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13. Shinkai reported the following pK_a values⁸ of *p*-nitro-calix[4]arene such as $pK_1=2.9$, $pK_2=10.9$, $pK_3=12.3$, and pK_4 more than 14. Even though we were not dealing *p*-nitrocalix[4]arene here, we might correlate the difference of the pK_a of calixarene **1** with the values obtained for *p*-nitrocalix[4]arene. The difference between pK_1 to pK_2 is 8, but it is only 1.4 between pK_2 to pK_3 . This suggests that the third proton from calix[4]arene might be lost as easy as the second one. That would explain why we could not detect the dianion species, but the mixture of mono and trianions.
14. A multiplet at 3.4 ppm was attributed from *n*-butyllithium, which was confirmed by the separate experiment.
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Structural Properties of TiO₂ Films Grown by Pulsed Laser DepositionHa-Sub Yoon, Seong Kyu Kim, and Hoong-Sun Im^{†*}

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Pure titanium dioxide (TiO₂) films were prepared by pulsed laser deposition on a single crystal Si(100) substrate. We have investigated the growth of crystalline titanium dioxide films with respect to substrate temperature and ambient oxygen pressure. The structural properties of the films were analyzed by X-ray diffraction. We found that the anatase as well as the rutile phases could be formed from the original rutile phase of the target TiO₂. At 0.75 torr of ambient oxygen pressure, the structure of TiO₂ film was amorphous at room temperature, anatase between 300 and 600 °C, a mixture of anatase and rutile between 700 and 800 °C, and only rutile at 900 °C and above. However, at a low ambient oxygen pressure, the rutile phase became dominant; the only rutile phase was obtained at the ambient oxygen pressure of 0.01 torr and the substrate temperature of 800 °C. Therefore, the film structures were largely influenced by substrate temperature and ambient oxygen pressure.

Introduction

Titanium dioxide (TiO₂) has various attractive properties such as high refractive index, high permittivity, semiconductor properties and chemical stability. Because of these properties TiO₂ films find wide applications. They have been used as gas sensors, antireflection coating, dielec-

tric materials in optoelectronics, protective layers in integrated circuits, and photocatalysts in solar energy conversion and in environmental cleaning. The bulk TiO₂ has three crystalline polymorphs: the rutile, the anatase and the brookite. The rutile is known to be the most stable phase, while the anatase phase is less stable and forms at lower temperatures. The brookite phase can form only under extreme conditions.

The films have been prepared by various techniques such

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as chemical vapor deposition (CVD),¹⁻⁸ electron beam evaporation,⁹⁻¹² and reactive sputtering¹³⁻¹⁶ and their optical and electrical properties have been extensively investigated. The structural properties of TiO₂ films obtained by these methods depend largely upon the process parameters-the substrate nature, substrate temperatures, annealing conditions, etc. For an instance, with the plasma enhanced chemical vapor deposition (PECVD) on a glass substrate at temperatures below 300 °C, 300-400 °C, 500 °C, and above 600 °C, the films with the structures of amorphous, anatase, anatase-rutile mixture, and rutile phases were obtained, respectively.⁶ And with the reactive sputtering method,¹³ TiO₂ films deposited on Si substrate were amorphous at room temperature and predominantly anatase at temperatures between 200 °C and 400 °C. When these films were annealed in air for 1 hour at 850 °C, the anatase phases were converted to the rutile phases.⁸

In recent years, a few groups have reported the structural and compositional properties of TiO₂ thin films prepared by the pulsed laser deposition (PLD).¹⁷⁻²¹ With this technique, the studies have concentrated on producing oxygen deficient TiO_{2-x} thin films since TiO_{2-x} films show n-type semiconductor property. In those reports, we find a lack of understanding in the detailed mechanism of the phase formation during the TiO₂ film growth. Therefore, for the better understanding, we have investigated the effects of the growth conditions involved in the deposition process of PLD such as ambient oxygen pressure and substrate temperature. In this paper, we discuss the influence of the deposition parameters on the structural properties of TiO₂ films prepared *in-situ* by PLD.

Experimental procedures

The experimental set-up is fully described elsewhere,²² and therefore only a brief description is given here. It uses second harmonic pulses (532 nm, 10 ns) from a Q-switched Nd:YAG laser at the repetition rate of 10 Hz. A pellet of stoichiometric TiO₂ was used as the target for the laser ablation. The pellet (2 cm in diameter and 1 inch thick) was made by pressing and sintering commercially available high-purity (99.9%) TiO₂ powder at 750 °C for 6 hours. The target was then transferred into a stainless steel vacuum chamber which is evacuated with a diffusion pump. The base pressure is usually in the 10⁻⁶ torr range. The Si substrate was mounted inside the vacuum chamber and its temperature was regulated between room temperature and 900 °C by using a D.C. power supply (5 A, 100 V). The target-to-substrate distance was fixed at 15 mm. In order to avoid texturing on the target surface, the target holder allowed the rotation of the TiO₂ pellet. The incidence angle of the laser beam was 45 degree. Just prior to deposition, the Si substrate was cleaned with diluted HF solution and distilled water. Oxygen was dosed into the chamber through a precision leak valve to provide the ambient pressures of 0.01 torr to 0.75 torr. The laser fluence per pulse at the target was 2 J/cm². This gave the deposition rate of about 15 Å/sec at the substrate temperature of 500 °C and the oxygen pressure of 0.75 torr. The crystal structure of the film was determined with a X-ray diffractometer (XRD) [Regaku Rotaflex RTP 300 RC] using Cu Kα radiation and 4 degree

glancing angle of the incidence. X-ray photoemission spectroscopy (XPS) was performed to determine the stoichiometry of the films with a VSW instrument (Scientific Instruments Ltd.) under ultrahigh vacuum condition. For the measurement, X-ray source is a nonmonochromated dual anode type radiation, Al Kα (1486.6 eV) and Mg Kα (1253.6 eV). The binding energy of the emitted photoelectrons is analyzed with a concentric hemispherical analyzer. XPS spectrum of the characteristic core level peak is obtained with the fixed analyzer transmission (FAT) mode with the pass energy of 22 eV.

Results and Discussion

Using PLD technique, non-stoichiometric TiO_{2-x} thin films can be deposited depending on the deposition conditions. Usually, under the ambient oxygen gas stoichiometric TiO₂ thin films have been obtained. XPS data have been successfully applied to determine the stoichiometry of TiO₂ thin films.^{16,21} We have investigated the core level electronic structure of Ti in TiO₂ film using XPS, from which one can get the chemical state of Ti. Figure 1 shows the XPS of TiO₂ film prepared by PLD in the Ti 2p region. The Ti 2p_{3/2} and Ti 2p_{1/2} levels are located at 459.38±0.5 eV and 465.14±0.5 eV, respectively. The measured binding energy of the Ti 2p peaks and the splitting of the doublet (ΔBE=5.76±0.05 eV) indicate an oxidation state of 4+ for titanium. The XPS shown in Figure 1 is typical for the investigated TiO₂ films prepared by different techniques. Very similar doublets with the same binding energy are obtained for TiO₂ films prepared by the dip coating (DC), the reactive evaporation (RE), and the ion plating (IP).¹² Small differences are found in the full width at half maximum (FWHM) of the Ti 2p_{3/2} peak. Representative values of the FWHM are 1.4 eV for PLD films, 1.3 eV for IP films and 1.2 eV for RE and DC TiO₂ films, suggesting small differences in the oxidation state or the structural arrangement of the atoms.

Figure 2 shows the XRD pattern for the target TiO₂. It is consistent with the reference (PDF Card, #21-1276) data for the rutile TiO₂. After the laser deposition onto the Si sub-

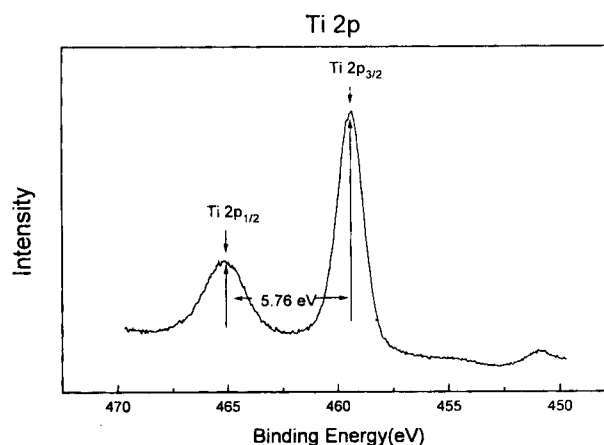


Figure 1. XPS spectrum of the Ti 2p doublet for a TiO₂ film produced by PLD. The splitting of the doublet (ΔBE=5.76) is written inside.

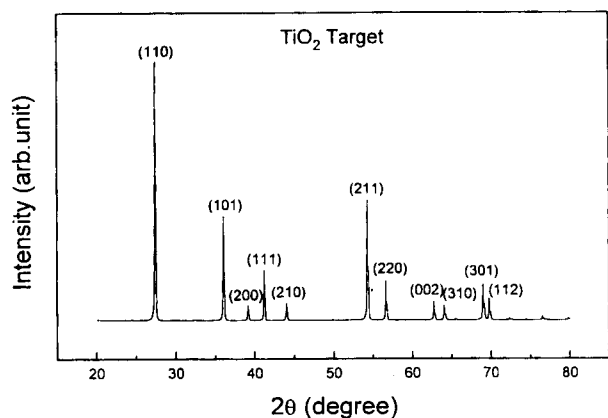


Figure 2. X-ray diffraction patterns of bulk TiO_2 , showing the typical rutile phases of TiO_2 . Each phase is assigned from the reference data.

strate for 600 seconds, the XRD spectra of the TiO_2 films show different features depending on the substrate temperature or the ambient oxygen pressure. Figure 3 shows the XRD patterns of the films in a series of substrate temperatures when the oxygen pressure is 0.75 torr. With reference to the standard data, we assign the peaks for the anatase and the rutile phases of TiO_2 with the structural planes. Below 300 °C, the film is amorphous. Between 300 °C and 600 °C, the anatase peaks grow with increasing temperatures. The broad peaks at 300 °C and 400 °C are for the anatase and they become narrower as the substrate temperature is raised. Apparently, the narrowing of the peaks follows a gradual process rather than a rapid phase transition. Even if the anatase phase is dominant in this range, the small fraction of the rutile phase ($2\theta=55^\circ$) exists in the film. About 700 °C, a peak for the rutile phase ($2\theta=27^\circ$: (110)) begins to appear, and finally dominates at 900 °C. Although initially broad, it grows narrow as the substrate temperature is raised. These observations suggest that at low temperatures the anatase phases are more favorable than the rutile phases. As the substrate temperature goes up, the thermodynamically more stable rutile is formed. The same

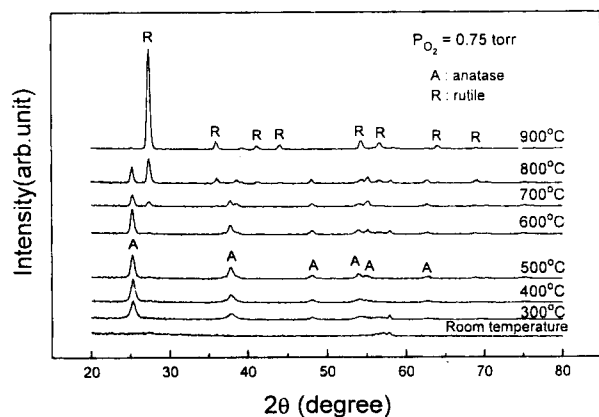


Figure 3. X-ray diffraction patterns of the TiO_2 films deposited on Si substrate at ambient oxygen pressure of 0.75 torr. Each deposition temperature is indicated on each data. The laser power of 2 J/cm^2 was used.

trend has been reported for the thin films deposited by PECVD.⁶

In Figure 3 we find that the *in-situ* PLD process induced the phase transformation in such a way that the films were converted from the anatase phase to the rutile-dominated mixtures and to the rutile phases with increasing the substrate temperature. The fact that the rutile phase is formed only at high temperatures (>600 °C) implies that it has a higher activation energy of formation than the anatase does.

In growing crystalline film, substrate heating is generally used. According to a theory for nucleation and growth of film, the energy of the nucleation site is a function of the substrate temperature.²³ It is generally accepted that thin films begin to form at nucleation sites on surface. The density of the sites is inversely proportional to the site energy.²⁴ At 0.75 torr, the anatase appears at temperatures between 300-800 °C but is absent at 900 °C and the rutile phases start to form at 700 °C. These facts indicate that the energy of the nucleation site is insufficient to allow the rutile phase formation below 700 °C by PLD. Therefore, the anatase phases are initially nucleated and grow at the low temperature. But as the substrate temperature goes up, the rutile which is thermodynamically more stable can be formed. This fact is also reflected in the trend of the line narrowing; the anatase peaks are broad at 400 °C but grow narrow as the film adopts the more single crystalline phase at the higher temperatures.

XRD patterns of the films in several ambient oxygen pressures at the substrate temperature of 800 °C are shown in Figure 4. At 0.75 torr, both the anatase and the rutile peaks are observed. At the low oxygen pressures, the rutile peaks are predominantly observed at the same temperature. Especially, at 0.01 torr almost the same strong peaks of the rutile phase are observed as those obtained under the condition of 900 °C and 0.75 torr. These results mean that the rutile phase can be formed easily at the lower oxygen pressure. The phase formation is found to be dependent on the ambient oxygen pressure with the same energy of the nucleation site which is a function of the substrate temperature. In these experiments, no deposition parameter has been changed except the ambient pressure. Under these con-

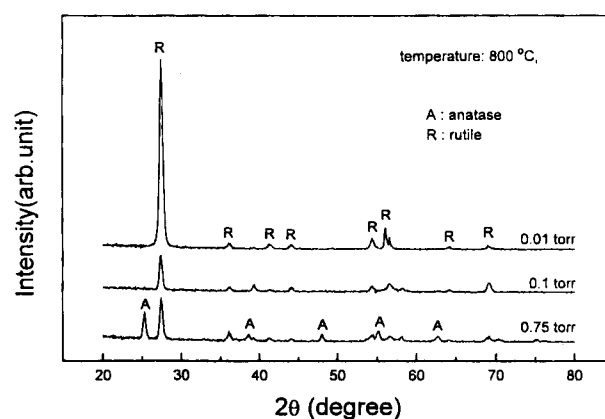


Figure 4. X-ray diffraction patterns of the TiO_2 films deposited on Si substrate at the deposition temperature of 800 °C. Each ambient pressure is shown on each data. The laser power of 2 J/cm^2 was used.

ditions, only the characteristics of ablated particles, such as the kinetic energy of the particles, could be changed. This difference causes the change of the phase formation condition. The systematic studies are being performed to investigate the effect of the kinetic energy of the ablated particles on the phase formation.

Conclusions

The single phases of the anatase and the rutile TiO₂ film were deposited on Si(100) substrates by PLD. The measured binding energies of the Ti 2p peaks and the splitting of the doublet ($\Delta BE = 5.76 \pm 0.05$ eV) indicate an oxidation state of 4+ for titanium.

At the oxygen pressure of 0.75 torr, the deposited films display three types of structure, *i.e.*, the rutile (above 900 °C), the rutile-anatase mixture (700-800 °C), the anatase phase (300-600 °C). When TiO₂ thin film is deposited at low ambient oxygen pressure, however, only the rutile phase can be obtained at the lower substrate temperature.

The behavior of temperature dependence to form the crystalline structures of TiO₂ thin film indicates that at high ambient oxygen pressure, the energy of nucleation site plays an important role in the phase formation. When the ambient oxygen pressure is low, however, another factor, such as the kinetic energy of laser ablated particles, becomes important to form the crystalline structure.

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