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Preparation of TiO_2/TiN/TiO_2 thin films for multifunctional heat mirror using pulsed laser deposition

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Titanium oxide (TiO_2) and titanium nitride (TiN) films have been prepared as a heat mirror, which has a high transmittance in the visible region and a high reflectance in the infrared region, using pulsed neodymium doped yttrium aluminum garnet (Nd:YAG) laser deposition (PLD). The results of X-ray diffraction analysis suggest that crystalline TiO_2 and TiN thin films are formed on a glass substrate under precisely controlled process parameters such as gas pressure and substrate temperature. The depth profiles obtained by X-ray photoelectron spectroscopy suggest that TiO_2(30 nm)/$TiO_{2-x}N_x$(30 nm)/TiO_2(30 nm) thin films as a heat mirror can be prepared using PLD. The results of UV-VIS spectrometry and Fourier transform infrared spectrometry suggest that a highly improved visible transmittance can be obtained using a double-layer TiO_2 coating owing to a strong suppression of visible reflectance, together with a good heat mirror performance represented by an IR transmittance of approximately 60%. Furthermore, multifunctional performance can be expected through the precise control of the crystalline structure of the TiO_2 top layer that serves as a photocatalyst.
Key words: Heat mirror, Titanium oxide, Plasma process, Pulsed laser deposition

1. INTRODUCTION

Recently, several types of heat mirror, which have a high transmittance in the visible region and a high reflectance in the infrared region, have been developed for economical and ecological house windows. The optical requirements for the heat mirror are a high transmittance in the visible region, 380–760 nm in wavelength, and a high reflectance in the infrared and ultraviolet regions. These requirements have been realized using thin film structures on a glass substrate using a doped oxide semiconductor, such as Sn-doped In_2O_3 or Al-doped ZnO, or using a thin film of noble metals, such as Au, Ag, Cu, Al, TiN and ZrN, or their metal-like nitrides sandwiched between antireflection coatings made of a transition-metal oxide. In particular, TiO_2/TiN/TiO_2 stacked films on a glass substrate have attracting attention because of their stability optical properties and ease of manufacture, such as by plasma ion assisted deposition [1], rf magnetron sputtering [2, 3, 4] or evaporation [5]. Fu et al. produced oxide-metal-oxide and oxide-nitride-oxide heat mirrors by plasma ion assisted deposition (PIAD) [1]. They observed an optimum durability for TiO_2/TiN/TiO_2 heat mirrors, despite the spectral performance of these mirrors being lower than that of metal-based heat mirrors in terms of transmittance in the visible and infrared regions. Tazawa et al. fabricated these mirrors by rf magnetron sputtering [2]. They defined the evaluation function and investigated the thickness of the upper TiO_2 layer in the heat mirror structure TiO_2/TiN/TiO_2 on a glass substrate, and a 377.5 nm thick upper TiO_2 layer was recommended for realizing heat mirrors. Wang et al. designed a metal-based transparent heat mirror for ultraviolet curing applications using evaporation deposition [5]. In their comprehensive analysis of material properties, TiO_2/Ag/TiO_2 nano-multilayers with an ultraviolet (UV) transmission of 81% (at 365 nm) and an IR reflectivity of 90% (at 1600 nm) were prepared by conventional evaporation.

However, most research and design studies on hot mirrors focused on their high transparency in the visible region and high reflectance in the infrared region. Few studies emphasized the relationship between film quality and transparency. Pulsed laser deposition (PLD) has become a widely used technique for thin films deposition during the past years owing to its advantages of a simple system setup, a wider range of deposition conditions, a wider choice of materials and higher instantaneous deposition rates. In particular, this method shows a high reproducibility in the preparation of crystalline thin films. Because of this versatility, we have developed several types of functional thin film, such as tungsten carbide, silicon carbide, chromium carbide, titanium carbide, cubic boron nitride, carbon nitride and silicon nitride films, using PLD [6-7].

In this study, we prepared heat mirrors comprising TiO_2/TiN/TiO_2 stacks on a glass substrate using PLD, and evaluated their crystalline structure, the nitrogen states in their lattice and the composition of their films using

X-ray diffraction (XRD) analysis and X-ray photoelectron spectroscopy (XPS). From results of those analyses, we found the optimum conditions for fabricating TiO_2/TiN/TiO_2 thin films as a heat mirror.

2. EXPERIMENT

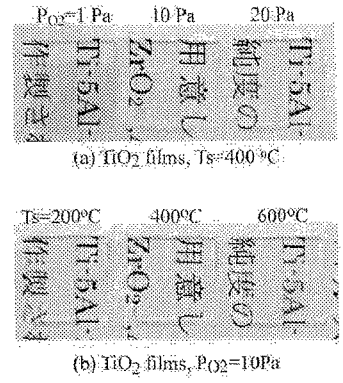
In this experiment, TiO_2, TiN and TiO_2/TiN/TiO_2 heat mirror thin films were prepared by PLD. The details of the experimental facility are reported elsewhere [6-7]. The chamber was evacuated to a base pressure (below 4×10^{-4} Pa) using a turbo molecular pump and a rotary pump, and the reaction gases oxygen (O_2: 99.99%) and nitrogen (N_2: 99.99%) were fed into the chamber. A pulsed Nd:YAG laser (Continuum SureliteIII; wavelength of 532 nm, pulse duration of 3.5 ns and maximum output energy of 340 mJ) was used to irradiate TiN (purity 99.9 %) and/or a TiO_2 (99.99%) targets. Their irradiated area was 2.8 mm^2. Si(100) and SiO_2 (Corning 7059) substrates were located 6.0 cm from the targets.

The crystalline structure and crystallographic orientation of the TiO_2 and TiN thin films were characterized by XRD (RIGAKU RINT2100V) analysis using CuKα radiation. The composition of the films was measured by XPS (JEOL JPS9010). The optical transmittance spectra of the films were measured using an ultraviolet and visible light spectrophotometer (UV-VIS; Hitachi U-3300) and a Fourier transform infrared spectrometer (FT-IR; Shimadzu FTIR8900).

3. RESULTS AND DISCUSSION

Figure 1 shows photographs of the films prepared using the TiO_2 target by PLD at different oxygen gas pressures (P_{O2}) and substrate temperatures (Ts) on a glass substrate. As shown in Fig. 1(a), the TiO_2 film is green at a low oxygen gas pressure (P_{O2} = 1 Pa) at Ts = 400 °C. With increasing P_{O2}, the film changes from green to transparent. Film color is independent of Ts at P_{O2} = 10 Pa, as shown in Fig. 1(b); however, the film prepared at Ts = 400 °C and P_{O2} = 10 Pa is glaucous. Figure 2 shows photographs of the films prepared using the TiN target by PLD at different nitrogen gas pressures (P_{N2}) and Ts values. As shown in Fig. 2(a), the film has a dark green-brown color at P_{O2} = 1 Pa and Ts = 400 °C. With increasing P_{O2}, the film changes from green-brown to transparent. Film color weakly depends on Ts at P_{O2} = 10 Pa; however, the film is glaucous and becomes green with increasing Ts, as shown in Fig. 2(b).

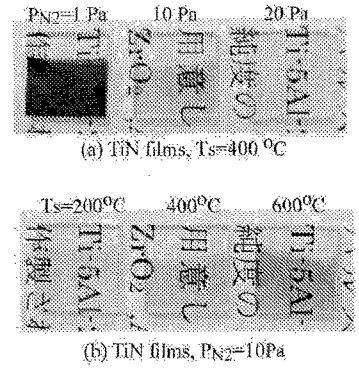
Figure 3 shows XRD patterns of the TiO_2 films deposited using the TiO_2 target on the Si substrate at Ts = 400 °C at different P_{O2} values. At P_{O2} = 1 Pa, crystalline anatase TiO_2(101), (004), (200) peaks and a crystalline rutile TiO_2(110) peak are observed. At P_{O2} = 10 Pa, the crystalline rutile TiO_2(110) peak disappears and only the crystalline anatase TiO_2(101), (004) and (200) peaks are observed. At P_{O2} = 20 Pa, all the crystalline peaks disappear. In general, an anatase TiO_2 thin film has a good performance as a photocatalyst. Therefore, the optimum conditions for preparing a multifunctional heat mirror, which also performs as a photocatalyst, are P_{O2} = 10 Pa and Ts = 400 °C. Figure 4 shows XRD patterns of the TiN films deposited using the TiN target on a Si substrate at Ts = 400 °C at varying the P_{N2}. At P_{N2} = 1 Pa, very small crystalline TiN(111) and (200) peaks are



(a) TiO_2 films, Ts=400 °C

(b) TiO_2 films, P_{O2}=10Pa

Fig. 1 Photographs of the films prepared using TiO_2 target by PLD method as a parameter of (a) oxygen gas pressure (P_{O2}) at Ts=400°C, and (b) substrate temperature (Ts) at P_{O2} = 10 Pa on the glass substrate.



(a) TiN films, Ts=400 °C

(b) TiN films, P_{N2}=10Pa

Fig. 2 Photographs of the films prepared using TiN target by PLD method as a parameter of (a) oxygen gas pressure (P_{N2}) at Ts=400°C, and (b) substrate temperature (Ts) at P_{N2} = 10 Pa on the glass substrate.

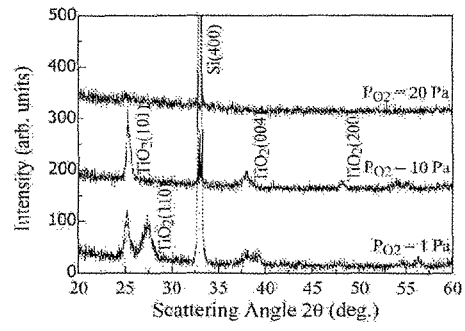


Fig. 3 XRD patterns of the TiO_2 films using TiO_2 target deposited on Si substrate at Ts=400°C as a parameter of the oxygen gas pressure.

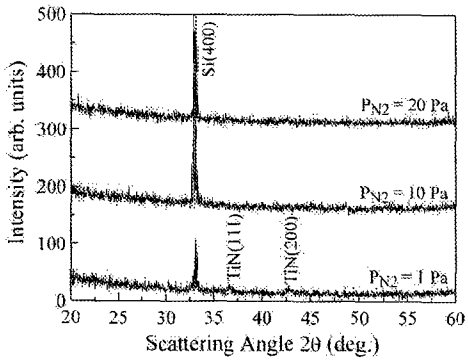


Fig. 4 XRD patterns of the TiN films using TiN target deposited on Si substrate at Ts=400°C as a parameter of the nitrogen gas pressure.

observed. However, these peaks disappear with increasing P_{N2}. Therefore, the optimum conditions for preparing a heat mirror are P_{N2} = 1 Pa and Ts = 400 °C.

XPS analysis was carried out to determine the composition of the film and identify the valence states of the various species present therein. XPS spectra of Ti $2p_{3/2}$, O 1s and N 1s peaks of the film prepared on a SiO_2 glass substrate are shown in Fig. 5. The films were sputtered for 60 s by the bombardment of Ar ions accelerated by applying 600 V to eliminate the oxygen layer on the film surface. XPS spectra of Ti $2p_{3/2}$ and O 1s in the TiO_2 film are shown in Figs. 5(a) and 5(b), respectively. The spectra show the presence of a symmetrical peak of Ti 2p incorporated with TiO_2 (460 eV) and that of O 1s incorporated with TiO_2 (531 eV). XPS spectra of Ti $2p_{3/2}$ and N 1s in the TiN film deposited on the glass substrate are shown in Figs. 5(c) and 5(d), respectively. The spectra show the presence of a large symmetrical peak of Ti 2p incorporated with TiN (458 eV) and a small asymmetrical peak of N 1s (397 eV). Peak intensity and binding energy are independent of P_{N2} and Ts (data not shown).

Film thickness was measured using an α-step system. The thickness of the TiO_2 film was almost 150 nm, and that of the TiN film was 120 nm at a deposition time of 30 min (data not shown). The deposition rates of the film were almost 0.08 nm/s for the TiO_2 film and 0.07 nm/s for the TiN film. These deposition rates are independent of P_{O2}, P_{N2} and Ts. Tazawa et al. suggested that the optimum thickness of a multilayer heat mirror is TiO_2(30 nm)/TiN(30 nm)/TiO_2(30 nm) [2]. From these experimental results, TiO_2/TiN/TiO_2 thin films as a heat mirror were prepared using as follows. First, a TiO_2 film was prepared using a TiO_2 target at P_{O2}=10 Pa, and then TiN thin films were prepared using a TiN target at P_{N2}=1 Pa. A TiO_2 film was also prepared using a TiO_2 target at P_{O2}=10 Pa. In these experiments, the deposition time was 7 min and Ts = 400 °C. Figure 6 shows XPS spectra of the prepared heat mirror films for different Ar ion

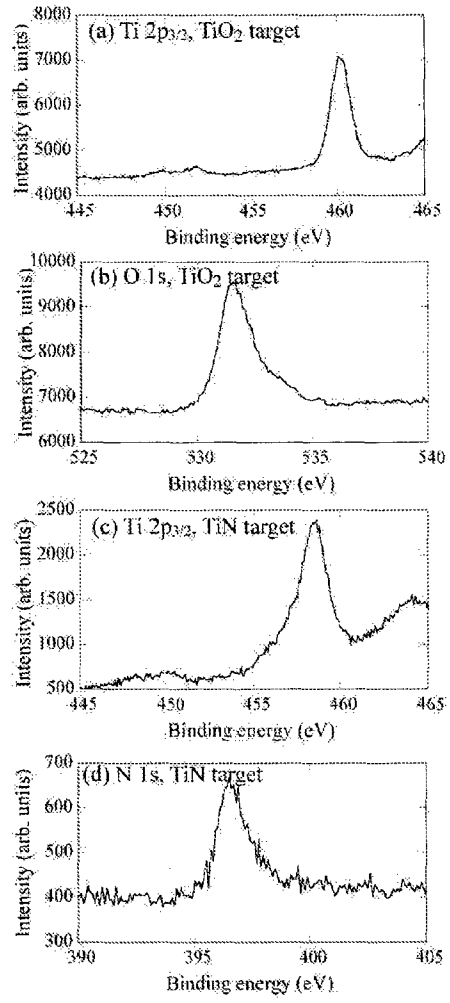


Fig. 5 XPS spectrum of the films deposited at Ts=400°C and P_{O2} or P_{N2} = 10 Pa on glass substrate. (a) Ti $2p_{3/2}$ in TiO_2 film, (b) O 1s in TiO_2 film, (c) Ti $2p_{3/2}$ in TiN film, (d) N 1s in TiN film.

sputter etching times. The acceleration voltage of the sputter etching was 600 V and the etching rate was 0.05 nm/s. As shown in Fig. 6, the intensity of the spectra of Si $2p_{3/2}$ increased after an etching time (t_e) of 2000 s. The spectra of Ti $2p_{3/2}$ and N 1s changed with t_e. In particular, a distinct peak of the N 1s spectra appeared at t_e = 1000-1500 s. The O 1s spectra of the film are independent of t_e (data not shown). These results suggest that TiO_2(30 nm)/$TiO_{2-x}N_x$(30 nm)/TiO_2(30 nm) thin films can be prepared using PLD. The thickness of the prepared multilayer heat mirror film was approximately 90 nm. As a result, the second phase is not TiN but $TiO_{2-x}N_x$. The reason for this phenomenon is not clear yet, but may be oxygen diffusion.

The optical transmittance of the deposited heat mirror was measured between 300 and 1100 nm and between 1.2 and 2.5 μm, as shown in Figs. 7(a) and 7(b), respectively. A highly improved visible transmittance was obtained using the double layer TiO_2 coating owing to the strong

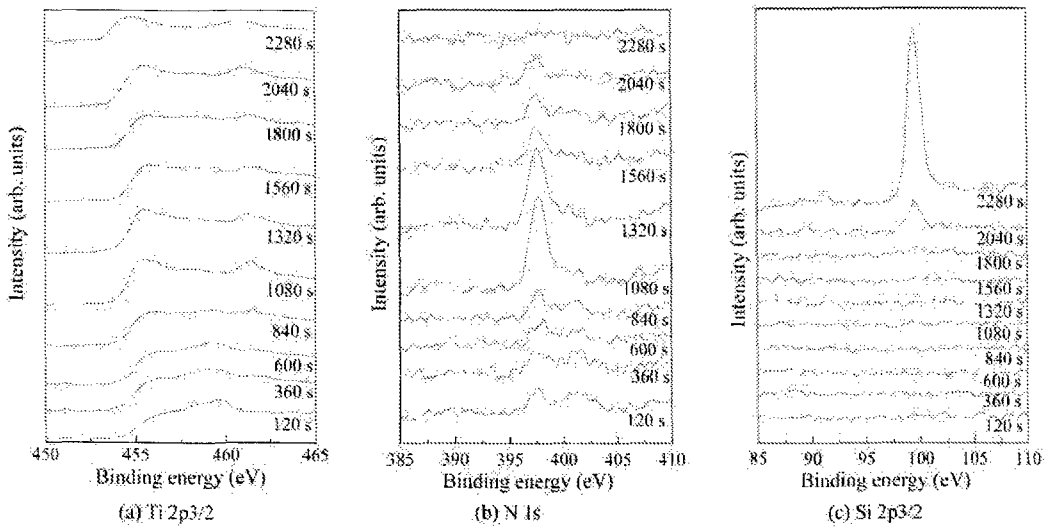


Fig. 6 XPS spectra of the prepared heat mirror film as a parameter of Ar ion sputter etching time. (a) Ti $2p_{3/2}$, (b) N 1s, (c) Si 2p3/2.

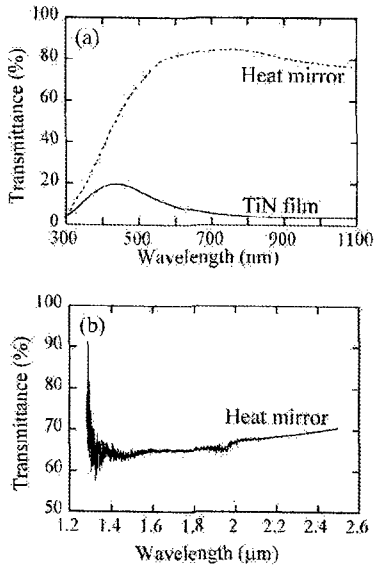


Fig. 7 The optical transmittance of the deposited heat mirror on the grass substrate using (a) UV-VIS spectrometer (300-1100 nm) and (b) FT-IR (1.2-2.5 μm).

suppression of visible reflectance, as shown in Fig. 7(a), together with the good heat mirror performance represented by the IR transmittance of approximately 60% shown in Fig. 7(b). It is inferred that multifunctional performance can be expected for the heat mirror through the precise control of the crystal structure and the photocatalytic properties of the TiO_2 top layer.

4. CONCLUSIONS

TiO_2 and TiN thin films have been prepared as a heat mirror, which has a high transmittance in the visible region and a high reflectance in the infrared region, using PLD. The results of XRD analysis suggest that crystalline TiO_2 and TiN thin films are formed on a glass substrate under precisely controlled process parameters such as P_{O2}, P_{N2} and Ts. XPS results suggest that TiO_2(30 nm)/$TiO_{2-x}N_x$(30 nm)/TiO_2(30 nm) thin films can be prepared using PLD. The optical transmittance of the deposited heat mirror, measured by UV-VIS and FT-IR spectrometries suggests that a highly improved visible transmittance was obtained using a double layer TiO_2 coating owing to the strong suppression of visible reflectance, together with the good heat mirror performance represented by an IR transmittance of approximately 60%. Furthermore, it is suggested that multifunctional performance can be expected through the precise control of the crystal structure of the TiO_2 top layer that serves as a photocatalyst.

5.ACKNOWLEDGEMENTS

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6. References

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