Optical Properties of Au Nanoparticle Dispersed TiO$_2$ Films Prepared by Laser Ablation

Akihiko Ito*, Hiroshi Masumoto and Takashi Goto

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Au-nanoparticle dispersed TiO$_2$ (Au/TiO$_2$) films were prepared by laser ablation using Au-powder mixed TiO$_2$ (rutile) sintered targets. The Au content in the films was controlled in the range from 3 to 37 mol% by changing the target composition. As-deposited TiO$_2$ matrix of the films was amorphous-like anatase, and changed to a well-crystallized anatase phase after heat treatments at 1173 K. The diameters of Au nanoparticles increased from 1.5 to 4.1 nm with increasing the heat-treatment temperature from 573 to 1173 K. Optical absorption spectra by surface plasmon resonance from Au nanoparticles were observed in the heat-treated films. The red-shift of absorption peak from 590 to 635 nm was observed due to the increase in the diameter of Au nanoparticles and refractive index of TiO$_2$ matrix with increasing the heat-treatment temperature.

Table 1 Deposition parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser source</td>
<td>Nd:YAG (THG)</td>
</tr>
<tr>
<td>Repetition frequency</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Peak FWHM</td>
<td>4–6 nm</td>
</tr>
<tr>
<td>Energy density</td>
<td>$6.0 \times 10^4$ J/m$^2$</td>
</tr>
<tr>
<td>Substrate</td>
<td>Quartz glass, NaCl</td>
</tr>
<tr>
<td>Oxygen pressure</td>
<td>13 Pa</td>
</tr>
<tr>
<td>Target distance</td>
<td>60 mm</td>
</tr>
<tr>
<td>Substrate temp.</td>
<td>room temperature</td>
</tr>
</tbody>
</table>

(Received April 28, 2003; Accepted June 4, 2003)

Keywords: laser ablation, surface plasmon resonance, gold nanoparticle, titanium oxide, anatase, optical property

1. Introduction

Metal nanoparticle dispersed dielectric films can exhibit specific absorption in a visible-light range due to surface plasmon resonance between photons and electrons at the metal surface. The absorption depends on the plasma frequency of metals, nanoparticle sizes and refractive indexes of the dielectric matrix. These materials often have large third-order optical nonlinear susceptibilities which can be applied to control optical properties offering optical switching devices.

These composite (nanocomposite) films have been prepared by several methods including multi-target co-sputtering$^{[1-3]}$, alternative sputtering$^{[4]}$, sol-gel$^{[5-9]}$ and ion implantation.$^{[10]}$ On the other hand, laser ablation has an advantage to fabricate nanocomposites because a large amount of atom clusters or nanoparticles are synthesized during the ablation process.$^{[11]}$ Several metal nanoparticle dispersed films have been prepared by alternative ablation using double targets of a metal and a dielectric material.$^{[12-14]}$ However, no previous study has reported on the preparation of optical nonlinear films by laser ablation particularly using a single mixture target. Since the usage of the single target has advantageous to control the composition and microstructure of films, a photo-catalytic film was prepared by laser ablation using a single Pt–TiO$_2$ mixture target.$^{[15]}$

In this paper, Au-nanoparticle dispersed TiO$_2$ films were prepared by laser ablation using Au/TiO$_2$ sintered targets, and the relationship between microstructure and optical property was investigated.

2. Experimental Procedure

The experimental set-up was mainly consisted of a vacuum chamber and a laser system. Deposition parameters are listed in Table 1. A third harmonic wavelength (355 nm) of a Q-switch pulsed Nd:YAG laser at a repetition frequency of 10 Hz was used. The laser beam was introduced into the vacuum chamber at an angle of 45$^\circ$ through a quartz glass window with spherical lens and focused onto the target. The focal spot size was 2 mm in diameter and the power density was about $6 \times 10^4$ J/m$^2$.

Au powder (99.9% in purity, 10$\mu$m in dia.) and TiO$_2$ powder (rutile-phase, 99.99%, 1 to 2$\mu$m in dia.) were used for preparation of targets. These powders were weighed, mixed, pressed into pellets and sintered at 1373 to 1473 K for 7.2 ks. Au contents were varied from 0.5 to 60 mol%.

Au/TiO$_2$ films were deposited onto quartz and NaCl substrates at room temperature. The base pressure was $3.0 \times 10^{-7}$ Pa, and the deposition was carried out in an oxygen atmosphere at 13 Pa. The distance between target and substrate was 60 mm. The target and substrate stages were rotated at 5 rpm. The as-deposited specimens were heat-treated at 573 to 1173 K for 3.6 ks in air using a rapid thermal annealing furnace (RTA, ULBAC MILA-5730).

The crystal phase was studied by X-ray diffraction (XRD, Rigaku RAD-2C). The composition was examined by electron probe micro analysis (EPMA, JEOL JXA-8621MX) and transmission electron microscopy (TEM) attached with energy dispersive X-ray analysis (EDX, JEOL JEM2000FX). The microstructure was observed by TEM. The diameter and size distribution of Au particles was determined by TEM observation. The optical absorption spectra were measured in the range between 200 and 2500 nm using a ultraviolet (UV)-visible light (Vis) spectrophotometer (Shimadzu UV-3101PC). The refractive index at the
wavelength of 633 nm was studied by ellipsometry (Geartner L115B).

3. Results and Discussion

Figure 1 shows the XRD patterns of Au/TiO$_2$ films. As-deposited films showed a halo pattern from a quartz substrate. After heat treatments at 573 to 1173 K for 3.6 ks in air, the TiO$_2$ matrix was crystallized into an anatase phase. With increasing the heat-treatment temperature, the peaks of Au (cubic) became more significant due to the crystallization and the increase in diameter of Au nanoparticles. Broadening of the Au (111) peak could be yielded from overlapping with (004) and (112) peaks of TiO$_2$ (anatase).

Figure 2 shows the relationship between Au content in the target and that in the film analyzed by EPMA and TEM-EDX. The Au contents in the film were slightly smaller than those in the target, and increased linearly with increasing those in the target below 40 mol%.

Figure 3 shows the in-plane views of TEM micrographs and the diffraction patterns of Au/TiO$_2$ films. Broad Debye rings of the as-deposited film were assigned to Au (cubic) and TiO$_2$ (anatase). The size of Au particles increased with increasing the heat treatments from 873 to 1173 K. The diffraction spots from the crystallized Au and TiO$_2$ (anatase)
were clearly observed after the heat treatment at 1173 K. It is generally known that anatase TiO$_2$ would transform into rutile at 673 to 1273 K. However, the Au/TiO$_2$ films were crystallized to anatase after the heat treatment at 1173 K for 3.6 ks in air. Pal et al. reported that an anatase film 50 nm in thickness showed no phase change after a heat treatment at 1473 K. The phase transformation from anatase to rutile might be affected by thickness and microstructure probably due to stress between film and substrate and/or between TiO$_2$ matrix and Au particles. Further study should be needed to understand the phase transformation of TiO$_2$. Figure 4 shows the size distributions of Au nanoparticles measured by TEM observation. The mean diameter of Au nanoparticles in the Au/TiO$_2$ films increased from 1.3 to 4.1 nm with increasing the heat-treatment temperature. Figure 5 shows the wavelength dependence of absorbance for as-deposited and heat-treated Au/TiO$_2$ films (17 mol% Au). No absorption peak was observed in the as-deposited film. The absorption peak due to the surface plasmon resonance of Au nanoparticles was observed at a wavelength ($\lambda_{\text{SPR}}$) around 630 nm after the heat treatments. The $\lambda_{\text{SPR}}$ increased at most 40 nm and the peak height increased with increasing the heat-treatment temperature.

Table 2 summarizes previous reports on the preparation and several properties of Au/TiO$_2$ films. To date Au/TiO$_2$ films have been prepared by co-sputtering or sol-gel methods. Although Au/TiO$_2$ films with a wide range of Au content were obtained by co-sputtering, the relationship between Au size and optical properties has not been studied. In the Au/TiO$_2$ films by sol-gel, on the other hand, Au contents were not well-controlled; the sizes of Au particles were in a limited range between 10 and 30 nm, and therefore the $\lambda_{\text{SPR}}$ could not be varied in a wide wavelength range. The laser ablation used in this study has controlled the content and size of Au nanoparticles easily in a wide range.

The optical absorbance of the Au/TiO$_2$ films may be given by eq. (1).
\[ \alpha(\lambda) = \frac{18\pi n_{\text{TiO}_2}^3}{\lambda} \left( \epsilon'_{\text{Au}}^u + \frac{\epsilon''_{\text{Au}}^u}{(\epsilon'_{\text{Au}}^u + 2n_{\text{TiO}_2}^2)^2 + \epsilon''_{\text{Au}}^u} \right) \]  

(1)

where \( n_{\text{TiO}_2} \) is the refractive index of TiO\(_2\) matrix. \( \epsilon'_{\text{Au}} \) and \( \epsilon''_{\text{Au}} \) are the real and imaginary part of complex dielectric constant of Au nanoparticle (\( \epsilon_{\text{Au}} \)), respectively. The frequency (\( \omega \)) dependent of \( \epsilon_{\text{Au}} \) may be calculated from eq. (2).

\[ \epsilon_{\text{Au}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega \tau} + \epsilon_{\text{bound}}(\omega) \]  

(2)

where \( \epsilon_{\text{bound}} \) is the dielectric constant of bound electrons\(^{16}\). \( \omega_p \) and \( \omega \) are the plasma and the relaxation frequency represented by eqs. (3) and (4), respectively.

\[ \omega_p^2 = \frac{N e^4}{\varepsilon_0 m^*} \]  

(3)

\[ \omega = \frac{v_F}{d} \]  

(4)

where \( N \), \( e^* \) and \( \tau \) are the density, the effective mass and the mean relaxation time of free electrons, respectively. The \( v_F \) is the Fermi velocity and \( d \) is the diameter of Au nanoparticles.

The refractive index of TiO\(_2\) matrix increased from 2.43 to 2.55 with increasing the heat-treatment temperature from 573 to 1173 K. The heat treatment (annealing) may cause the decrease of oxide vacancy and the increase in crystallinity of TiO\(_2\) matrix. The diameter of Au nanoparticles increased from 1.5 to 4.1 nm by the heat treatments. The \( \lambda_{\text{SPR}} \) was calculated from eq. (1). Figure 6 depicts the effect of heat-treatment temperature on \( \lambda_{\text{SPR}} \) together with the diameter of Au nanoparticles and the refractive index of TiO\(_2\) matrix. The experimental values of \( \lambda_{\text{SPR}} \) were in good agreement with calculated values. The \( \lambda_{\text{SPR}} \) of the Au/TiO\(_2\) film (37 mol\%Au) after the heat treatments was around 630 to 675 nm. The trend how the \( \lambda_{\text{SPR}} \) changes with the heat-treatment temperature was different from that of the Au/TiO\(_2\) film (17 mol\%Au). The \( \lambda_{\text{SPR}} \) of the Au/TiO\(_2\) films (37 mol\%Au) heat-treated at 873 K increased from 630 to 675 nm (red-shift), whereas that heat-treated at 1173 K decreased from 675 to 635 nm (blue-shift), respectively. Figure 7 shows a TEM micrograph of the Au/TiO\(_2\) film (37 mol\%Au) heat-treated at 1173 K for 3.6 ks in air. The diameter of Au nanoparticles increased over 20 nm and agglomerated forming a number of elongated particles. The red-shift might be caused of the increase in the size of Au nanoparticles, while the blue-shift might be associated with the change of the shape of Au nanoparticles. Further study should be necessary to understand the shift of \( \lambda_{\text{SPR}} \) depending on the change of size and shape of Au nanoparticles.

4. Conclusion

Au nanoparticles dispersed TiO\(_2\) (Au/TiO\(_2\)) films were synthesized by laser ablation. The Au content was controlled from 3 to 37 mol\%Au by changing the composition of targets. The Au/TiO\(_2\) films without heat treatment consisted of Au nanoparticles 1.3 nm in diameter and amorphous-like anatase TiO\(_2\). After heat treatments, the TiO\(_2\) matrix was crystallized to anatase in a single phase. With increasing the heat-treatment temperature from 573 to 1173 K, the diameter of Au nanoparticles increased from 1.5 to 4.1 nm and the refractive index of TiO\(_2\) matrix from 2.43 to 2.55. The optical absorption due to the surface plasmon resonance was observed at the wavelength around 590 to 675 nm. The absorption peak positions shifted depending on heat-treatment conditions due to the increase in the diameter of Au nanoparticles and refractive index of TiO\(_2\) matrix.

Acknowledgments

This research was supported in part by a COE program at Institute for Materials Research, Tohoku University. The authors thanks Messrs Y. Murakami and S. Ito at Laboratory for Advanced Materials, Institute for Materials Research for EPMA analysis and TEM observation, respectively.
References