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Epitaxial growth of rutile films on Si(100) substrates by thermal oxidation of evaporated titanium films in argon flux

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Abstract. Thick (2000–3000 Å) titanium oxide films were synthesized on Si (100) substrates and characterized using x-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS). Epitaxial rutile-type TiO_2 (100) films were prepared by an electron beam evaporating a titanium film (1000 Å) in vacuum at 400 °C, followed by oxidation in argon flux at the flow rate of 30 sccm to temperatures of 500–700 °C. RBS analyses show that stoichiometric TiO_2 films were formed by the oxidation of titanium films and 2θ–θ scan and pole figure of XRD confirm that the rutile-type TiO_2 films have the orientation relationship with the substrates (100)TiO_2‖(100)Si and (110)TiO_2‖(110)Si.

Metal oxides have found roles in an extremely wide variety of technologically important areas, from catalysis and gas sensing to diverse applications in water detoxification and solar energy conversion. There are already many techniques which have been reported for the synthesis of titanium oxide films, including sol-gel processing [1], reactive sputtering [2], magnetron sputtering [3], low-pressure chemical vapour deposition [4, 5], dual ion-beam sputtering [6], dynamic ion-beam mixing [7] and ion beam enhanced deposition [8]. Very recently, a few groups have also reported on the preparation of titanium dioxide by ion beam techniques [8], solid-state reactions of titanium/silicon oxide/silicon structure [9], metal–organic chemical vapour deposition (MOCVD) [10, 11]. Meanwhile, a lot of work has also been performed on oxidation of titanium film by furnace oxidation [12, 13] and rapid thermal oxidation [14]. It was reported to be very difficult to synthesize highly-oriented rutile-type titanium oxide unless the special substrates with a close lattice match were selected [15, 16]. This is probably because the evaporated titanium atomic energy is low and atomic mobility in the growing film is inhibited. It has also been found that with the application of transverse current injection (TCI) during deposition, the randomly arranged round structure tended to be arranged in long strings parallel to the current field lines [17]. Ion-beam bombardment during film deposition has been observed to produce beneficial modification in a number of characteristics and properties, such as improved adhesion, densification of films grown at low substrate temperatures and control of orientation. It also offers the possibility to control composition, lattice parameters and grain size [18]. Both TCI and ion-beam-assisted deposition (IAD) can supply additional energy to the deposited atoms during film growth. Until now, to the best of our knowledge, there is no

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reported work on the successful preparation of epitaxial or highly-oriented rutile-type titanium dioxide films, by thermal oxidation of evaporated titanium films. In this paper, we focused on the growth of epitaxial rutile-type titanium dioxide film by a low-cost, easy-to-manipulate and applicable-to-large-area deposition technique, deposition of titanium film and subsequent oxidation in an argon flux.

The titanium films were deposited using an ultra-high vacuum (UHV) molecular beam epitaxy (MBE) system at a base pressure of 10^{-7} pa. High-purity titanium was used as source material for electron beam evaporation deposition. The silicon (100) wafers were cleaned ultrasonically in an acetone bath for 10 min, then a methanol bath for 10 min and finally immersed in de-ionized water. The cleaned silicon wafers were directly used for substrates. We intentionally did not to remove the natural oxide layer on silicon surface because titanium oxide could be more easily formed by heating of the $Ti/SiO_2/Si$ structure [8]. The thickness of all of the deposited titanium films is approximately 1000 Å, and was monitored by a quartz-crystal microbalance and calibrated by Rutherford backscattering spectrometry (RBS) analysis. The deposited titanium films were then oxidized for 1 h using a conventional furnace in argon flux at a flow rate of 30 sccm. The quartz tube was first evacuated to low vacuum (less than 1 Pa) and then pure argon gas was introduced into the tube. 2.5 h were used to increase temperature to the expected temperatures or decrease the temperature down to room temperature. Therefore the total time of oxidation for a sample is 6 h. The samples were kept in an argon flux in the process of increasing and decreasing the temperature. The film structures were then characterized by x-ray diffraction (XRD) and XRD pole figure in air by an X'Pert-MRD four-circle x-ray diffractometer (Philips). The XRD analysis in the θ–2θ configuration was carried out using a step of 0.02° with Cu Kα1. The Kα2 was filtered by a monochromator. RBS/Channeling were carried out using 2.0 MeV $^4He^+$ ions from a 3 MV single stage accelerator at TIARA in JAERI/Takasaki.

The experimental (symbols) and simulated (full curve) RBS spectra of the as deposited and the oxidized titanium films on Si (100) at 400 °C, 500 °C and 800 °C are shown in figure 1. The atomic fraction distributions of titanium and oxygen as a function of depth of these films obtained by RUMP [19] simulation are shown in figure 2. The RBS spectra of the samples oxidized at 600 and 700 °C are not shown in these two figures because they are similar to that of the film oxidized at 500 °C. We can clearly observe that the oxidation of the titanium film is not complete (O:Ti < 0.5) and the titanium at a depth close to the interface is not oxidized after oxidation at 400 °C. The oxidation at 500 °C for 1 h is complete—the titanium film at all depths is completely oxidized and mainly composed of TiO_2. The simulated result show that the titanium dioxide film formed by oxidation at 500 °C and 600–700 °C are stoichiometric at most depths. However, there is a thin interlayer containing titanium, oxygen and silicon. For the film oxidized at different temperatures, the thickness and the relative atomic fractions of the interlayer are different. In the case of the film oxidized at 500 °C, the thickness of the interlayer is about 750 Å and the atomic fraction ratios of Ti:O:Si are roughly 1:2:1.5. The depth closer to Si substrates contains more Si in the oxidized film. For the film oxidized at 700 °C, the thickness of the interlayer is over 1000 Å. The higher oxidation temperature makes Si diffuse outward from the substrates to the film's surface. RBS data also show that the thickness of the titanium oxide films were approximately 1.9 times larger than that of the titanium films deposited on the silicon substrate when the oxidation temperature is higher than 500 °C, i.e. oxidation is complete. This value is in agreement with that, 1.7, reported by K Yokota *et al* [9]. They formed titanium oxide by heating the $Ti/SiO_2/Si$ structure to temperatures of 700–1000 °C in flowing dry oxygen for 1–6 h.

Figure 3 shows XRD analyses of the titanium dioxide film prepared by oxidation at 700 °C. We can clearly see from figure 3(*a*) that the 2θ–θ scan shows only (200) and (400) orientations

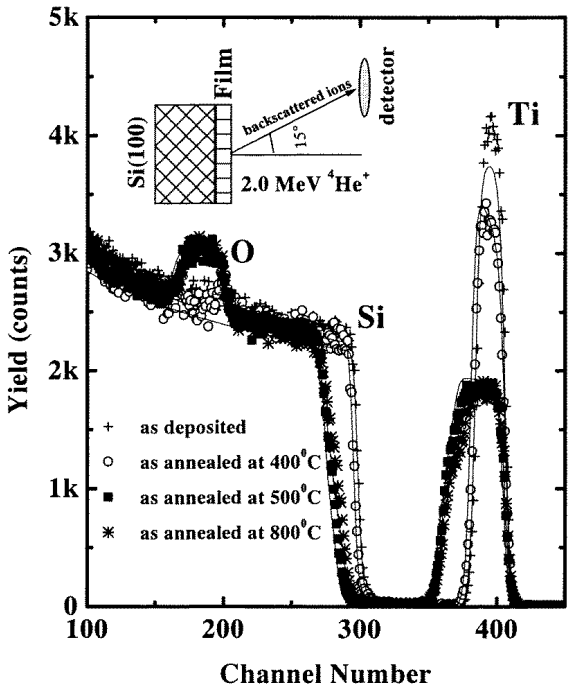

Figure 1. RBS spectra of as-deposited titanium film on Si (100) and those as annealed at different temperatures, 400 °C, 500 °C and 800 °C.

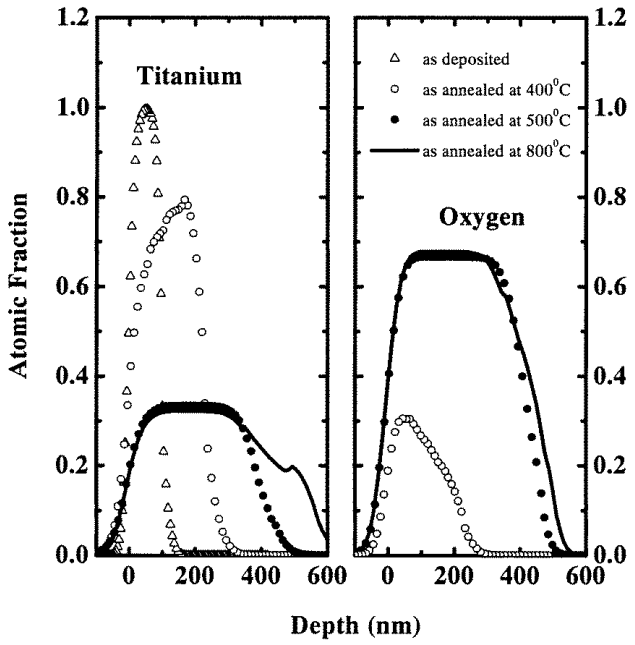

Figure 2. The depth distributions of titanium and oxygen after oxidation at different temperatures, 400 °C, 500 °C and 800 °C.

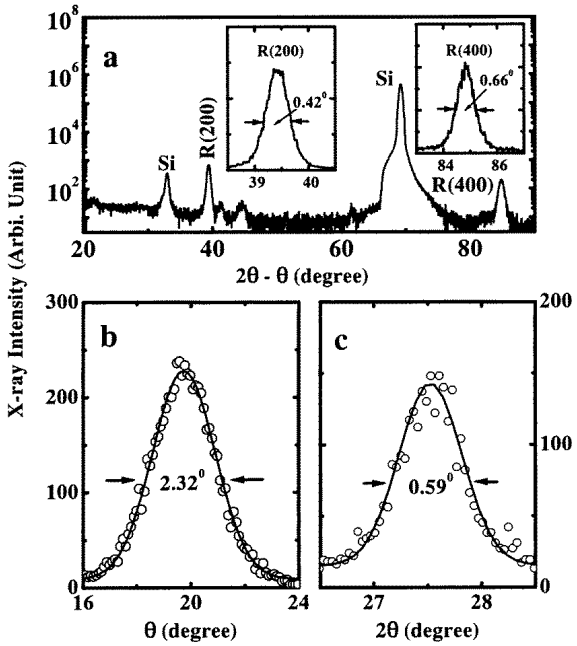

Figure 3. (a). The 2θ–θ scan of the titanium dioxide film on Si (100) prepared by oxidation at 700 °C. The two insets show the details of rutile (200) and rutile (400) peaks. (b) The rocking curve of TiO_2 (200) and (c) the Brag peak of TiO_2 (110) formed after oxidation at 700 °C for 1 h.

of rutile-type titanium dioxide. This suggests that the TiO_2 film grow epitaxially. The details of these two peaks are shown in the insets of figure 3(*a*). The other two peaks, located at 33.03° and 69.19°, are Si (200) and Si (400), respectively. The rocking curves (θ scan at a certain 2θ angle) of TiO_2 (200) and the Bragg peak of the inter plane (110) are shown in figures 3(*b*) and 3(*c*), respectively. The rocking curve of TiO_2 (200) shows a full-width half-maximum (FWHM) of 2.32° and the Bragg peak of (110) shows a FWHM of 0.59°. Both peaks show the distributions of Gaussian function, and they confirm a high-quality film, although further improvement is necessary indicated by relative wide FWHM of the rocking curve of TiO_2 (200).

Figure 4 shows the 2θ–θ scans of the titanium oxide films oxidized at different temperatures, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C. We can see that the XRD patterns of the films oxidized at 500 °C, 600 °C and 700 °C show only (100) orientations. The sharp peak and high intensity suggest high-quality films. From the different intensities of the rutile (200) peaks, we can see the improvement of the crystalline quality with the increase of temperature of oxidation. These indicate that highly-oriented rutile-type titanium dioxide film could be grown on Si (100) by titanium evaporation and subsequent oxidation in the temperature range 500–700 °C.

The orientation relationship was further measured by scanning of the azimuth rotation angle, φ, from 0–360° at the fixing 2θ positions of 27.46° and 47.34° for TiO_2 (110) and Si (220), respectively (see figure 5). The tilt angles, χ, for TiO_2 (110) and Si (220) are the same: 45.00°. It is seen that the (110) peaks of TiO_2 and (220) peaks of Si (100) substrate show fourfold symmetry and locate at almost the same φ positions, although the intensities are quite different. This result confirms that the major portion of the TiO_2 has the orientation relation with the substrates (100)TiO_2‖(100)Si and (110)TiO_2‖(110)Si.

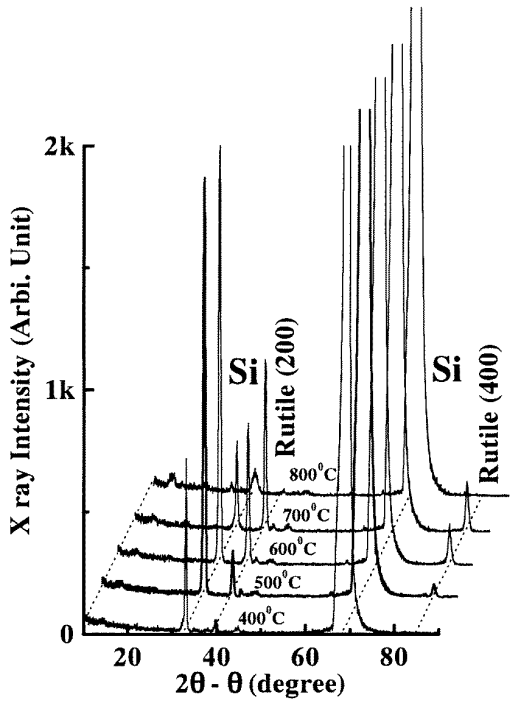

Figure 4. X-ray diffraction data on titanium films on Si (100) after oxidation at different temperatures, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C.

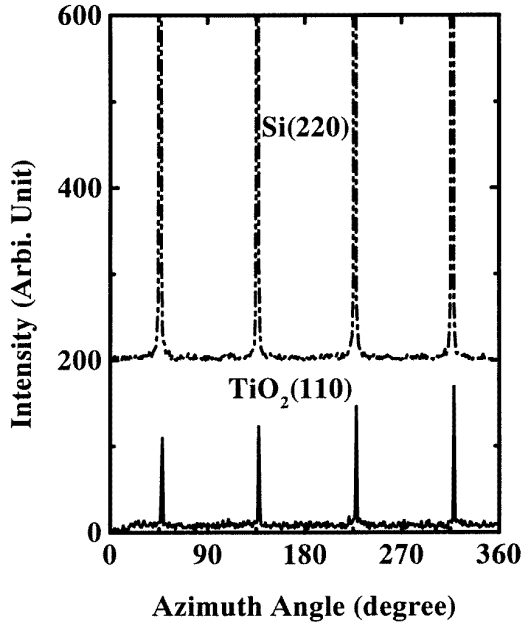

Figure 5. φ scan of (110) pole of the rutile TiO_2 and (220) pole of the silicon substrate oxidized at 700 °C. The full curve and broken curves stand for the data of the rutile film and the substrate, respectively.

In conclusion, we report a low-cost, easy-to-manipulate and applicable-to-large-area deposition technique to prepare epitaxial (100) rutile-type titanium dioxide films on Si(100). Epitaxial TiO_2 (100) films were prepared by an electron beam evaporating titanium film (1000 Å) in vacuum ($<10^{-7}$ Pa), followed by oxidation in an argon flux of 30 sccm. RBS data show that the stoichiometric titanium dioxide films were formed when the oxidation temperature is in the range of 500–700 °C. XRD data confirm that epitaxial rutile (200) films can be grown by oxidation in the temperature range of 500–700 °C and that these films have the orientation relation with the Si (100) substrate $(100)TiO_2 \| (100)Si$ and $(110)TiO_2 \| (110)Si$. The mechanism of the effect of argon flux on the growth of epitaxial rutile-type titanium dioxide films is unknown. It is a completely new and simple technique to prepare epitaxial titanium dioxide films, although it needs further optimization and explanation. This method may also be very useful for film growth of other metal oxide films.

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