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Preparation of TiO_2-anatase film on Si(001) substrate with TiN and $SrTiO_3$ as buffer layers

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Abstract

An epitaxial TiO_2-anatase thin film was grown on the Si(001) substrate with $SrTiO_3$/TiN as the buffer layers by the pulsed laser deposition technique under an oxygen gas supply. The typical thicknesses of TiO_2-anatase, $SrTiO_3$ and TiN layers were 760 nm, 450 nm and 230 nm, respectively. The characterization of the epitaxial TiO_2-anatase film was performed using the x-ray diffraction method. The crystallographic relationships between the TiO_2-anatase film and $SrTiO_3$/TiN buffer layers were analysed by the θ–2θ scan and pole figure measurement. The growth direction of the films was determined as $TiO_2\langle 001\rangle/SrTiO_3\langle 001\rangle/TiN\langle 001\rangle/Si\langle 001\rangle$ and their in-plane relationship $TiO_2\{110\}\|SrTiO_3\{100\}\|TiN\{100\}\|Si\{100\}$. The crystalline quality of TiO_2-anatase was examined by the rocking curve analysis. The composition of the thin film packaging was characterized by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV ^{4}He beam. The simulation of the RBS data points to the possible intermixing of Ti (from TiN) and Si.

1. Introduction

The potential utilization of titanium dioxide (TiO_2) thin films for wide ranging technological applications has been widely reported. Special interest has been focused on the anatase structure of TiO_2 for photocatalytic application due to its higher band-gap (3.3 eV) compared to that of the rutile structure (3.1 eV) [1]. Sumita *et al* [2] showed that a multilayer structure of TiO_2 consisting of the rutile and anatase crystals could elevate its photocatalytic efficiency. O'Regan and Grätzel [3] demonstrated that an electrode made of TiO_2 in anatase form can be useful for a photoelectrochemical solar cell. Recent study has pointed out the dependence of the charge transfer processes on anatase electrodes [4].

Several techniques such as pulsed-laser deposition (PLD) [5], chemical vapour deposition (CVD) [6], sol–gel processing [7], reactive evaporation [8], reactive sputtering [9], ion beam mixing (IBM) and ion beam assisted deposition (IBAD) [10] and the hot wall technique [11] have been implemented for preparation of the TiO_2 films. It is well known that the film properties are strongly dependent upon the film processing and substrate preparation. It has also been accepted that the misfit in lattice constants of both substrate and deposited film plays

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important role for the epitaxial growth of the TiO_2 films. If there exists a large difference between the lattice constants of the substrate and TiO_2 film the epitaxial growth of TiO_2 can only be realized with difficulty [12].

The purpose of this study was to inspect possibility of the epitaxial growth of the TiO_2-anatase film on the multilayer system consisting of the Si(001) wafer and TiN and $SrTiO_3$ buffer layers. To our best knowledge, this is the first report on such an attempt, following the previous work of Chen [6] reporting successful preparation of a high quality TiO_2-anatase(004) film grown on an $SrTiO_3$(100) single crystal. In the present case the growth mechanism of the TiO_2 film on the $SrTiO_3$/TiN/Si(001) multilayer substrate is more complicated because of the complex thin double-layer $SrTiO_3$/TiN stage. The epitaxial growth of TiO_2 with a good crystalline quality can be achieved only if the $SrTiO_3$/TiN buffer layers are well mutually accommodated with only a minimal interface strain.

2. Experiment

The TiO_2/$SrTiO_3$/TiN/Si(001) multilayer thin film system has been grown using the laser ablation technique. For deposition of the TiO_2-anatase film the Nd-YAG laser was employed; for the $SrTiO_3$ and TiN buffer films grown on Si(001) the KrF excimer laser was used. The detailed procedure of the film growth is the following.

Prior to the deposition, the Si(001) substrates were cleaned ultrasonically in acetone and ethanol rinses, each specimen for 15 minutes, to remove hydrocarbons present at the surface. The substrates were then etched ultrasonically in a 5% fluoric acid solution and washed in deionized water again each sample for 15 minutes, for hydrogen passivity.

In the first deposition step the pulsed KrF-excimer laser beam (Lambda Physik LPX-210i, with 248 nm wavelength, 30 ns pulse duration and 0.05–0.2 J cm^{-2} energy range) was focused on to the TiN target (with 50 mm diameter, 5 mm thickness and 99.99% purity) for deposition of the TiN layer. The TiN target and Si(001) substrate were fixed to the target and substrate holders respectively and inserted into the vacuum chamber, which was evacuated to a background pressure $<2.7 \times 10^{-3}$ Pa. The Si substrate was heated up to 873 K and kept at this temperature during the deposition. To prevent the degradation of the surface of the target and to prepare smooth homogeneous film both target and substrate were slowly rotated (10 rpm) during the laser ablation. Before deposition the target was pre-cleaned (using the plasma ablation for few minutes) to remove the contamination from the surface (during the ablation the substrate was screened by a shutter).

In the second deposition step a similar procedure was used for preparation of the $SrTiO_3$ buffer layer. After deposition the multilayer $SrTiO_3$/TiN/Si(001) system was analysed by the x-ray diffraction technique, which confirmed epitaxial growth of both layers (see below).

Growth of the TiO_2 film on the $SrTiO_3$/TiN/Si(001) multilayer sequence was performed using the Nd-YAG laser (with 532 nm wavelength, 145 μs pulse width and 10 Hz frequency). The $SrTiO_3$/TiN/Si(001) substrate was fixed to the substrate holder and placed at a distance of about 50 mm from the titanium-metal target (with 50 mm diameter, 5 mm thickness and 99.99% purity). The background pressure in the chamber was 1.3×10^{-3} Pa, the temperature of the substrate was fixed to 823 K. During the deposition the oxygen gas was supplied to the chamber at the constant pressure of 4.6 Pa. The supply was automatically controlled using MKS type 250-pressure controller. Similarly as for TiN and $SrTiO_3$ also the Ti target was slowly rotated to avoid damage of the surface and irregularity in the ablation rate. After the deposition the sample was cooled down to RT and kept then under the oxygen pressure for about 1 h.

Generally, preparation of thin films using the laser ablation technique proceeds in three separate processes [13]: (1) absorption of energetic photons at the surface of the target results in ablation of the target material, (2) transportation of the material towards the substrate; and (3) condensation and crystal growth on the substrate. Besides the selection of the optimal substrate, as mentioned above, also other parameters such as oxygen pressure, substrate temperature and deposition rate are important factors that influence the growth morphology, crystalline structure and final stoichiometry of the deposited films [14]. In this work the deposition of the TiN and $SrTiO_3$ buffer layers and TiO_2-anatase film growth was inspected varying the above-mentioned parameters. The optimal conditions were achieved with the Nd-YAG laser energy set at 0.05 J/cm^2 and the KrF-excimer energy 0.15 J/cm^2 (the other parameters are cited above).

It should be noted that in the present experiment several substrates (i.e., Si(001), α-Al_2O_3 m-plane and c-plane) were analysed in order to find a suitable backing for the $SrTiO_3$/TiN buffer layer combination. The x-ray diffraction examination showed that though the TiN layer can grow on all mentioned substrates epitaxially in good crystal quality, the $SrTiO_3$ adlayer can grow epitaxially only on TiN/Si(001). For all other combinations (i.e. TiN/α-Al_2O_3 m-plane and TiN/α-Al_2O_3 c-plane) the $SrTiO_3$ layer grows in disordered polycrystalline form. This indicates that the selection of the suitable substrate plays a crucial role for the epitaxial growth (and crystallographic orientation) of TiO_2. For further study only the $SrTiO_3$/TiN/Si(001) multilayer combination was selected.

In this experiment, the crystal structure of the films was examined by the x-ray diffraction method (XRD) in an X'pert diffractometer (Philips PW 3040, Cu Kα = 0.154 056 nm). The film thickness and its composition were analysed by Rutherford backscattering (RBS) using 2.0 MeV $^4He^+$ ions. The size of the beam was about 1 mm in diameter and the beam current typically was about 10 nA. Backscattered particles were detected by a standard surface barrier detector at 165° to the incident beam. The energy resolution of the surface barrier detector was about 15 keV.

3. Results and discussion

In figure 1, a θ–2θ scan of the $TiO_2/SrTiO_3$/TiN/Si(001) thin multilayer system is shown. One can see that five reflections at different 2θ angles were registered. In addition to the Si substrate peak ($2\theta = 69.29°$) other four relatively strong peaks originating from the multilayer system are seen. Peaks at $2\theta = 22.47°$ and $2\theta = 46.85°$ identify reflections from the $SrTiO_3$(100) and (200) crystallographic planes, peaks at $2\theta = 37.87°$ and $2\theta = 42.4°$ from TiO_2-anatase(004) and TiN(200), respectively. The measurement indicates that the TiO_2-anatase(004), TiN(200) and $SrTiO_3$(200) layers were grown epitaxially in parallel texturing with the Si(001) substrate. The simplest possible epitaxial relationship, determined by XRD, is the following: TiO_2-anatase(001)/$SrTiO_3$(001)/TiN(001)/Si(001). It should be noted that the 2θ angles of the observed reflection peaks do not correspond precisely to the data tabulated in the JCPDS-ICDD (Joint Committee on Powder Diffraction Standard—International Centre for Diffraction Data—copyright PSI International) cards. This suggests that the films were grown under (compressive or tensile) stress during the deposition of the ablated material. It is documented on the lattice constant of the deposited films calculated using Bragg's formulae and the experimental 2θ data (see table 1).

In figure 2, rocking curves of the Si substrate and TiO_2, $SrTiO_3$ and TiN films are shown. One can see that with an exception of the substrate the other ω scans show broad curves. The full widths at half maximum (FWHM) of the rocking curves are following: 5.1424°, 4.3424° and 4.5717° for TiO_2-anatase(400), $SrTiO_3$(200) and TiN(200) films respectively. The data give

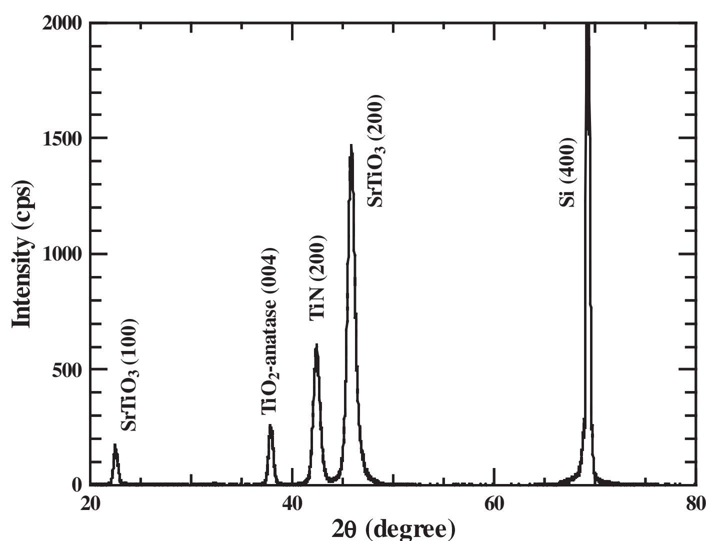


Figure 1. θ–2θ x-ray diffraction shows epitaxial growth of TiO_2-anatase(004) on Si(001) with TiN and $SrTiO_3$ as buffer layers. The growth of the films has been performed using pulsed laser deposition.

Table 1. Summary of structural properties of the sample examined by XRD and RBS.

Sample film thickness[a] (nm)	Crystal structure	Lattice constant: Calculated (nm)[c]	Lattice constant: JCPDS[d] data (nm)	Grain size[b] (nm)
Si —	Cubic	0.3895	0.3903	—
Ti N 227	Cubic	0.4261	0.4242	3.25
$SrTiO_3$ 1247	Cubic	0.3955	0.3905	3.47
TiO_2	Tetragonal	$a = 0.3778$ $c = 0.9495$ $a = 0.3785$ $c = 0.9.5139$	2.85	761

[a] Calculated based on best fitting of simulated curve of SIMNRA computer program to RBS data.
[b] Calculated from ω curve data and using Scherrer formula $B = 0.9\lambda/d\cos\theta$.
[c] Calculated from θ–2θ scan data and Bragg's equation.
[d] Joint Committee on Powder Diffraction Standards.

evidence about the relatively good crystallographic alignment of the crystallites. The size of the crystallites could be calculated using Scherrer formulae [15] $B = 0.9\lambda/d\cos\theta$, where B is the FWHM of the reflection, λ is the wavelength of the incident x-radiation, θ is the diffraction angle of the films and the substrate and d is the size of the crystallites. The crystallite size ranged from 2.85 to 3.47 nm (see table 1).

The growth of TiN (200) and $SrTiO_3$ (200) buffer layers on Si(001) substrate is a good agreement with those reported elsewhere [13, 16] and the growth of these films seems to be in similar manner because the crystal structures of these elements are similar. The existence of the strong reflections from the planes TiN(200) and $SrTiO_3$(200) (see figure 1) indicates

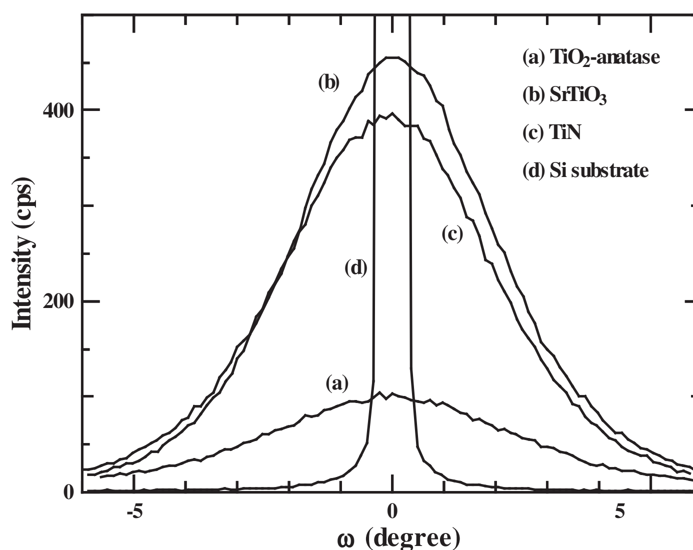
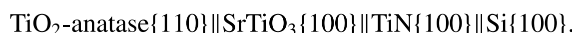


Figure 2. ω scan of growth panes of (a) TiO_2(004), (b) TiN (200), (c) $SrTiO_3$ (200), and (d) Si substrate.

that these planes are crystallographically oriented to the Si(001) single crystal. The pole figure measurement showed (not shown) that both buffer films are grown epitaxially with cube-on-cube texturing and that the TiO_2(101) is oriented at 45° to the $SrTiO_3$(111). The crystallographic relationship to these films is therefore

$$TiO_2\text{-anatase}\langle 001\rangle/SrTiO_3\langle 001\rangle/TiN\langle 001\rangle/Si\langle 001\rangle$$

with orientation relationship



$$TiO_2\text{-anatase}\{110\}\|SrTiO_3\{100\}\|TiN\{100\}\|Si\{100\}.$$

One can see that TiO_2-anatase and $SrTiO_3$ are different in their crystal structure. The crystal structure of TiO_2-anatase has tetragonal symmetry in which each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions [1]. The crystal structure of $SrTiO_3$, on the other hand, is perovskite type with a cubic cell [17]. Chen *et al* [6] suggested that the oxygen atoms from $SrTiO_3$ and TiO_2-anatase form a common atomic network via an oxygen bridging mechanism. Although these materials are different in structure, there is a resemblance in their sublattice anions. In their structures all oxygen atoms are close packed and metallic atoms are located in appropriate octahedral sites. The tetragonal structure of anatase has lattice parameter $a = 0.3785$ and $c = 0.9514$ nm respectively (JCPDS-ICDD No 21-1272) and the cubic structure of $SrTiO_3$ has lattice parameter $a = 0.3904$ nm (JCPDS-ICDD No 35-0734). The lattice mismatch between TiO_2-anatase and $SrTiO_3$ is around 3%. This small value of lattice mismatch makes hetero-epitaxy possible. Once the gas plume of TiO_2 reacts with $SrTiO_3$ (via oxygen bridging) an inevitable formation of oxygen atoms network occurs. The oxygen atoms of TiO_2 align themselves with the existing oxygen of the $SrTiO_3$ film in order to form initial structural network of oxygen atoms and TiO_2 film formation can occur.

The symmetrical tetragonal structure of TiO_2-rutile has lattice constant $a = 0.459\,33$ and $c = 0.295\,92$ nm (JCPDS-ICDD No 21-1276), The lattice mismatch between TiO_2-rutile and $SrTiO_3$ is about 17%. The rutile phases of the deposited TiO_2 film were not detected by the x-ray diffraction measurement, which might be caused by a larger lattice

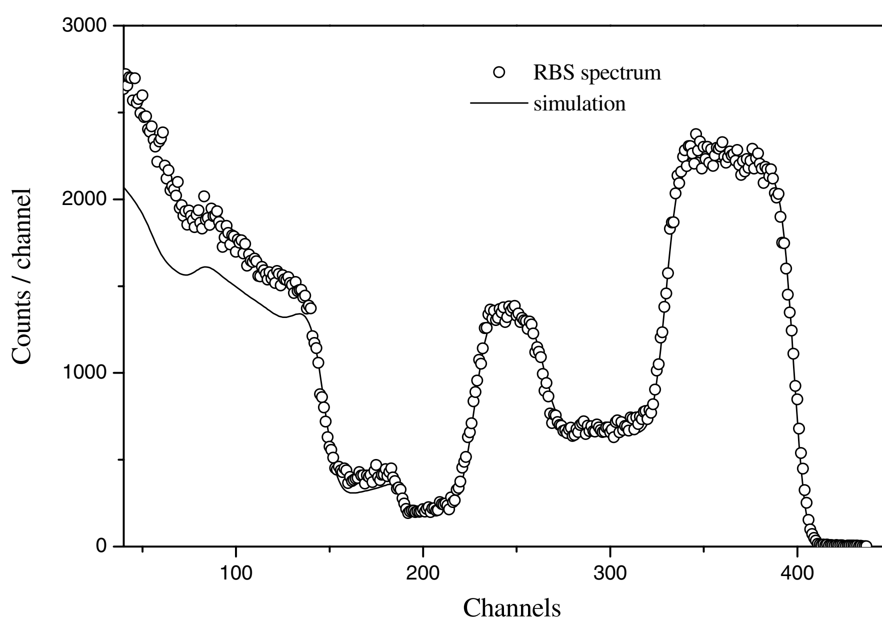


Figure 3. 2.0 MeV $^{4}He^{+}$ RBS spectrum (165° laboratory scattering angle) with that from SIMNRA simulation of TiO_2/TiN/$SrTiO_3$ on the Si(001) substrate.

mismatch between TiO_2-rutile and $SrTiO_3$ compared with TiO_2-anatase and $SrTiO_3$. During the deposition the TiO_2 film will therefore prefer the 'less-stressful way' selecting the anatase variant.

The film composition and thickness was examined by RBS, see figure 3. The experiment was performed using 2.0 MeV of $^{4}He^{+}$ ions. The thicknesses of the films estimated by the SIMNRA simulation computer program are 762, 450 and 227 nm for TiO_2, $SrTiO_3$ and TiN films respectively. It should be noted that the thickness was evaluated using the density of the bulk materials, i.e., the real thickness of the films should be bigger. As can be seen from figure 3 the pattern of the RBS spectra is complicated. The spectrum could be fitted well (using SIMNRA simulation tools) only under the assumption that interdiffusion with about 200 nm thickness between the first buffer layer TiN and the substrate Si occurs. The interdiffusion mechanism is however not clear. The possibility of the formation of a new thin interfacial layer was inspected by XRD; however no significant signal was registered.

4. Conclusion

In this work we report on the growth of the TiO_2-anatase thin film deposited on the $SrTiO_3$/TiN/Si(001) single crystal multilayer system. X-ray diffraction measurement confirmed that the TiO_2 film was grown epitaxially and that its crystalline quality, as follows from the ω measurement, is relatively good (i.e. FWHM = 5.142°). The analysis of the lattice constant however showed that the film is strained. The grain size of the films is in the range of 2.85 to 3.47 nm resulting in an about 5% broadening of the TiO_2(200) reflection peak. The RBS measurement suggested that intermixing between TiN and the substrate might occur. The new intermixed film was however not confirmed by XRD study.

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