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Surface-properties relationship in sputtered Ag thin films: Influence of the thickness and the annealing temperature in nitrogen

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ABSTRACT

Metal layers with high roughness and electrical conductivity are required as back-reflector electrodes in several optoelectronic devices. The metal layer thickness and the process temperature should be adjusted to reduce the material and energetic costs for the electrode preparation. Here, Ag thin films with thickness ranging from 30 to 200 nm have been deposited by sputtering at room temperature on glass substrates. The structure, morphology, optical and electrical properties of the films have been analyzed in the as-grown conditions and after thermal treatment in flowing nitrogen at various temperatures in the 150–550 °C range. The surface texture has been characterized by the root-mean-square roughness and the correlation length coefficients, which are directly related to the electrical resistivity and the light-scattering parameter (reflectance haze) for the various samples. The increment in the reflectance haze has been used to detect surface agglomeration processes that are found dependent on both the film thickness and the annealing temperature. A good compromise between light-scattering and electrical conductivity has been achieved with 70 nm-thick Ag films after 350 °C heating.

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1. Introduction

Silver thin films can achieve unique optical and electrical properties, such as maximum reflectance in the visible region and minimum resistivity, in comparison with other metallic coatings [1,2]. These properties make Ag layers ideal reflecting and conductive electrodes for several optoelectronic devices [3,4], particularly for thin-film solar cells [5–7]. Other characteristic of the Ag layers is that they suffer agglomeration processes at high temperatures, which restructure and reshape the surface in order to reduce the overall energy of the system [8]. The agglomeration is initiated by grain-boundary grooving, and it proceeds towards rougher surfaces when the grooves become deeper, which gives increased light scattering and decreased conductivity with respect to the initial smooth layer. Then, Ag agglomeration is avoided in applications where maximum specular reflection and maximum conductivity are required [4], but it is desirable to increase diffuse reflection at the back-contact electrode of thin-film photovoltaic devices [7]. In thin-film solar cells, the use of a rough or textured back reflector enables to increase the photocurrent and efficiency by increasing the optical path length of the incident light at different directions within the photoactive materials [9,10].

The temperature onset and depth extent of the agglomeration processes have been found to be dependent on several factors, mainly the Ag layer thickness, the substrate and the heating atmosphere [11–16]. The film density and its adherence to the substrate are essential issues, as a faster degradation of the Ag layer is related to a higher proportion of initial voids that can grow by the heating and/or the formation of micrometric holes by film dewetting [11]. Besides, different criteria can be used to determine the agglomeration onset. One of them is the abrupt change in resistivity when the surface scattering of the conduction electrons increases. For Ag thin films on SiO_2 in vacuum, such temperature onset was below 300 °C when the films were thinner than 70 nm, but it increased to above 600 °C for ∼90 nm thick layers [12,13]. Similar results have been obtained for Ag layers on Ti-coated Si substrates heated in nitrogen [14]. Otherwise, the visible reflectance drop and/or the increment in the surface roughness are more reliable parameters to determine the agglomeration in thicker films and oxidizing atmospheres, where the resistivity changes can be smaller and also attributed to oxidation processes. In this way, for 150–250 nm thick Ag films on GaN and glass substrates, agglomeration has been detected from the reflectance shift after heating in air at 250 °C [15,16].

When the objective is to achieve metallic electrodes with high roughness and electrical conductivity, as required for back-contacts in thin-film solar cells, Ag layer thicknesses above 200 nm and temperatures above 400 °C are typically used [7,17,18]. The minimization of these values is searched to reduce the material and

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energetic costs for the electrode preparation. Besides, an effective monitoring of the resultant surface morphology is desirable, as well as the accurate prediction of light distribution in the rough coating, especially to check the homogeneity of the electrode properties on large areas. For this purpose, atomic force microscopy (AFM) is considered a suitable tool due to the progress in fast and precise monitoring [19], together with the advanced data analysis to describe the surface characteristics from the AFM image [20]. The relationship between the morphological and optical properties should be clearly established to allow a good control of the light scattering through the surface roughness. Besides, the influence of the morphology on the electrical conductivity should be determined for complete electrode optimization.

In the present work, Ag thin films with various thicknesses from 30 to 200 nm have been prepared by sputtering on unheated glass substrates, and post-deposition annealing has been performed at several temperatures ranging from 150 to 550 °C in nitrogen. The structure, morphology, optical and electrical properties of the films have been analyzed as a function of the layer thickness and the heating temperature to determine the effect of agglomeration processes. AFM measurements have been used to calculate the main parameters of the surface morphology and to link them to the conductivity and light-scattering properties. The final objective is to determine the best way to achieve high diffuse reflectance without significant conductivity losses, minimizing the electrode layer thickness and the heating temperature.

2. Experimental details

Ag thin films have been deposited on unheated soda lime glasses (SLG) by DC magnetron sputtering of a metallic target (Ag, 99.99% purity). The preparation processes were performed under an argon gas pressure of 0.6 Pa by setting the power density at 100 mW/cm^2, which is low enough to maintain the substrate at room temperature, and adjusting the deposition time to obtain various layer thicknesses within the 30–200 nm range. Post-deposition annealing has been carried out in a tubular furnace at several temperatures from 150 to 550 °C during 30 min in flowing nitrogen. Argon gas has also been used for several annealing experiments, which gave the same results as under nitrogen atmosphere.

The sheet resistance of the layers has been determined with a four point probe system Veeco FPP5000, and the film thickness value by profilometry with a Dektak 3030 instrument. The optical characterization was accomplished in a Perkin Elmer Lambda 9 double-beam spectrophotometer, with an integrating sphere to measure both the diffuse and the total reflectance of the various samples in the wavelength range from 300 to 1500 nm. The crystallographic structure has been analyzed by X-ray diffraction (XRD) using the nickel filtered Kα1 emission line of copper (λ = 1.54056 Å) in a Philips X'pert instrument. Morphological characterization has been performed with a Park XE-100 atomic force microscope.

3. Results and discussion

Fig. 1 shows the XRD patterns obtained for the Ag layers with different thicknesses in the as-grown conditions. There are two diffraction peaks corresponding to the (1 1 1) and (2 0 0) lines of the Ag powder diffraction standard [21]. The mean crystallite size, S, determined from the full width at half maximum (FWHM) of the main (1 1 1) peak, increases from 30 to 75 nm with the growing film thickness from 30 to 200 nm. Besides, the $I_{(111)}/(I_{(111)}+I_{(200)})$ intensities ratio is in the 0.84–0.90 range for the various samples, above the 0.67 value reported for the Ag powder reference. These observations are according to the previous works which indicated that Ag thin films grow preferentially with the (1 1 1) crystallographic planes parallel to the substrate [22–24] because such planes have the lowest surface energy [8].

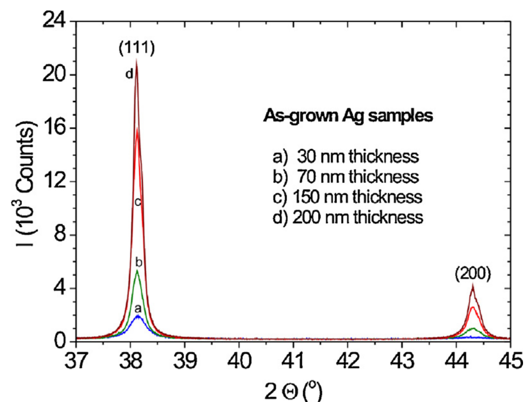

Fig. 1. XRD patterns for the Ag layers grown by sputtering at room temperature with different thicknesses.

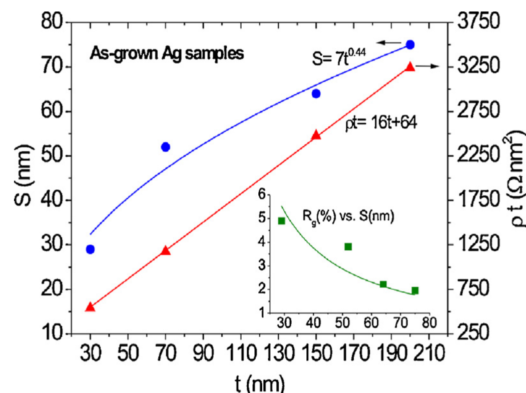

Fig. 2. Evolution of the mean crystallite size, S, and the electrical resistivity, ρ, as a function of the film thickness, t, for the as-grown Ag layers. The inset shows the reflection coefficient at grain boundaries, R_g, obtained for the different crystallite sizes.

The mean crystallite sizes (S) determined by XRD have been represented as a function of the layer thickness (t) in Fig. 2, where they show a good fit to the dynamical scaling law $S \propto t^B$ [25]. The growth exponent B = 0.44 is within the 0.2–0.7 range that has been reported for other metallic thin films [25–27]. Fig. 2 includes also the evolution of the electrical resistivity (ρ) with the layer thickness, for which a linear relationship $\rho t = at + b$ has been found. Such behaviour is related to the grain-boundary scattering that enables to increase the film resistivity with respect to the metal bulk value (ρ_b) in the form $\rho t = \rho_b t + C_g$, by means of the grain-boundary parameter $C_g = (3/2)(\rho_b \lambda_b) n R_g/(1 - R_g)$; being λ_b the mean free path for electrons in the metal bulk, R_g the reflection coefficient at the grain boundary, and n the thickness to grain size ratio that is taken as the unity in a first approximation [28,29]. For the present samples, the linear fit gives $\rho_b = 1.6 \times 10^{-6}$ Ω cm as the bulk silver resistivity and R_g = 5% for the reflection coefficient assuming n = 1. In a subsequent approximation, the experimental values of $n = t/S$ have been used to calculate the evolution of the reflection coefficient with the crystallite size, and this is depicted in the inset of Fig. 2, where R_g is found decreasing from 5 to 2% as S increases from 30 to 75 nm. It is interesting to note that the grain-boundary reflection decreases rapidly when the crystallite size increases up to the mean free path (for S > 50 nm) and then the film resistivity approaches to the bulk value [29].

The optical characteristics of the as-grown samples have been collected in Fig. 3, including both the diffuse reflectance (R_{dif}) and

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