Available online at www.sciencedirect.com

SCIENCE DIRECT

Surface & Coatings Technology 200 (2005) 276–279

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

# Stability of reactively sputtered silver oxide films

J.F. Pierson*, C. Rousselot

*Département CREST, Institut FEMTO-ST (UMR CNRS 6174), Université de Franche-Comté, Pôle Universitaire, BP 71427, 25211 Montbéliard cedex, France*

Available online 9 March 2005

**Abstract**

Silver oxide films were deposited on glass substrates by RF magnetron sputtering of a silver target in various Ar–$O_2$ reactive mixtures. At low oxygen flow rate, the films were biphased (Ag+$Ag_2O$) while single $Ag_2O$ films were synthesised at higher oxygen flow rate. Films coming from the same deposition run were annealed in air at 200 and 300 °C. Whatever, the deposition conditions and the annealing temperature, $Ag_2O$ grains were either partially or fully decomposed into metallic silver and oxygen. Furthermore, the intensity of the $Ag_2O$ diffraction peaks decreased when a bias voltage was applied to the substrate holder. These results showed that the $Ag_2O$ phase is not stable during a thermal treatment or when submitted to an ion bombardment.


*Keywords:* Reactive sputtering; Silver oxide; Thermal stability; Bias voltage

## 1. Introduction

The binary Ag–O system contains several defined compounds: $Ag_2O$, $Ag_3O_4$ [1], AgO, $Ag_4O_3$ [2] and $Ag_2O_3$. Among these different compounds, $Ag_2O$ is the most stable. It crystallises in a simple cubic structure ($a$=0.472 nm). This silver oxide is a p-type semi conductor with a band gap close to 1.2 eV. This material has been widely used in photography and as positive electrode in batteries. Now, recent interest in silver oxide is related to its potential use in optical memories. The synthesis of $Ag_2O$ thin films can be achieved using various deposition processes [3–6]. Among the different processes, the reactive sputtering one is probably the most powerful. Indeed, it allows the deposition of films with high quality, controlled composition and properties. Although numerous studies have been devoted to the sputtering of a silver target in reactive mixtures containing oxygen, few information are reported in the literature concerning the effect of the bias voltage on the structure of silver oxide films. On the other hand, it is well known that $Ag_2O$ decomposes easily in metallic silver and oxygen when heated at low temperature [7].

In this study, silver oxide films are deposited by reactive sputtering. Their stability is firstly examined after annealing in air at two temperatures for different deposition conditions and secondly when a bias voltage is applied to the substrate holder during the films deposition.

## 2. Experimental

Silver oxide coatings were deposited on glass substrates by RF (13.56 MHz) reactive sputtering of a 200 mm diameter metallic target, using an Alcatel SCM 650 sputtering system. Details on the deposition reactor, substrates cleaning and deposition procedure can be found elsewhere [8]. In this study, the following deposition conditions were kept constant: the argon flow rate (25 sccm), the substrate–target distance (60 mm), the RF power applied to the target (600 W). On the other hand, the oxygen flow rate ($Q(O_2)$) introduced in the deposition chamber was ranging between 0 and 15 sccm. Thus, the total pressure was varied from 0.9 to 1.1 Pa. During the films deposition, the substrates could be RF biased with a bias voltage ($V_b$) ranging between 0 and −70 V. Annealing in air of films coming from the same deposition run were performed in a conventional furnace at 200 and 300 °C during 4 h. The heating rate

* Corresponding author. Tel.: +33 3 81 99 46 72; fax: +33 3 81 99 46 73.
*E-mail address:* jean-francois.pierson@pu-pm.univ-fcomte.fr (J.F. Pierson).

0257-8972/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2005.02.005

from room temperature to annealing one was fixed at 250 °C $h^{-1}$.

The films thickness was measured by tactile profilometry. The structure of as-deposited and annealed films was investigated by X-ray diffraction (XRD) in $\theta/2\theta$ mode using Cu Kα radiation. The crystal size is estimated from the full width at half maximum (FWHM) of the X-ray diffraction line using the Debye–Scherrer formula, neglecting peak broadening due to residual stresses in the films.

## 3. Results and discussion

### 3.1. As-deposited films synthesised without bias

As for Cu–O films [8], the solubility of oxygen into silver is very low. Indeed, a weak diffraction peak of $Ag_2O$ (111) is detected as soon as oxygen is introduced into the deposition chamber (Fig. 1a). Note that the detection of $Ag_2O$ (200) is difficult because its position is very close to

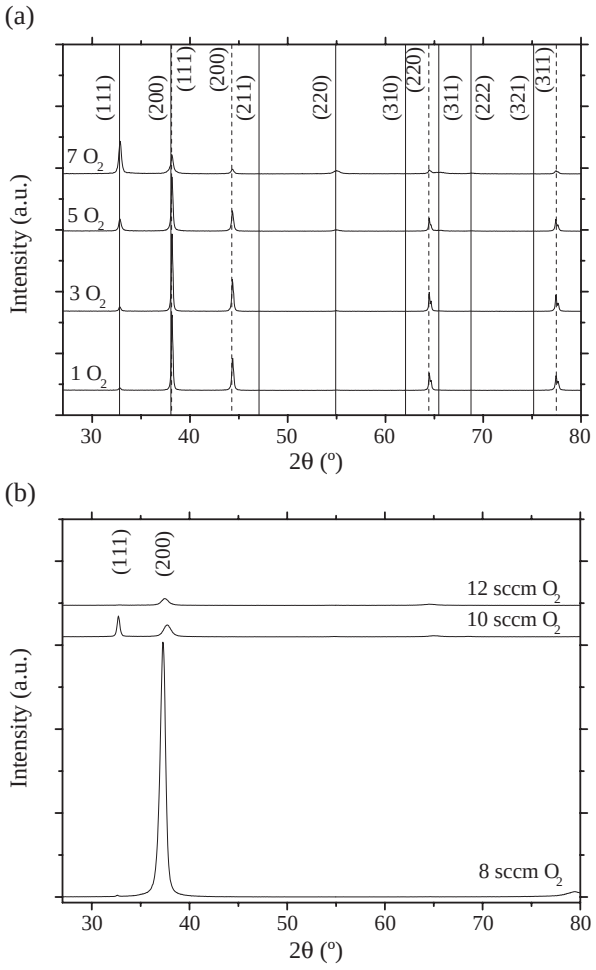


Fig. 1. Influence of the oxygen flow rate on X-ray diffractograms of films deposited without bias voltage. $0<Q(O_2)\leq 7$ sccm (a) and $8\leq Q(O_2)\leq 12$ sccm (b). Vertical solid and dash lines correspond to the position of diffraction peak of $Ag_2O$ and Ag, respectively.

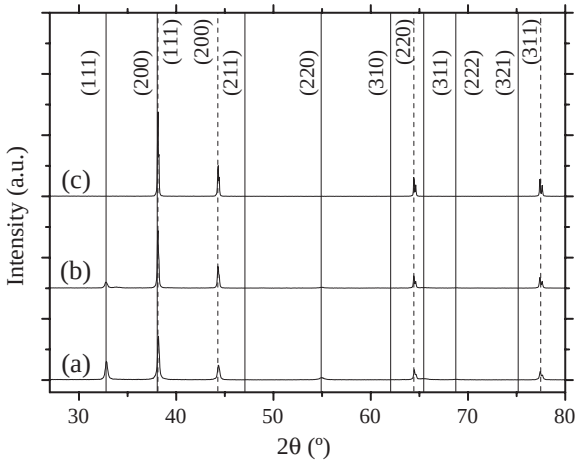


Fig. 2. Effect of annealing in air on the structure of films deposited using $Q(O_2)$=6 sccm. As-deposited film (a), 200 °C annealed film (b) and 300 °C annealed film (c). Vertical solid and dash lines correspond to the position of diffraction peak of $Ag_2O$ and Ag, respectively.

that of Ag (111). The increase of the oxygen flow rate induces a progressive increase of the $Ag_2O$ diffraction peaks intensity while those of silver decrease. When $Q(O_2)$=7 sccm, the Ag (200) diffraction peak is still unambiguously detected indicating, that in this range of oxygen flow rate, the films are biphased: Ag+$Ag_2O$. When $Q(O_2)$ increases up to 8 sccm, the silver diffraction peaks disappear and the films become transparent, indicating that they are composed of single silver oxide $Ag_2O$ (Fig. 1b). $Ag_2O$ films deposited with $Q(O_2)$=8 sccm show a strong preferred orientation in the [100] direction. The crystal size of $Ag_2O$ grains has been estimated to nearly 14 nm. The strong texture of $Ag_2O$ films disappears gradually for higher oxygen flow rates (Fig. 1b). Whatever the oxygen flow rate, the sole crystalline oxide detected by XRD is $Ag_2O$. Thus, in the deposition conditions tested in this study, the reactive sputtering method cannot be used to synthesise pure silver oxide such as: AgO, $Ag_3O_4$ or $Ag_2O_3$.

### 3.2. Stability of silver oxide films during air annealing

Since two kinds of coatings are deposited by varying $Q(O_2)$ (biphased Ag+$Ag_2O$ and single $Ag_2O$), the thermal treatments have been performed for both films. Fig. 2 displays X-ray diffractograms of films deposited with $Q(O_2)$=6 sccm (i.e., biphased films) before and after air annealing at 200 and 300 °C. For as-deposited films, the use of this oxygen flow rate leads to the deposition of biphased film according to the occurrence of diffraction peaks at nearly 32.8 and 44.3° which are related to $Ag_2O$ (111) and Ag (200) peaks, respectively. It appears clearly in Fig. 2 that the intensity of the $Ag_2O$ (111) peak decreases with the annealing temperature. Simultaneously, the intensity of the Ag (200) peak increases, indicating that $Ag_2O$ is not stable at temperature as low as 200 °C. When the annealing temperature is fixed at 300 °C, no $Ag_2O$ diffraction peak is