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Optical Properties of Au/SiO_2 Nano-Composite Films Prepared by Induction-Coil-Coupled Plasma Sputtering

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Au/SiO_2 nano-composite thin films with 3 to 65 vol% Au were prepared by induction-coil-coupled plasma sputtering, and the effect of heat-treatment on the nano-structure and optical property of the films were investigated. The mean diameter of the Au particles in the as-deposited films was about 8 nm and increased from 10 to 30 nm after the heat treatments at 900°C. The optical absorption was greatly improved by the heat-treatment due to the increase of Au particle sizes. At the heat-treatment of 900°C, Au/SiO_2 films containing 3 to 65 vol% Au showed absorption peaks at the wavelength of 540 to 560 nm, while no absorption peak was observed in the as-deposited films containing more than 12 vol% Au. The intensity of the absorption peak for the Au/SiO_2 films heat treated at 900°C increased with increasing Au content, showing a maximum value around the Au content of 37 vol%.

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1. Introduction

Nano metal-particle dispersed glasses are attractive candidates for optical logic devices, such as optical switches, shutters and wave-guides because of their nonlinear optical properties. The metal particles would cause the surface plasmon resonance (SPR) accompanying specific optical absorption peaks. The volume fraction and microstructure of the dispersed metal particles as well as the dielectric constant of the matrix glasses strongly affect the optical absorption of the composite thin films. A variety of techniques including melt quenching[1,2] ion implantation,[3–5] sol-gel[6–11] and sputtering[12–16] have been employed to fabricate Au/SiO_2 composite thin films. In order to increase the optical absorption of the composite thin films, the content of metal particles should be increased as high as possible. However, it is difficult to control the content of metal particles using the above-mentioned methods. Particularly, in a single target sputtering method, the content can be hardly increased due to higher vapor pressures of metals than that of glasses. In order to further increase the metal content in composite films, a multi-target sputtering technique has been used[14–16] to deposit Au and SiO_2 layers alternatively; however, few study[16] has been reported on the optical properties of Au/SiO_2 composite thin films over a wide range of Au content.

We have prepared Au/SiO_2 multilayer films over a wide ranged Au content by using induction-coil-coupled plasma sputtering.[17] The absorption peak due to SPR of Au particles was observed at the wavelength of 560 nm in the as-deposited Au/SiO_2 films. The mean diameter of Au particles was typically small than 8 nm in the as-deposited Au/SiO_2 films. The absorption would become more significant with increasing Au content. However, in the as-deposited Au/SiO_2 films, the absorption peak disappeared when the Au content was higher than 12 vol% due to percolation of Au particles in the SiO_2 layers. By heat-treating as-deposited films, the percolation value may shift to higher Au content by an appropriate distribution of Au particle sizes. In the present study, the as-deposited Au/SiO_2 films were heat-treated to maximize the Au content without connecting Au particles. The effect of heat treatment on the microstructure and the optical properties of the Au/SiO_2 films were investigated.

2. Experimental Procedure

Au/SiO_2 multilayer films were prepared by induction-coil-coupled plasma sputtering (ULVAC, MB95-1010). The sputtering system has a pair of conventional dc magnetron cathodes in which a circular radio-frequency (RF)-induction coil is enhanced in front of the cathodes.[17] The induction coils and target magnetron cathodes were excited at the RF of 13.56 MHz in combination with a magnetic field produced by a Sm–Co magnet placed below the target. The deposition rates of Au and SiO_2 layers were controlled independently using a shutter in front of the targets. The deposition conditions are summarized in Table 1.

The deposition time of each Au layer was fixed at 8 s. The Au content in the film was controlled by adjusting the deposition time for a single SiO_2 layer, while the total deposition time for the SiO_2 layers was always 3000 s.

Table 1 Preparation condition of the Au/SiO_2 thin films.

Target	Au, SiO_2
Substrate	Si, Quartz
Chamber pressure (Pa)	$<5 \times 10^{-4}$
Working pressure (Pa)	1.6×10^{-1}
Au: RF coil (W)	50
RF Target (W)	50
SiO_2: RF coil (W)	200
RF Target (W)	200
Ar flow rate (m^3/s)	8.3×10^{-8}
O_2 flow rate (m^3/s)	5.8×10^{-8}
Rotation (min^{-1})	10
Working distance (mm)	180

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Table 2 Preparation condition of the Au/SiO_2 thin films expressed as $[Au_{(x)}SiO_{2(y)}] \times z$, in which the total deposition time of SiO_2 was fixed at 3000 s.

Deposition time of one Au layer x/s	Deposition time of one SiO_2 layer y/s	Layer number of Au or SiO_2 z	Total deposition time of Au layer w/s	Au content C_{Au}/vol%
8	600	5	40	3
8	300	10	80	5
8	150	20	160	10
8	120	25	200	12
8	75	40	320	38
8	60	50	400	37
8	40	75	600	45
8	30	100	800	65

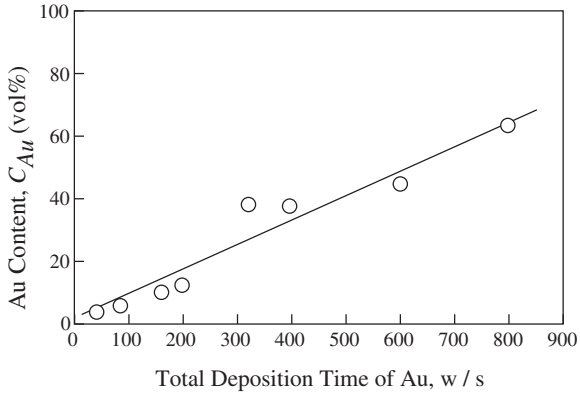

Fig. 1 Au content in the Au/SiO_2 nano-composition thin films as a function of the total deposition time of Au.

Numbers of Au and SiO_2 layers increased with decreasing the deposition time of a single SiO_2 layer. Table 2 summarizes the preparation conditions of the Au/SiO_2 multilayer films. The as-deposited films were heat-treated at 500–900°C in air for 1 h by a rapid thermal annealing (RTA) system, where heating rate was 15°C/s.

X-ray diffraction (XRD) measurements were conducted with Cu Kα radiation in the θ–2θ mode. The mean diameter (D) of Au particles was estimated using the Scherrer's equation,

$$D = 0.9\lambda/\beta\cos\theta$$

where λ is the X-ray wavelength, β the full width at half maximum (FWHM), and θ the diffraction angle. The microstructure of the film was observed by transmission electron microscopy (TEM) (JEOL, JEM-2000EX II). The composition was determined by an energy dispersion X-ray (EDX) spectroscopy (JEOL, TN-5500) attached to TEM. Optical absorption spectra were measured in the range of 200–2500 nm by a spectrometer at room temperature.

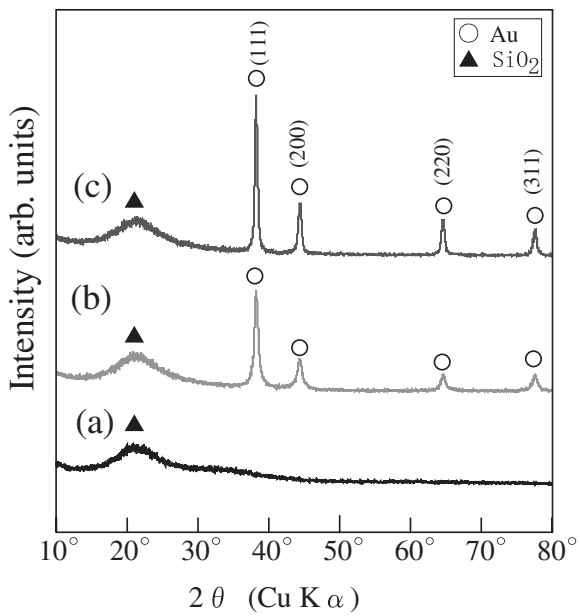

Fig. 2 XRD patterns of the Au/SiO_2 thin films containing 37 vol% Au. As-deposited (a) and heat-treated for 1 h at 700°C (b) and at 900°C (c).

3. Results and Discussion

Figure 1 shows the total volume fraction of Au in the Au/SiO_2 multilayer films as a function of total Au deposition time. The Au content increased from 3 to 65 vol%, as the total Au deposition time increased. The as-deposited Au/SiO_2 multilayers showed a light brown color and became deeper brown with increasing Au content. After heat treatments above 500°C for 1 h, a ruby-like color was observed.

Figure 2 shows the XRD patterns of the as-deposited Au/SiO_2 film containing 37 vol% Au and those heat treated at 700 and 900°C for 1 h. In the as-deposited film (a), since the mean diameter of Au particle was less than 8 nm,[17] no diffraction peak was observed except the typical halo pattern of SiO_2 glass around 22°. After the heat treatment at 700°C for 1 h, four diffraction peaks were observed at 38.1°, 44.4°, 64.6° and 77.6°, corresponding to (111), (200), (220) and (311) refections of the Au phase, respectively. Those peaks became stronger and sharper with increasing heat treatment temperature due to the increase in the size of Au particles. The calculated Au particle sizes by the Scherrer's equation were 17 and 21 nm after the heat treatment at 700 and 900°C, respectively. Figure 3 showed the relationship between Au content and the calculated mean diameter of Au particles for the Au/SiO_2 thin film containing various Au content after the heat treatment at 900°C for 1 h. The mean diameters of Au particles increased with increasing Au content from 10 to 30 nm.

Figure 4 shows the nano-structure of the Au/SiO_2 thin film containing 37 vol% Au before and after the heat treatment at 900°C for 1 h. The in-plane and cross-sectional TEM micrographs showed that the nano-structure changed with a significant grain growth of Au particles after the heat treatment. The mean diameter of Au particles in the as-deposited film was 8 nm (Fig. 4a, b). Since the deposition time for one SiO_2 layer was 60 s and then the thickness of each SiO_2 layer was too thin, no layer-by-layer structure was observed in the as-deposited films. When the Au/SiO_2 thin film was heat treated at 900°C for 1 h, the Au particles became significantly large, resulting in an Au-particle-aggregated microstructure in SiO_2 matrix. The sizes of the Au particles ranged from 10 to 60 nm (Fig. 4c, d). The mean

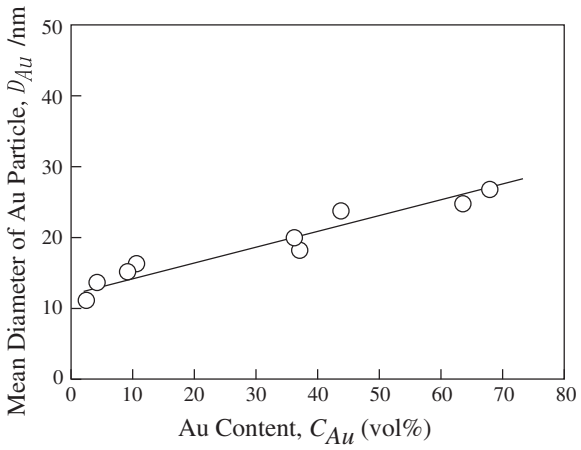

Fig. 3 Relationship between Au content and the mean diameter of Au particle for the Au/SiO_2 thin films heat-treated at 900°C for 1.

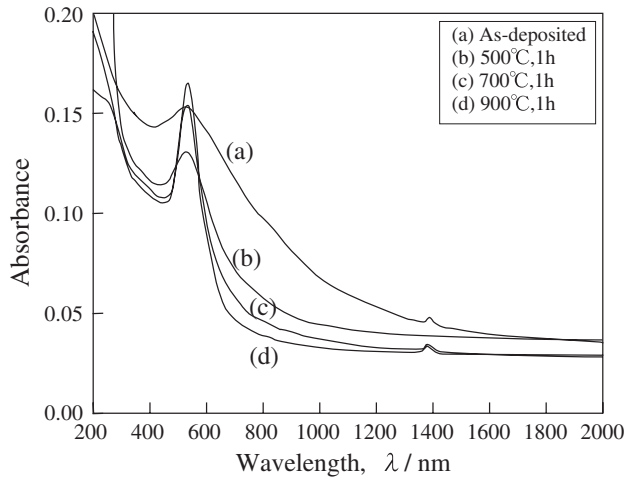

Fig. 5 Optical absorption spectra of Au/SiO_2 thin films containing 3 vol% Au. As-deposited (a) and heat-treated for 1 h at 500°C (b), at 700°C (c) and at 900°C (d).

diameters of the Au particle after the heat treatment estimated from TEM micrographs were almost in agreement with those calculated from the Scherrer's equation.

Figures 5 and 6 show the optical absorption spectra before and after the heat treatments for the Au/SiO_2 thin films with 3 and 37 vol% Au, respectively. The as-deposited film of 3 vol% Au showed a broad absorption peak at the wavelength of 560 nm. The peak became sharper with increasing the heat-treatment temperature. The Au/SiO_2 thin films of 37 vol% Au showed the similar tendency, although no peak was observed in the as-deposited film. The improvement of the absorption properties could be attributed to the growth of the Au particles with increasing the heat-treatment temperature.[13,14]

Figures 7 and 8 compare the optical absorption spectra of the Au/SiO_2 thin films before and after the heat-treatment at 900°C for 1 h. The as-deposited Au/SiO_2 films containing 5 to 10 vol% Au showed a small optical absorption peak at the wavelength of 560 nm, whereas the absorption peak disappeared for the films of Au content more than 12 vol%. The mean diameter of Au particles in the as-deposited films was always less than 8 nm regardless of the Au content, and the

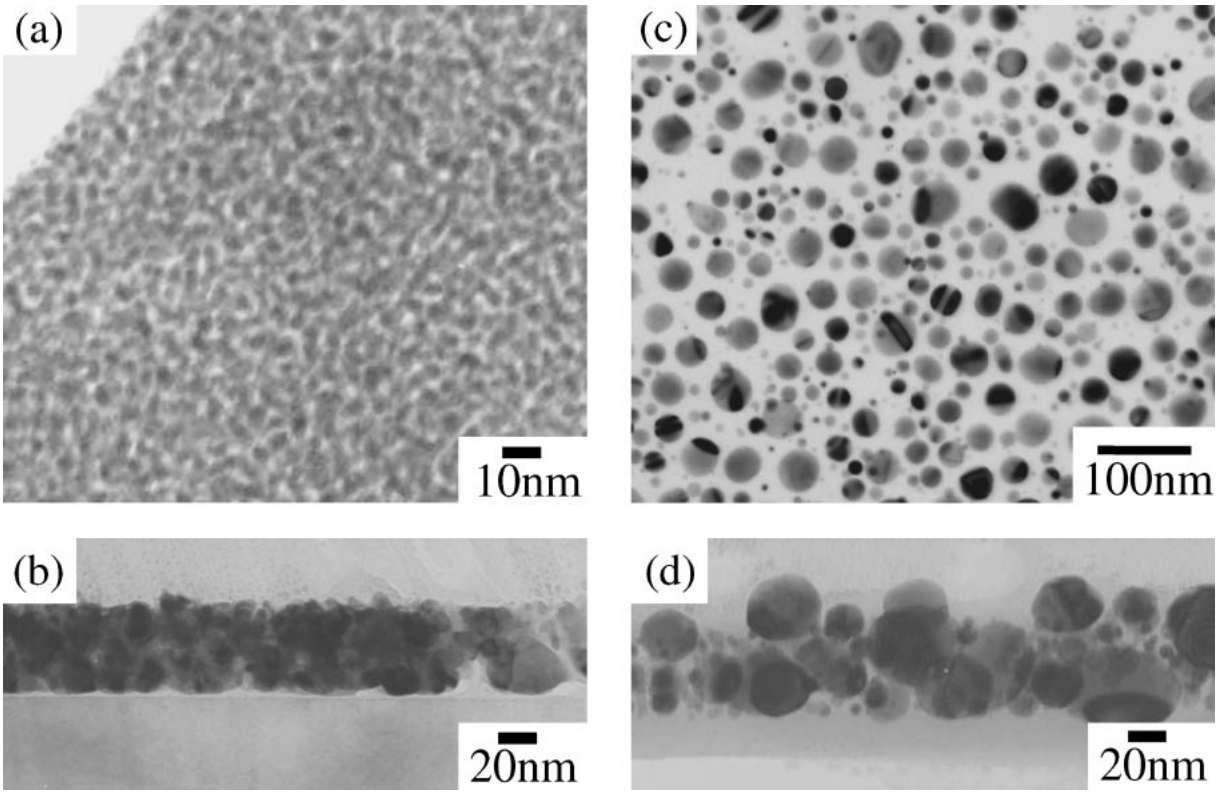

Fig. 4 TEM micrographs of Au/SiO_2 thin films containing 37 vol% Au. (a) and (b): as deposited, (c) and (d): heat-treated at 900°C for 1 h. (a) and (c): in-plane, (b) and (d): cross-section.

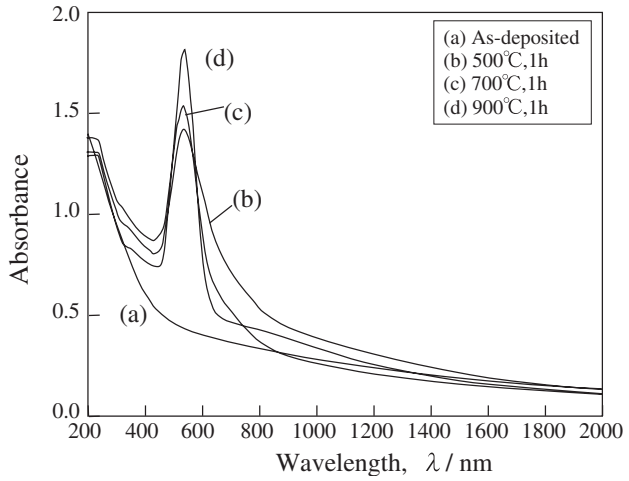

Fig. 6 Optical absorption spectra of Au/SiO_2 thin films containing 37 vol% Au. As-deposited (a) and heat-treated for 1 h at 500°C (b), at 700°C (c) and at 900°C (d).

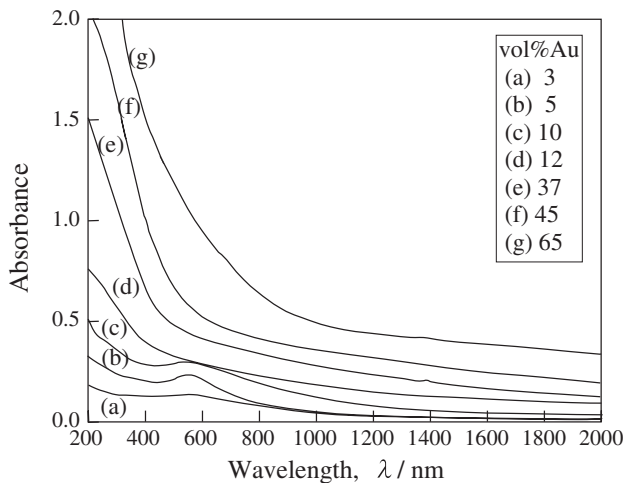

Fig. 7 Optical absorption spectra of the as-deposited Au/SiO_2 thin films.

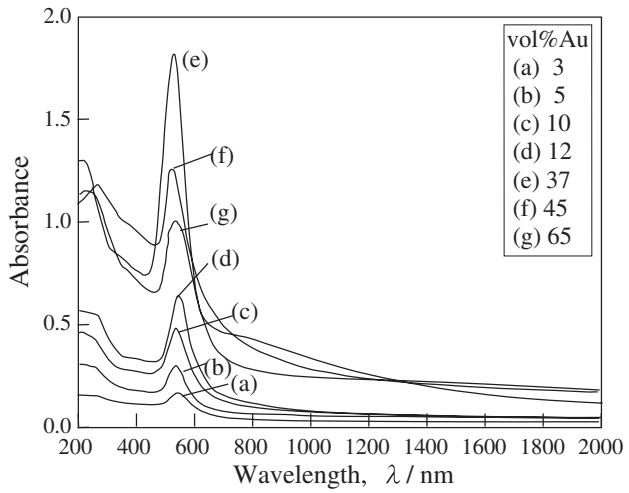

Fig. 8 Optical absorption spectra of the Au/SiO_2 thin films after the heat treatment at 900°C for 1 h.

films containing the Au content less than 12 vol% showed a layer-by-layer structure.[17] The increase in Au content reduced the distance between the Au layers, *i.e.*, the thickness of SiO_2 layer. For the as-deposited Au/SiO_2 film containing 5 to 10 vol% Au, there should be no change of the absorption peak positions, and the intensity of the absorption peak would increase with increasing Au content. When the Au content was more than 12 vol% by increasing the number of Au and SiO_2 layers, the Au particles between the SiO_2 layers were connected. Therefore, the layer-by-layer structure was not constructed for the as-deposited Au/SiO_2 thin films containing Au more than 37 vol% as shown in Fig. 4(b). Since the surface plasmon resonance occurs only in the composite films containing dispersed metal particles, the absorption peak disappeared for the as-deposited films containing more than 12 vol% Au.

When the as-deposited films with 37 vol% Au were heat-treated at 900°C for 1 h, the mean diameter of Au particle increased to 20 nm and consequently the Au particles were dispersed separately in the SiO_2 matrix as shown Figs. 4(c) and (d). The change from the network structure to the Au particle-dispersed structure by the heat-treatment has caused the improvement of absorption peaks. All the heat-treated films showed the absorption peaks at the wavelength of 540 to 560 nm as shown in Fig. 8. The intensity of the absorption peak increased with increasing Au content up to 37 vol%, whereas the intensity of the absorption peak decreased as the Au content was increased more than 45 vol%. The decrease in the intensity of the optical absorption peaks at the high Au contents must be due to the residual presence of connected Au.

Liao *et al.*[16] have prepared Au/SiO_2 composite films with Au contents from 4 to 74 vol% using multitarget magnetron sputtering and reported the maximum intensity of the optical absorption peak at 40 vol% Au for the heat-treated Au/SiO_2 films. The maximum intensity of the optical absorption peak in the present work was comparable with that reported, although the thickness of our film was about half of theirs. A trough absorption around the wavelength of about 500 nm was observed in their film instead of the absorption peak when the Au content was higher than 63 vol% Au. Therefore, absorption properties of the high Au containing films in the present study could be preferable to their films.

4. Conclusions

Au/SiO_2 multilayer composite films with 3 to 65 vol% Au were prepared by induction-coil-coupled plasma sputtering and heat treated to investigate. The heat-treatment caused the growth of Au particles, resulting the change of nano-structure from connection to dispersion of Au particles in the SiO_2 matrix. The optical absorption properties of the heat-treated films were greatly improved as compared with those of as-deposited films. The Au/SiO_2 films containing 3 to 65 vol% Au showed the significant absorption peaks at the wavelength of 540 to 560 nm after the heat-treatment at 900°C for 1 h, while no absorption peak was observed in the as-deposited films with more than 12 vol% Au.

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