Titanium Oxide Thin Film Preparation by Pulsed Laser Deposition Method Using a Powder Target

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Titanium oxide thin films were prepared by a pulsed laser deposition method using a Ti powder material target. Atomic force microscopy images of the films appeared to be nearly same as those of films prepared using a Ti bulk target. X-ray diffraction and X-ray photoelectron spectroscopy measurements suggested that polycrystalline titanium dioxide (TiO₂) thin films can be prepared using a Ti powder target, and that their properties depend on substrate temperature and the argon and oxygen gas mixture. These results suggest that titanium oxide thin films can be prepared using a Ti powder target and their quality was almost the same as those of compared with the films prepared using a Ti bulk target.

Key words: Superfluid, Liquid helium, arc discharge, bubble, carbon nano material

1. INTRODUCTION

Physical vapor deposition (PVD) refers to a variety of well-known film deposition methods, and these deposition mechanisms have been thoroughly studied [1-11]. In particular, pulsed laser deposition (PLD) is a widely used technique for the deposition of thin films because of its advantages such as a simple system setup, operability under a wide range of deposition conditions, wider choice of materials offered, and higher instantaneous deposition rates. The PLD method uses a high power pulsed laser beam that is focused inside a vacuum chamber such that it strikes the target material. This method shows high reproducibility for the preparation of crystalline thin films. The versatility of the PLD method has enabled the development of various functional thin films, such as tungsten carbide, silicon carbide, chromium carbide, titanium carbide, cubic boron nitride, carbon nitride and silicon nitride using the PVD method [12-21].

In the PLD method, high density bulk targets, (≥3 g/cm³ and ≥95% in density) are generally used. Therefore, when preparing a thin film with certain element ingredients using this method, it is necessary to form new targets by other methods, such as spark plasma sintering. The target cooling method, which increases material hardness by using liquid nitrogen and liquid helium at a very low temperature, has also been successfully applied to the preparation of functional thin films, including organic electroluminescence films. However, these target making systems require considerable time, and are usually expensive. Therefore, the PLD method may become more attractive if powder material targets are used.

Sputtering deposition using powder targets has been used in the preparation of magneto-optics thin films. Kajima et al prepared ferromagnetic nanocomposite oxide sputtered films by using a Bi₂O₃-Fe₂O₃-PbTiO₃ ternary system and powder targets [22]. They suggested that films prepared using powder targets worked well as thin film capacitors. However, film properties, such as crystallinity, composition ratio, hardness, roughness of the film surface, and adhesion between the films and the substrates, were not studied.

In this study, titanium oxide (TiO₂) thin films were prepared using a PLD method with Ti powder and bulk targets, and film properties, such as crystallinity, composition ratio and surface roughness were compared. In the PLD process, the emission spectra were measured using a monochromator. Crystallinity, composition ratio and surface roughness of the films were measured by X-ray diffraction (XRD) and atomic force microscopy (AFM). On the basis of these results, the mechanisms of thin film deposition using powder targets were explored.

2. EXPERIMENTAL

The schematic of the experimental apparatus is shown in Fig. 1. The deposition chamber was fabricated of stainless steel with a diameter of 400 mm and a length of 370 mm. The chamber was evacuated to a base pressure (below 4×10⁻⁴ Pa) by using a turbo molecular pump and a rotary pump. A pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-230-10;
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wavelength 532 nm, pulse duration 1-2 ns, maximum output energy 650 mJ) was used to irradiate the powder Ti (purity 99.9 %) targets. In addition, we used a bulk Ti (purity 99.9 %) target to compare the properties of the films prepared using these two targets. The radiated area on the targets was maintained at 0.32 cm². The laser fluences used were 0.36, 0.53 and 0.62J/cm². Si(100) and SiO₂ (TEMPAX float) substrates were located 2.2 cm from the targets. Prior to loading into the deposition chamber, the substrates were cleaned using an ultrasonic agitator with repeated bathing in ethanol, followed by rinsing in high-purity deionized water. The substrates were maintained at room temperature. The deposition conditions are shown in table 1.

The surface morphology of the films was observed using an atomic force microscope (AFM, JOEL;JSPM4210). The crystalline structure and composition of the films were measured by XRD (RIGAKU RINT2100V) analysis. The film thickness was measured using alpha-Step (Kosaka Laboratory Ltd. Surfconder ET4000A).

Table 1 Experimental conditions

<table>
<thead>
<tr>
<th>Target</th>
<th>Ti powder (Purity 99.99 %, Particle size 45 nm)</th>
<th>Ti bulk (Purity 99.99 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser</td>
<td>Nd:YAG laser (532 nm, 10 Hz)</td>
<td></td>
</tr>
<tr>
<td>Laser Spot Size</td>
<td>0.32 cm²</td>
<td></td>
</tr>
<tr>
<td>Laser Fluence</td>
<td>0.2~1.0 J/cm²</td>
<td></td>
</tr>
<tr>
<td>Gas Pressure</td>
<td>Vacuum (5×10⁻⁵ Pa), 10 Pa</td>
<td></td>
</tr>
<tr>
<td>Gas Mixture</td>
<td>Ar:O₂ = 10:0, 9:1, 5:5, 1:9, 0:10</td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>Si(100)</td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>Room temperature</td>
<td></td>
</tr>
<tr>
<td>Target-Substrate</td>
<td>2.2 cm</td>
<td></td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION
3.1 Surface morphology of prepared films

The effect of laser fluence on the surface morphology of the films prepared using on the laser fluence using a Ti powder target at room temperature in pure Ar gas as measured by AFM, shown in Fig. 2. The measurements were performed in non-contact AFM mode. The results suggest that the films were smooth and the mean roughness was several nanometers. In addition, the films were found to be composed of small particles of about 10 nm in diameter. The surface morphology of the films prepared using a Ti bulk target at room temperature was also smooth and the mean roughness was several nanometers, not shown here. The figure shows that surface morphology strongly depends on laser fluence. In addition, the films were composed of small coagulated particles. In our deposition condition, some droplets were observed on the prepared films. However, size and density of them on the film prepared using powder target were almost similar to that of bulk target in the parameter range.

![Fig. 2 Surface morphology of the prepared film at the laser fluence of 0.4J/cm² the using a Ti powder target at room temperature.](image)

![Fig. 3 Mean roughness of the prepared film](image)
The dependence of the deposition rate on laser fluence is similar to that of mean roughness as compared with Fig. 4. These results suggest that both deposition processes using Ti powder and bulk targets are almost the same, and depend on laser fluence.

3.2 XRD measurement

Fig. 5 shows the effect of laser fluence on XRD patterns of films prepared using the Ti powder target. The substrate was maintained at room temperature, and the gas pressure was maintained at 10 Pa using pure O$_2$ gas. As the result, TiO peaks were observed, and the crystallinity of the films was independent of laser fluence. The effect of laser fluence on XRD patterns of films prepared using the Ti bulk target not shown here, also show that the XRD pattern of the film prepared using a Ti bulk target are different from those prepared using a Ti powder target, and some TiO peaks were observed. These patterns and peak intensites were independent of laser fluence.

Figure 6 shows XRD pattern of the films prepared using the Ti powder target on the substrate temperature. In this deposition, the gas pressure was 10 Pa and the Ar and O$_2$ gas mixture ratio was 9:1. At room temperature, a weak anatase peak for TiO$_2$ was observed. This suggests that films prepared under these conditions are almost amorphous. At a substrate temperature of 400°C, several strong anatase peaks for TiO$_2$ were observed. Moreover, certain weak rutile peaks for TiO$_2$ were observed. At a substrate temperature of 700°C, only rutile peaks for TiO$_2$ were observed. These results suggest that the crystallinity of the films prepared using a Ti powder target strongly depends on substrate temperature.

Fig. 7 shows the effect of gas mixture on XRD patterns of films prepared using the Ti bulk target. The substrate temperature was 700°C, and the total gas pressure was 10 Pa. In pure Ar gas, TiO peaks were observed along with the Si substrate peaks, however, rutile TiO$_2$ peaks increased with an increase in the O$_2$ content in the gas mixture. These results suggest that the oxygen atomic concentration of films prepared using a Ti powder target depends on the O$_2$ gas mixture.
4. CONCLUSION
The discharge characteristics and optical em TiO₂ thin films were prepared using a PLD method with Ti powder and Ti bulk targets. The deposition rate and surface morphology of the prepared films increased with increasing laser fluence in case of both Ti powder and Ti bulk targets. The deposition rate of the films prepared using the powder target was higher than that of films prepared using the bulk target at the low laser fluence, and the dependence of the deposition rate on laser fluence is similar to that of mean roughness. XRD measurements showed that TiOₓ peaks can be observed for films prepared using both Ti powder and Ti bulk targets. However, the crystallinity of the prepared films depended upon gas mixture and substrate temperature. These results suggest that TiO₂ films can be prepared by a PLD method using a Ti powder target material.

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References

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