #1737 glass substrate was cleaned ultrasonically in acetone, 2-propanol, and de-ionized water, followed by treatment in a UV/ozone cleaner. The substrate was transferred to a nitrogen-filled glove box, immersed in 5 mM MPTMS toluene solution for 30 min, and then rinsed in toluene and dried overnight to provide the substrate with an MPTMS interlayer. The deposition of Ag films on the substrates, with and without the interlayer was carried out by vacuum evaporation below

$3.0 \times 10^{-4}$  Pa using an Ag wire (99.99% purity) evaporation source. The thickness and deposition rate (0.40 nm/s) of the films were controlled by a quartz crystal monitor.

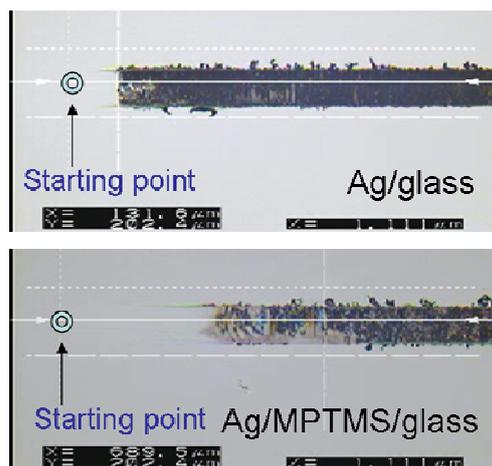
Formation of MPTMS layer was confirmed by contact angle measurement using 10  $\mu$ l water droplets, and the layer thickness was estimated by ellipsometry, as described somewhere else [7]. After deposition of 60-nm-thick Ag thin film, adhesion strength of the film on the substrate was examined by microscratch tester with a diamond stylus of R25  $\mu$ m. The surface morphology of the films was observed using an atomic force microscope (AFM). The average rms roughness ( $R_{rms}$ ) was calculated based on images (5  $\mu$ m  $\times$  5  $\mu$ m) from three different locations on the sample surface. Electrical resistivity was measured at room temperature using a four-point probe method. Optical transmittance was investigated with UV/Vis spectrophotometer.

### 3. Results and Discussion

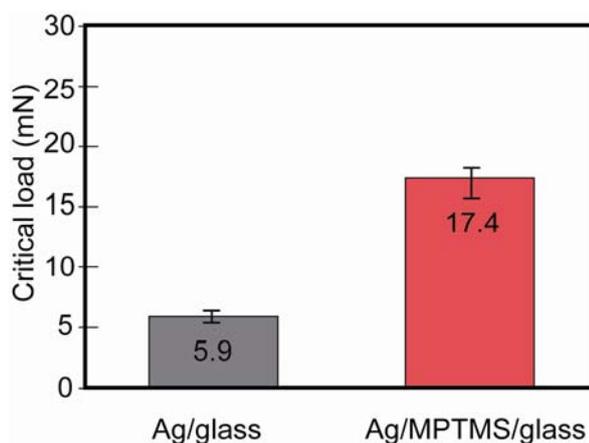
#### 3.1. Formation of MPTMS layer on glass substrate

To confirm formation of MPTMS layer on glass substrate, we measured a static water contact angle, and the measured value was  $64^\circ$ , which is close to a value ( $66^\circ$ ) for MPTMS layer on  $\text{SiO}_2/\text{Si}$  substrate in our previous study [7]. As a thickness, we obtained a value of 1.4 nm  $\pm$  0.6 nm which is slightly larger than that in previous study. As a result, we consider that the substrate surface is covered with MPTMS layer.

Next, we investigated adhesion strength at the interface of 60-nm-thick Ag thin film and the glass substrate. Figure 1 shows photos of representative samples after the scratch test. It is recognized that a Ag film without an MPTMS interlayer delaminated easily. Figure 2 shows average critical load for delamination of Ag films. It is found that the critical load becomes three times larger for the sample with MPTMS interlayer than that without the interlayer, which was also observed for Ag films on  $\text{SiO}_2/\text{Si}$  substrates [6]. As the reason, we consider that the interlayer enhanced the adhesion strength by anchoring effect of the MPTMS molecule. Therefore we think this enhanced adhesion is one of the proofs of the formation of the MPTMS layer.



**Figure 1.** Sample surfaces after the scratch test.

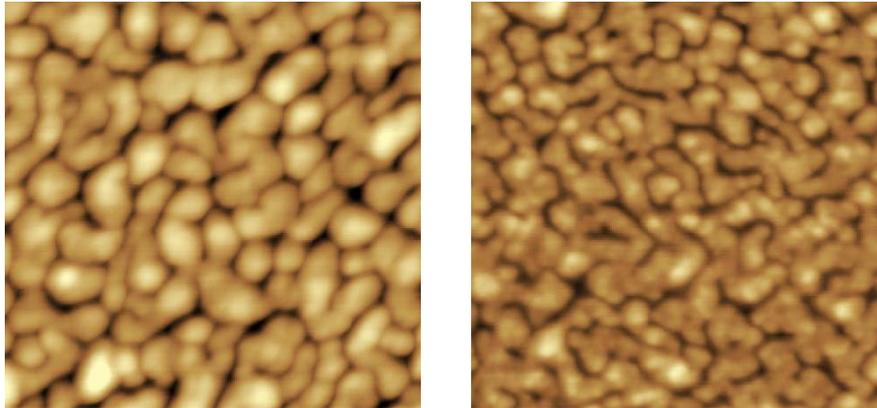


**Figure 2.** Critical load for delamination of Ag films on investigation of adhesion strength.

#### 3.2. Characterization of Ag thin films on glass substrate with MPTMS interlayer

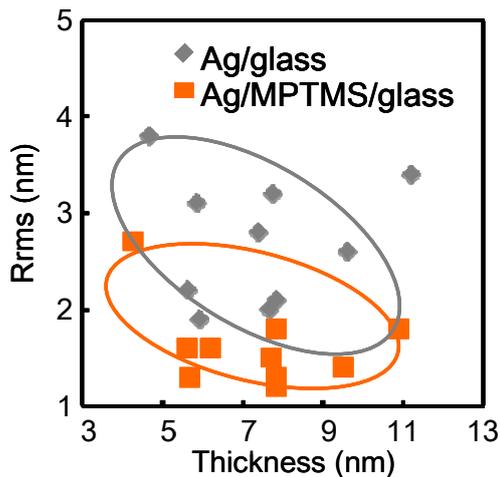
First, morphological analysis was carried out for the deposited samples. Figure 3 shows AFM images of 6-nm-thick Ag thin films with and without MPTMS interlayer. It is clearly observed that Ag grains are grown larger in round shape and look isolated each other on glass substrate without the interlayer.

However, they are smaller in peanut shape being connected each other on the MPTMS interlayer. This suggests that initial nucleation density was higher on MPTMS interlayer. At 8-nm-thick Ag films, grains were connected on both surfaces, but height from the substrate was smaller for Ag film with the interlayer. Therefore, it is suggested that growth of Ag thin films seems to be flatter by MPTMS interlayer, which was found on SiO<sub>2</sub>/Si substrates, too.

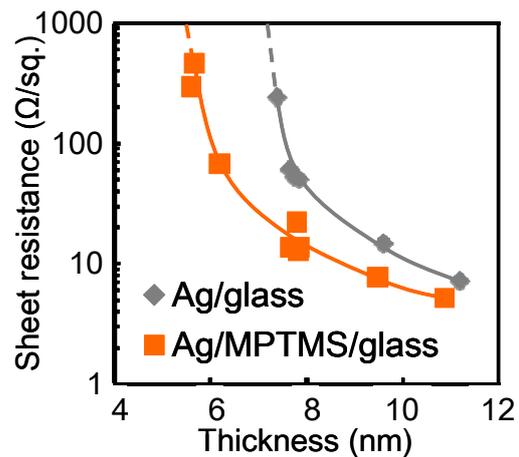


**Figure 3.** AFM images of 6-nm-thick Ag thin films on glass substrates with (right) and without (left) the MPTMS interlayer. Image size is 0.5 $\mu$ m x 0.5 $\mu$ m.

Further result of AFM analysis is shown in Figure 4. It is shown that the root-mean-square roughness of Ag film with the MPTMS interlayer is lower than that of Ag film without the interlayer at the same thickness. Then, the values of roughness decrease with increase of the film thickness because the films become more continuous. Consequently, we confirm that a Ag film grows flatter on a glass substrate with the MPTMS interlayer. As the reason, we consider that Ag atoms arrived on the substrate are less mobile due to a strong interaction with mercapto moiety of MPTMS, which causes a higher nuclei density.



**Figure 4.** Root-mean-square roughness of the samples at each Ag film thickness.



**Figure 5.** Sheet resistance of the samples as a function of Ag film thickness.

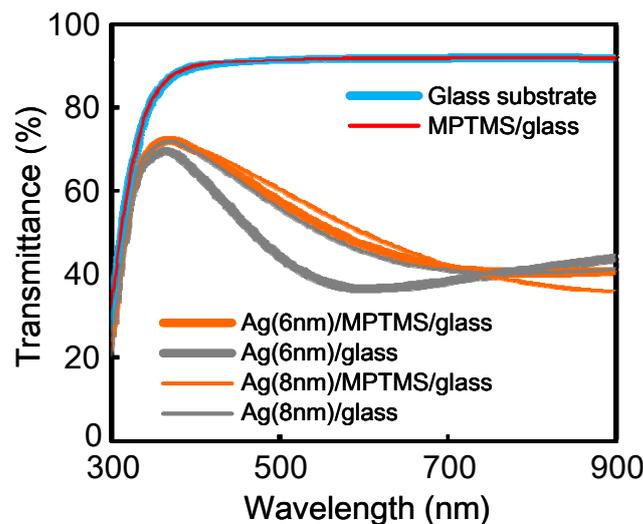
Then we compare an electrical property of both samples. Figure 5 shows the sheet resistance of Ag films with and without the MPTMS interlayer. In general, very thin films are discontinuous, and their resistance is too high to be measured. Above a critical thickness, films become continuous and their sheet resistances decrease with increasing thickness. It is found that the Ag film with the interlayer shows lower sheet resistance in any thickness. The figure shows that the Ag film without the interlayer becomes continuous at a thickness of 7.4 nm, on the other hand, that with the interlayer becomes continuous at a thickness of 5.6 nm. Namely, critical thickness was found to be 2 nm smaller. Thus, we confirmed that a thinner Ag film becomes continuous film by the presence of the MPTMS interlayer.

The sheet resistance of 6 and 8-nm-thick Ag films are summarized in Table 1 where the average values are shown with the highest and the lowest values in parenthesis. At 6 nm, a sheet resistance of Ag films without the MPTMS interlayer was too high to be measured, but that with the interlayer was relatively low. This difference coincides with microstructure of the films shown in Figure 3; Ag grains were isolated on glass substrate but connected on the interlayer.

As a result, we confirm the usefulness of MPTMS interlayer on glass substrate to obtain flat Ag film with a smaller critical thickness. We consider the following mechanism for this smaller critical thickness. By interaction with mercapto group of MPTMS layer, migration of arrived Ag atoms is suppressed. This causes formation of more nuclei on the substrate, and a continuous film can be obtained with fewer atoms.

**Table 1.** Sheet resistance of the samples

Sample	Sheet resistance ( $\Omega/\text{sq}$ )
Ag(6nm)/MPTMS/glass	67 (63 – 73)
Ag(6nm)/ glass	-
Ag(8nm)/MPTMS/glass	13 (13 – 14)
Ag(8nm)/ glass	54 (50 – 60)



**Figure 6.** Transmittance spectra of the samples.

Next, transmittance of the films was measured. The transmission spectra of glass substrate and glass substrate with the MPTMS interlayer were the same in a region from 300 to 900 nm. Then, Ag films

with a thickness of 8 nm with and without the interlayer were compared. As a result, there was no remarkable difference on their spectra and transmittance was higher than 70% at 400nm, and about 60% at 500nm, including absorption by the glass substrate. The transmittance of a 6-nm-thick Ag film does not show any increase compared to that of an 8-nm-thick film. Because the sheet resistance of the Ag film (8 nm) with the interlayer is much lower than that of the others as shown in Table 1, it is concluded that introduction of the MPTMS interlayer is very useful to prepare the Ag thin film with properties of a low sheet resistance and a high transmittance. And the best sample structure in the present study was found to be Ag (8 nm) film with MPTMS interlayer. According to a reference where Ag film was deposited on ITO film [8], sheet resistance and transmittance were reported to be 27  $\Omega$ /sq. and about 60% ( $\lambda=400$  nm), respectively. Therefore, the sheet resistance of Ag film (8 nm) with the interlayer in the present study was found to be half with similar transmittance value. We now proceed to apply this film as electrode of an organic light emitting diode.

#### 4. Conclusions

We have found flatter growth of Ag thin films on glass substrates with MPTMS interlayer due to the suppressed surface migration of Ag atoms by an interaction with mercapto moiety of MPTMS. As a result, Ag film with MPTMS interlayer showed a lower sheet resistance compared to a Ag film without the interlayer when the Ag thickness was the same. In addition, optical transmittance does not change by the presence of the MPTMS layer. Therefore, with this interlayer, we can prepare Ag thin film with a lower sheet resistance for the same optical transmittance. This is believed to be preferable for the use as semi-transparent electrode in display devices.

#### Acknowledgments

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