Surface plasmon resonance from self-assembled Ag nanodots prepared by one-step pulsed laser deposition

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Self-assembled Ag nanodots in vitreous matrix were prepared on various substrates, e.g. Si(100), glass, or copper microgrid by one-step pulsed laser deposition (PLD). A 266nm beam from Nd:YAG laser was irradiated on the target comprising mechanically activated mixtures of Ag and matrix sources. Microstructure of the thin film containing assembled Ag nanodots was characterized in detail. Intensity and peak width of the surface plasmon resonance at around 400nm depend sensitively on the operational condition of PLD, e.g. gas species (N_2 or Ar) and pressure (between 5mPa and 1kPa) in the chamber. The relationship between dots assemblage and surface plasmon resonance spectra was discussed in terms of the geometry of the nanodots, and physical and chemical properties of the deposited film. Optimization of operational condition given above, and target preparation for controlled dot assembly, and hence sharp and strong plasmon resonance was explored.
Key words: Surface plasmon resonance, Ag, nanodot, Pulsed laser deposition

1. INTRODUCTION

When we embed metal nano crystals in a dielectric matrix, the resultant nano-composite exhibits surface plasmon resonance (SPR) absorption. The composite is also applied to non-linear optical devices [1,2]. These composites are conventionally synthesized either by quenching and heat treatments, sol-gel processes [3], sputtering [4], or by ion implantation [5]. Most of these techniques are multi-step and often needs post-treatment to optimize the properties.

In this paper, we present a method of preparing nano-composite films comprising metal Ag nanodots embedded in glass matrix by one-step pulsed laser deposition (PLD) from an Ag-glass mixed target. We then evaluate the structural and optical properties of the composite thin film obtained by systematically varying the conditions for target preparation and PLD deposition to optimize the SPR properties.

2. EXPERIMENTAL

Ag-glass target was prepared from Ag powder (KANTO CHEMICAL, Co., Inc.) and glass frit CY: SiO_2-Al_2O_3-B_2O_3-CaO-Na_2O-K_2O (NIPPON FRIT CO., LTD) or borax (BO : $Na_2B_4O_7$ (KANTO CHEMICAL, Co., Inc.)). The mixtures were mechanically activated by a multi-ring mill (MICROS®, Nara Machinery, Co., Ltd) for 2h. The milled products were pressed into a pellet at 97.7MPa and heated in N_2-4%H_2 atmosphere. Sample name and preparation condition was summarized in Table I.

The film deposition was carried out under nitrogen atmosphere between 0.005Pa and 1000Pa by using a Nd:YAG laser (BM Industries). The wavelength was 266nm, frequency 10Hz, pulse duration 10ns, and the output power was 100mJ/pulse. Distance from target to substrate (d_{TS}) was 100mm. Deposition time was varied from 3min to 60min. Either Si(100) or cover glass was used as a substrate. Morphology of the film was analyzed by a transmission electron microscope (TEM; Philips, TECNAI F20). Specimens were deposited on the Cu-based micro-grid for the purpose of TEM observation. Crystallographical properties of a thin film were examined by an X-ray diffractometer (Rigaku, RAD) with an incident angle $0.5°$. Optical property of the composite was measured by UV-Vis spectrometer (JASCO, V-550).

Table I   Target preparation condition

Target	Ag volume Fraction(%)	MICROS (rpm, h)	Heating (temp, h)
Ag15CY	15	1000, 2	600, 1
Ag30CY-1	30	800, 1	400, 1
Ag30CY-2	30	1000, 2	600, 3
Ag30CY-3	30	1800, 2	600, 3
Ag30BO	30	1000, 2	500, 3

3. RESULTS

Microstructure of the prepared thin film was analyzed by TEM. As shown in Fig. 1, well-dispersed nanodots with their diameter 16 ± 3.9nm in the amorphous matrix was observed. We also observed the fringe pattern with the line spacing about 0.238nm corresponding to Ag(111). From XRD profiles of the Ag15CY target, we observed Ag(111) and Ag(200) diffraction peaks, as shown in Fig. 2. The interplanar spacing of Ag(111) is 0.236nm from XRD, in accordance with the line spacing

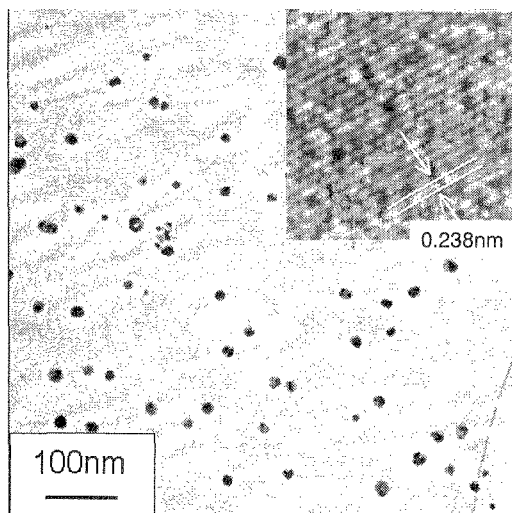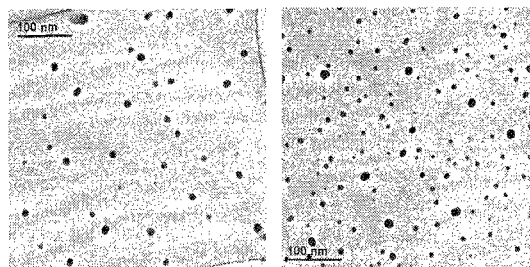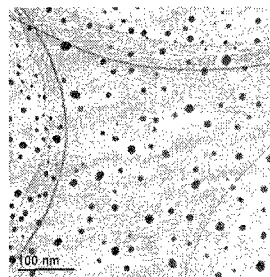we observed by TEM. We therefore conclude that the nanodots observed in TEM comprise crystalline Ag metal.

Fig. 1   TEM images of Ag15CY thin film
(Ar 100Pa 3min)

(a) Ag30CY-1F   (b) Ag30CY-2F

(c) Ag30CY-3F

Fig. 3   TEM images of Ag30CY thin film
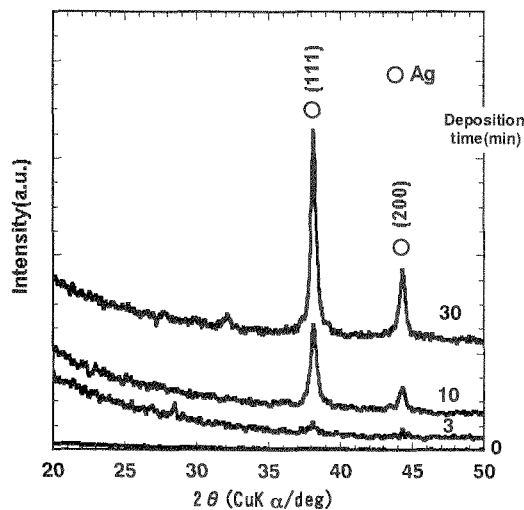(N$_2$ 0.05Pa 3min)

Fig. 2   Thin film XRD profiles of Ag15CY thin film
(Ar 100Pa 3min)

Table II   Dot size distribution of the samples

	dot size(nm)	dot number (μ m^{-2})	Area ratio R$_A$
Ag30CY-1F	12.6±2.5	164	0.02
Ag30CY-2F	10.0±3.2	551	0.043
Ag30CY-3F	11.2±2.8	613	0.065

amount of debris formed.

Optical properties of the films deposited for 30min were measured by UV-Vis spectra. In Fig. 4, we observe two absorption peaks at 454 and 590nm from Ag30CY-1F. The peak at the shorter wavelength is attributed to the SPR of Ag nanodots, while those at 590nm to the Ag thin film [6]. The second peak appeared due to the film inhomogeneity to allow continuous Ag film formation.

In Ag30CY-2F and 3F, the absorption peak is observed at 436nm. The shape of the peak in Ag30CY-2F is much sharper and stronger than in Ag30CY-3F, although the microstructures of the two samples are similar. It is therefore clear that the optical property of this kind of composites is determined not only by the microstructure of the composites, but also by the dielectric environment of interface between Ag nanodots and matrix.

Effects of N$_2$ pressure on the dot size and assembly are demonstrated in Fig. 5. At 0.005Pa, bimodal nanodots are observed. Nanodots with their diameter ca 5nm were mainly generated, while those of about 15nm were also observed. When the pressure increases from 0.005Pa to 10Pa, dot size was increased up to 7.3± 2.7nm. We recognize that the dot size distribution

To examine the effect of target preparation condition, thin films were deposited under the same condition from three different targets, Ag30CY-1 to 3. Microstructures of the films were examined in Fig. 3. The variation of the dot size, dot number, and the area ratio R$_A$ was summarized in Table II. The relative area covered by the Ag dots, i.e. the fractional dot area, R$_A$, was determined from the transmission electron micrograph. In each sample, nanodots with their diameter about 10nm are observed. In Ag30CY-1F, however, the number of dots was far less than those in Ag30CY-2F and 3F, presumably due to the larger
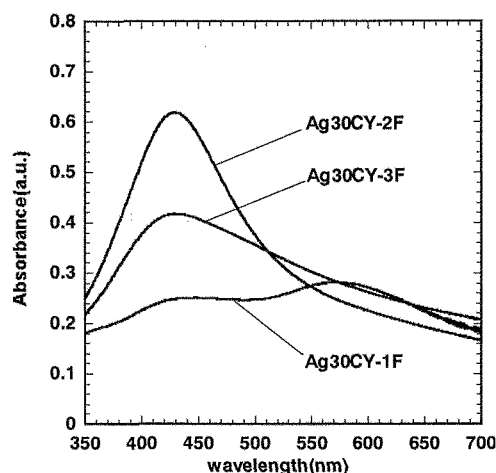
Fig. 4   UV-Vis spectra of Ag30CY thin film (N$_2$ 0.05Pa 30min)

becomes homogeneous. At 1000Pa, aggregation of nano-clusters ablated from the target and ambient gas occurred so that the thin film with monodispersity was destroyed.

Fig. 6 shows optical properties of the three samples. The numerical values are summarized in Table III, where α denotes the secondary derivative of the peak intensity. The larger α/I value, therefore, means a sharper SPR peak. As the deposition pressure decreased, the peak intensity increased. However, the value of α/I is larger at 10Pa than in 0.005Pa. At 0.005Pa, absorption spectra exhibit a long tail at the longer wavelength side. This is attributed to heterogeneity of Ag nanodots [7]. No absorption peak was observed on the sample prepared at 1000Pa, because of aggregation.

4. DISCUSSION

As shown in Fig. 4, SPR properties of the nanodot thin film is very sensitive to the condition of target preparation, even when the microstructure of the thin film is not too much different. The different SPR is, therefore, attributed to the properties invisible by TEM, e.g. difference in dielectric property of the matrix.

For SPR, the electric field induced by the incident light beam forces to oscillate the free electrons. As the movement of the electrons is restricted by the particle surface, all the free electrons will behave like a harmonic oscillator. In this study, Ag$^+$ exists at the interface between the Ag nanodots and the matrix. Due to the attractive force to Ag$^+$, the electron oscillation is suppressed. Higher Ag$^+$ concentration in the matrix is, therefore, unfavorable for SPR, as in the case of Ag30CY-3F.

As shown in Fig. 5, the film formed at 10Pa exhibits most homogeneous dot size distribution of the three films. At 0.005Pa, main dot size was smaller than in 10Pa. We observe, however, another Ag nanodot group as large as 15nm. Generally, smaller particles are obtained under the lower gaseous pressure. What we observed was just the opposite.

Two different influences of the increasing deposition pressure are conceivable in the present study, i.e., (1)
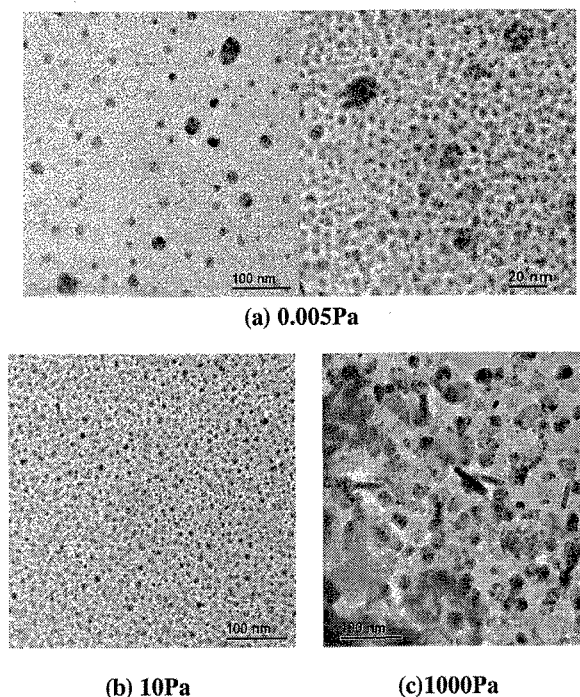

(a) 0.005Pa

(b) 10Pa   **(c)1000Pa**

Fig. 5   TEM images of Ag30BO Thin Film deposited at various N$_2$ pressure (deposition time 60min)
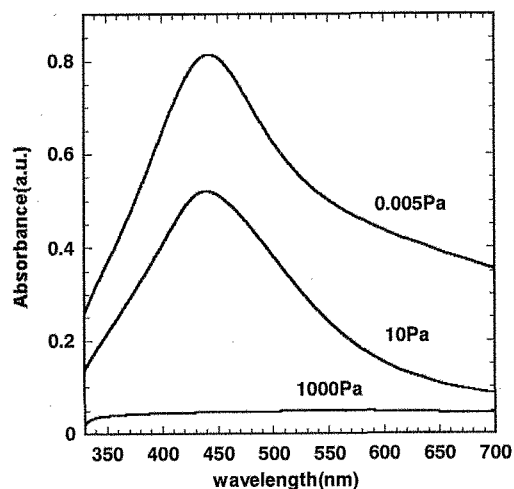

Fig. 6   UV-Vis spectra of Ag30BO thin film (N$_2$ 60min)

Table III   Numerical values of absorption spectra

Pressure (Pa)	Peak position(nm)	Peak intensity	α /I (-1×10^{-5})
0.005	443	0.814	28.1
10	440.5	0.520	31.5

increasing dot size as discussed above and (2) the increase in the electrical charges generated by the ionized gaseous species in the chamber. The charge is transferred to the clusters by collision. The coalescence of Ag nanodots in air or on the substrate is prevented by the electrostatic repulsive force. This was exerted by the surface charge deposited on the matrix species enveloping nano-dots.

At 0.005Pa, main dots are smaller than those prepared at 10Pa, since the collision frequency between the metallic species or dots and gas molecules is small enough. When the pressure increased up to 10Pa, the dot size increased by about 50%, but the dot size became uniform presumably because of the surface charge concentration is high enough.

The intensity of SPR resonance peak was larger for the film prepared at lower pressure, as shown in Fig. 6. Therefore, homogeneity of dot size does not play a significant role on the SPR peak intensity. Instead, the peak intensity becomes stronger when the number of Ag nano-dots increases. Under the same quantity of silver, the number of dots increases and peak intensity becomes larger when the dot size becomes smaller.

Blue shifts of SPR peak occur when the dot size becomes smaller. In order to fabricate composites with the sharp and strong absorption desirable for optical devices, we therefore pay effort primarily to minimize the dot size and narrower the size distribution.

The microstructure of Ag nanodots were compared with those obtained from a target with pure Ag. Significant coalescence is observed after 30min deposition, as shown in Fig. 7. As a consequence, we observe a broad SPR peak at around 600nm. Since the solid matrix does not exist, dots do not have any protection from coalescence.
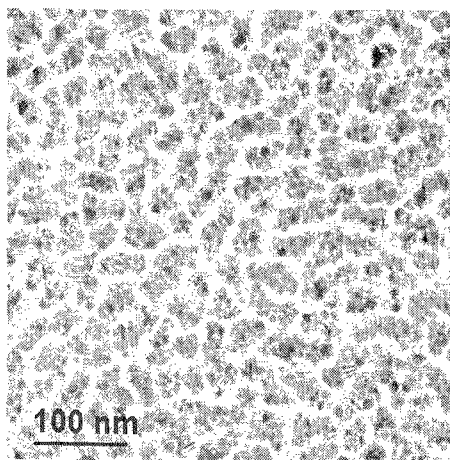
composite maintained its microstructure with well dispersed nano-dots even after prolonged deposition time. When the film is deposited under 0.005Pa, the dot size became bimodal and absorption peak intensity increased. When the deposition pressure is increased to 10Pa, the dot size increased and the size distribution became homogeneous. These changes were explained in terms of the two factors, i.e. the dot growth and inhibition of coalescence by increasing pressure.

6. REFERENCE

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Fig. 7 TEM image of Ag thin film (Ar 1Pa 30min)

5. SUMMARY

We prepared nanocomposite films comprising metal Ag nanodots embedded in a glass matrix by one-step pulsed laser deposition from an Ag-glass mixed target. By changing the target preparation condition, we observed sharpest and greatest peak in Ag30CY-2F, milled by MICROS for 1000rpm for 2h. Glass matrix prevented Ag nanodots from coalescence, and the