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# TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirrors by laser ablation of single TiN target

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**Abstract** Titanium oxide (TiO<sub>2</sub>) and titanium nitride (TiN) multilayered films grown by pulsed laser deposition (PLD) technique have been tested as a heat mirror, which have a high transmittance in the visible region and a high reflectance in the infrared. Three layer TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirrors were grown on Corning glass substrates ablating single TiN target. Switching of TiO<sub>2</sub>-to-TiN layers composition was achieved by changing gas atmosphere (oxygen-to-nitrogen). Grown TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirrors are highly transparent in visible (above 60% at 525nm), opaque in infrared (10% at 2600nm) and in the range from 400 nm to 2600 nm they possess almost the same properties as films prepared using two targets: TiO<sub>2</sub> and TiN. XPS confirms similarity of chemical composition of multilayered TiO<sub>2</sub>/TiN films prepared by single TiN and two TiO<sub>2</sub> and TiN targets techniques. Furthermore, multifunctional self cleaning properties of TiO<sub>2</sub>/TiN heat mirrors are expected through the precise control of the composition of the top TiO<sub>2</sub> layer operating as a photocatalyst.

## 1 Introduction

Today considerable amounts of energy are used globally to heat or cool the interior of buildings. In an advanced country where there are a lot of large-scale buildings, even a small reduction of the energy consumption would result in large savings. Energy control strategy of buildings has traditionally been the window, which allows the energy not to escape outside the building in cold climates and allows the solar energy not to enter the building in warm climates. In the future, advanced windows will be more frequently used to control the indoor climate. Therefore, several types of heat mirrors have been developed for economical and ecological windows. The optical requirements of the heat mirror are a high transmittance in visible and a high reflectance in infrared and ultraviolet lights. These requirements have been realized by thin film coatings on glass substrate using doped oxide semiconductors, thin films of noble metals, or metal-like nitrides sandwiched between the antireflection coatings of the transition metal oxide [1-7]. In particular, TiO<sub>2</sub>/TiN/TiO<sub>2</sub> stacked films on glass substrate have been attracting the attention of researchers because of the stability of the optical properties and rather easy manufacturing process.

We have prepared the TiO<sub>2</sub>/TiN/TiO<sub>2</sub> films using pulsed laser deposition (PLD) method [8]. The PLD has become a widely used technique for thin films deposition due to the advantages of a simple system setup, wide ranging deposition conditions, a wider choice of materials and higher instantaneous deposition rates. Our previous results suggest that films microcrystalline structure as well as oxygen and nitrogen concentration ratio can be controlled by changing gas atmosphere [9]. Thin TiO<sub>2</sub> and TiN single layer and multilayered films on glass substrates have been prepared by PLD using two TiO<sub>2</sub> and TiN targets under precisely controlled processing parameters such as gas pressure and substrate temperature. XPS analysis has proved strict stoichiometry of three layer TiO<sub>2</sub>(30nm)/TiN(30nm)/TiO<sub>2</sub>(30nm) films. The optical transmittance of the deposited heat mirrors,

measured by UV-VIS and FTIR spectrometers, demonstrate improved visible transmittance that higher than 80%. However, IR light transmittance of 60% was not low enough to meet parameters required for heat mirrors [1-7].

In this study, we prepared TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirrors by PLD on glass substrates using a single TiN ceramic target. Switching of TiO<sub>2</sub>-to-TiN layers composition was achieved by changing gas atmosphere (oxygen-to-nitrogen). We present basic optical properties of single layer TiO<sub>2</sub> and TiN films as well as TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirror in the range from 400 nm to 2600 nm. Moreover, we experimentally prove the catalytic properties of TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirror.

## 2 Experimental

In this experiment, single layer TiO<sub>2</sub>, TiN films and three layer TiO<sub>2</sub>/TiN/TiO<sub>2</sub> films were prepared by conventional PLD method. The deposition chamber was evacuated to a base pressure (below  $4 \times 10^{-5}$  mbar) using a turbo molecular and rotary pumps, and after that, the reaction gases of pure oxygen and pure nitrogen were fed into the chamber. A pulsed KrF excimer laser (Lambda Physik-300, wavelength of 248 nm, pulse duration of 25 ns, maximum output energy of 300 mJ) was used to ablate TiO<sub>2</sub> (purity 99.9 %) and TiN (purity 99.9 %) ceramic targets. Glass substrates (Corning 7059) were placed at 8.5 cm from the targets. The substrate was cleaned using an ultrasonic agitator by repeated bathing in acetone and then rinsed in deionized water prior to loading into the deposition chamber. The substrates were heated to 150°C using resistive heater.

The optical transmittance spectra of the films were measured using a Fourier transform infrared spectrometer (FTIR, Nicolet 5700). The composition of the films was measured by X-ray photoelectron spectroscopy (XPS, JEOL JPS9010). Film thickness was measured by the profilometer (Tencor alpha-step 200). The photocatalytic activity of the films was evaluated by degrading the methylene blue in aqueous solution.

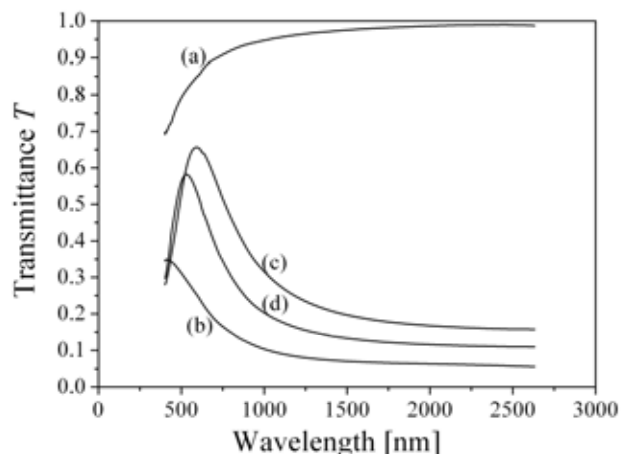
## 3 Experimental Results

### 3.1 TiO<sub>2</sub> film deposition using TiN target

In our previous study [9], XPS measurements (not shown here) of the TiO<sub>2</sub> film obtained from TiN target in oxygen gas suggested that peaks of Ti 2p (460 eV) and O 1s (531 eV) are related to TiO<sub>2</sub>. On the other hand, peak of N 1s (397 eV) was not detected clearly. Film composition Ti-to-O ratio was found to be 1:2. These results prove that accurate switching of the composition of prepared film from TiN to TiO<sub>2</sub> has been achieved by changing gas atmosphere (oxygen-to-nitrogen).

Film deposition was performed in  $1.4 \times 10^{-2}$  mbar pure oxygen atmosphere and deposition time was 5 min. Thickness of the TiO<sub>2</sub> film was almost 20 nm. Therefore, deposition rate of the TiO<sub>2</sub> films using TiN target was found to be around 4nm/min.

The optical transmittance of TiO<sub>2</sub> film deposited from a single TiN target is shown in Fig. 1(a). The transmittance of the film increases with a wavelength in visible – near IR region (400 nm – 1000 nm), and after that it saturates. The maximum transmittance in IR is almost 98%.



**Figure 1.** The optical transmittance of single layer TiO<sub>2</sub> (a) and TiN (b) films deposited from a single TiN target. Transmittance of TiO<sub>2</sub>(60nm)/TiN(14nm)/TiO<sub>2</sub>(60nm) heat mirrors deposited from a single TiN target (c) and from two TiO<sub>2</sub> and TiN ceramic targets (d).

### 3.2 TiN film deposition using TiN target

As we reported previously [10], XPS measurements of Ti  $2p_{3/2}$  and N 1s peaks in the TiN film made from the TiN target in nitrogen gas showed the presence of Ti  $2p_{3/2}$  and N 1s peaks associated with TiN (458 eV and 397 eV respectively, not shown here). In addition, film color was yellow-gold and composition Ti:N ratio was about 1:1.

The transmittance of TiN films deposited from TiN target is shown in Fig. 1(b). 35 nm thick TiN film was deposited in  $3.0 \times 10^{-2}$  mbar nitrogen atmosphere. Deposition rate of TiN films using TiN target was about 3.5 nm/min. In visible – near IR range, the transmittance of TiN film decreases with wavelength increase and then it saturates at the level below 5%.

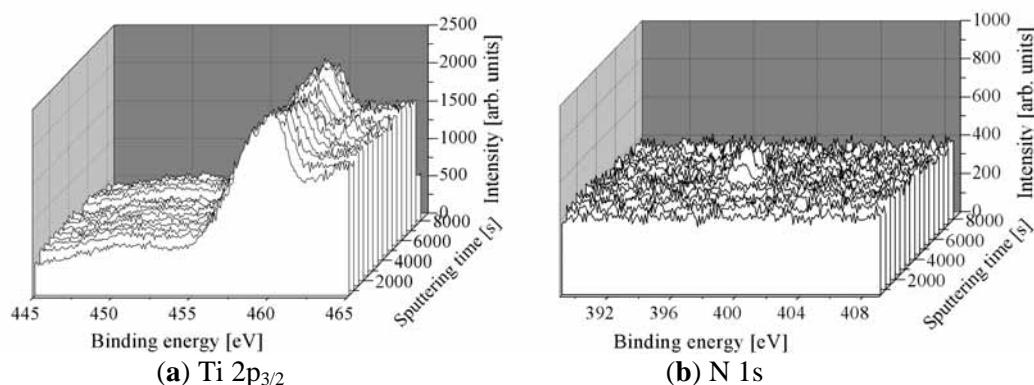
### 3.3 Multilayer TiO<sub>2</sub>/TiN/TiO<sub>2</sub> thin films deposition

Using these calibration experiments, multilayer TiO<sub>2</sub>/TiN/TiO<sub>2</sub> thin films were prepared as follows. First, 60 nm thick TiO<sub>2</sub> film was grown in  $1.4 \times 10^{-2}$  mbar oxygen atmosphere. Then, 14 nm thick TiN film was deposited in  $3.0 \times 10^{-2}$  mbar nitrogen atmosphere. Finally, 60 nm thick TiO<sub>2</sub> film was grown at  $1.4 \times 10^{-2}$  mbar oxygen pressure. In this deposition process, the same single TiN target was used and substrate temperature was kept at 150°C. Precise calibration of the deposition rate suggests that three layer TiO<sub>2</sub>(60nm)/TiN(14nm)/TiO<sub>2</sub>(60nm) heat mirror was obtained. Fig. 1(c) presents the transmittance of the film in the range from 400 nm to 2600 nm. Transmittance of the visible light is about 65% at 525nm and 15% in IR at 2600 nm.

For comparison, we also prepared TiO<sub>2</sub>(60nm)/TiN(14nm)/TiO<sub>2</sub>(60nm) film using two TiO<sub>2</sub> and TiN ceramic targets in the same deposition system. First, 60 nm thick TiO<sub>2</sub> film was grown using TiO<sub>2</sub> target in oxygen atmosphere, and then the target was changed to TiN without opening the reaction chamber. 14 nm thick TiN layer was deposited in nitrogen atmosphere. After that, changing the TiN target back to the TiO<sub>2</sub> one, TiO<sub>2</sub> layer with the thickness of 60 nm was grown again in oxygen gas. Transmittance of this film is shown in Fig. 1(d). It is about 60% at 525 nm and around 10% at 2600 nm. Shapes of these two spectra are almost the same, but the peak transmittance of heat mirror made from two TiO<sub>2</sub> and TiN targets is about 5% lower compared to that grown from a single TiN target.

XPS analyses were carried out with Ar ion etching to determine the composition of multilayer films and identify the valence states of various species present therein. Fig. 2 shows the XPS spectra of Ti  $2p_{3/2}$  and N 1s peaks in the TiO<sub>2</sub>/TiN/TiO<sub>2</sub> multilayer film grown from a single TiN target. As shown in Fig. 2, Ti  $2p_{3/2}$  associated with TiO<sub>2</sub> (460 eV) is clearly obtained at an etching time  $t_e$  of 0-3000 s. In addition, O 1s peak associated with TiO<sub>2</sub> (531 eV) is still detected (not shown here). After that, a distinct peak of the N 1s spectra appeared at  $t_e = 3500-5000$  s. Ti  $2p_{3/2}$  peak associated with TiN shifts toward lower energy and N 1s peak associated with TiN becomes visible at 397 eV. At  $t_e = 5500-8000$  s, Ti  $2p_{3/2}$  peak associated with TiO<sub>2</sub> is clearly obtained, which is similar to that at  $t_e = 0-3500$  s. After that, the intensity of the Si  $2p_{3/2}$  peak increases at  $t_e > 8000$  s (not shown here).

Ti  $2p_{3/2}$  and N 1s peaks in TiO<sub>2</sub>/TiN/TiO<sub>2</sub> multilayer film prepared by pulsed laser ablation of two

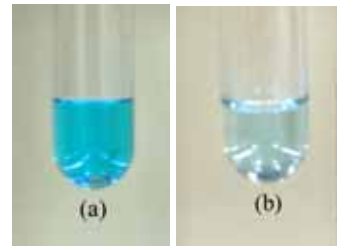


**Figure 2.** XPS spectra of the TiO<sub>2</sub>/TiN/TiO<sub>2</sub> film prepared using a single TiN target.

TiO<sub>2</sub> and TiN targets also have been measured by same XPS system (not shown here). The dependence of XPS profiles on etching time  $t_e$  is almost the same compared to the XPS spectra of the film made from a single TiN target shown in Fig. 2. These results suggest that chemical composition of the TiO<sub>2</sub>/TiN/TiO<sub>2</sub> multilayer thin films fabricated from a single TiN target is similar to the three layer film prepared using two TiO<sub>2</sub> and TiN targets.

### 3.4 Photocatalytic properties

The photocatalytic properties of TiO<sub>2</sub>(60nm)/TiN(14nm)/TiO<sub>2</sub>(60nm) films were evaluated by measuring the decomposition of methylene blue in aqueous solution on the film surface under UV light [9]. The films were dipped into an aqueous methylene blue solution with the concentration of 30 mmol/l and irradiated with a black light lamp (362 nm, 50 mW/cm<sup>2</sup>). Fig. 3 shows the aqueous methylene blue solution changed its colour after dipping the TiO<sub>2</sub>/TiN/TiO<sub>2</sub> film grown from a single TiN target. This observation clearly proves that single TiN target PLD-made TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirror possesses decomposition ability of methylene blue under UV light irradiation.



**Figure 3.** Colour of an aqueous methylene blue solution with dipped TiO<sub>2</sub>(60nm) / TiN(14nm) / TiO<sub>2</sub>(60nm) film without UV light (a), and after UV light irradiation (b).

## 4 Conclusions

Stoichiometric TiO<sub>2</sub>/TiN/TiO<sub>2</sub> multilayer films demonstrating high heat mirror performance have been pulsed laser deposited on to the Corning glass substrates using a single TiN target. Films combine high transmittance in the visible range and high opaqueness in the infrared. XPS results prove that highly stoichiometric TiO<sub>2</sub>/TiN multilayers can be sintered using pulsed laser ablation of a single TiN target. Fabricated TiO<sub>2</sub>/TiN/TiO<sub>2</sub> heat mirror demonstrates UV-photocatalytic properties.

## 5 Acknowledgements

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