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Ag and AgO thin film formation in Ag⁺–triethanolamine solutions

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Abstract

Thin film formation in aqueous Ag–triethanolamine (TEA) solutions has been studied. It was found that this bath can be used to deposit both Ag and AgO thin films on glass or polyester substrates. Uniform, specularly reflective films with thickness up to 1.2 μm were obtained from a single bath at 50°C. X-ray and some basic optical investigations were carried out for both films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silver films; Silver oxide films; Thin films; Chemical bath depositions

1. Introduction

In recent years, thin film technology has become more and more attractive for the scientists. Thin film materials with semiconducting, metallic, insulating or optical properties are already in use in industry, medical science and technology, space science and technology, etc. There are numerous methods and techniques to deposit materials in a thin film form, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), electro-chemical deposition (ECD), chemical bath deposition, and many more. Among all of them, there is little doubt that chemical bath deposition (sometimes called solution growth or

electroless deposition) is the simplest and most economical one.

We have exploited this technique in our laboratory for several years, and were able to develop suitable techniques and to fabricate a significant number of useful inorganic thin film materials, such as Ag₂S, Cu_xS, Cu₂Se, Cu₂O, Sb₂S₃, HgS, PbSe on glass, metal or polyester substrates [1–7].

Thin films of the noble metals, such as Au, Ag and Cu are important materials in the field of spectrally selective coatings and energy savings applications. It is also suggested that the high electrical conductivity of these films will be used in the near future to produce highly transparent electrically heatable windshields for automobiles [8]. Also, thin films of some metal oxides are known to have spectrally selective characteristics suitable for applications in photothermal and architectural applications [9].

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In this paper, we report a simple solution growth technique for fabrication of silver and silver peroxide thin films on glass or polyester substrates. The technique is based on a hydrolytic decomposition of silver triethanolamine (TEA) complexes formed in aqueous solutions. This technique is suitable for any size or shape of substrates. Uniform, specularly reflective mirror-like films of both Ag and AgO (or Ag_2O_2) were produced on glass and polyester substrates.

2. Experimental procedure

2.1. Chemical bath and growth of films

The proposed solution growth technique is very simple and does not require any special equipment or set-up. A bath container can be a 50 ml beaker or a large-volume container, depending on the size and

(or) number of substrates to be immersed into the bath. Also, the deposition of the films can be carried out at room temperature (although this would slow down the deposition rate) or at fairly mild temperatures of 40–55°C.

Here is the composition of a typical small bath. One gram of solid AgNO_3 was dissolved in approximately 5 ml of deionized water in a 100-ml beaker. Then TEA was added slowly, with constant stirring, just until the brownish solution became clear, i.e. until the initially formed precipitate (of $\text{AgOH} \gg \text{Ag}_2\text{O}$) was dissolved. At that point deionized water was added to make a total volume of 80 ml. The substrates, (glass or polyester strips) previously pretreated, as explained below, were vertically placed into the beaker and the bath was brought and kept at 45–50°C on a hot plate. In a few minutes, precipitation in the solution began, and both sides of the substrates were coated with white shiny deposit of Ag. After about 90 min, the reaction completely stopped. The coated substrates were then removed

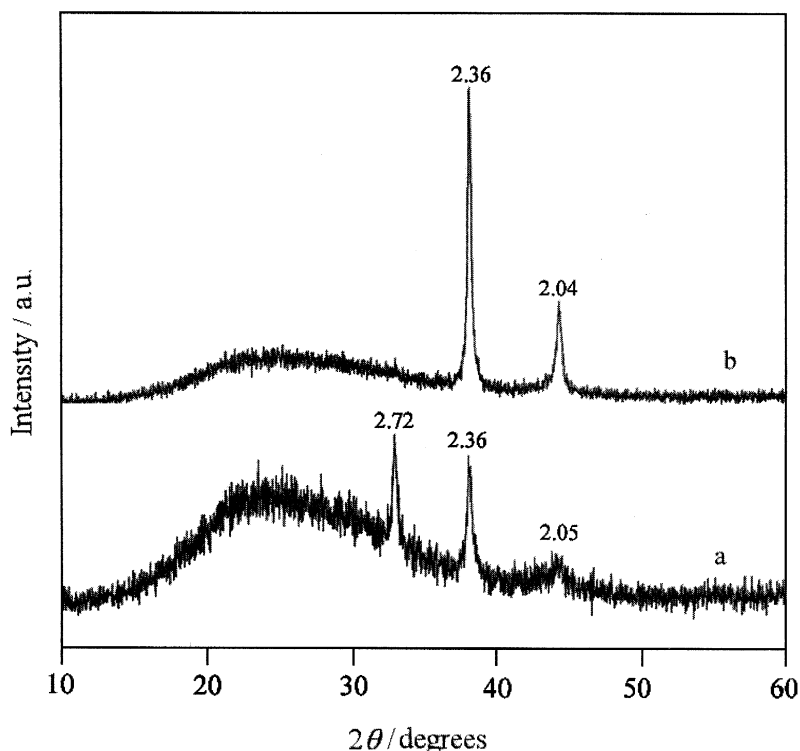


Fig. 1. X-ray diffractograms of as-deposited Ag and AgO films on glass substrates: (a) AgO film, 1.5 μm thick; (b) Ag film, 1.2 μm thick.

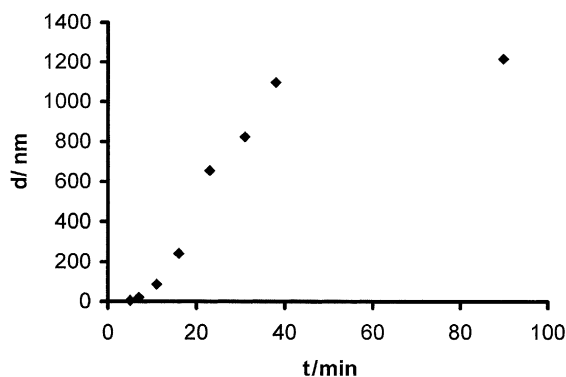


Fig. 2. Dependence of thickness of Ag films on deposition time from a single bath at 50°C.

from the bath, washed with deionized water and dried in air.

Following exactly the same procedure, with just a little less TEA added to the silver ions (some precipitate is left undissolved) results in deposition of AgO films, or possibly a mixture of AgO and some of the undissolved Ag₂O.

2.2. Pretreatment of substrates

Poor wetting of the substrates which results in poor adhesion or growth of non-uniform films is a common problem with this technique. In this work, standard microscope glass slides, 75 × 25 × 1.0 mm, and similar size strips of clear polyester films (commonly used as overhead transparencies) were used as substrates. Glass substrates were first soaked into sulfochromic acid overnight. Then they were washed in deionized water and soaked into 0.03% aqueous solution of tin(II) chloride for about 20 min. After that the glass substrates were washed with deionized water, dried in air, and annealed at 200–250°C for 30 min. Polyester substrates were first washed with detergent, rinsed with deionized water and then soaked into 0.03% aqueous solution of tin(II) chloride for 20 min. Then they were washed with deionized water and dried in air.

After this treatment, the deposited films onto the substrates had very good adhesion and uniformity.

2.3. Characterization of the films

The thickness of the films was estimated gravimetrically, assuming the same density as that of a

bulk AgO or Ag (7.44 g/cm³ for AgO and 10.5 g/cm³ for Ag). The deposited film was removed from the surface by rubbing with a cotton swab moistened in 10% nitric acid.

Identification of as-deposited films was done by X-ray diffractometry on a Jeol Model JDX Diffractometer using nickel filtered CuK_α radiation ($\alpha = 1.54050 \times 10^{-10}$ m). Optical transmission and absorption spectra were taken in the spectral range of 0.3–3.0 μm on a Cary 5 UV–VIS–NIR Spectrophotometer against plain glass or clear polyester film as a reference.

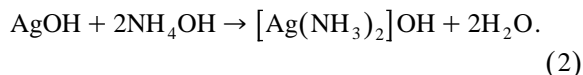
3. Results and discussion

3.1. Chemical considerations

It is known that silver ions can be complexed by NH₃ according to the following reaction



in excess of NH₄OH



According to this, we assumed that the complexing reactions of silver ions with TEA follow a similar pathway

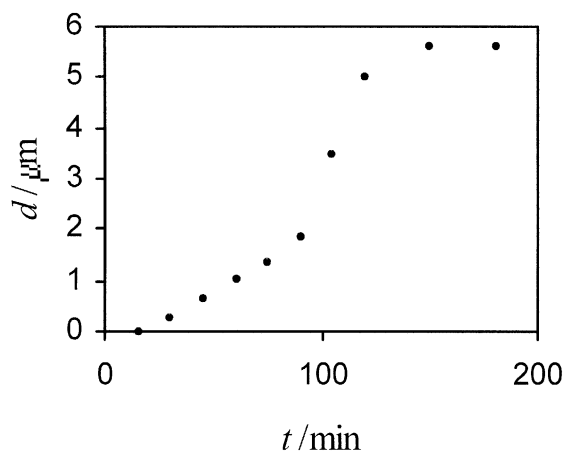
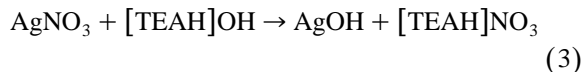


Fig. 3. Dependence of thickness of AgO films on deposition time from a single bath at 50°C.

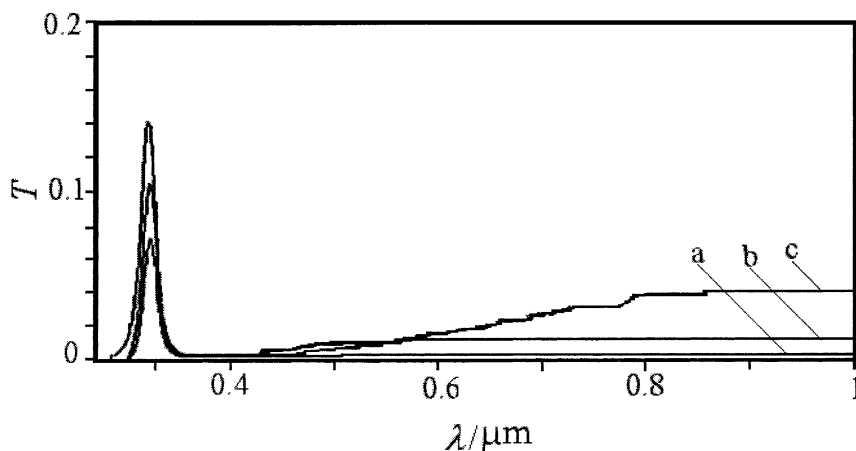
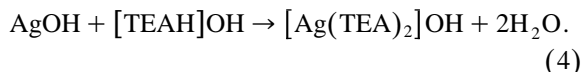


Fig. 4. UV–VIS–NIR spectra of as-deposited AgO films on glass substrates. (a) 0.3, (b) 0.8, (c) 1.2 μm thick.

in excess of TEA



We suggest that this silver complex then undergoes a thermal and hydrolytic decomposition, and depending on the experimental conditions, either Ag or AgO (or possibly a mixture of AgO and Ag_2O) is deposited onto the substrate. At this time, we cannot predict the exact mechanism of Ag–TEA complex decomposition. However, the following has been established beyond doubt: the final product depends on the amount of TEA in solution. If enough TEA is added to completely dissolve the previously formed precipitate of AgOH, i.e., Ag_2O , then an Ag film is deposited onto the substrates. Just a couple of drops less of TEA produces a film of AgO (or AgO + Ag_2O) onto the substrates.

3.2. X-ray, optical and other considerations

X-ray diffractograms from film samples are shown in Fig. 1. The observed diffraction peaks were compared against standard JCPDS-ICDD diffraction patterns from PDF-2 sets 1–43 database. The dA values are shown above the reflections. The reflections shown on Fig. 1a correspond with those of Ag. The reflections marked on Fig. 1b correspond with those belonging to AgO. However, the peak at $dA = 2.36$ could also belong to Ag_2O . Keeping in mind that AgO films were deposited from a bath in which

some Ag_2O was left undissolved, we allow the possibility that the deposited film could also contain some Ag_2O .

Fig. 2 shows the dependence of Ag film thickness on deposition time. Under the experimental conditions previously described, the terminal thickness of Ag films achieved from a single bath is about 1.2 μm . Fig. 3 shows the dependence of thickness of AgO films on deposition time.

The transmittance UV–VIS–NIR spectra of AgO films with different thickness are shown in Fig. 4. The maximum transmittance is in the UV region, at about 300 nm. Depending on thickness, the transmittance of AgO films in the visible and near infrared

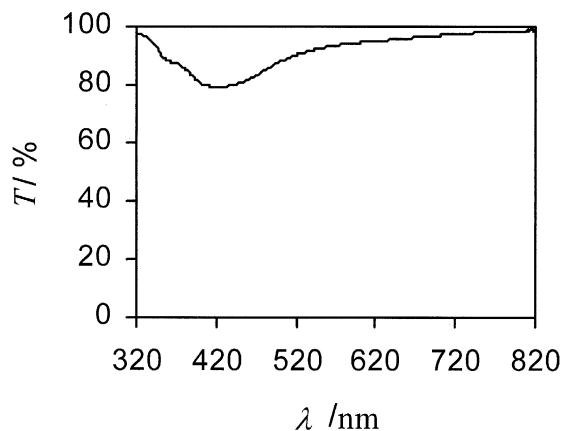


Fig. 5. UV–VIS–NIR spectrum of an 8 nm thick, as-deposited Ag film on glass substrate.

part of the electromagnetic spectrum is either very small (for thinner films) or close to zero (for thicker films). In a similar way, Fig. 5 shows the transmission spectrum of a very thin Ag film (about 8 nm). Thicker films of Ag were not transparent.

4. Conclusion

Ag and AgO thin films can be deposited from aqueous Ag–TEA solutions depending on the amount of TEA added. We presented a simple and economic technique that offers a possibility for large area depositions at a fairly low temperature (about 50°C). The obtained films are uniform and specularly reflective. The identification of the deposited materials was determined by X-ray diffractometry. In addition, some basic optical observations for these films are reported.

We believe that these films can be successfully used in photothermal, architectural and other areas where spectrally selective films are of interest. It is also noteworthy that we were able to deposit Ag and AgO on flexible, transparent polyester sheets. In this way, electrically conductive surface of the polyester films is obtained (in the case of Ag deposition) or spectrally selective AgO films on a flexible substrate.

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