



ELSEVIER

Solar Energy Materials & Solar Cells 70 (2001) 363–368

Solar Energy Materials
& Solar Cells

www.elsevier.com/locate/solmat

Preparation of Au/ZnO nanocomposites by radio frequency co-sputtering

U. Pal^{a,*}, E. Aguila Almanza^a, O. Vázquez Cuchillo^a,
N. Koshizaki^b, T. Sasaki^b, S. Terauchi^b

^a*Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, Mexico*

^b*National Institute of Materials and Chemical Research (NIMC), AIST, MITI, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan*

Abstract

Au/ZnO nanocomposite films were prepared by co-sputtering of ZnO and gold wires. The composite films were transparent and red in color due to surface plasmon resonance absorption of small Au particles. The composite films were annealed at different temperatures in argon atmosphere to study the evolution of the size of Au particles and subsequent change in their optical properties. With the increase of annealing temperature, the size of the Au particles increased and the intensity of plasmon resonance absorption peak increased. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thin films; Nanocomposites; Colloidal metal particles

1. Introduction

Glasses doped with semiconductor [1,2] or colloidal metal [3,4] particles show high nonlinear optical properties and are attractive candidates for utilization in optical devices. Due to the low solubility restriction, generally, the concentration of colloid particles is low in glass prepared by conventional melting method [3]. In materials for the production of nonlinear optical devices, it is important to ensure a certain concentration of such colloidal particles in the matrix. Though, a large amount of colloidal particles can be incorporated in glass matrix by ion-implantation, the defects created by high energy ions modify their optical properties drastically. On the

*Corresponding author. Tel.: +52-22-45-76-45; fax: +52-22-44-89-47.

E-mail address: upal@sirio.ifuap.buap.mx (U. Pal).

other hand, by alternate, or co-sputtering, we can control the amount of dopant easily without modifying the optical properties of the host material.

It is known that colloidal Au particles have a large third-order nonlinear susceptibility and pico-second near-resonance nonlinear response [5], which implies their use in nonlinear optical devices [6]. The growth of colloidal Au particles increases its third-order optical susceptibility and absorption coefficient [4]. It is therefore important to study the growth of Au particles and its effect on the optical properties with the variation of growth condition and post-growth treatments.

Though, silica or quartz glass have been used vastly as matrix material to prepare colloidal metal particles, there are only a few reports on the use of function matrix material like ZnO for this purpose [7] and the effect of such functional host on the optical properties of small metal particles is not well known. In the present work, we report the synthesis of Au/ZnO nanocomposite by radio frequency co-sputtering technique. Formation and growth of nanometer size colloidal gold particles in ZnO matrix and their evolution on post deposition thermal annealing have been studied by X-ray diffraction, electron microscopy and optical absorption techniques.

2. Experimental

Au/ZnO composite films were prepared on quartz glass substrates by co-sputtering of ZnO and Au wires using a Shimadzu HSR-521 sputtering unit. Three pieces of Au wires of 7.5 mm length (0.4 mm diameter) were placed on a 100 mm diameter ZnO (99.99%) target and sputtered simultaneously for 60 min with a 100 W RF Power at 10-mTorr argon pressure. In this way the composite films of about 1.2 μm thickness were obtained. For transmission electron microscopy (TEM) and transmission electron diffraction (TED) observations, the composite films of about 25 nm thick were deposited on NaCl substrates and transferred subsequently to the microscopic copper grids. The as-grown films were annealed at 320°C, 500°C and 700°C for 2 h in argon atmosphere. The crystallinity of the films were examined by X-ray diffraction (XRD) analysis using the CuK_{α} radiation of a Rigaku, RAD-C diffractometer. A JEOL, JEM2000-FXII electron microscope was used for TEM and TED observations on the films. A Shimadzu UV-VIS 3101PC double beam spectrophotometer is used to record the absorption spectra of the films.

3. Results and discussion

Fig. 1 shows the TEM micrographs of the films annealed at different temperatures. We can observe the formation of Au nanoparticle in the matrix. Depending on the temperature of annealing the average size of the nanoparticles varied from 17.9 to 8.7 nm. In general, the size of the nanoparticles increased with the increase of annealing temperature. Fig. 2 shows the size distribution of nanoparticles measured from the TEM images. Increase of particle size on increasing the annealing

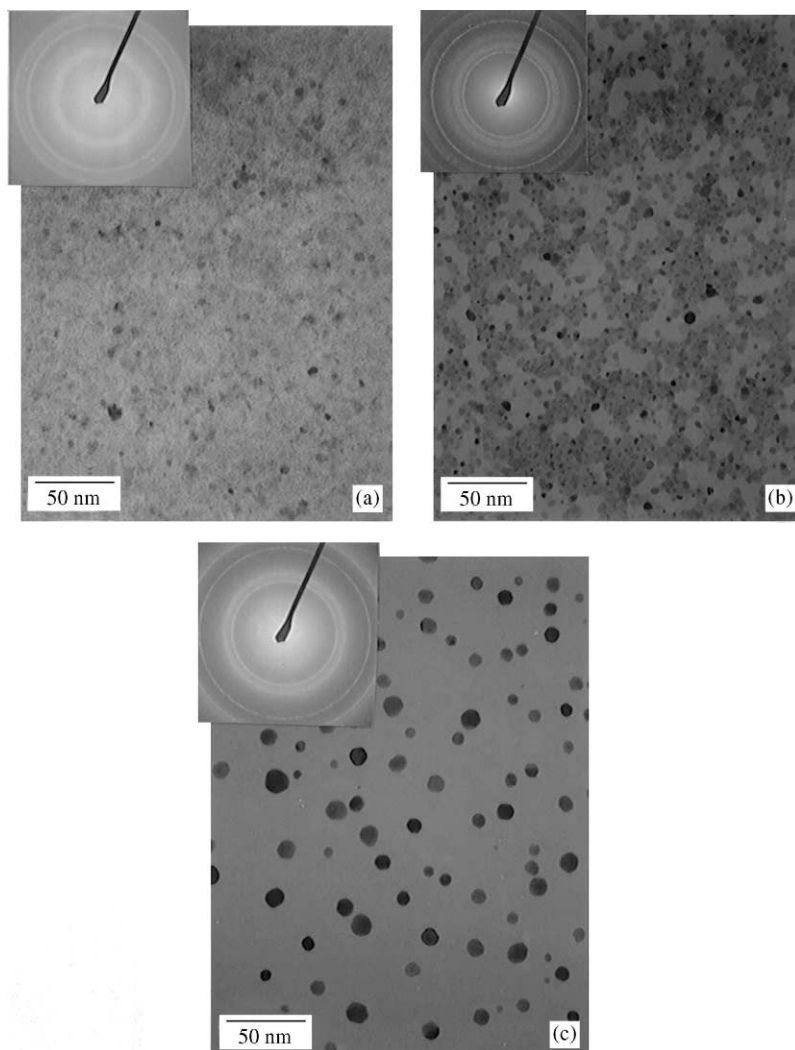


Fig. 1. TEM micrographs for the Au/ZnO composite films (a) as-grown, (b) annealed at 500°C and (c) annealed at 700°C. The inserts show the corresponding TED patterns.

temperature is clear from the size distributions. From this result, it is clear that adjusting the temperature of annealing can control the diameter of the nanoparticles.

Fig. 3 shows the XRD patterns for the sample before and after annealing at different temperatures. The composite films were polycrystalline in nature. There appeared the peaks correspond to Au and AuO in the diffraction patterns along with the peaks of ZnO matrix. With the increase of annealing temperature, the intensity of the reflections correspond to ZnO are increased. Furthermore, the intensity of AuO

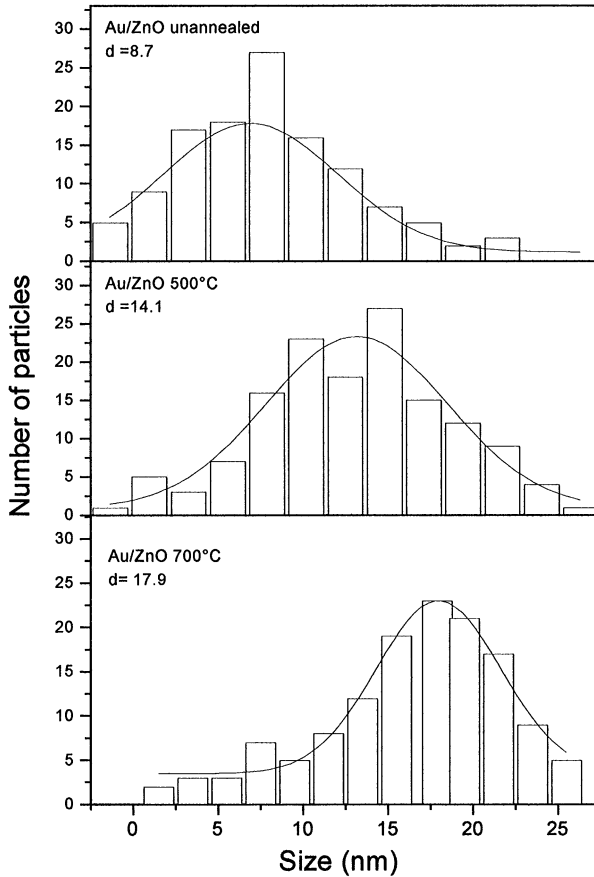


Fig. 2. Size distribution of the nanoparticles in (a) as-grown, (b) 320°C annealed and (c) 700°C annealed samples.

peaks decreased and the intensity of the peaks which correspond to Au increased. So, we can say, that the Au incorporated in the ZnO matrix remains in partially oxidized state. On annealing the films at high temperatures along with the increase of the crystallinity of ZnO matrix, the oxide bonds in AuO broke and the oxide reduced to metallic gold. The crystallinity of gold also increased on annealing, which is also clear from the TED patterns of the samples inserted in Fig. 1.

Fig. 4 shows the optical absorption spectra measured at different temperatures for the Au/ZnO composite films. The spectra were recorded using a quartz glass as reference material. Though the ZnO films without Au particles showed no absorption in the wavelength region > 400 nm, the composite films containing Au revealed an absorption peak at about 540 nm (2.30 eV). Distinct from the spectra of bulk Au due to d-d transition, there is evidence that the absorption peak is due to the surface plasmon resonance of Au particles in the matrix. With the increase of

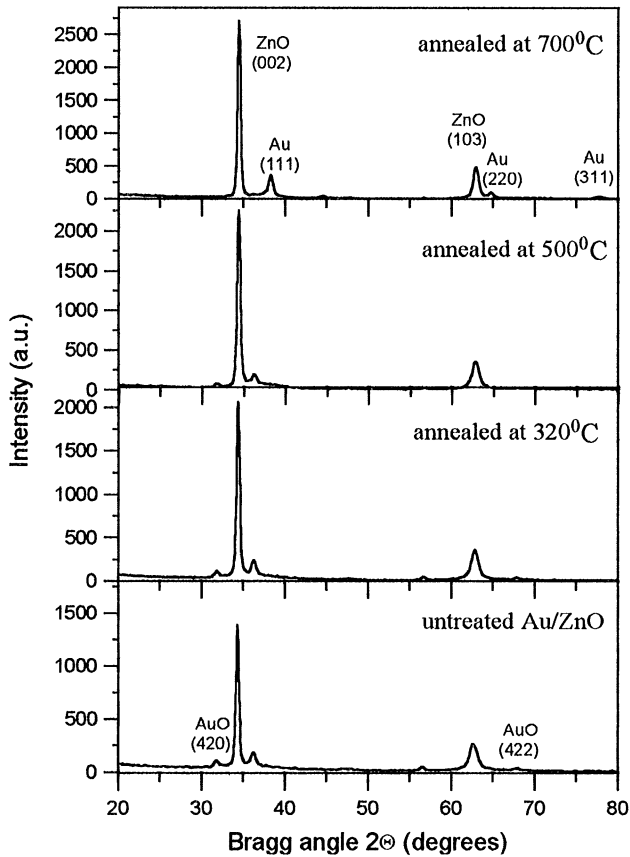


Fig. 3. XRD patterns for the (a) as-grown, (b) 320°C annealed (c) 500°C and (d) 700°C annealed samples.

annealing temperature, the intensity of the peak increased and its position shifted gradually towards higher wavelengths. Such changes in the peak intensity and position are attributed to the change in Au particle size. As observed from the size distribution of particles, the average diameter of the particles increased with the increase of annealing temperature and the peak position of the plasmon resonance absorption for bigger particles shifted to longer wavelengths. A similar growth of Au colloid particles in SiO₂ matrix on thermal annealing has also been observed by other workers for their ion implanted samples [4,6,8].

4. Conclusions

Au/ZnO nanocomposite films were grown by RF co-sputtering technique. The nanoparticles formed in the matrix were mostly the elemental Au with an oxide layer at the particle-matrix interface. Controlling the temperature of post-deposition

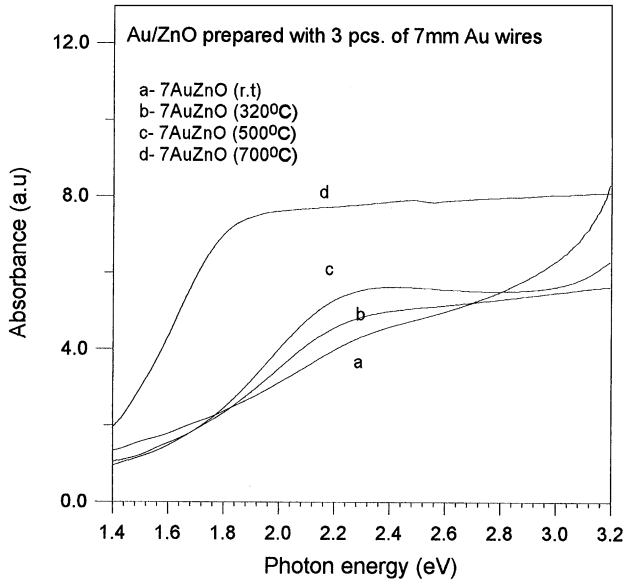


Fig. 4. Optical absorption spectra for the samples annealed at different temperatures.

annealing can control the size of the nanoparticles. The optical absorption spectra of the nanoparticles exhibit characteristic size dependence in the position and amplitude of the surface plasmon resonance.

Acknowledgements

The work is partially supported by CONACyT (Grant No. 28380-E), Mexico and AIST, MITI, Japan.

References

- [1] R.K. Jain, R.C. Rind, *J. Opt. Soc. Am.* 73 (1983) 647.
- [2] B.L. Justus, M.E. Seaver, J.A. Ruller, A.J. Campillo, *Appl. Phys. Lett.* 57 (1990) 1381.
- [3] F. Hache, D. Ricard, C. Flytzanis, U. Kreibig, *Appl. Phys.* A47 (1988) 347.
- [4] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, K. Fuji, J. Hayakawa, M. Satou, *J. Appl. Phys.* 75 (1994) 3075.
- [5] D. Ricard, Ph. Roussignol, Chr. Flytzanis, *Opt. Lett.* 10 (1985) 511.
- [6] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, J. Hayakawa, M. Satou, *Jpn. J. Appl. Phys.* 30 (1991) L742.
- [7] T. Yoshino, S. Takanezawa, T. Ohmori, H. Masuda, *Jpn. J. Appl. Phys.* 35 (1996) L1512.
- [8] K. Fukumi, A. Chayahara, M. Adachi, K. Kadono, T. Sakaguchi, M. Miya, Y. Horino, N. Kitamura, J. Hayakawa, K. Fujii, M. Satou, *Mater. Res. Soc. Symp. Proc.* 235 (1992) 389.