

Optical and electrical properties of sputtered Ag films on PET webs

C. Charton*, M. Fahland

Fraunhofer Institut für Elektronenstrahl und Plasmatechnik, Winterbergstrasse 28, D-01277 Dresden, Germany

Abstract

Optical and electrical properties of Ag films deposited onto PET webs by sputtering are studied in dependence on the process parameters during deposition. The Ag layers were deposited onto a commercially available PET substrate (Melinex[®] 400) by DC magnetron sputtering. The optical properties of the samples were analyzed by ellipsometry and VIS/NIR spectroscopy. The electrical properties of the thin Ag films were characterized by four-point-probe measurements. The optical constants for bulk Ag were found to describe the thin films accurately only above a critical thickness d_c . This critical thickness depends on the process parameters during deposition and is found to vary between 12 and 18 nm. The results indicate, that the critical thickness marks a transition in the growth mode of Ag thin films from well separated islands to a continuous film. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ag; Film growth; Sputtering; Solar control; Web coating

1. Introduction

Sputtered Ag films are applied for several types of optical layer stacks. Ag is widely used especially in transparent and heat reflecting layer stacks of the solar-control or low-e type. These layer stacks are applied in glazing units for buildings, automobiles as well as for solar energy engineering purposes for passive heat gain [1–4]. The typical design of a transparent and heat reflecting layer stack includes a metal layer to reflect the infrared radiation. The metal layer must be thin enough to have a sufficient transmittance in the visible wavelength range. This metal layer is embedded between two dielectric layers, which act as antireflection coatings in the visible wavelength range to increase the transmission.

During the last decade these transparent and heat reflecting layer stacks are becoming more and more

important, since they can contribute to a reduction of the global CO₂ emission. In Germany, for example, a new law concerning energy conservation was introduced in 1995 [5] which prescribes the use of coated glass panes for new buildings in order to reduce the radiative heat loss through windows.

Since absorption is combined with the emission of heat, the absorption of these layer systems must be very small. Therefore the material for the metal layer in these systems is normally Ag, because Ag is characterized in contrast to other noble metals by a very low absorption in the visible wavelength range.

If a three-dimensional surface must be equipped with a transparent heat reflecting layer stack several problems occur if the substrate is coated directly. This concerns the handling of the substrates and the layer homogeneity. The problems can be resolved if a coated PET web is laminated to the curved surface. This is of special interest for automotive applications. It is also possible to retrofit existing glazing with transparent heat reflecting layer stacks on coated PET webs. Complete insulating glazing units with coated glass panes

* Corresponding author. Fax: +49-351-2586-55-133.
E-mail address: charton.c@fep.fhg.de (C. Charton).

can additionally be equipped with a coated web, further improving the insulation function. In this case, the coated web is mounted between the two glass panes of the insulating glazing unit [6].

In this study, only results for single Ag films on a PET substrate are presented. Results for complete layer stacks of the solar-control or low-e type will not be presented. This has two main reasons, the first is that from reflection and transmission measurements of a three layer stack the properties of the embedded Ag film cannot be determined unambiguously. The second reason is that the neighboring layers to the Ag film alter the electrical and optical properties of the Ag. This is a well-known phenomenon and was confirmed by additional investigations. For single Ag layers on a PET surface outgassing of the PET during deposition might influence the film growth. To prevent outgassing several Ag films were deposited on PET coated with TiO₂. In this case, the TiO₂ acts as a barrier layer. The result was that no influence of outgassing on the film properties could be detected, but that surface roughness of the underlayer has a pronounced influence on the properties of the Ag film.

The topic of this study was the determination of the electrical and optical properties of Ag films on PET webs and the correlation between optical layer properties and process parameters during deposition.

2. Experimental procedure

DC magnetron sputtering of the Ag films was performed in a web coater with a deposition width of 200 mm. Fig. 1 shows a sketch of the web coater LBA 200. It consists of a winding chamber and three deposition chambers, which are separately pumped by turbomolecular pumps. The base pressure of the vacuum chamber after 1 h of pumping is 1×10^{-3} Pa. Optical sensors for transmission and reflection measurements are installed in the winding chamber and allow an in-situ control of the deposited layers. The optical in-situ measurements are carried out with a Chromex 250 IS spectrometer from Princeton Instruments. The dispersive element is a grating and a CCD camera serves as the detector.

With the unwinder and the rewinder in the winding chamber an adjustable tension is applied to the web to ensure a good heat transport to the cooling drum. This prevents the web from melting during the deposition process. The web speed can be varied between 0.05 and 30 m/min. As a substrate for the Ag films a commercially available PET from DuPont (Melinex[®] 400) with a thickness of 75 μm was used. The sputter source is a magnetron from Sierra Applied Sciences and has a target surface of 12.7×35.6 cm. The distance between target and substrate is 5.5 cm. The Ag target has a

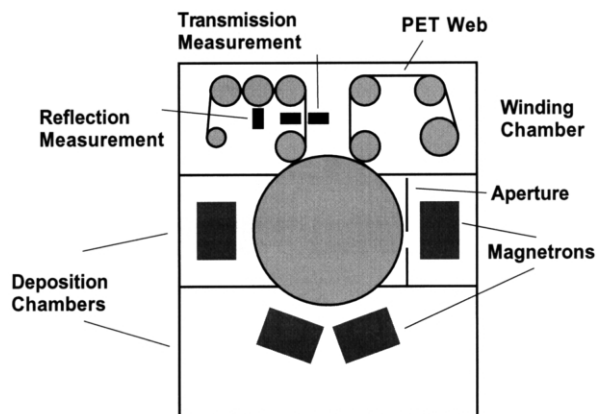


Fig. 1. Sketch of the laboratory roll coater LBA 200.

purity of 99.95% and the Ar gas has a purity of 99.996%. For the deposition of the Ag films an aperture is inserted between the magnetron and the substrate (see Fig. 1), reducing the effective coating length to 22 mm. This was necessary because Ag has a very high deposition rate and without an aperture the web speed would be too slow to enable the deposition of the thinnest Ag layers. The thickness of the Ag films can be controlled via the web speed and the electrical power from the magnetron fed into the plasma. The power supply is a DCG 200 from ENI which is connected to the target surface serving as cathode and to the chamber wall serving as anode.

Ellipsometric investigations were carried out with the Vase[®] ellipsometer from Woollam in the wavelength range from 290 to 1050 nm. Additional transmission and reflection measurements were performed with the double-beam spectrometer Lambda 900 from Perkin-Elmer between 380 and 1800 nm. For the electrical sheet resistance measurements of the Ag films a Veeco FFP 500 four-point-probe was used. With the four-point-probe the conductivity can be determined with an accuracy of $\pm 2\%$.

Since both surfaces of the PET web have a different topography, all Ag films were deposited on the inside of the PET web. The outside of the Melinex[®] 400 PET web has been treated with a corona discharge by the PET supplier and, thus shows a greater surface roughness. As a consequence the sheet resistance of an Ag film deposited on the outside of the PET web is higher compared to an Ag film deposited on the inside.

For the ex-situ analysis of the Ag films an eventual alteration of the film properties through a reaction of the film surface with the atmosphere has to be avoided. Sulfur and oxygen from the atmosphere can react with the surface of the Ag film, leading to a change in the optical properties of the film surface [7,8], which should be visible in transmission and reflection spectra.

An Ag film with a thickness of 20 nm was deposited on PET to analyze if oxidation has a major influence

on the ex-situ measurements. Transmission and reflection data were determined in-situ. Afterwards the vacuum vessel was vented while continuing the optical measurements with the in-situ spectrometer for 2.5 h. During this period of time no change in the transmission and reflection data could be detected. As a consequence all optical and electrical ex-situ measurements were carried out within this period of time after exposure to air of the Ag films to prevent a possible falsification of the measurements.

3. Results

The films were analyzed by ellipsometric measurements in the wavelength range from 290 to 1050 nm at three different angles of incidence to determine the optical constants and the thickness of Ag. The Ag films deposited on PET can be described by the optical constants from Palik et al. [9] if the thickness exceeds a certain threshold value. In the following, this threshold value was denoted as the critical thickness d_c . Such a critical thickness has also been detected by Yamamoto et al. [10]. It has been interpreted as a transition from an optically anisotropic to an optically isotropic state, which is linked to a transition in the growth mode of the thin film from well-separated islands to a continuous film.

Transmission and reflection data of the thin Ag films were measured in order to investigate the critical thickness in detail.

Fig. 2a,b shows the transmission and reflection spectra in the wavelength range between 380 and 1800 nm of two Ag films with a thickness well above ($d = 16$ nm) and below ($d = 6$ nm) the critical thickness. The layers were deposited at a sputtering power of 500 W and at an Ar pressure of 0.71 Pa. In addition to the measured spectra, calculated spectra corresponding to the optical constants from [9] are shown. For the film with the thickness of 16 nm, the measured and calculated spectra are in good accordance. For the thickness of 6 nm, considerable deviations between the measured and calculated spectra are detected. For wavelengths above 600 nm the difference between measured and calculated reflectance increases. In the infrared spectral region the measured reflectance is approximately 20% lower as expected after the calculation. The transmission below 1060 nm is lower and above 1060 nm higher than the calculated values. This indicates that the model assumptions of a homogeneous, plane parallel and isotropic Ag film, which were made for the calculation, fail below the critical thickness d_c . To explain the optical properties of aggregated metal films below the critical thickness additional investigations were re-

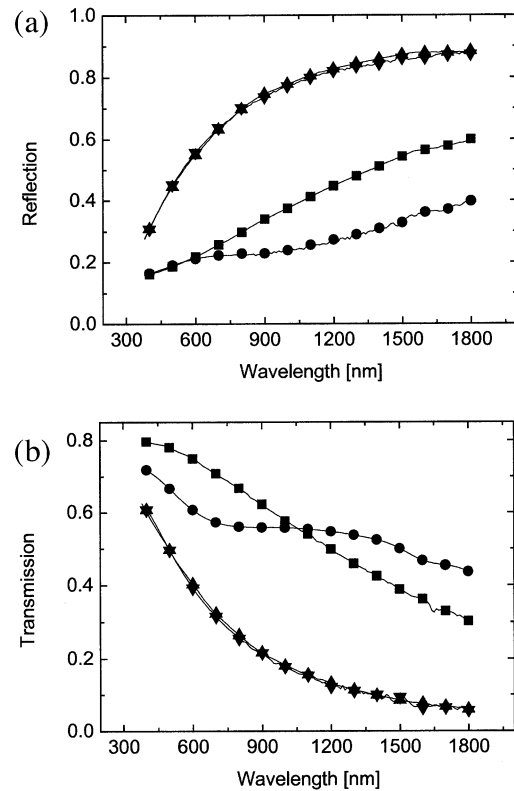


Fig. 2. Comparison between calculated and measured reflection (a) and transmission (b) data for the Ag/PET system. The thicknesses of the Ag-layers were chosen above (16 nm) and below (6 nm) the critical thickness d_c . (a) ■: Calculated reflection ($d = 6$ nm); ●: measured reflection ($d = 6$ nm); ▲: calculated reflection ($d = 16$ nm); ▼: measured reflection ($d = 16$ nm). (b) ■: Calculated transmission ($d = 6$ nm); ●: measured transmission ($d = 6$ nm); ▲: calculated transmission ($d = 16$ nm); and ▼: measured transmission ($d = 16$ nm).

quired, which can be found in the work of Abelés et al. [11].

To determine the critical thickness, transmission and reflection spectra of the Ag films were measured and the mean square deviation between the measured and the corresponding calculated spectra was determined. The result is shown in Fig. 3. The mean square deviation above a thickness of 7 nm can be approximated by a Boltzmann-function of the following type:

$$y = \frac{(A_1 - A_2)}{1 + e^{(x-x_0)/d_x}} + A_2. \quad (1)$$

Since the mean square deviation decreases continuously, the critical thickness d_c was defined as the thickness where the mean square deviation between the measured and calculated spectrum reaches a value of 20% above the minimum (parameter A_2 from Eq. (1)) which is reached asymptotically for thick Ag films.

To analyze the critical thickness and its dependence

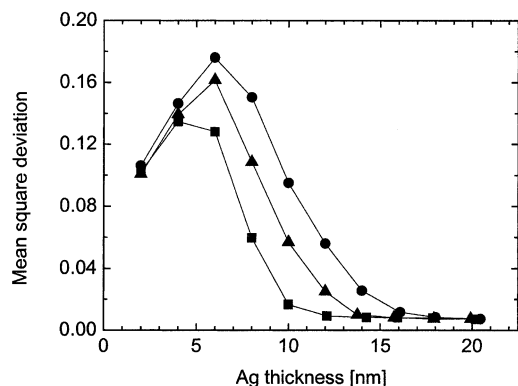


Fig. 3. Mean square deviation between the measured and calculated spectra for the Ag/PET system in dependence on the Ag-layer thickness and the deposition parameters. The mean square deviation was evaluated in the wavelength range between 380 and 1800 nm. ■: $P = 500$ W, $p = 0.71$ Pa; ●: $P = 500$ W, $p = 2.5$ Pa; and ▲: $P = 200$ W, $p = 2.5$ Pa.

on the deposition parameters, Ag films with a thickness between 2 and 20 nm were deposited on PET and characterized by VIS/NIR spectroscopy. Reflectance and transmittance spectra allow a thickness determination with a precision of $\pm 3\%$. Three different sets of process parameters were used, which are listed in Table 1.

The global tendency for the three parameter sets is similar, for small Ag film thicknesses the mean square deviation is large, it goes through a local maximum at a thickness between 5 and 6 nm, it decreases rapidly with further increasing film thickness and asymptotically reaches a minimum of 0.008. This minimum value is the same for all three sets of parameters.

An analysis of the absorption of the Ag films (see Fig. 4) shows a tendency correlated to the critical thickness d_c . Ag films with a thickness below d_c show a much larger absorption than the calculated value with the dispersion data from [9]. The absorption (A) of the Ag films can be calculated from the transmission (T) and reflection (R) data ($A = 1 - T - R$) with an accuracy of ± 0.005 .

These results could be explained with different growth modes for the Ag films. It is well known that three different growth modes exist for thin evaporated

Ag films [12]. At first, Ag islands are formed on the substrate, the second phase is the linking between individual islands with well separated 'island clusters' and the third phase is the transition to a closed film.

It has been shown, that the optical properties of aggregated metal films differ considerably from closed films, they show for instance a much higher activity in surface-enhanced Raman spectroscopy (SERS) [13] and much higher absorption than the closed films [14]. Therefore it can be assumed that the critical thickness d_c marks the transition between an aggregated and a closed film.

The experiments reveal two general tendencies for the critical thickness and its dependence on the process parameters. If the parameter sets (I) and (II) from Table 1 are compared, the critical thickness shifts from 11.6 to 18.2 nm with an increase in the sputtering pressure from 0.71 to 2.5 Pa as the sputtering power is kept constant. A comparison between the parameter sets (I) and (III) shows an increase in the critical thickness from 14.1 to 18.2 nm for a reduction of the sputtering power from 2000 to 500 W at a constant sputtering pressure.

It can be deduced that the energy of the Ag atoms impinging on the substrate surface has a major influence on the film formation and thus on the critical thickness. The energy of the Ag atoms is determined by their initial energy at the target surface and by the energy loss through collisions on the way to the substrate surface.

The conductivity of the Ag films reflects the different growth modes (see Fig. 5). The onset of electrical conductivity is correlated to the absorption maximum of the Ag films. Below the critical thickness the increase of the conductivity with increasing film thickness is relatively steep, which can be explained with the merging of individual islands. Above the critical thickness the increase in the conductivity is reduced. For a thickness of 20 nm the conductivity is approximately one-third of the conductivity of the bulk material. The weak increase in the conductivity above d_c can be correlated to the growth of the Ag grains in the film, reducing the grain boundary scattering of electrons and thus improving the conductivity of the films.

Table 1
Dependence of the critical thickness on the process parameters

	Pressure [Pa]	Sputtering power [W]	Discharge voltage [V]	Discharge current [A]	Dynamic deposition rate [nm [*] m/min]	Critical thickness d_c [nm]
I	2.5	500	384	1.30	5.6	18.2
II	0.7	500	465	1.07	6.8	11.6
III	2.5	2000	473	4.22	24.3	14.1

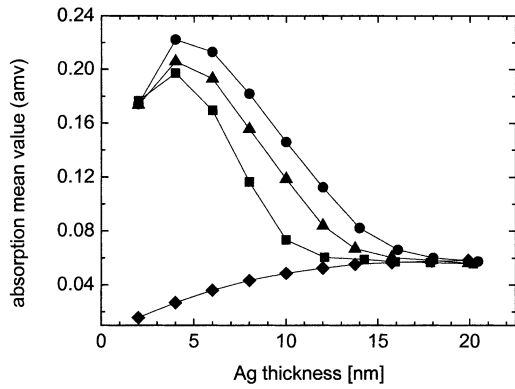


Fig. 4. Thickness and process parameter dependence of the absorption mean value (amv) in the Ag/PET system in comparison to the calculated values. The absorption was evaluated in the visible wavelength range (380–780 nm). ■: amv ($P = 500$ W, $p = 0.71$ Pa); ●: amv ($P = 500$ W, $p = 2.5$ Pa); ▲: amv ($P = 2000$ W, $p = 2.5$ Pa); and ▼: amv (calculation).

The growth of the grains was detected with X-ray diffraction. The full width at half maximum of the Ag (111) peak was compared with an Ag reference sample.

Fig. 6 shows the grain size and conductivity as a function of the Ag thickness. Up to a thickness of 20 nm the grain size is smaller for the lower sputtering pressure. This relation is inverted for larger film thicknesses and for an Ag film thickness of 100 nm the grain size for the high sputtering pressure is two times larger than the grain size of the films deposited at low pressure. The conductivity is linked to the dependence of the grain size on the Ag film thickness. The defect density in the Ag films is higher the lower the sputtering pressure and as a consequence the higher the energy of the impinging Ag atoms.

This means that the Ag films are closed earlier at a higher energy of the impinging Ag atoms, but simultaneously the conductivity for thicknesses above 20 nm is reduced in comparison to Ag films deposited at higher

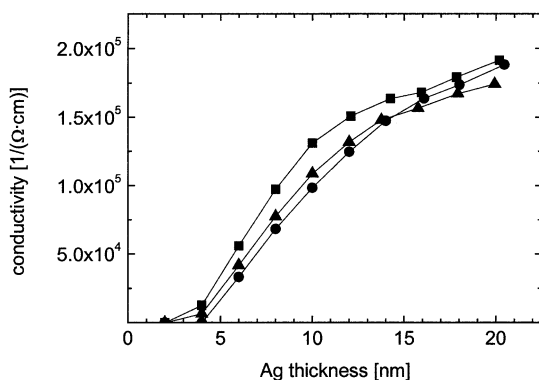


Fig. 5. Conductivity of Ag deposited on PET in dependence on the Ag thickness and the process parameters during deposition. ■: $P = 500$ W, $p = 0.71$ Pa; ●: $P = 500$ W, $p = 2.5$ Pa; and ▲: $P = 2000$ W, $p = 2.5$ Pa.

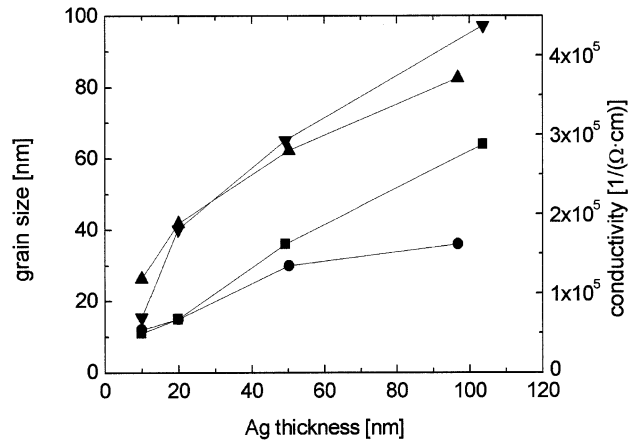


Fig. 6. Correlation between the grain size and the conductivity of Ag deposited on PET in dependence of the Ag thickness and the process parameters. ■: grain size ($P = 500$ W, $p = 0.73$ Pa); ●: grain size ($P = 500$ W, $p = 0.17$ Pa); ▲: conductivity ($P = 500$ W, $p = 0.17$ Pa); and ▼: conductivity ($P = 500$ W, $p = 0.73$ Pa).

sputtering pressures. As a consequence the optimization of the process parameters, for Ag films with minimum absorption and good conductivity depends on the required Ag film thickness.

4. Discussion

After a simplified sputtering model from Mahan et al. [15] the average energy of the Ag atoms at the target surface can be calculated from Eq. (2):

$$E_{\text{ave}} = U_{\text{sb}} \cdot \ln\left(\frac{\gamma E}{U_{\text{sb}}}\right) \quad \text{with} \quad \gamma = \frac{4 \cdot m_{\text{Ag}} \cdot m_{\text{Ar}}}{(m_{\text{Ag}} + m_{\text{Ar}})^2} \quad (2)$$

E_{ave} is the average energy at the target surface, U_{sb} is the surface binding energy of the Ag atoms, E is the energy of the Ar ions bombarding the target surface and γ is the energy transfer mass factor.

Because of the logarithmic dependence of the energy E of the bombarding Ar ions the average energy of the emitted Ag atoms at the target surface varies only slightly.

The upper limit for the energy of the bombarding Ar ions is given by the discharge voltage. With the discharge voltage from Table 1, the energy of the sputtered Ag atoms at the target surface is between 14.1 and 14.8 eV, this is a variation of $\pm 2.4\%$. This small variation in the energy E_{ave} with the discharge voltage cannot explain the shifts in the critical thickness.

The major influence on the energy of the Ag atoms impinging on the substrate surface is determined by the number of collisions of the Ag atoms with the sputtering gas. The number of collisions is proportional to the

Table 2

Pressure [Pa]	Number of collisions [cm ⁻¹]
0.71	1.01
2.5	3.57

gas density, which is a function of pressure and temperature at constant volume.

$$\frac{N}{V} = n = \frac{p}{kT}. \quad (3)$$

For a constant pressure the number of collisions between Ag and Ar at a temperature of 300 K is shown in Table 2.

The target substrate distance is 5.5 cm and thus the gas density has an order of magnitude where the energy loss of the Ag atoms is determined by the number of collisions.

For large changes in the discharge current, the temperature of the sputtering gas and thus the gas density becomes dependent on the sputtering rate, as Rossnagel et al. found out [16]. The reason is that the gas is heated as the sputtered atoms are thermalized. This effect is very prominent for the sputtering of Ag, since Ag has a very high sputter yield.

For a simplified estimation of the reduction in the gas density, it will be assumed that the critical thickness depends only on the energy of the impinging Ag atoms and thus on the gas density. For a linear dependence of the critical thickness on the gas density and a temperature of 300 K for a sputtering power of 500 W, the temperature for the sputtering power of 2000 W can be estimated to be approximately 570 K. This is consistent with the results from [16], where a comparable change in the power density resulted in a doubled gas temperature.

The change of the critical thickness with the process parameters sputtering pressure and power can thus be explained by the energy of the Ag atoms impinging on the substrate and the dependence of this energy on the gas density.

Besides the dependency of the critical thickness on the gas density, discussed above, the Ar plasma should influence the film formation. This requires the energy analysis of Ar ions and Ar atoms bombarding the Ag film during the growth process. The results concerning the influence of the plasma on the Ag film formation will be published in the future.

5. Conclusion

Ag films were deposited by DC magnetron sputtering onto a PET web and the optical and electrical layer properties were studied. Ellipsometric measurements showed that the Ag films can be described by the optical constants from Palik et al. [9], if the critical thickness is exceeded. The critical thickness depends on the gas density of the sputtering gas, which is a function of pressure and sputtering power. The critical thickness decreases with increasing sputtering power and decreasing Ar pressure. Whereas, the critical thickness itself depends on the process parameters, the optical properties of the films above d_c are independent of the process parameters. It is assumed that the critical thickness marks the transition from island growth to a closed film. This is in accordance with the results of the electrical measurements. Below the critical thickness the conductivity increases rapidly with increasing Ag film thickness and above the critical thickness a slower increase in the conductivity is detected, which is due to a growth of the Ag grains in the film.

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