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Photoluminescence of reactively sputtered Ag_2O films

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ABSTRACT

Ag_2O thin films were deposited on glass substrates by radio frequency magnetron sputtering of a silver target in a reactive Ar–O_2 mixture. Spectrophotometry results suggest a direct band gap of 3.32 eV. Photoluminescence measurements reveal optical instability and thermal quenching of the luminescence intensity. Electrical characterization by 4-point probe and Hall effect measurements showed that the films are insulators.

1. Introduction

Metal oxides come in many forms and are generally easy and inexpensive to manufacture, stable at room temperature and in air, and mostly harmless to living organisms. Many metal oxides are semiconductors with optical and electrical properties suitable for a wide range of applications, such as light emitting diodes, monitors and television screens, touch screens, and solar cells. Most of the commonly used metal oxides are n-type semiconductors, such as tin-doped indium oxide and aluminum-doped zinc oxide, which are both used as transparent conducting oxides. The general lack of p-type metal oxides is thought to originate from the strong localization of the upper edge of the valence band to oxide ions [1]. Some of the few known p-type oxides are silver oxide (Ag_2O), cuprous oxide (Cu_2O) and nickel oxide (NiO). P-type oxides might be used to form oxide heterojunctions in applications such as transparent electronics or solar cells.

A number of silver oxide phases have been reported, such as AgO (usually in the form $Ag^{I}Ag^{III}O_2$ [2]), Ag_2O, Ag_3O_4, Ag_4O_3 and Ag_2O_3, of which Ag_2O is found to be the most thermodynamically stable one [3]. The fabrication methods include magnetron sputtering [3–7], pulsed laser deposition [8], chemical bath deposition [9,10], electrodeposition [11], electron cyclotron resonance oxygen plasma assisted e-beam evaporation [12], and post-deposition oxygen plasma processing of silver surfaces [13,14].

In the literature one finds a considerable variation in the reported band gap of Ag_2O, ranging from 1.2 eV [15] to 3.4 eV [6] depending on the deposition and characterization methods employed. This range covers several photovoltaic applications, from absorbers, which have an optimal band gap of 1.4 eV for single junction solar cells, to transparent conducting oxides with more than 3 eV band gaps. The abundant silver oxide phases — some of which also crystallize in several structures — and the lack of detailed crystal structure analysis in many of the published studies are most likely the main reasons for the wide range in reported band gap values.

In this study Ag_2O films were prepared by reactive radio frequency magnetron sputtering of a silver target. We found that the Ag_2O films are transparent, highly resistive, and have direct band gaps of around 3.3 eV.

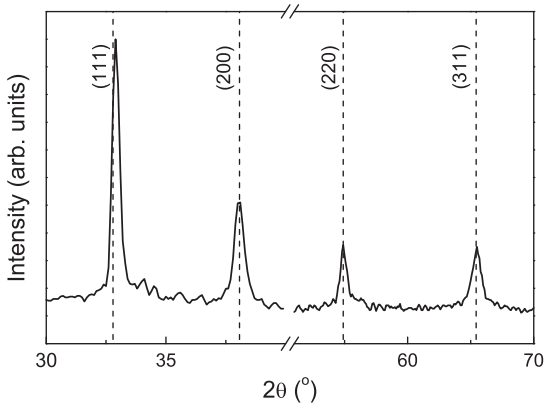

Fig. 1. Typical XRD pattern of the silver oxide films. The dashed vertical lines indicate expected peaks for the cubic Ag_2O phase.

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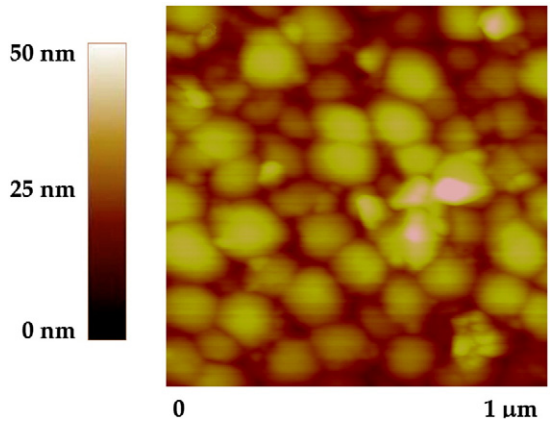

Fig. 2. AFM height image of a 1.3 µm-thick Ag_2O film sputtered at room temperature.

2. Experiment

Silver oxide films were deposited on glass substrates by RF magnetron sputtering of a silver target (3″, 99.99% purity) in a reactive Ar–O_2 mixture. The sputtering was done in a Semicore Tri-axis Pro 439 sputtering system, having a 50 L chamber and a distance of around 10 cm between the substrate and the target. The base pressure was ~10^{-4} Pa, while the deposition pressure was 0.99 Pa, as measured by a Baratron absolute gauge. The argon and oxygen flow rates were kept at 20 sccm and 13 sccm (standard cubic centimeters a minute), respectively. The sputtering power was 250 W with a deposition time of 3 min and a deposition temperature of 180 °C. The sputtering was followed by a short anneal in air of 3 min at 250 °C. The typical sample size and film thickness were 2.5 cm × 4 cm and 250 nm, respectively.

The film thickness was measured by tactile profilometry using a Veeco Dektak 8 Stylus Profiler, whereas the film structure was studied by grazing incidence X-ray diffraction (XRD) using a Bruker D8 DISCOVER instrument (Cu K_α). Atomic force microscopy (AFM) was performed by employing a Veeco D3100 microscope running in tapping mode, while the optical transmittance was determined by a Shimadzu Solidspec-3700 UV–vis–NIR spectrophotometer. The temperature dependent photoluminescence was investigated in the range 10–300 K by using a 325 nm wavelength cw He–Cd laser with an output power of 10 mW as excitation source. The electrical properties were examined with a Jandel RM3-AR 4-point probe and a LakeShore 7704A Hall Measurement System.

3. Results and discussion

3.1. Film structure

Fig. 1 shows a typical XRD pattern of the sputtered films. The dashed vertical lines indicate expected peaks for the cubic Ag_2O phase (ICDD PDF4 pattern 00-041-1104 [16]). The relative intensity and width of the XRD peaks reveal a randomly oriented polycrystalline nature.

The mean crystallite size of the films was determined to be 22 nm from the full-width at half maximum of the main diffraction peak using the Scherrer equation, neglecting the peak broadening due to internal strain in the films.

Fig. 2 shows an AFM height image of a 1.3 µm-thick Ag_2O film sputtered at room temperature. The grain sizes are in the range 100–200 nm, considerably larger than the crystallite size of 22 nm, indicating a polycrystalline nature of the grains.

The deposition rate is around 80 nm/min.

3.2. Optical and electrical properties

Fig. 3 shows transmittance spectra (a), absorption spectra (b) and band gap estimation assuming direct optical transitions (c) of the Ag_2O films. These films were deposited on fused silica with thicknesses of around 300 nm. The Taucplot in Fig. 3(c) shows the square of $\alpha h\nu$ versus $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. To a first approximation, any direct optical band gap should appear as a straight line, which — when extrapolated to the x-axis — gives an estimate of the band gap. Fig. 3(c) indicates a direct band gap of 3.32 eV, which is in good agreement with the direct band gap estimate of 3.29 eV for a mixed phase AgO–Ag_2O film found by Rivers et al. [12]. The films in Ref. [12] were prepared by e-beam evaporation of silver in the presence of an electron cyclotron resonance oxygen plasma. Other studies done on magnetron sputtered silver oxide films suggest optical band gaps of 2.23 eV (RF sputtering) [5] and 3.4 eV (DC sputtering) [6].

Photoluminescence measurements reveal optical instability of the films. More specifically, the spectral contents and intensity change under continuous exposure to UV photo excitation, most notably in the higher photon energy region of the spectra. Saturation of optically induced changes occurs within several tens of seconds for the less than 1 W/cm^2 intensity used in our experiments. Fig. 4 shows typical saturated photoluminescence spectra of the Ag_2O films, recorded at 10 K using 325 nm excitation light, with several characteristic peaks in the region from 2.5 to 3.4 eV.

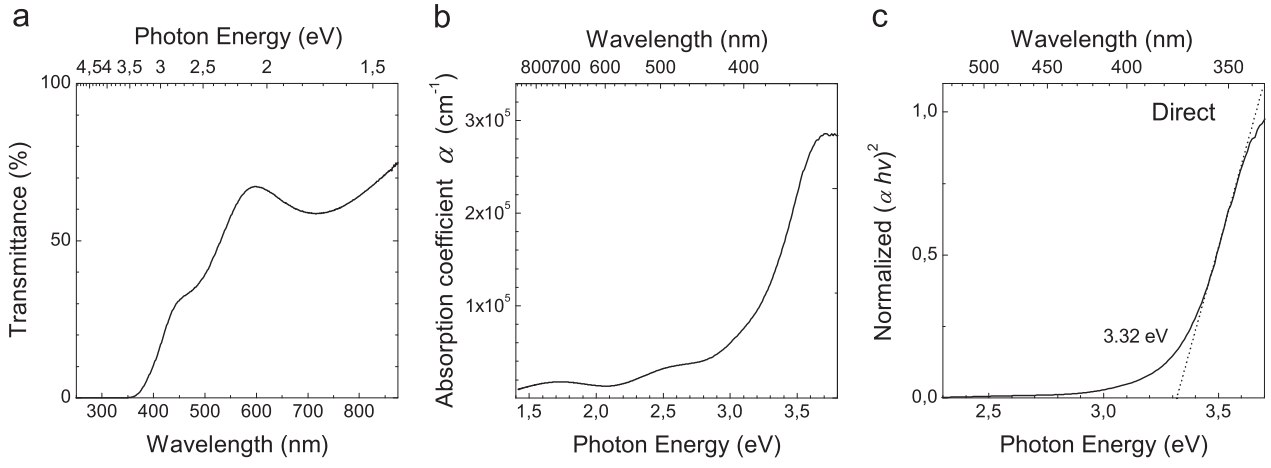

Fig. 3. Transmittance spectra (a), absorption spectra (b), and band gap estimation assuming direct optical transitions (c) of 300 nm-thick Ag_2O films.