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Ion beam induced chemical and morphological changes in TiO_2 films deposited on Si(1 1 1) surface by pulsed laser deposition

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ABSTRACT

We have investigated TiO_2 films prepared by pulsed laser deposition method on Si(1 1 1) surface using X-ray diffraction (XRD), Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and ion beam sputtering techniques. Our XRD data along with Raman indicated that the deposited TiO_2 is in anatase phase. The binding energy position of Ti 2p also supports the anatase phase formation. AFM topography of as deposited film indicates the formation of non uniform TiO_2 growth with the formation of voids on Si(1 1 1) substrate. After sputtering with argon ion beam, surface erosion occurs and voids have disappeared. The Ti 2p core level of sputtered TiO_2 exhibits the formation of Ti_2O_3, TiO and pure Ti on the surface. High binding energy shoulder of O 1s peak becomes sharp after sputtering. Ti LMM Auger peaks become broader after sputtering but no shift in kinetic energy is observed.

1. Introduction

Titania or titanium dioxide (TiO_2) possesses unique chemical and physical properties such as high chemical stability, high dielectric constant, high electrical stability, excellent transmittance in the visible region etc. It has been studied extensively due to its numerous applications in optoelectronic devices such as solar energy conversion, anti-reflection coatings, high-temperature optical filters, optical wave guides, self-cleaning protective coatings, sensors and highly efficient catalysts [1–7]. TiO_2 is one of the potential candidates to replace SiO_2 gate dielectric in semiconductor charge storage memory devices [8–12] due to its high dielectric constant (70–80) [13]. The dielectric constant of TiO_2 increases from amorphous to anatase to rutile phase. The large variation in dielectric constant of TiO_2 films has been attributed to differences in film thickness, and to the formation of low-permittivity SiO_x at the interface [11]. The reduced TiO_2 surface with oxygen vacancies is of particular interest for its photocatalysis applications such as dehydration of formic acid and dissociation of water molecules [14–16]. Interestingly, the band gap and dielectric constant of TiO_2 are tunable over a wide range. The chemical and physical properties of TiO_2 depend on the method of preparation. The band gap of TiO_2 changes from 3.2 to 3.5 eV depending on the crystal structure. TiO_2 can exist in three crystallographic phases: anatase, rutile and brookite [9,17–19]. The first two polymorphs have a tetragonal symmetry whereas Brookite has orthorhombic symmetry and usually not found in thin films.

TiO_2 thin films have been synthesized by using numerous methods including plasma oxidation [20], chemical vapor deposition (CVD) [21], metal organic chemical vapor deposition (MOCVD) [22], sputtering [23], atomic layer deposition (ALD) [24], plasma-enhanced ALD (PEALD) [25] and pulsed laser deposition (PLD) [26]. Among the above mentioned techniques, PLD provides thin films with good mechanical rigidity and with high specific surface area [27,28]. The stochiometry of the films deposited by PLD method is same as that of the bulk target used for ablation. During ablation oxygen may be lost and thus oxygen partial pressure is maintained in the chamber to obtain stochiometric oxide films.

TiO_2 thin films prepared by pulsed laser deposition has previously been studied by various research groups [29–33]. However, chemical properties and the crystal structure of TiO_2 films depend on the substrate, deposition pressure and temperatures used. The anatase and rutile multi phase structures were observed in TiO_2 thin films by several groups [29,30,33]. Luca et al. [33] have reported

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the increase of anatase phase with increase in oxygen partial pressure. They have also reported [33] that O:Ti ratio ranges from 1.78 to 2.0 depending on the deposition temperature and pressure. Very few studies have discussed the relationship between the valance states of Ti and the deposition condition during PLD synthesis of TiO_x thin films [33]. Variation in deposition parameters such as pressure and temperature results in the formation of TiO_2 films with different chemical and structural properties [30,33,34].

Low energy inert gas ion bombardment introduces chemical and morphological changes on surface or near surface region of materials [35,36]. Ion beam sputtering is widely used for surface patterning, surface cleaning and depth profiling of materials used in industries and in basic science research. Ion bombardment on oxide surfaces leads to the reduction of stoichiometric oxides. Such reduction of TiO_2 finds applications in catalysis, dehydration and water dissociation etc. Therefore, the preparation and characterization of reduced TiO_2 surface is important for industrial applications as well as for basic chemistry research. Chemistry of Ti is very complicated due to the possibility of multiple integral and fractional valence states.

In this paper we report the chemical modification of PLD grown TiO_2 poly-crystalline films deposited on Si(1 1 1) from TiO_2 target.

2. Experimental procedure

TiO_2 thin films of 300Å were deposited on Si(1 1 1) surface by conventional PLD method. Prior to the deposition Si substrate was degassed by flashing at 900 °C in Ultra High Vacuum (UHV) to remove surface oxides. The target used for ablation were high purity (99.99%) anatase TiO_2 pellets prepared from commercially available powder. The deposition chamber was back filled with oxygen to a pressure of 1.0×10^{-3} mbar during ablation to maintain oxygen stoichiometry in the deposited film. The substrate temperature was maintained at 500 °C during the film growth. The estimated film thickness using crystal balance is about 300Å.

The deposited film was structurally characterized using X-ray diffraction (XRD). As the sample studied in this case is a thin film of TiO_2 of thickness 300Å on Si(1 1 1) substrate, most of the XRD signal comes from the substrate due to the bulk sensitivity of the technique. Actual TiO_2 reflections are of very low intensity. Fig. 1(a) shows the XRD pattern of TiO_2/Si(1 1 1) emphasizing the TiO_2 peaks. The strong peaks at 33° and 69° correspond to Si(1 1 1) and Si(4 0 0) reflections respectively and two peaks at 25.2° and 38° correspond to (1 0 1) and (0 0 4) reflections respectively of anatase TiO_2 which are in agreement with previously published XRD data [37–43].

The Raman spectrum of TiO_2/Si(1 1 1) is shown in Fig. 1(b) which has been indexed using previously published Raman data on TiO_2 [38]. As expected, Si substrate exhibits Raman peaks around 300, 520 and 965 cm^{-1}. A sharp and intense peak observed at 144 cm^{-1} corresponds to E_g mode of anatase TiO_2. B_{1g} mode is observed at around 390 cm^{-1} and another peak of E_g mode is seen at 630 cm^{-1}. Observed XRD pattern and Raman spectrum confirm the formation of anatase TiO_2 which contains edge shared oxygen octahedra whose centre is occupied by Ti^{4+} ion as shown in Fig. 2.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a VG ESCA machine equipped with argon ion source, twin anode X-ray source and a hemispherical analyser. Ion beam sputtering was done using a 3 keV argon ion beam in-situ in the preparation chamber maintained at a base vacuum of 2.0×10^{-8} mbar. Argon ion current was fixed at 10 μA using an argon pressure of 5.0×10^{-6} mbar. Angle of incidence of the argon ion beam on the sample surface is about 15° measured from the surface normal of the sample. Sputtering was done in a de-focussed mode with a large spot size to cover whole of the sample. Sample

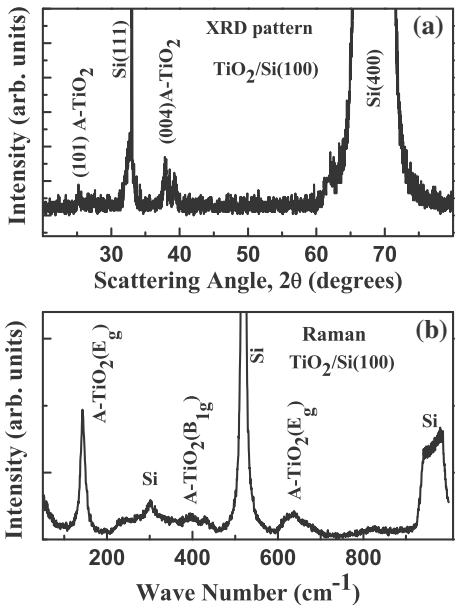

Fig. 1. (a) X-ray diffraction pattern of TiO_2/Si(1 1 1) (b) Raman spectrum of TiO_2/Si(1 1 1).

has been sputtered for 10 min for which the ion fluence is given by 6.0×10^{15} ions/cm^2. The samples have been transferred to the analysis chamber having a base vacuum of 2.0×10^{-10} mbar, immediately after sputtering for XPS measurements. Ti 2p, O 1s, wide range Valence Band (VB) region including Ti 3s, Ti 3p, O 2s and Ti LMM Auger spectra were recorded along with the wide energy survey scans in Fixed Analyzer Transmission (FAT) mode using AlK_α radiation. The total resolution of the spectrometer is 0.8 eV measured as the full width at half maximum (FWHM) of $3d_{5/2}$ peak of clean silver. Binding Energy (B.E.) was calibrated using Au $4f_{7/2}$ at 83.96 eV. This calibration also agrees with the adsorbed C 1s reference taken at 284.6 eV. The surface morphology was studied by AFM (Nanoscope III, Veeco) in tapping mode uisng SiN tip (dimension 5–10 nm) immediately after taking out the samples from XPS chamber.

3. Results and discussion

The survey scans of as deposited and sputtered TiO_2/Si(1 1 1) are shown in Fig. 3. Both the spectra show sharp and intense features corresponding to Ti and Oxygen. Intensity of the C 1s peak is

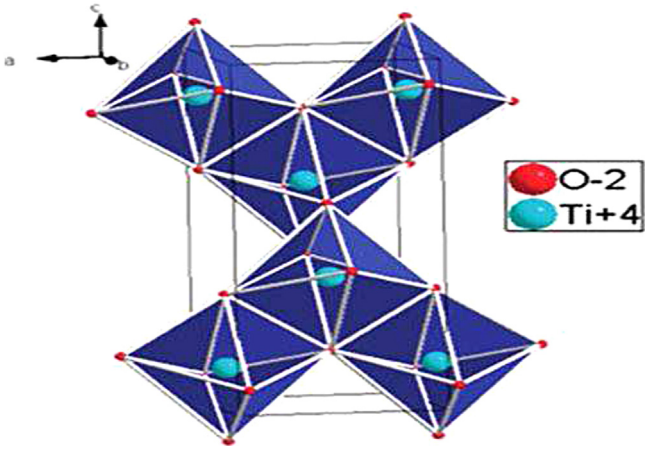

Fig. 2. Crystal structure of anatase TiO_2.