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Synthesis of Cu/ZnO nanocomposites by r.f. co-sputtering technique

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Abstract

Cu/ZnO composite films with different Cu contents were prepared on quartz glass substrates by r.f. co-sputtering technique. The as-grown films were annealed at different temperatures in argon atmosphere for 2 h. TEM images revealed the formation of nanoparticles, which are distributed homogeneously in the ZnO matrix. The size of the nanoparticles increased with the increase of Cu content in the films and with the temperature of annealing. X-ray diffraction spectra revealed the peaks of partially oxidized copper along with the peaks that correspond to ZnO matrix. Optical absorption spectra of the films revealed the characteristic plasmon resonance absorption peak of small Cu particles. The intensity of the plasmon resonance peak increased either on increasing the Cu content in the films or on increasing the annealing temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thin films; Nanocomposites

1. Introduction

The metal nanoparticles have been used for a long time in preparing colored glasses for decoration purposes and for optical elements such as filters. There has been a great interest on the growth and study of metal nano-cluster composites in recent years due to their large non-linear optical susceptibility [1–3]. Several techniques, for example, ion-implantation [3–5], chemical [6], sol-gel [7] and sputtering [8–9] have been employed by different groups to prepare metal nanocomposites. The effect of post growth treatments on the evolution of nano-clusters is also being investigated [10]. In most of the works, SiO_2 has been used as

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the matrix material due to its thermal and chemical stability. However, incorporation of metal nano-clusters in functional matrices like ZnO, TiO_2, MgO is relatively recent [11–12]. Effects of such functional host on the optical and electrical properties of metal nano-clusters are not yet clear and a study on that would be of scientific interest.

In the present work, we report the synthesis of Cu/ZnO nanocomposite films by r.f. co-sputtering technique. The composite films were deposited on quartz glass substrates with different Cu contents. The effects of Cu content and post-growth thermal treatment on the growth of nanoparticles and their optical properties have been studied.

2. Experiments

Cu/ZnO composite films were prepared on quartz glass substrates by co-sputtering of ZnO and Cu wires. Copper wires of 2.0 mm length (0.25 mm diameter, 99.998% pure) were placed symmetrically on an ZnO (5 cm diameter, 99.995% pure) target and sputtered simultaneously for 2 h with a 200 W r.f. power at 20 mTorr argon pressure. The content of Cu in the films was varied by changing the number of Cu pieces on the ZnO target, keeping the time of sputtering fixed. Depending on the content of Cu, the thickness of the films varied from 0.18 to 0.24 μm. The as-grown films with different Cu contents were annealed at different temperatures (150°C, 300°C and 400°C) for 2 h in argon atmosphere. For transmission electron microscopy (TEM) and transmission electron diffraction (TED) studies, the composite films of about 25 nm thickness were deposited on carbon coated NaCl pellets. The films were transferred to Cu grids by floating them on the surface of water. The samples prepared for electron microscoy were also annealed at different temperatures in argon atmosphere. The crystallinity of the films was examined by a Simens D5000 X-ray diffractometer using CuK_{α} radiation (Rigaku, RAD-C). A JEOL 2010 electron microscope was used for TEM and TED observations on the films. Optical absorption spectra of the films were measured by a Shimadzu UV-VIS 3101PC double beam spectrophotometer, using a quartz substrate in its reference beam.

3. Results and discussion

Fig. 1 shows the XRD patterns of the composite films with different Cu contents and annealed at 300°C. We can observe that the films were polycrystalline in nature. In the XRD spectra, the peaks corresponding to Cu, CuO and Cu_2O were revealed along with the peaks of ZnO. Though the films were grown in argon atmosphere, the incorporated Cu in the matrix was oxidized to some extent by reacting with the oxygen of the ZnO matrix. With the increase of Cu content in the films, the XRD peak intensity increased initially and then reduced for the films of highest Cu content. The initial increase of diffraction peak intensity is due to the increase of film

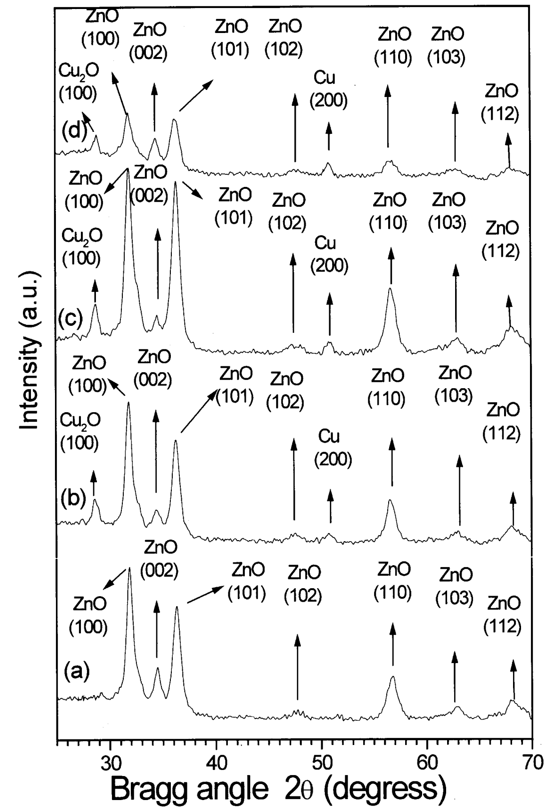

Fig. 1. XRD patterns of Cu/ZnO composites prepared with (a) no Cu, (b) 4 pieces of Cu wires, (c) 8 pieces of Cu wires, and (d) 16 pieces of Cu wires. All the films were annealed at 300°C.

thickness with the increase of copper content in the films. For the films prepared with highest Cu content (prepared with 16 pieces of Cu wires), the decrease of the intensity of diffraction peaks might be due to the reduction of crystallite size of the matrix on excessive Cu incorporation. Fig. 2 shows the XRD patterns of the as-grown composite film prepared with 16 pieces of Cu wires and annealed at 400°C. On annealing the film, the intensity of all the peaks increased. In Fig. 3, the typical TEM micrographs of the as-grown ZnO film, and composite film prepared with 16 pieces of Cu wires, that were annealed at 400°C temperature are presented. We can observe the formation of nanoparticles dispersed homogeneously in the matrix. The size of the particles increased with the increase of annealing temperature. The size of the nanoparticles were measured from the TEM images and their distribution are presented in Fig. 4. The increase of average diameter of the particles with the increase of annealing temperature is clear in Fig. 4. The increase of the size of Cu particles at higher temperatures might be due to the segregation of dispersed Cu in

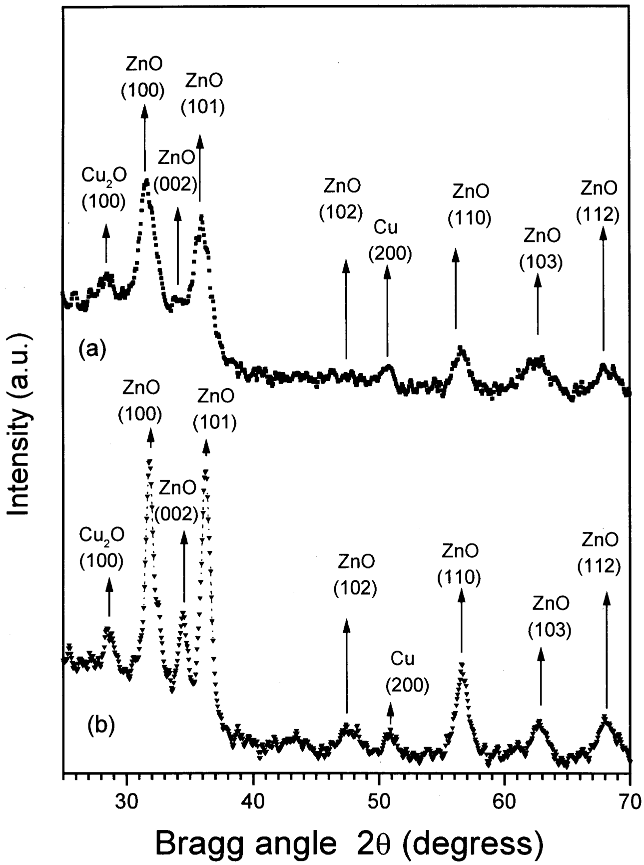

Fig. 2. XRD patterns of Cu/ZnO composites prepared with 16 pieces of Cu wires (a) as-grown and (b) annealed at 400°C.

the matrix. The increase of particle size with the increase of Cu content is demonstrated in the size distribution of particles in Fig. 5. Therefore, the size of the nanoparticles could be controlled either by controlling the content of copper in the composite films or by controlling the temperature of annealing. In Fig. 6, typical TED patterns for a sample prepared with 16 pieces of Cu wires, before and after annealing at 400^0C are presented. Appearance of more elemental Cu lines in the TED pattern after annealing the sample at 400°C indicates the breaking of oxide bond at this temperature.

In Fig. 7, the optical absorption spectra for the films prepared with different Cu contents are presented. The peak that appeared at about 560 nm wavelength correspond to the plasmon resonance absorption of small Cu particles [4]. With the increase of Cu content in the films, the peak became more intense and sharper. For the films prepared with lower copper contents, the plasmon resonance absorption

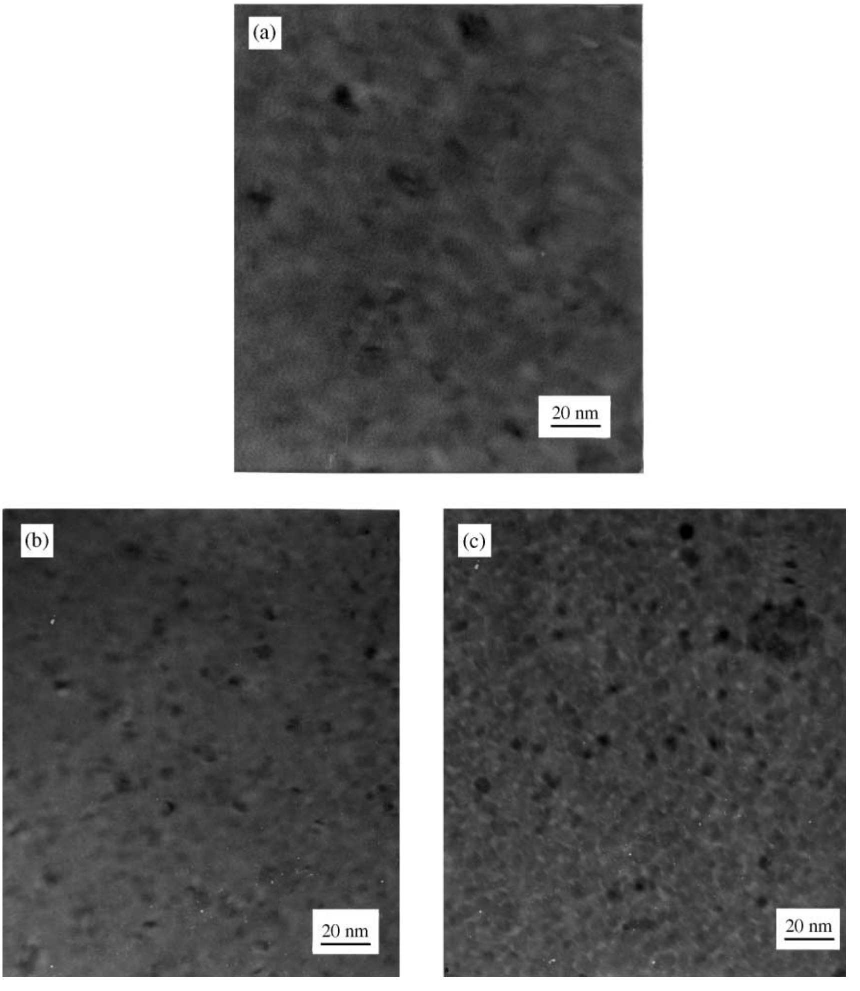

Fig. 3. Typical TEM micrographs of (a) as-grown ZnO film (b) as-grown composite film prepared with 16 pieces of Cu wires and (c) the composite film prepared with 16 pieces of Cu wires, annealed at 400°C.

bands are broader, sometimes revealing two humps. The broadness of the bands is due to broad size distribution of nanoparticles. The appearance of two humps might be due to the presence of two types of size distribution of the nanoparticles in the same sample. In Fig. 8, the optical absorption spectra for the film prepared with 16 pieces of Cu wires and annealed at different temperatures are presented. Increase in the intensity of the plasmon resonance absorption peak with the increase of annealing temperature indicates the growth of particles on annealing. The growth of particles on annealing is also clear from the shift of the plasmon resonance peak position on increasing the annealing temperature. Though, the copper incorporated

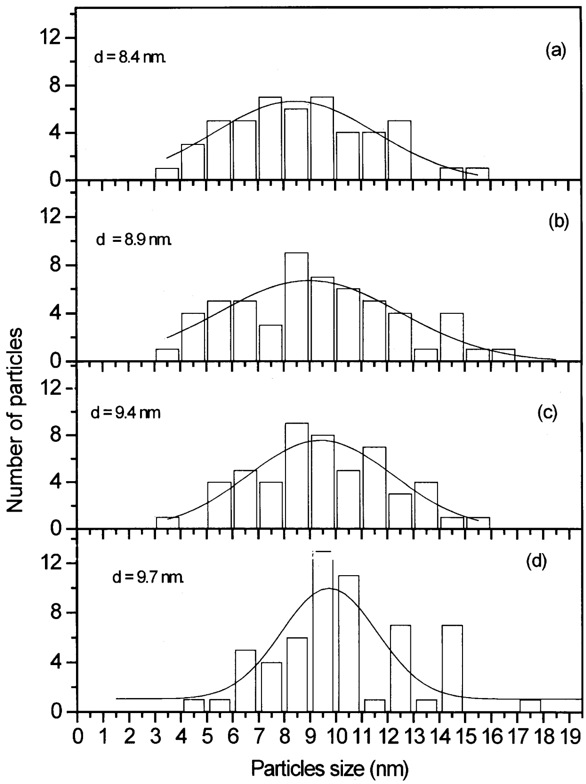

Fig. 4. Particle size distribution for the films prepared with 16 pieces of Cu wires and annealed at different temperatures (a) as-grown, (b) annealed at 150°C, (c) annealed at 300°C and (d) annealed at 400°C.

in the ZnO matrix remained mainly in its oxide state, a fraction of it must be retained in the elemental state even in as-grown samples. On annealing the samples at high temperatures, the oxide bonds break, and the content of elemental copper in the films increase. Therefore, we can assume that the nanoparticles formed in the ZnO matrix are the partially oxidized copper particles. The particles might have an elemental core and an oxide cap layer.

4. Conclusions

Cu/ZnO nanocomposite films were grown successfully by r.f. co-sputtering technique. Depending on the content of Cu, partially oxidized Cu nanoparticles of different sizes were formed in the ZnO matrix. The size and the density of the particles depended on the content of Cu in the composite films and also on the temperature of annealing. From the TED and absorption results, we can assume that

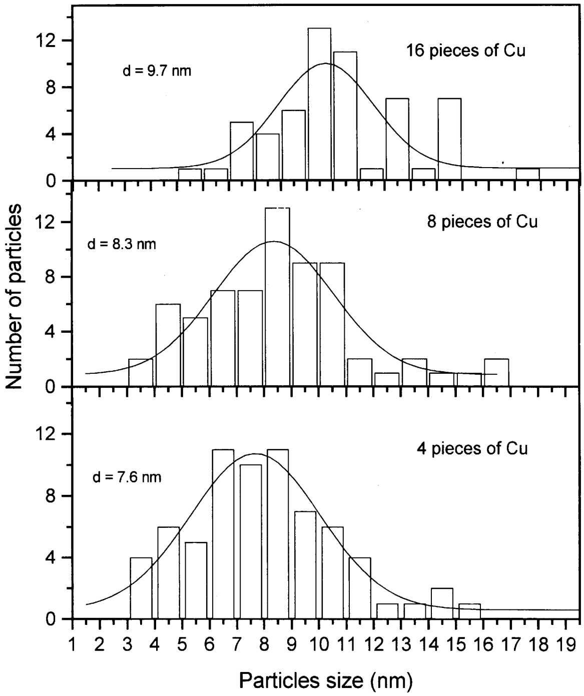

Fig. 5. Particle size distribution for the films prepared with different Cu contents and annealed at 400°C.

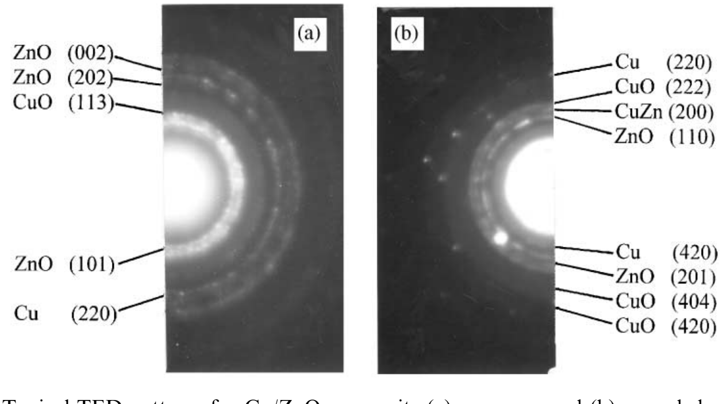

Fig. 6. Typical TED patterns for Cu/ZnO composite (a) as-grown and (b) annealed at 400°C.

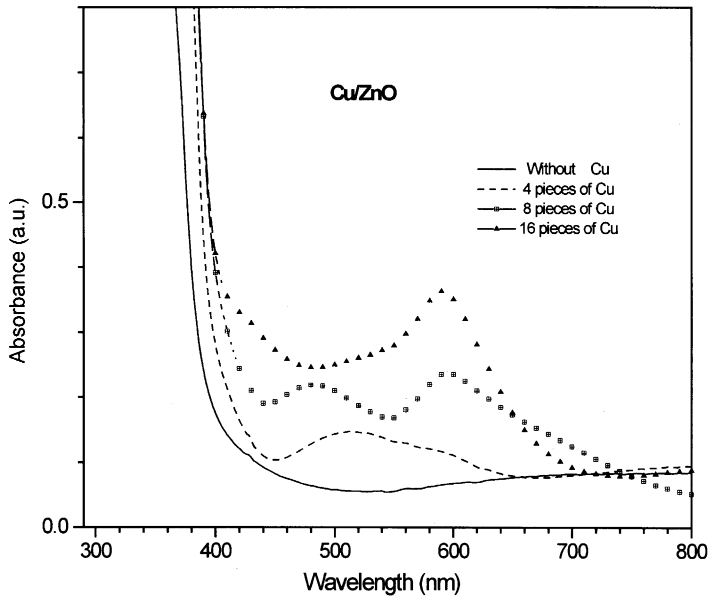

Fig. 7. Optical absorption spectra for the composite films prepared with different Cu contents and annealed at 400°C.

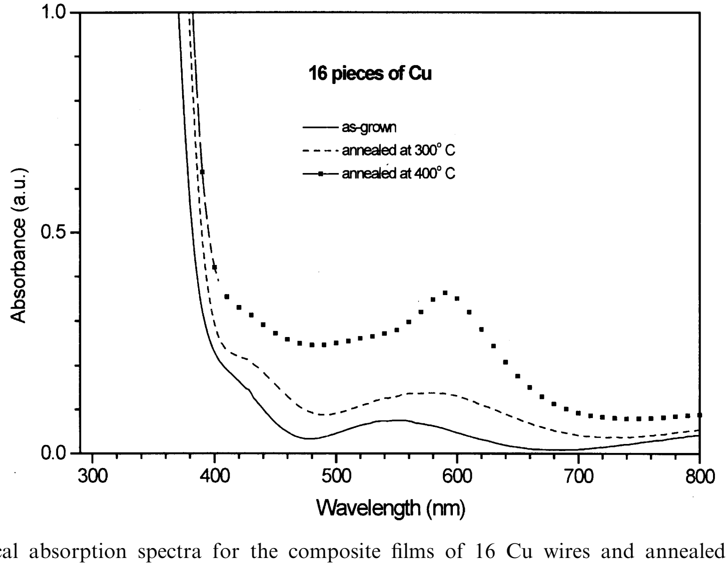

Fig. 8. Optical absorption spectra for the composite films of 16 Cu wires and annealed at different temperatures.

the nanoparticles have an elemental Cu core and an oxide cap layer around them. A further study is needed to verify the structure of the nanoparticles.

Acknowledgements

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