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Sputtered cuprous oxide thin films and nitrogen doping by ion implantation

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ABSTRACT

The structural, optical and electrical properties of sputtered cuprous oxide thin films have been optimized through post-deposition thermal treatments. Moreover we have studied the effects of nitrogen doping introduced by ion implantation followed by the optimized oxidant thermal annealing. Three concentrations have been used, 0.6 N%, 1.2 N%, and 2.5 N%. Along with the preservation of the Cu_2O phase, a slight optical band gap narrowing and a significant conductivity enhancement has been observed with respect to the undoped samples. These results can be justified by the absence of further oxygen vacancies promoted by dopant introduction and by the substitution of O atoms by N ones. This lattice configuration has been guaranteed by the post implantation annealing in oxidant atmosphere. The used doping technique represents an original out-of-equilibrium approach toward the formation of low-resistivity contacts on Cu_2O films for photovoltaic applications.

1. Introduction

Metal oxides exhibit a wide range of functional properties, depending on their crystalline structure and bonding between the metal cation and oxygen, with electrical properties ranging from insulating to highly conductive. Hence, metal oxides have unfolded a remarkable progress in the ability to develop devices with new functionalities that are difficult to realize with standard semiconductors (i.e. Si and Ge) based technology [1]. In particular, copper oxides-based materials attract great interest for their potential uses in numerous technological fields such as photovoltaic [2], transparent electronics [3], heterogeneous catalysis [4,5], solid state gas sensors [6] and electrode for lithium batteries [7]. Among the wide variety of metal oxides, copper oxides have unique features such as low cost, non toxicity and the abundant availability of the constituent atoms. In particular it is a non-stoichiometric spontaneously p-type semiconductor, predominately due to copper vacancies, and it has the advantages of direct optical band gap with an energy value of about 2.1 eV [8,9] and high electrical hole mobility exceeding 100 $cm^2 V^{-1} s^{-1}$ [9] that make this material interesting for photovoltaic cells [10,11] and for electrophoresis of water. As an example, thin film solar cells based on the hetero-junction between p-type Cu_2O and n-type transparent conductive oxide (TCO) have received great attention [12].

Substantial efforts have been devoted to improve the physical properties of Cu_2O and to avoid the co-formation of CuO (which is deleterious for the film electrical conductivity), by tailoring the synthesis parameters and the post growth treatments [13,14]. Moreover, it has been demonstrated that the electric and optical properties of Cu_2O thin films could be tuned by doping with foreign atoms [15]; in particular nitrogen, due to its abundance and non toxicity, attracted great attention. For example it has been recently observed that nitrogen doped cuprous oxide films form low resistivity ohmic contacts on metals [16]. However, controversial results and interpretations have been reported about the role of nitrogen in the optical and electrical properties. For instance, Ishizuka et al. [17] reported that nitrogen atoms in Cu_2O films act as p-dopant elements with no effects on optical band gap; on the contrary, Nakano et al. [18] found that their introduction induces optical band gap widening without significant modulation of the electrical properties.

In the present work we studied the optimization of structural, optical and electrical properties of Cu_2O thin films synthesized by non-reactive magnetron sputtering through the investigation of several post-deposition thermal annealing in oxygen atmosphere. Moreover, we have analyzed the effects of nitrogen doping, introduced by ion implantation, on the properties of Cu_2O films. To our knowledge the investigation of such doping technique in cuprous oxide films has not been reported and it has permitted us to observe a peculiar lattice configuration never obtained by other doping methods.

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2. Experimental details

Copper oxide thin films were deposited by radio frequency (RF) magnetron sputtering of a Cu_2O target (99.99% purity) on Corning glass substrates. During the deposition the substrate temperature was kept at 100 °C, the argon pressure was 5.0×10^{-3} mbar and the RF power was 200 W. The thickness of the as deposited films, estimated by Rutherford backscattering spectrometry (RBS), was fixed at 80 nm.

Nitrogen was introduced in the as deposited films by ion implantation, with a 400 kV HVEE ion implanter. The ion energy was set at 46 keV according to SRIM (The Stopping and Range of Ions in Matter) simulation, in order to centre the nitrogen distribution inside the film thickness. The obtained Gaussian distribution was centered at the film depth of 40 nm (exactly at the center of the film thickness), corresponding to the projected range, and a full width at half maximum (FWHM) of 25 nm, corresponding to the ion straggling in the film thickness. The implanted doses, 0.45×10^{16} N/cm^2, 0.91×10^{16} N/cm^2 and 1.89×10^{16} N/cm^2, were set by controlling the ion current density and the implantation time. The used doses correspond to the average values of 0.6 N%, 1.2 N% and 2.5 N% respectively.

Post deposition thermal annealing in O_2 atmosphere was performed at 200 °C, 250 °C, and 300 °C for 1 h and 4 h in a conventional furnace. These thermal treatments, for the undoped and doped films, allowed to optimize the stoichiometry and the crystalline structure.

The crystalline structure was analyzed by x-ray diffraction (XRD) performed with a Bruker-AXS D5005 diffractometer, by a Cu K_α radiation at 1.54 Å and a grazing incidence angle of 1°.

The optical direct transmittance (T) and specular reflectance (R) of the samples were measured, in order to evaluate the optical absorption coefficient, by using a VARIAN Cary 500 double beam UV–Vis-NIR spectrophotometer in the wavelength range from 200 nm to 2000 nm. Direct transmittance spectra were normalized to 100% baseline obtained by mounting the empty sample holder, while for the reflectance spectra a calibrated standard sample was used as reference. Absorption coefficient, α, was evaluated by the following relation.

$$\alpha = (1/d)\log[(T_s/T)(1\text{-}R)] \quad (1)$$

where T_s is the direct optical transmittance of the bare substrate and d is the sample thickness. In this way the effects due to the presence of the interface between the corning glass substrate and the film are taken into account.

Sheet resistance measurements were performed with a Keithley 4200-SCS (Semiconductor Characterization System) at room temperature by using the 4-point collinear probe technique. The charge carriers concentrations and Hall mobilities were measured by the Van der Pauw method, using a Hall effect system equipped with a Keithley 220 current source and 1 T magnetic field.

3. Results and discussion

3.1. Undoped films

Thin films have been deposited by direct sputtering of a Cu_2O target in a non-reactive atmosphere. The Corning glass substrate was heated at 100 °C during the deposition, in order to obtain an optimal crystalline quality. For these deposition conditions, the thickness uniformity and chemical composition of Cu_2O thin films were verified by Rutherford backscattering spectrometry (data not shown). The film was then annealed in O_2 ambient in order to improve its optical, structural and electrical properties. The role of various annealing temperatures, 200 °C, 250 °C and 300 °C, combined with two different treatment durations (1 h and 4 h) was taken into account.

The crystalline structure of the annealed samples has been evaluated by XRD; the spectra are reported for all the temperatures in

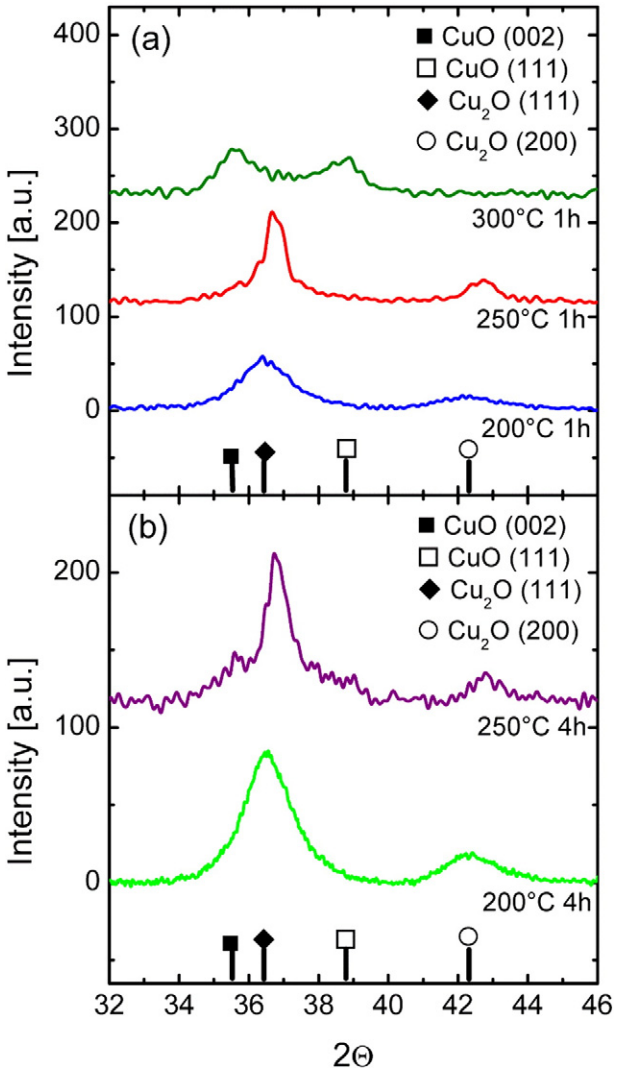

Fig. 1. (a) XRD patterns of undoped Cu_2O films annealed for 1 h at different temperatures. (b) XRD patterns of undoped Cu_2O films annealed for 4 h at 200° and 250 °C. The reference peaks of Cu_2O [JCPDS card no. 00-005-0667] and CuO [JCPDS card no. 01-0800076] phases are also indicated.

Fig. 1(a) and (b), for 1 h and 4 h respectively. In all the cases the samples are polycrystalline, but with different peculiar patterns.

After annealing for 1 h at 200 °C the XRD spectrum shows only diffraction peaks associable to the most intense peaks of the polycrystalline Cu_2O phase (JCPDS card No. 00-005-0667), which are relative to the families of (111) and (200) planes. The same (111) and (200) peaks of the Cu_2O phase are still the only ones detected in the diffraction pattern for the sample annealed for 1 h at 250 °C, as shown in Fig. 1(a). In this case both peaks are more intense by a factor of two and narrower. In particular, by using the Debye–Scherrer formula, an increase of grain size by a factor of 3 is estimated. Moreover, it is evident a slight shift of about 0.2° of 2θ toward higher angles in respect to the tabulated positions of Cu_2O (JCPDS card No. 00-005-0667), that can be associated to a strain accumulated in the film. These facts suggest that at higher annealing temperature, a higher number of larger crystalline Cu_2O grains are favored.

By further increasing the annealing temperature at 300 °C for 1 h, the peaks relative to the Cu_2O phase disappear and the only detectable XRD signals are relative to the (111) and (002) peaks of the monoclinic CuO phase (JCPDS Card No. 01-0800076), see Fig. 1(a). At this temperature all the Cu_2O film, reacting with the oxygen in the furnace, is oxidized into CuO [14].