Available online at www.sciencedirect.com
SCIENCE DIRECT®
PERGAMON
International Journal of Hydrogen Energy 28 (2003) 637–640
International Journal of HYDROGEN ENERGY
www.elsevier.com/locate/ijhydene

Synthesis and characterization of Au nanoparticles in Al_2O_3 matrix

J. García-Serrano[a], U. Pal[b,*]

[a] *Centro de Investigaciones en Materiales y Metalurgia (CIMyM), Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo Km. 4.5, Pachuca, Hgo 42074, Mexico*

[b] *Instituto de Fisica, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue 72570, Mexico*

Received 1 December 2001; received in revised form 1 March 2002; accepted 1 May 2002

Abstract

Al_2O_3 thin films containing dispersed Au metal particles were prepared on quartz glass substrates by radio-frequency (r.f.) co-sputtering technique and subsequent annealing at different temperatures (200°C, 400°C and 600°C) in argon atmosphere. Transmission electron microscope images demonstrated a homogeneous distribution of nanoparticles in the matrix with average size varied from 3.2 to 46 nm depending on the temperature of annealing. Optical absorption measurements revealed a band in between 500 and 550 nm due to the surface plasmon resonance of the Au particles in the Al_2O_3 matrix. The transmission electron diffraction study of some composite films revealed that the nanoparticles formed in the films are in crystalline state. Effects of the incorporated metal particles on the optical properties of the composite films in the visible spectral range were investigated.

Keywords: Nanoparticles; Gold; Surface plasmon; Nanostructures

1. Introduction

Nanocomposite films that consist of small metal particles embedded in metal oxides have attracted attention because they are expected to have many useful electronic and optical properties as a result of quantum size effects [1,2]. These systems find useful applications in catalysis, photocatalysis, sensors and novel optoelectronic devices. Glasses doped with semiconductor [3,4] or colloidal metal [2,5–7] particles, for example, show high optical nonlinearity, and are attractive candidates for utilization in optical devices. Recently, several workers [8,9] have reported the preparation of semiconductor-doped metal oxide nanocomposites which might have potential applications as catalysis and photoelectrodes [10,11].

Nanoparticles often exhibit novel properties, which are different from the bulk materials properties. Many of these properties show strong dependence on size, shape and surface [12]. The characterization of these properties can ultimately lead to identifying many potential uses, particularly in the field of optical devices. Research in this area is motivated by the possibility of designing nanostructured materials that possess novel electronic, optical, magnetic, photochemical and catalytic properties. Such materials are essential for technological advances in photonics, quantum electronics, nonlinear optics and information storage and processing.

In this work, we report on the preparation and characterization of Au nanoparticles formed in Al_2O_3 matrix. Nanometer sized Au particles embedded in Al_2O_3 matrix were prepared on quartz glass substrates by r.f. co-sputtering technique and annealed subsequently at different temperatures. Formation and growth of Au nanoparticles in Al_2O_3 matrix and their evolution on post-deposition thermal annealing have been studied by transmission electron microscopy (TEM), transmission electron diffraction (TED) and optical absorption techniques.

* Corresponding author. Tel.: +52-22-45-76-45; fax: +52-22-44-89-47.
E-mail address: upal@sirio.ifuap.buap.mx (U. Pal).

0360-3199/03/$ 30.00
PII: S0360-3199(02)00138-6

2. Experimental

Al_2O_3 thin films containing dispersed Au metal particles were deposited on quartz glass substrates by r.f. co-sputtering technique. Three pieces of Au wires of 0.5 mm diameter were placed symmetrically on a 50 mm diameter Al_2O_3 target and sputtered with 150 W r.f. power at 15 mTorr Argon gas pressure. The content of Au in the films varied by changing the length of Au wires (1, 3 and 6 mm) on the Al_2O_3 target, keeping the deposition time for 6 h. The thickness of the as-deposited films was measured by a surface profilometer. Some as-deposited films with different Au content were annealed at 200, 400 and 600°C for 2 h in argon atmosphere. For TEM and TED study, the films were deposited on carbon-coated NaCl substrates and transferred subsequently to the copper grids. Optical absorption, TEM and TED techniques were used to characterize the films. Optical absorption spectra of the films were measured at room temperature using a Shimadzu UV-VIS-NIR 3101PC spectrophotometer over the 200–800 nm wavelength range. The microstructure of the composite was observed by a JOEL-2010 TEM.

3. Results and discussion

Fig. 1 show the variation of film thickness in the as-deposited composite films as a function of length of the Au wires placed on the Al_2O_3 target. We observed that the thickness of the films increased progressively with the increase of length of the Au co-targets used in the preparation of the samples.

Formation of Au nanoparticles in the films is evident from TEM images. Fig. 2 shows typical TEM microphotographs of as-deposited Au/Al_2O_3 composites films prepared with different Au content and the size distribution of the Au nanoparticles measured from the photographs. We can observe the formation of Au particles which are dispersed uniformly in the matrix. In the composite films prepared with Au wires of 1 mm, the size of the Au particles were in the range of 1–7 nm, and the average size was 3.2 nm. The increment in the Au content of the films caused a small increased in the average size of the Au particles. For the films prepared with Au wires of 3 mm, the average size of the nanoparticles was 5.1 nm.

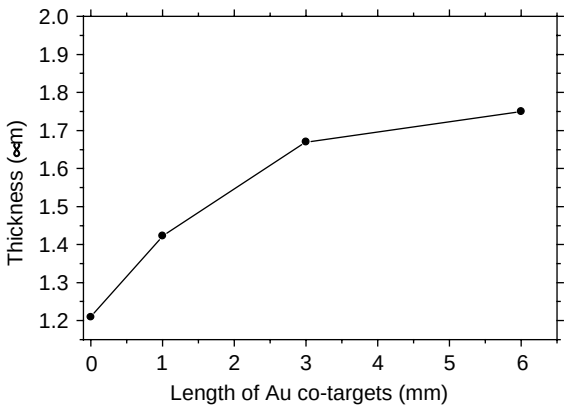

Fig. 1. Thickness of the as-deposited composite films as a function of the length of Au co-targets.

When the films were annealed at 200°C, the dimension of the particles did not increased noticeably. However, when the annealing temperature of the samples increased to 400°C and 600°C, a considerably increment in the dimension of the nanoparticles was observed. Fig. 3 shows TEM micrographs of the Au/Al_2O_3 composite thin films prepared with Au wires of 3 mm. It is evident that to annealing temperature of 400°C and 600°C, the small Au particles aggregated to form bigger particles, with an average size of 25 and 46 nm, respectively.

Formation of Au nanoparticles in the films is also evident from their optical absorption spectra, since, it is well known that small metallic particles show the optical absorption in the ultraviolet–visible region due to the excitation of the surface plasmon resonance (SPR) of the free electrons [13]. Fig. 4 shows the optical absorption spectra of the Au/Al_2O_3 thin films prepared with three pieces of Au wires of 6 mm. The spectra were recorded by using a quartz glass as reference material. The spectra revealed an absorption in the short wavelength region of < 450 nm, which is due to 5d to 6sp interband transition [9] and exhibit a broad absorption band at around 517 nm, which was assigned to the SPR of Au particles. The intensity of the SPR absorption band increased progressively with the increase of the annealing temperature of the films. This effect is attributed to the increment in the particle size caused as mentioned above, by the increases of the annealing temperature of the samples, since, the SPR absorption of small metal particles is originated from the collective motion of the conduction electrons interacted with external electromagnetic field of the incident radiation.

Fig. 5 shows the evolution of the optical absorption spectra of Au/Al_2O_3 thin films with the variation of the Au content. The intensity of the SPR absorption band increased with the increase of the Au content in the composite films. This behavior is due to the increase in the size of the Au particles on increasing the Au content in the composite films.

Electron diffraction pattern of as-grown composite films prepared with three pieces of Au of 1 mm indicated that the nanoparticles formed in this films are in crystalline state. The TED pattern showed concentric rings whose sequence corresponds to a face-centered-cubic phase. The values of interplanar spacing d_{hkl} calculated from the diameters of the diffraction rings agree well with those of bulk gold. In Fig. 6, a typical TED pattern of the Au nanoparticles is presented.

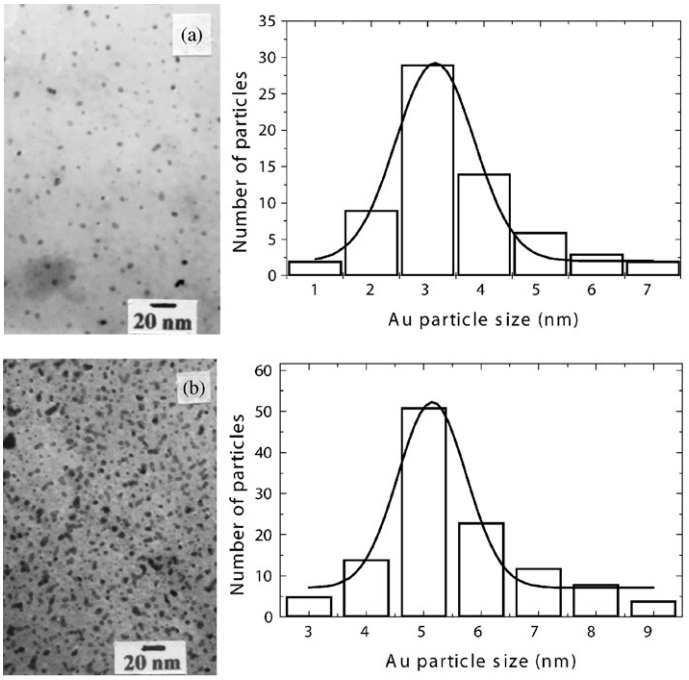

Fig. 2. Typical TEM micrographs of as-deposited Au/Al_2O_3 composite thin films prepared with three pieces of Au wires of: (a) 1 mm; and (b) 3 mm length and the size distribution of the Au nanoparticles in them.

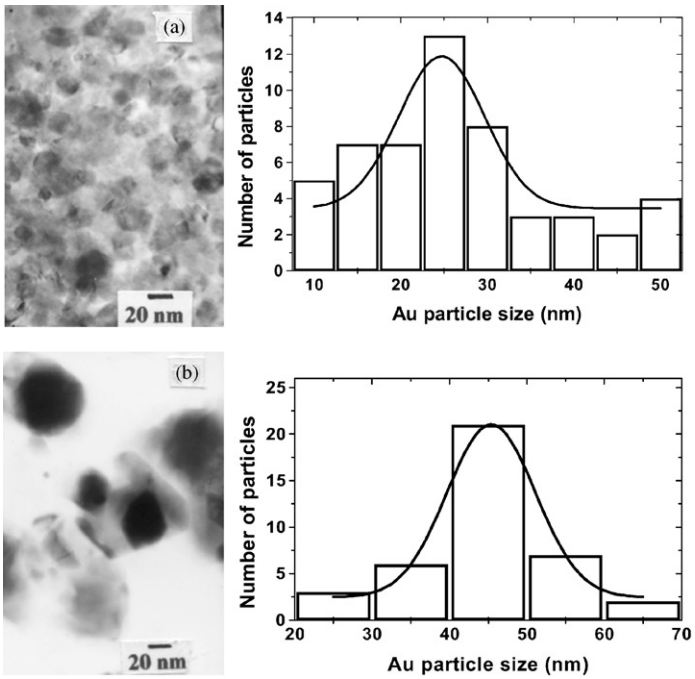

Fig. 3. Typical TEM images of Au/Al_2O_3 composite thin films prepared with three pieces of Au wires of 3 mm length and annealed at: (a) 400°C; and (b) 600°C, and their size distribution of the Au nanoparticles.

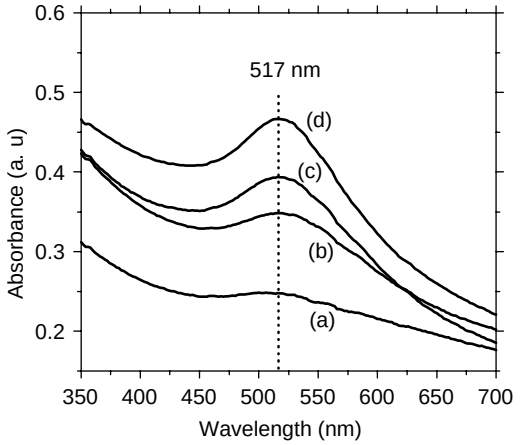

Fig. 4. Optical absorption spectra of: (a) as-grown; (b) 200°C; (c) 400°C; and (d) 600°C annealed Au nano-particles dispersed in Al_2O_3 thin films.

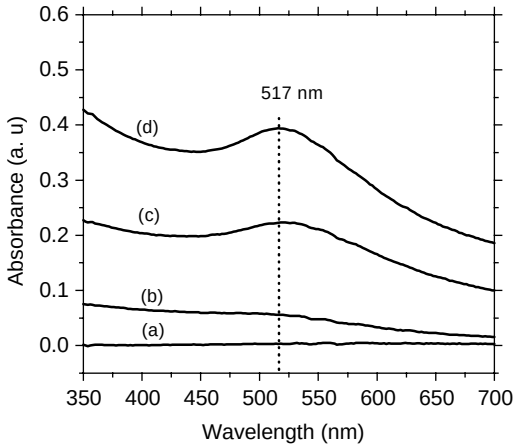

Fig. 5. Optical absorption spectra of Al_2O_3 thin films annealed at 400°C and prepared with: (a) only Al_2O_3; (b) Au wires of 1 mm; (c) Au wires of 3 mm; and (d) Au wires of 6 mm.

4. Conclusions

In conclusion, Au nanoparticles were formed in Al_2O_3 matrix by r.f co-sputtering technique. The formation of Au nanoparticles was demonstrated by TEM, TED and optical absorption. The intensity of the SPR absorption band characteristic of Au nanoparticles increased with the increase of particles size. The position of the SPR absorption band is independent of Au particle size. The TED pattern of the as-grown composite films prepared with three pieces of Au of 1 mm revealed that the nanoparticles formed in this films correspond to Au in crystallized state, the pattern showed concentric circles characteristic of a face-centered-cubic phase.

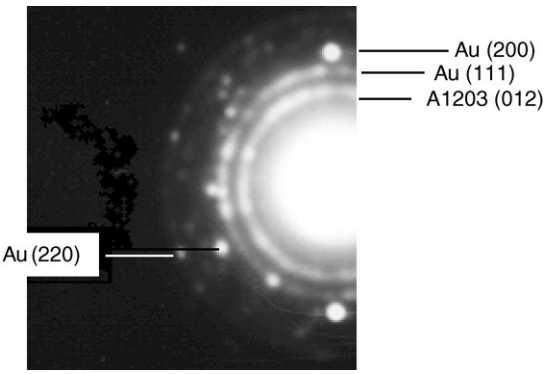

Fig. 6. A typical TED pattern of Au nanoparticles formed in as-grown composite films prepared with three pieces of Au of 1 mm.

Acknowledgements

Authors are thankful to Nancy Castillo, Department of Physics, CINVESTAV, México for taking TEM images. The work is partially supported by the Univesidad Autónoma del Estado de Hidalgo (project PAU2000).

References

[1] Zhoo G, Kozuka H, Yoko T. Thin Solid Films 1996;277:147.
[2] Fukumi K, Chayahara A, Kadono K, Sakaguchi T, Hirono Y. J Appl Phys 1994;75:3075.
[3] Jain RK, Rind RC. J Opt Soc Am 1983;73:647.
[4] Justus BL, Seaver ME, Ruller JA, Campillo AJ. Appl Phys Lett 1990;57:1381.
[5] White CW, McHargue CJ, Sklad PS, Boetner LA, Farlow GC. Mat Sci Rep 1989;4:43.
[6] Haglund RF, Magruder RH, Morgan SH, Henderson DH, Séller RA, Yang Y, Zuhr RA. Nucl Instrum Methods B 1992;65:405.
[7] Matsuoka J, Mizutani A, Kaneko S, Nasu H, Kamiya K, Kadono K, Sakaguchi T, Miya M. J Ceram Soc Jpn 1993;101:53.
[8] Pal U, Aguila Almanza E, Vázquez Cuchillo O, Koshizaki N, Sasaki T, Terauchi S. Sol Energy Mater Sol Cells 2001;70:363.
[9] Vázquez Cuchillo O, Pal U, Vázquez Lopez C. Sol Energy Mater Sol Cells 2001;70:369.
[10] Matsumoto Y, Ishikawa Y, Nishida M, Li S. J Phys Chem B 2000;104:4204.
[11] Matsumoto Y. MRS Bull 2000;25:47.
[12] Wang Y, Herron N. J Phys Chem 1991;95:525.
[13] Kreibig U, Vollmer M. Optical properties of metallic clusters. Berlin: Springer, 1995. p. 13.