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Characterization of copper oxide nanolayers deposited by direct current magnetron sputtering

A.R. Rastkar *, A.R. Niknam, B. Shokri

Shahid Beheshti University, G.C., Laser-Plasma Research Institute, Tehran, 1983963113, Iran

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ABSTRACT

Direct current reactive magnetron sputtering was used to deposit the thin layers of copper oxide (Cu_2O) on glass substrates. A solid disc of pure copper as the target was sputtered in an argon gas under sputtering pressures varying from 0.133 to 4 Pa. The effects of the sputtering power and pressure on the structural and optical properties of Cu_2O thin films were systematically studied. The deposited layers were characterized using X-ray diffraction, atomic force microscopy, profilometry and spectrophotometry. The optical transmission of the films was measured in the visible region. The increase in pressure resulted in a higher growth rate than increasing sputtering power. The increase in power produced Cu_2O thin films that were detrimental to the optical transmission of the films.

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconductor with a band gap of approximately 2.0 eV and a cubic crystal structure [1]. The high optical absorption coefficient and low cost of production of Cu_2O thin films have made them good candidates for electro chromic devices, solar cells [2,3] and oxygen sensors [4]. Depending on the method used for the growth of cuprous oxide, the growth of cuprous oxide may finally result in the production of a combination of copper (I) oxide Cu_2O and copper (II) oxide CuO [2]. Cu_2O thin films are also highly transparent. They are slightly yellowish and usually absorb wavelengths less than 600 nm, while CuO strongly absorbs the whole visible spectrum and is black in appearance.

Direct current (dc) and radio frequency (rf) sputtering [5–7], thermal evaporation [8,9] solution growth [10], and sol–gel [11] and electro depositions [12,13] have been used to deposit Cu_2O thin films. Direct current (dc) reactive magnetron sputtering is one of the promising methods for the preparation of Cu_2O thin films due to the easier control of deposition parameters and relatively high deposition rates and less heating of the substrate. The physical properties of the sputtered films depend on the sputtering parameters such as pressure and power. Furthermore, in sputtering deposition, the nature of the substrate, deposition temperature, deposition pressure and vacuum quality are some of the influencing parameters on the film properties. In a constant magnetic field, the distance between the target and substrate, the deposition time, and the voltage and pressure play significant roles in governing the properties of metallic films.

In this paper the effects of different parameters of magnetron sputtering in the presence of a constant magnetic field on the thickness and light absorption of copper oxide nanolayers deposited on glass are studied.

2. Experimental techniques

Our experiments were performed in a dc sputtering system designed and developed in our laboratory with a cylindrical reaction chamber of 18 cm in diameter and 20 cm in height. Voltage and target distance were adjustable in the system. We designed and constructed a circular planar unbalanced dc magnetron sputtering source with a target diameter of 70 mm and permanent magnets. The target was oxygen free high conductivity copper with a purity of 99.99%. Two inner and outer ring magnets were used to produce a magnetic field keeping the electron in a helical motion. The vacuum system was pumped down to an ultimate base pressure of 5×10^{-4} Pa using a combination of diffusion and rotary pumps. The level of vacuum in the reaction chamber was measured with Pirani and Penning gauges.

All thin films were deposited on clear white microscope glass slides as substrates. Ar (99.95%) was used as the sputtering gas across the target surface. During the experiments, the substrates were at room temperature between 19 and 25 °C which was measured by thermometer and there was no external heating. The oxygen as the reactive gas came from the impurity of the fed argon gas. The partial pressures of oxygen reported in the literature for the formation of copper oxide is in the range of impurity levels in the sputtering gas that we employed in the experiments. The total working pressure was as low as 1 to 4 Pa.

The impurities in cylinders of argon gas reported by the majority of manufacturers are mainly oxygen, oxygen containing compounds and water vapor. Most of argon is produced through distillation of

* Corresponding author.
E-mail address: a_rastkar@sbu.ac.ir (A.R. Rastkar).

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compressed air at subzero temperature. The boiling point of argon (−185 °C) is between the boiling point of nitrogen (−195 °C) and oxygen (− 182 °C). Nitrogen has the lowest boiling point and is vaporized first. Therefore the main impurity in the vaporized argon is oxygen. Hydrogen is used for oxygen removal, which in turn produces water vapor. Even after all drying and filtering treatments for improving the purity, final impurities are mainly and inevitably oxygen, oxygen containing compounds and water vapor. Moreover oxygen containing compounds and water vapor will be converted into reactive radicals of oxygen under the application of plasma. Therefore, it can be suggested that the oxygen radicals produced from oxygen molecules and other impurities will contribute to the oxidation process and participate in the production of Cu_2O layers [14]. We assume that the most impurities in the cylinder of the argon to be oxygen. In addition, our local supplier reports the impurities of the argon gas in ppm in the ranges of $O_2<50$, $N_2<10$, $H_2<5$, $CO_2<30$, $CO<30$, $N_2O<0.2$, $CH_4<0.1$, $THC<0.5$ and $H_2O<50$. It can be seen that the oxygen is the most abundant element in the impurities that participate in the oxidation process.

In fact, in the present work, the idea is the utilization of industrial gases instead of very pure argon gas for reducing the cost and eliminates the precise control of the very low flow rate of the oxygen gas.

There are different devices to control the flow of oxygen entering to the systems at very low levels. These instruments may loss their proper function during the operation of a system. Hence, one solution is a previously prepared mixture of the required gases having certain composition rather than controlling the required amounts of fed gases. If we assume that we need a mixture of oxygen and argon, it can be calculated that the oxygen impurity in the industrial argon gas will have the required level for the oxidation of Cu without fluctuation during the deposition. This in turn, dismisses the necessity of the precise control of oxygen. We believe that such utilization of oxygen impurity in the cylinder of the argon gas is not less repeatable than using low flow rate of separate oxygen source in deposition processes.

The partial pressure of 0.05% oxygen in a total pressure of 1 Pa of the argon gas is equal to 0.0005 Pa. The selection of this percentage is approximately similar to the lowest partial pressures reported in other studies. This partial pressure was increased to 0.002 Pa by increasing the total working pressure to 4 Pa.

The working pressure during sputtering was from 0.133 to 4 Pa. The voltage of the dc magnetron sputtering system varied from 0.4 to 1.2 kV. The measured power at voltages of 400, 600, 800 and 950 were approximately 320, 480, 640 and 760 W, respectively.

Structural and chemical characterizations of the films were performed by X-ray diffractometry (XRD) (Philips, PW 1730/10) using two theta reflections of Cu kα line (1.54 Å). Film thicknesses were measured using a Dektak 8000 profilometer manufactured by Sloan Technology (a subsidiary of Veeco Instrument Inc.). The topography of the films was studied by a Suisse made Easy Scan 2 atomic force microscopy (AFM) system with contact mode AFM tip (Vista probes; CL-25). The tip was mounted on a cantilever holder chip of monolithic silicon and was shaped like a polygon based pyramid with the height of 10–15 μm, 0.2 N/m spring constant, resonant frequencies of 12 kHz and the tip radius of ~10 nm.

The optical transmittance of the copper and oxide films was studied in the wavelength range of 400–900 nm using a Hitachi U-3501 model spectrophotometer. In this equipment, a deuterium discharge tube was used to produce UV light and an iodine tungsten lamp was used for the production of visible and near-infrared light. All measurements were made in the laboratory at room temperature.

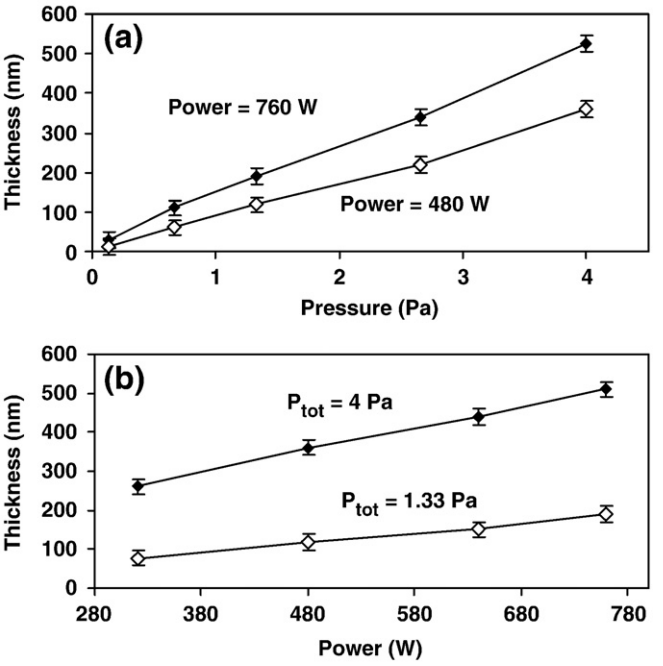

Fig. 2. Effects of (a) pressure and (b) power variations on the thicknesses of Cu_2O thin layers.

3. Results and discussions

3.1. Composition and structure

A typical X-ray diffraction pattern of the layers deposited at the total pressures of 1.33 and 4 Pa under the electrical power of 760 W is shown in Fig. 1. The identified peaks of the patterns coincide with Cu_2O diffraction pattern rather than that of CuO or Cu. This implies that the layers were mostly formed of Cu_2O compound.

The Cu (111) peak is very close to the peak of Cu_2O (200). Therefore, the second smaller peak identified in the XRD pattern and some of other similar small peaks around 2-theta of 42 to 43°, especially in the data taken from the sample prepared at 1.33 Pa, may belong to a very low amount of not reacted Cu. The glass substrates were amorphous and did not contribute to the XRD peaks in the patterns. However, in most samples the peaks are not strong enough to be distinguished from the background. This might be attributed to the very fine structure and/or very thin layers of the copper oxide.

Furthermore, it has been reported that the increase in the total pressure influences the composition of the copper oxide. Based on the observed color changes, some authors have reported the co-deposition of Cu_2O and CuO at powers of 600 W [15]. Our XRD results strongly suggest the existence of Cu_2O compound only as the CuO was not detected in the deposited layers. Therefore, CuO did not exist in the layers or it has been too low to be detected by X-ray diffraction.

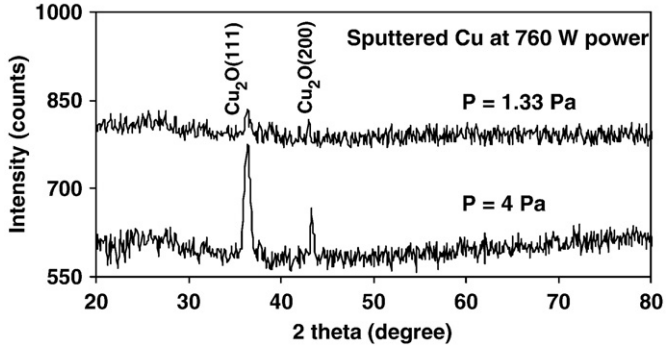

Fig. 1. XRD patterns of Cu_2O thin layers deposited at a power of 760 W and pressures of 1.33 and 4 Pa using dc magnetron sputtering.