Preparation of Au/SiO₂ Nano-Composite Multilayers by Helicon Plasma Sputtering and Their Optical Properties

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Au/SiO₂ nano-composite multilayers were prepared by helicon plasma sputtering. The Au particles dispersed in the SiO₂ matrix grew with increasing deposition time in the initial time less than 10 s, then changed from network-like to film-like microstructure with increasing deposition time. The optimum deposition time for preparing the Au particles was 8 s, and the size of Au particles was about 6 to 8 nm. The absorption peak due to the surface plasmon resonance of Au particles was observed at the wavelength of 560 nm in the optical absorption spectra for the as-deposited Au/SiO₂ thin films containing 3.3 to 10.3 vol% Au. The intensity of the absorption peak increased with increasing Au content, and the optimum Au content was about 10.3 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 due to nonlinear optical properties. The significant optical nonlinearity is resulted from the surface plasmon resonance (SPR) of metal particles, and the SPR effect yields the absorption peak in the optical absorption spectra. The volume fraction and microstructure of the dispersed metal particles strongly affect the optical absorption of composite thin films containing dispersed metal particles and glass matrix.

The fabrication technique of nonlinear optical thin films should be appropriately selected to adapt device performance requirements. A variety of techniques including melt quenching,^{1,2)} ion implantation,³⁻⁵⁾ sol-gel⁶⁻¹¹⁾ and sputtering¹²⁻¹⁶⁾ have been employed to fabricate metal/glasses composite thin films. However, it is difficult to control the concentrations of metal particles using quenching, ion implantation and sol-gel methods. Due to the different sputtering rates between metals and glasses, the ordinary sputtering method using a single target would be also difficult to increase metal contents in thin films. Recently, a helicon plasma sputtering method has received considerable attention for the fabrication of high quality optical thin films,¹⁷⁾ because of its highly precise controllability in deposition rates and the low plasma damage for film surface. In this method, the deposition rates of various targets can be controlled independently using shutters placed in the front of the targets, and then we have successfully prepared TiO₂/SiO₂ multilayer optical filters with graded refractive index profiles.¹⁸⁾ Hence, the helicon plasma sputtering is expected as a powerful method to control the concentration and the size of metal particles.

In the present study, the Au/SiO₂ nano-composite multilayers with various compositions were prepared using helicon plasma sputtering. In order to obtain excellent optical absorption properties, the film structure was optimized by controlling the concentration, size and shape of Au particles.

2. Experimental Procedure

Au/SiO₂ nano-composite multilayers schematically shown in Fig. 1 were prepared using a helicon plasma sputtering system (ULVAC, MB95-1010). This sputtering system utilizes a pair of helicon cathodes described elsewhere.¹⁷⁾ The induction coils and target magnetron cathodes were excited at the radio frequency (rf) of 13.56 MHz in combination with a magnetic field produced by an Sm-Co magnet placed below the target. Au (99.99%, ϕ 50 mm) and SiO₂ (99.99%, ϕ 50 mm) targets placed on a copper backing plate were installed in the helicon cathodes. The deposition rates of Au and SiO₂ layers were controlled independently using a shutter in front of the targets. Au and SiO₂ layers were deposited alternately on quartz or silicon wafer substrates. The distance between target and substrate was held constant at 180 mm. The sputtering chamber was initially pumped down to a base pressure of 5×10^{-4} Pa, then argon and oxygen gases were introduced up to the working pressure of 1.6×10^{-1} Pa. Oxygen gas was fed into the chamber in an active ionic state by a radical gun with rf magnetron, and was maintained at 5.8×10^{-8} m³/s with rf power of 50 W. The flow rates of argon gas in two cathodes were kept at 8.3×10^{-8} m³/s. During the deposition of Au/SiO₂ thin films, the rf power of the target was controlled

Fig. 1 Schematic diagram of Au/SiO₂ nano-composite multilayer.

as the same as the power of the rf-induction coil of the cathode. The rf power of 50 W and 50 to 200 W were applied to Au and SiO₂ targets, respectively.

Transmission electron microscopy (TEM) (JEOL, JEM-2000EX II) was employed to investigate the microstructure of the Au/SiO₂ thin films. The composition of specimens was determined by energy dispersion X-ray (EDX) spectrometer (JEOL, TN-5500) attached to the TEM. Thin specimens were prepared for plan-view and cross-sectional TEM observations. The thin specimens for the cross-sectional TEM observation were prepared by bonding two films facing each surface, and then cut and ground followed by mechanical dimpling, and finally ion-milling until to perforation. All ion-milling was performed on a liquid-nitrogen cooled stage using 6 kV argon ions with a incident angle at 12°. The in-plane observation was directly performed using a thin film deposited on a NaCl substrate, in which the thin film was separated from the substrate and attached onto the meshed copper grids in de-ionized water.

Optical absorption spectra were measured in the range of 200 to 2500 nm by a spectrometer at room temperature. The film thickness was measured by a surface profiler (Talystep).

3. Results

Figure 2 shows TEM dark field images and the selected area electron diffraction patterns of an Au layer which is sandwiched between SiO₂ layer. The deposition time of the SiO₂/Au/SiO₂ thin films deposited on NaCl substrates was changed from 5 to 15 s, while the SiO₂ layers were deposited for 300 s. As shown in the dark field images, Au particles dispersed uniformly in the SiO₂ matrix. With increasing the deposition time of the Au layer, Au particles became larger in size and the number also increased, corresponding to the increase in the diffraction intensity of Au.

Figure 3 compares the microstructure change of Au particles with different deposition times. The Au particles in the film deposited for 5 s were nearly circular with 3 to 5 nm in diameter and uniformly dispersed in the matrix. At the deposition time of 10 s, the Au particles grew to 6 to 9 nm, showing a network-like microstructure. No obvious change in the size of the Au particles was observed in the films deposited for more than 10 s; however, the Au layer showed a film-like microstructure. Consequently, the deposition time of one single Au layer should be within 10 s to disperse Au particles

Fig. 2 TEM micrographs and the selected area electron diffraction patterns of SiO₂/Au/SiO₂ thin films deposited on NaCl substrates for 5 s (a), 10 s (b) and 15 s (c).

Fig. 3 TEM micrographs of SiO₂/Au/SiO₂ thin films deposited on NaCl substrates for 5 s (a), 10 s (b) and 15 s (c).

Fig. 4 Effect of rf power on the deposition rate of SiO₂.

uniformly in the SiO₂ matrix.

Figure 4 shows the effect of rf power on the deposition rate of SiO₂ matrix. The deposition rate of SiO₂ increased with increasing the rf power to the SiO₂ target and the coil, being 0.017 nm/s at the greatest rf power (200 W). The following two conditions should be needed to prepare the Au/SiO₂ nano-composite multilayers in which Au particles disperse uniformly in the SiO₂ matrix. (i) The deposition time of one Au layer should be shorter than 10 s at 50 W (rf power), and (ii) the thickness of one SiO₂ layer should be larger than the diameters of Au particles. For example, the diameter of Au particles dispersed in the SiO₂ matrix was 6 to 9 nm when the deposition time for one Au layer was 8 s. The deposition time for SiO₂ at 200 W should be longer than 600 s to obtain one SiO₂ layer in 10 nm thickness.

The Au/SiO₂ nano-composite multilayers were prepared by alternatively depositing Au and SiO₂ layers for 5 times, in which each SiO₂ layer was deposited for 600 s at 200 W, and each Au layer for x s ($x = 2$ to 10) at 50 W. Hereafter, the Au/SiO₂ nano-composite multilayers were denoted as $[\text{Au}_{(x)}\text{SiO}_{2(600)}] \times z$. The footnotes (x and y) express the deposition times for one Au and SiO₂ layers, respectively, and z is the number of Au or SiO₂ layers. Figure 5 shows the volume fraction of Au in the $[\text{Au}_{(x)}\text{SiO}_{2(600)}] \times 5$ multilayers. The Au content increased with increasing the deposition time for one Au layer, being 0.7, 2.1, 3.5 and 5.3 vol% Au when the Au layer was deposited for 2, 5, 8 and 10 s, respectively. The thicknesses of the multilayers were all about 55 to 60 nm.

Figure 6 shows the optical absorption spectra of the $[\text{Au}_{(x)}\text{SiO}_{2(600)}] \times 5$ multilayers. No absorption peak was observed in the spectrum for the film $x = 2$ (Fig. 6(a)) due to too small Au content (0.7 vol%). When the Au layers were deposited for 5 s, the thin film $x = 5$ (Fig. 6(b)) showed a weak shoulder at the wavelength of about 600 nm. The absorption peak was observed clearly at the wavelength of 560 nm for the thin film $x = 8$ (Fig. 6(c)). When the deposition time of one Au layer was further increased to 10 s, the thin film $x = 10$ (Fig. 6(d)) showed a high absorption over broad wavelength range due to the formation of network-like microstructure of Au particles as shown in Fig. 2(c).

Figure 7 shows the TEM micrographs of the $[\text{Au}_{(8)}\text{SiO}_{2(600)}]$

Fig. 5 Au content in the $[\text{Au}_{(x)}\text{SiO}_{2(600)}] \times 5$ multilayers as a function of the deposition time for one Au layer. Fig. 6 Optical absorption spectra of $[\text{Au}_{(x)}\text{SiO}_{2(600)}] \times 5$ multilayers. (a) $x = 2$, (b) $x = 5$, (c) $x = 8$ and (d) $x = 10$.

$\times 5$ multilayer. The cross-sectional TEM image in Fig. 7(b) shows the layer-by-layer microstructure of Au and SiO₂ with five layers. The thicknesses of the Au and SiO₂ layers were about 6 and 7 nm, respectively. The total thickness of the $[\text{Au}_{(8)}\text{SiO}_{2(600)}] \times 5$ multilayer was about 60 nm. As shown in Fig. 7(a), Au particles were dispersed uniformly with the diameter of 6 to 8 nm. The optimum deposition time for one Au layer was found to be 8 s at 50 W to obtain the optical thin films with high absorption properties.

In order to increase the Au content in the thin film, the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ ($z = 5, 10, 20, 25$) multilayers were prepared. The number of Au/SiO₂ stacking layers were increased from 5 to 25, in which the total deposition time for SiO₂ was constant (3000 s), and the deposition time of one Au layer was fixed at 8 s. The thickness of the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ ($z = 5, 10, 20, 25$) multilayers was measured to be 60 to 100 nm. Figure 8 shows the volume fraction of Au in the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers as a function of the total deposition time of Au. The Au content increased with increasing the total deposition time of Au, being 3.3, 5.3, 10.3 and 11.6 vol% Au for the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ ($z = 5, 10, 20, 25$) multilayers, respectively.

Figure 9 shows the optical absorption spectra of the

Fig. 7 TEM micrographs of the $[\text{Au}_{(8)}\text{SiO}_{2(600)}] \times 5$ multilayer deposited on Si substrate. (a) Lateral image and (b) Cross-sectional image.

Fig. 8 Au content in the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers as a function of the total deposition time of Au.

$[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers deposited alternatively for different times of Au and SiO_2 layers, in which total deposition time for the SiO_2 layer was 3000 s, and for the Au layer 8 s. The absorption peak due to the surface plasmon resonance of Au particles was observed slightly at the wavelength of 560 nm for the thin film $z = 5$ (Fig. 9(a)). The intensity of the absorption peak at the wavelength of 560 nm increased with increasing Au and SiO_2 layers, while no obvious change in the peak position. The absorption peak disappeared for the thin film $z = 25$ (Fig. 9(d)). This fact indicates that the optimum layer structure for the as-deposited thin films showing absorption peak with high intensity is $[\text{Au}_{(8)}\text{SiO}_{2(150)}] \times 20$ containing 10.3 vol% Au.

Figure 10 shows the TEM micrographs of the

Fig. 9 Optical absorption spectra of the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers. (a) $z = 5$, (b) $z = 10$, (c) $z = 20$ and (d) $z = 25$.

$[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers, $z = 10$ to 25. Since the deposition time of one Au layer was always fixed at 8 s, the diameters of Au particles were almost constant, 6 to 8 nm. Au particles dispersed uniformly in the SiO_2 matrix for all the films, while the number of the Au particle increased with increasing the number of the Au layers.

4. Discussion

P. Brault *et al.*¹⁹⁾ has investigated the nucleation and initial growth of platinum films deposited on an amorphous carbon membrane surface by plasma sputtering. They found that nano-particles nucleated homogeneously on the substrate as a first step, then grew with prolonging the deposition time. When the amount of the enlarged particles reached a density limit, a coalescence process by connecting the neighboring particles began to occur until to the formation of the thin film. Similar nucleation, growth and coalescence of the Au particles were also observed in the present Au/ SiO_2 thin films as shown in Fig. 3.

Au/ SiO_2 thin films have been prepared by several methods such as ion implantation,^{3,5)} sol-gel^{6–11)} and sputtering.^{14–16)} Generally, the heat-treatment after deposition of films was necessary to obtain the optical absorption characteristics. Tanahashi *et al.*,¹⁴⁾ however, reported that the absorption peak was observed in the 860 nm-thick Au/ SiO_2 films prepared by sputtering without heat treatment. In the present work, the as-deposited Au/ SiO_2 multilayers containing 3.3 to 10.3 vol% Au showed the optical absorption peak (Fig. 9), even though the thickness of films was significantly small, 60 to 100 nm. As shown in Figs. 7 and 10, those as-deposited multilayers showed the isolated dispersion of Au particle in 6 to 8 nm diameter in the SiO_2 matrix without connecting. The connecting of the Au particles would decrease the surface area of the Au particles. The uniform and isolated dispersion of Au particle may be responsible to the high absorption property due to the high surface area of the Au particle in the SiO_2 matrix.

It was reported that the absorption peak wavelength shifts toward longer wavelengths with increasing average particle diameters, irrespective of the particle concentration in the Au/ SiO_2 thin film.^{4,8,11,12)} In the present work, no

Fig. 10 TEM micrographs of the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers. (a) $z = 10$, (b) $z = 20$ and (c) $z = 25$.

obvious change in the absorption peak position for the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ multilayers were observed as shown in Fig. 9. Although the distance between the Au layers changed depending on z , the diameter of Au particles was always constant (Fig. 10). The intensity of the absorption peak increased with increasing the Au content as shown in Fig. 9. This is in agreement with the general trend,^{5,6,15) i.e.}, the optical absorption is in proportion to the surface area of the Au particles since the surface plasmon resonance (SPR) of metal particle is responsible to the optical absorption properties. If the Au particles between the SiO₂ layers have connected with increasing the number of Au and SiO₂ layers, the absorption peak would have disappeared. The Au particles must have connected in the $[\text{Au}_{(8)}\text{SiO}_{2(120)}] \times 25$ multilayer, because the absorption peak was disappeared as shown in Fig. 9(d).

It is known that the size of Au particle could be enlarged by heat-treatment rather than by controlling the preparing process. Tanahashi *et al.*¹⁴⁾ observed the growth of Au particles in the Au/SiO₂ thin films after heat-treatment. They found that the absorption at the peak of the wavelength around 530 nm increased and the full width at half-maximum (FWHM) of the absorption peak decreased with increasing the mean diameter of Au particles. This would yield the enhancement of the third-order nonlinear susceptibility ($\chi^{(3)}$). In the present study, the Au particles dispersed uniformly with high density in the SiO₂ matrix, and the diameter of the Au particles was always constant in the Au/SiO₂ nano-composite multilayers, typically smaller than 8 nm. We found that the optical absorption properties of the as-deposited Au/SiO₂ nano-composite multilayers were greatly improved by heat-treatment. The effect of heat-treatment on the absorption properties will be reported elsewhere.

5. Conclusions

Au/SiO₂ nano-composite thin films with multilayer structure were prepared by helicon plasma sputtering. The nanostructure and the composition of the Au/SiO₂ multilayers were controlled by changing deposition conditions. When the deposition time was shorter than 10 s, Au particles dispersed uniformly in the SiO₂ matrix, and the size of the Au particles

increased with increasing the deposition time of one Au layer. No further growth of the Au particles occurred by prolonging the deposition time of one Au layer, while the microstructure of the Au layers in the matrix changed from network-like to film-like microstructure. The optimum deposition time for preparing one Au layer was 8 s at rf power of 50 W, in which the diameter of Au particles was 6 to 8 nm. The absorption peak due to the surface plasmon resonance of Au particles was observed at the wavelength of 560 nm for the $[\text{Au}_{(8)}\text{SiO}_{2(3000/z)}] \times z$ ($z = 5$ to 20) thin films. The intensity of the absorption peak increased with increasing Au contents, and the optimum Au content was about 10.31 vol%.

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