

Synthesis and microstructure of metal oxide thin films containing metal nanoparticles by liquid phase deposition (LPD) method

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Abstract. Au nanoparticles dispersed SiO₂-TiO₂ composite films have been prepared by a novel wet process, Liquid Phase Deposition (LPD) method. The composite films were characterized by XRD, XPS, TEM, ICP, SEM and UV-VIS absorption spectroscopy. The results showed that the SiO₂-TiO₂ composite films containing Au^{III} and Au^I ionic species were co-deposited from a mixed solution of ammonium silicofluoride, ammonium hexafluorotitanate, boric acid and tetrachloroauric acid. The heat treatment induced the reduction of Au ions and formation of Au nanoparticles in the film. TEM observation revealed that the Au nanoparticles with 5-10 nm in diameter were found to be dispersed uniformly in the SiO₂-TiO₂ matrix. The optical absorption band due to the surface plasmon resonance of dispersed Au particles were observed at the wavelength of 550 nm and shifted toward longer wavelength with increasing heat treatment temperature.

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1 Introduction

Nanosized metal and semiconductor particles dispersed in a solid dielectric matrix, such as glasses or ceramics, have recently attracted significant interest because such material exhibit high resonant type third-order optical nonlinearity [1,2]. Especially, the anomalous electronic, optical and catalytic properties of noble metal nanoparticles have motivated many researches in this field for the past two decades due to their potential applications in electronics and photonics devices. These unique properties are known to be caused by quantum size effects of the embedded nanoparticles in the matrix, and interface and/or surface effects between nanoparticles and the matrix.

A variety of techniques for preparing fine particles in dielectric matrixes has been developed, *e.g.*, r.f. sputtering [3], ion implantation [4], sol-gel process [5]. Recently, direct deposition using ligand-exchange hydrolysis of metal-fluoro complex and the F⁻ consumption reaction with boric acid or aluminum metal (liquid phase deposition process, LPD [6,7]) has been developed for the preparation of metal oxide thin films. Since the film deposition process is proceeded through a heterogeneous nucleation stage in an aqueous solution that is a typical homogeneous system, composite films can be readily prepared from mixed solutions containing objective species such as

metal ions. Thus, it is a promising technique for the direct preparation of multicomponent and/or multilayered metal oxide films.

In this paper, we report on the synthesis and characterization of composite nanostructured thin films consisting of Au nanoparticles dispersed in SiO₂-TiO₂ matrix by the LPD method. TiO₂ and SiO₂ are commonly used materials in optical thin film filters and waveguiding layers in the visible and near infrared wavelength range because of their chemical stability and large refractive index difference [8]. Moreover, Au has been received much attention due to large third order nonlinear susceptibility [9]. The obtained composite films were characterized by inductive coupled plasma atomic emission spectrometry (ICP-AES), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV-VIS) absorption spectroscopy and scanning electron microscopy (SEM). The correlations between preparation conditions and microstructures of obtained films are described.

2 Experimental

As a parent solution, ammonium silicofluoride acid, (NH₄)₂SiF₆, ammonium hexafluorotitanate acid, (NH₄)₂TiF₆, and boric acid, H₃BO₃ were dissolved in distilled water at a concentration of 0.50 mol dm⁻³,

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respectively. Tetrachloroauric acid, HAuCl_4 , as a gold precursor was diluted with distilled water at a concentration of 2.43 mol dm^{-3} and then stored in dark at ambient temperature. These solutions were mixed with various concentrations and used as the treatment solution for deposition. The films were deposited at the concentration of 0.01 mol dm^{-3} for $(\text{NH}_4)_2\text{SiF}_6$, 0.02 mol dm^{-3} for $(\text{NH}_4)_2\text{TiF}_6$ and 0.30 mol dm^{-3} for H_3BO_3 . Non-alkali glass (corning 7059), silicon wafer (111) and polyvinyl carbonate sheet were used as substrate. The substrate was immersed into the treatment solution and suspended therein vertically for several hours at 30°C under dark condition. The substrate was then removed from the solution, washed with distilled water, and dried at ambient temperature. Heat treatment for the deposited films was performed under air flow for 1 hr at various temperatures.

The composition of the composite films was carried out by ICP-AES (SRS 1500 VR, Seiko Instruments Inc.). The samples for ICP measurement were dissolved in diluted aqua regia solution ($\text{HCl}:\text{HNO}_3 = 3:1$). XRD patterns were measured by 2θ method using $\text{Cu-K}\alpha$ radiation on a Rigaku RINT-2100 system equipped with a thin film attachment. Incident angle of X-rays to the sample was set to 1° . The chemical states of the species in the composite films were measured using a KRATOS, XSAM800 X-ray photoelectron spectrometer with $\text{Mg-K}\alpha$ radiation. All the XPS data were calibrated using the binding energy of C 1s contamination line (285 eV). The microstructure and surface morphology of the films were observed using a JEOL JEM-2010 TEM operating at 200 kV and Hitachi S-2500 SEM with an acceleration voltage of 20 kV, respectively. UV-VIS spectra of the samples were recorded using a UVVIDEC 660 spectrophotometer in 400-800 nm region.

3 Results and discussion

Highly transparent films were obtained after deposition. They showed light yellow color having a strong adherence to the substrate. Figure 1 shows SEM images for the as-deposited $\text{SiO}_2\text{-TiO}_2$ composite film and $\text{Au/SiO}_2\text{-TiO}_2$ composite film. The $\text{Au/SiO}_2\text{-TiO}_2$ composite film (Fig. 1(b)) is very homogeneous and constructed of small particles showing no cracks as compared with the $\text{SiO}_2\text{-TiO}_2$ film (Fig. 1(a)). The color of the films became intense with increasing the initial concentration of HAuCl_4 solution. Figure 2 shows the relationship between the initial concentration of HAuCl_4 in the treatment solution and the atomic ratio of $\text{Au}/(\text{Si}+\text{Ti})$ in the composite films obtained by ICP measurement. The $\text{Au}/(\text{Si}+\text{Ti})$ atomic ratio is found to increase up to 1.5 with increasing the HAuCl_4 concentration. This indicates that the content of Au in the composite films can be readily controlled by varying the initial concentration of HAuCl_4 solution. The color of the composite film gradually changed to deep yellow, purple and blue by heat treatment at 100, 200 $^\circ\text{C}$ and above, respectively. These color changes indicate the formation of Au metal particles in the composite films.

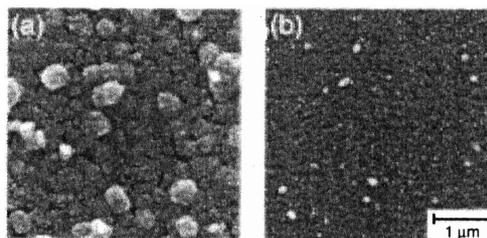


Fig. 1. SEM images for the as-deposited $\text{SiO}_2\text{-TiO}_2$ composite film (a), and $\text{Au/SiO}_2\text{-TiO}_2$ composite film (b).

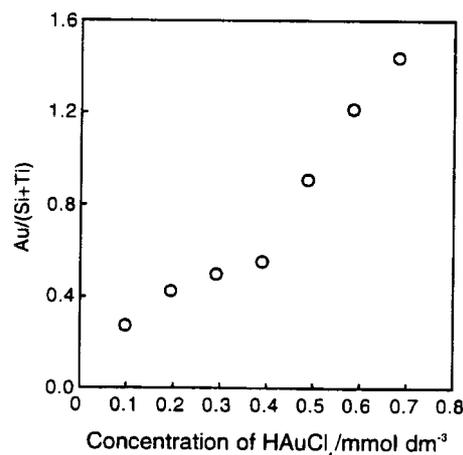


Fig. 2. Relationship between $\text{Au}/(\text{Si}+\text{Ti})$ atomic ratio of the deposited films and initial concentration of HAuCl_4 in the treatment solution.

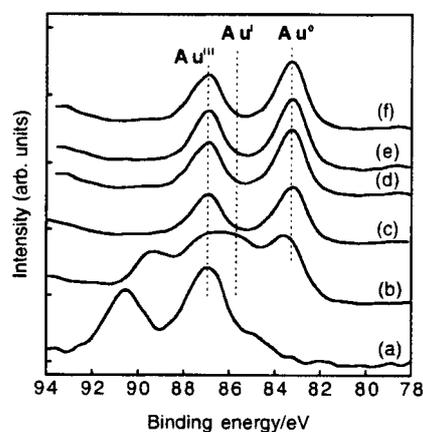


Fig. 3. Au 4f electron spectra of the $\text{Au/SiO}_2\text{-TiO}_2$ composite films heat-treated at various temperatures. (a); as-deposited film, (b) to (f); films heat-treated at 100, 200, 300, 400 and 500 $^\circ\text{C}$, respectively.

Figure 3 shows Au 4f electron spectra of the composite films heat-treated at various temperatures. For as-deposited film, the Au $4f_{7/2}$ peak was separated into 85.7 and 86.9 eV which are assigned to Au^I and Au^{III} ionic state, respectively [10]. For the film heat treated at 100 $^\circ\text{C}$ (Fig. 3(b)), the peak shifts to lower energy side as compared to the as-deposited sample, and new peak which is assigned to metallic Au (Au^0) is observed (83.5 eV). This

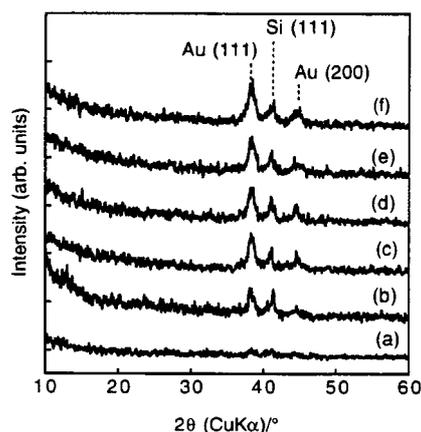


Fig. 4. X-ray diffraction patterns of the Au/SiO₂-TiO₂ composite films heat-treated at various temperatures. (a); as-deposited film, (b) to (f); films heat-treated at 100, 200, 300, 400 and 500 °C, respectively.

indicates that the Au^{III} ionic species in AuCl₄⁻ complex ions are partially reduced to Au^I ionic state and Au⁰ state by the heat treatment at 100 °C. For the films heat-treated at 200 to 500 °C, the spectra are completely assigned to metallic Au, indicating the complete reduction of Au ionic species in these films. Although not shown here, Si 2*p* and Ti 2*p*_{3/2} peak were observed at 103.3 eV and 459.0 eV, respectively, confirming the formation of SiO₂-TiO₂ composite film [11].

XRD patterns of the composite films heat-treated at various temperatures are shown in Fig. 4. For the as-deposited film, the film is found to be amorphous without any significant diffraction peak. After heat treatment at 100 °C, two distinct diffraction peaks are clearly observed at *ca.* 2θ = 38.1° and 44.4°, being assigned to (111) and (200) reflections of Au with fcc structure, respectively. As the heat treatment temperature increases, these peaks become more intense and the full-width at half maximum of the peaks decreases, indicating the growth of Au crystallites. The crystallite size of Au calculated by Scherrer equation using the width of Au (111) peak were 5 and 10 nm for the films heat-treated at 200 and 500 °C, respectively. TEM image of the deposited film heat-treated at 200 °C is shown in Fig. 5. The mean size of the Au particles is *ca.* 5 nm, which coincides well with those of the XRD analysis, and increased with increasing the heat treatment temperature.

It is well known that the small metal particles exhibit characteristic optical properties due to surface plasmon resonance of conduction electrons which results in an absorption peak in the UV-VIS region [12,13]. The variations of UV-VIS spectra of the composite films with heat treatment temperatures are shown in Fig. 6. A very weak shoulder was observed at *ca.* 520 nm for the film heat-treated at 100 °C. For the film heat-treated at 200 °C, the absorption peak is observed around 550 nm which is due to the surface plasmon resonance for Au nanoparticles [14]. With increasing heat treatment temperature from 300 to 500 °C, these absorption peaks become more

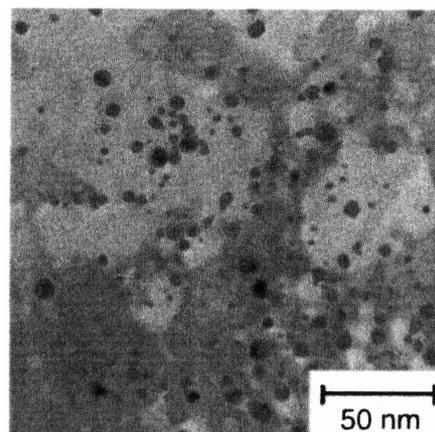


Fig. 5. TEM image of Au/SiO₂-TiO₂ composite film heat-treated at 200 °C for 1 hr.

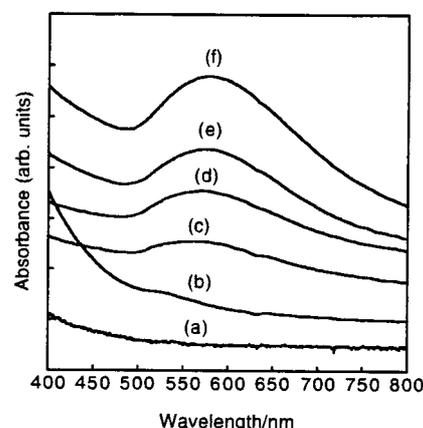


Fig. 6. UV-VIS spectra of the Au/SiO₂-TiO₂ composite films heat-treated at various temperatures. (a); as-deposited film, (b) to (f); films heat-treated at 100, 200, 300, 400 and 500 °C, respectively.

intense and peak wavelength shifts *ca.* 15 nm toward the longer wavelength.

In general, the plasmon absorption is very sensitive to chemical composition of particles, their size and shape, degree of aggregation, volume fraction of metal phase and relative permittivity of the surrounding matrix [15]. The size dependence of the peak position is explained by a size-dependent effective dielectric constant of a metal particle due to electron scattering at the particle surface [16]. In the present study, since the SiO₂-TiO₂ matrix was X-ray amorphous (Fig. 4), effect of relative permittivity of the matrix seems not to be significant. Therefore, the observed shift of the plasmon peak can be qualitatively explained by the changes in the effective dielectric constant of the composite film due to increase of mean size of the Au particles.

4 Conclusion

We have developed a very simple process for the preparation of Au nanoparticles dispersed in SiO₂-TiO₂

composite films by the LPD method. The SiO₂-TiO₂ composite films containing Au^{III} and Au^I ionic species were deposited from a mixed solution of (NH₄)₂SiF₆, (NH₄)₂TiF₆, H₃BO₃ and HAuCl₄ acid at ambient temperature and atmosphere. The Au content in the composite film was controlled readily by varying the initial concentration of HAuCl₄ solution. The Au ionic species were completely reduced to metallic Au particles by the heat treatment at 200 °C. The Au nanoparticles with 5-10 nm in diameter were dispersed homogeneously in the SiO₂-TiO₂ matrix and isolated individually. The absorption peak due to the surface plasmon resonance of Au particles were found to shift towards longer wavelength as the heat treatment temperature increases, which can be due to the increase of mean size of dispersed Au nanoparticles.

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