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Solution flow rate influence on properties of copper oxide thin films deposited by ultrasonic spray pyrolysis

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ABSTRACT

The present work is an investigation of the solution flow rate influence on copper oxide (CuO) thin film properties deposited by ultrasonic spray pyrolysis. A set of CuO thin films were deposited, with various solution flow rates, on glass substrate at 300 °C. The precursor solution is formed with copper salt dissolution in distilled water with 0.05 molarity. The solution flow rate was ranged from 10 to 30 ml/h. Films composition and structure were characterized by means of XRD (X Rays diffraction) and Raman scattering. The optical properties were studied using UV–visible spectroscopy. The electrical conductivity, carrier mobility and concentration were determined by Hall Effect measurements. The obtained results indicate that flow rate is a key parameter controlling CuO films growth mechanism and their physical properties. The prepared films are mainly composed with a CuO monophase, the crystallite size is reduced with increasing the flow rate. A ZnO/CuO heterojunction structure has been realized and its rectifying behavior is tested.

1. Introduction

It is well recognized that metal oxides play an important role in several areas of physics, chemistry and materials science. Currently, they found a wide application domains in microelectronics, piezoelectricity, photovoltaics, gas sensing and photocatalysis fields [1–4]. Among these metal oxides, copper oxide (CuO) is a promising material due to its low cost, non-toxicity and abundant availability of copper.

Copper oxide exists in two stable phases namely: CuO and Cu_2O with different proprieties [5]. CuO phase has a relatively low band gap (1.2–1.9 eV), it is a p-type semiconductor with a monoclinic structure. While Cu_2O phase is known to be a p-type semiconductor with cubic structure and a large direct band gap 2–2.6 eV. Both these oxides have found special interest for several applications such as: photocatalysis [6], high Tc superconductors [7], lithium batteries [8,9], magnetic storage [10], gas sensor [11] and solar cells [12].

Several techniques have been used to deposit CuO thin films namely: thermal oxidation [13], dip coating [14], chemical vapor deposition [15], plasma evaporation [16], electrodeposition [17], spray pyrolysis [18,19] and reactive sputtering [20]. Among these techniques, spray pyrolysis is a very attractive and versatile technique; it has been widely used to produce adherent, homogenous and stochiometric thin films. Ultrasonic spray pyrolysis technique has been extensively used for metal oxide thin films deposition [21–24]. It is a simple easy, low cost technique and do not require any sophisticated or vacuum equipments; it is also compatible with thin films materials mass production.

It is well recognized, that thin films physical properties are close related and largely influenced by the used technique and deposition conditions. Therefore, deposition

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parameters effect has been widely studied and optimized in order to produce CuO thin films with suitable properties for the application in hand. The most studied parameters are: precursor concentration [25] substrate temperature [26,27] and doping [28,29]. However fewer studies have been devoted to the influence of solution flow rate in ultrasonic spray pyrolysis technique.

Generally, in the whole commonly used deposition techniques, film growth steps namely nucleation, condensation and subsequent growth, are mainly controlled by two major parameters: the substrate temperature which controls the species energy and motion onto the substrate and the flux of arriving species on the substrate. In the case of spray pyrolysis, arriving species rate is controlled by the flow rate of the solution feeding the nozzle. Substrate temperature is extensively studied in the literature, while, to our knowledge, the flow rate influence is less studied. The lack of investigation related to this parameter is the motivation of the present study.

In the present work, CuO thin films have been deposited by ultrasonic spray pyrolysis. Solution flow rate effect on structural, morphological, optical and electrical proprieties of CuO films have been investigated. CuO is known to be a good ZnO partner to form an heterojunction used for gas sensor or solar cells application. Thereafter, preparation and characterization of ZnO/CuO heterojunction has been addressed at the end of this work.

2. Experimental details

CuO thin films were grown onto glass substrate, using a homemade spray ultrasonic system [22]. A solution of 0.05 morality was prepared by dissolving $CuCl_2.2H_2O$ precursor in distilled water. The total solution of 50 ml was sprayed during 20 min on heated glass substrates by ultrasonic nebulizer system (Sonics). The obtained stream is formed with uniform and fine droplets of 40 μm average diameter [30]. The substrates temperature was fixed at 300 °C. A set of samples was prepared by varying the solution flow rate from 10 to 30 ml/h with a step of 5 ml/h.

Films structural properties were determined by XRD using Philips X'Pert system with Cu Kα radiation (λ_{Cu}=0.154056 nm). The diffractometer reflections were taken at room temperature and the 2θ value were varied in the range 20–80°. Films morphology was analyzed using scanning electron microscope Jeol 5400 SEM microscope. The micro-Raman measurements were performed at room temperature using the 514.5 nm line of an argon ion laser as the excitation source (Renishaw). The laser power was kept at 10 mW. The optical transmission in the UV–visible range (200–2000 nm) measurements was performed using Shimadzu UV-3101 PC spectrophotometer. Films thicknesses and optical band gaps were estimated from fitting optical transmission data. Films electrical characterization was performed using Hall Effect measurement system, at room temperature (27 °C), to determine carriers concentration, mobility and electrical conductivity. ZnO/CuO heterojunction has been realized using CuO films prepared with a flow rate of 10 ml/h. ZnO films were also prepared by ultrasonic spray using the same deposition system. The sprayed solution was composed of 0.1 M dehydrate zinc acetate dissolved in methanol, the substrate temperature was fixed at 300 °C and flow rate of 10 ml/h, the obtained ZnO film have a thickness of 200 nm. The *I–V* characteristic of the obtained heterostructure was recorded using a curve tracer 370 Sony Tetronix.

3. Results and discussion

In Fig. 1 we have reported the prepared films thickness variation as a function of flow rate. In figure inset, we have drawn the variation of the deposition rate, the later is estimated from the ratio of film thickness on the deposition time fixed at 20 min. As can be seen, bellow 20 ml/h the deposition rate is almost constant and equal to 200 nm/min, while above this critical value the deposition rate varies linearly with the flow rate.

The XRD spectra recorded in different films are shown in Fig. 2. In the whole spectra, only two peaks assigned respectively to the planes (111) and (002) assigned to CuO tetragonal structure are present (PDF card #45-0937).

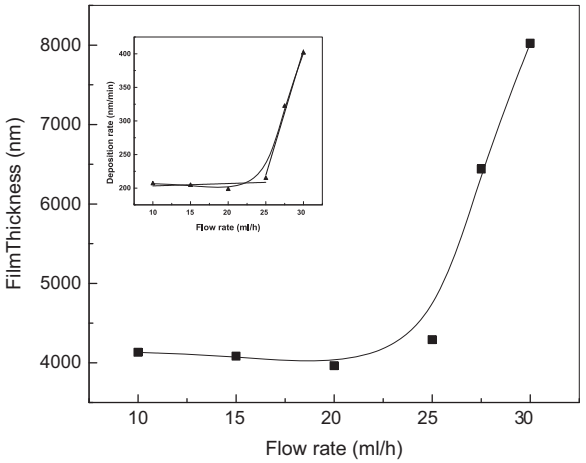

Fig. 1. Variation of film thickness as a function of solution flow rate, inset shows deposition rate dependence on solution flow rate.

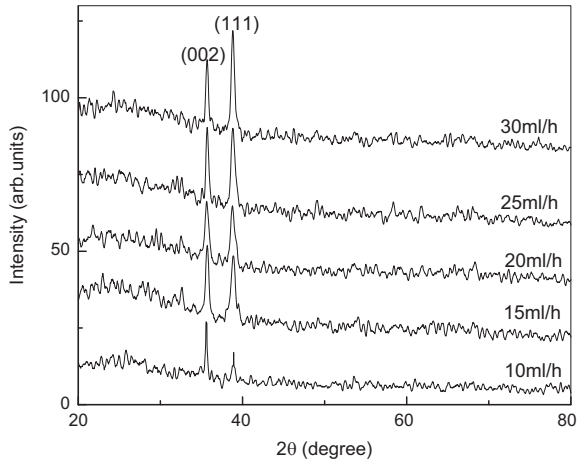

Fig. 2. XRD diffraction pattern of CuO thin films prepared with different solution flow rates.