Interface structure and phase of epitaxial $SrTiO_3$ (110) thin films grown directly on silicon

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The interface structure and phase between $SrTiO_3$ (110) on Si (100) have been investigated using high-resolution transmission electron microscopy and x-ray photoelectron spectroscopy. The $SrTiO_3$/Si interface was found to be epitaxially crystallized without any amorphous oxide layer. The formation of Sr silicate at the interface was suggested by considering the fact of the core-level spectra of the Si 2*p*, O 1*s*, and Sr 3*d*. Our results suggest that the presence of a coincident site lattice at the interface between Si and a Sr silicate and/or $SrTiO_3$ may help to stabilize $SrTiO_3$ in the epitaxial orientation reported in the work. © *2005 American Institute of Physics*.
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Interfacing perovskite oxide with silicon (Si) is a major challenge.[1,2] The system of $SrTiO_3$(STO)/Si can be used as a growth substrate for fabrication of thin films of other functional oxides and carbon nanotube transistors.[3–5] Those STO films grown directly on Si using various deposition techniques were usually polycrystalline with randomly oriented grains.[6–10] The pioneering work of McKee, Walker and Chisholm demonstrated the epitaxial growth of STO on Si (001) with a $SrSi_2$ submonolayer interface by molecular beam epitaxy (MBE) technique.[11] Extensive research has been carried out on the growth of STO (001) on Si (001) with various single buffer layers and/or multi-buffer layers.[4,12–15] Recently, both theoretical and experimental studies have shown that the resulting interfacial structures between silicon and the grown STO thin films depend upon the details of deposition conditions and specific growth sequences.[16–19] It suggests that differing synthesis routes may lead to epitaxial STO films with different atomic scale structure of the interface. Using MBE technique, Tambo *et al.* observed a $\theta-2\theta$ x-ray diffraction pattern of (110) oriented STO grown on a Si (100) at a substrate temperature of 500 °C.[20] Furthermore, an epitaxial STO(100) film was successfully grown on SrO/Si (100) at 500 °C in an oxygen atmosphere of 8×10^{-8} Torr in their work. In this letter, we have grown epitaxial STO (110) films on Si without any buffer layer by pulsed laser deposition (PLD) technique. We present the study of structure and phase at the STO/Si interface using various measurements.

A single-crystal STO target was used in our PLD deposition. The (100)-oriented Si substrates were chemically cleaned. The substrates were mounted on a directly heated sample holder made of stainless steel sheet. To remove the native oxide from the Si surface, the Si wafers were etched in a dilute HF solution prior to the loading into the chamber. Furthermore, the native oxide on the silicon substrate surface may be then completely removed by heating to 850 °C in 5×10^{-6} mbar. During STO film growth in a two step process, the substrate temperature was maintained at 760 °C. The initial growth of STO films was carried out under relatively low O_2 pressure of 1.4×10^{-3} mbar for 1 min to avoid the rapid oxidation of the Si substrates. Subsequently, the STO films were deposited in an oxygen pressure of 1.4×10^{-2} mbar for 2–40 min. The deposited film was cooled to room temperature in an oxygen atmosphere of 600 mbar. The total film thickness was 70–950 nm from the measurement of a Dektax^{3}ST surface profile. The x-ray diffraction (XRD) analysis was made using $\theta-2\theta$ scan on the Siemens D5000 x-ray diffractmeter. The in-plane alignments of the films were studied by low-angle Laue diffraction.[21] The interfacial microstructures were studied using high-resolution transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS).

Figure 1 shows a typical XRD $\theta-2\theta$ scan curve of STO thin films directly grown on (100)-oriented Si substrates. The STO films exhibit strong (110) diffraction peaks in addition to the silicon substrate diffraction, with no extra XRD peaks

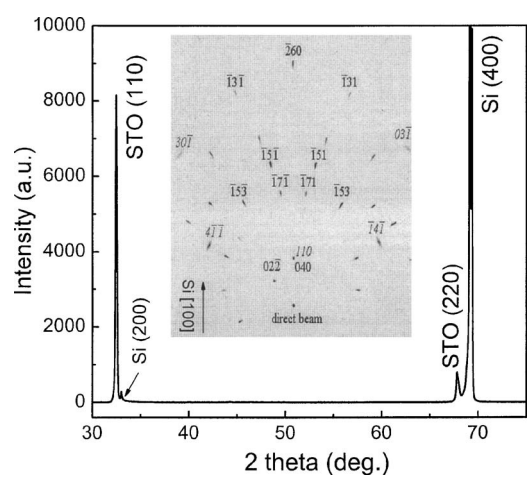

FIG. 1. X-ray diffraction $\theta-2\theta$ patterns of STO thin films grown directly on Si (100). The inset shows low-angle Laue diffraction pattern of STO thin films on Si. X-ray is incident at the film surface at ~8°. Si peaks are indexed as normal numbers while STO peaks are broader and indexed as italic numbers.

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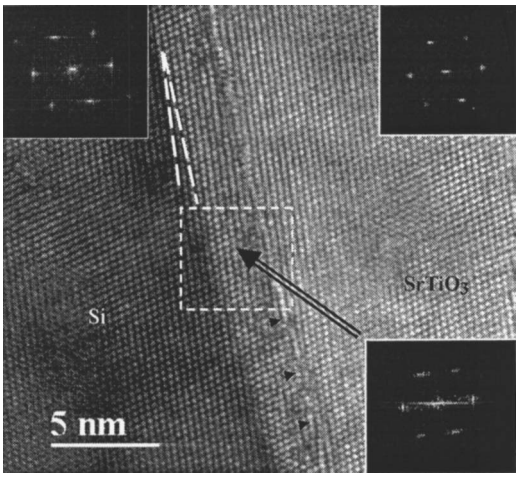

FIG. 2. Cross-sectional transmission electron microscopy (TEM) of the STO thin films grown on Si (100), and plots of corrsponding fast Fourier transform taken at the STO film, STO/Si interface and Si substrate, respectively. Si substrate miscut is observed, which is around 8° measured from this image. Periodic arrays of dislocations are marked with arrow heads.

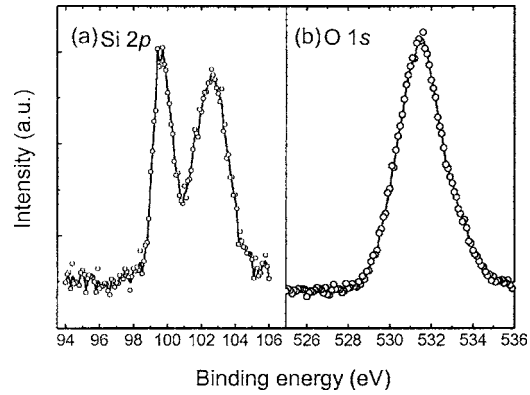

FIG. 3. XPS spectra for (a) Si 2*p* and (b) O 1*s* core levels at the interface of STO and Si.

from other crystalline orientations of the STO films. The inset in Fig. 1 shows the resulting Laue diffraction patterns of the STO thin films on Si. The spots for STO films and Si were labeled. Analysis of the Laue diffraction pattern for STO/Si reveals that the in-plane alignments are STO[001]∥Si[001] and STO[1$\bar{1}$0]∥Si[010]. It demonstrated that the epitaxial growth of STO thin films on Si without any buffer layer has been achieved through rotating the STO lattice by 45° with respect to the Si lattice. The lattice constants of STO and Si are $a_{STO}=0.3905$ and $a_{Si}=0.5429$ nm, respectively. As a result, a lattice mismatch between STO and Si is quite large $(|a_{STO}-a_{Si}|/a_{Si}\times 100\%=28\%)$. However, the lattice mismatch along the Si [010] direction reduces $(|a_{(1\bar{1}0)STO}-a_{Si}|/a_{Si}\times 100\%=1.7\%)$ after a 45° in-plane rotation. Extensive study has been carried out on the lattice mismatch and microstructure of STO/Si in Ref. 22. Their work demonstrated that the mode of growth was probably of two-dimensional growth followed by island nucleation since the film was deposited on the (001) plane of Si and the lattice mismatch between STO and Si is neither small nor large. In our further experiment, it is found that the lattice mismatch between the STO films and Si could be accommodated by the presence of interface dislocation.

Figure 2 shows a cross-sectional TEM image of the STO thin films grown on Si (100), and plots of corresponding fast Fourier transforms (FFTs) taken at the STO film (inset in the upper right), the STO/Si interface (lower right) and the Si substrate (upper left), respectively. The incident electron beam is parallel to the [110] direction of the silicon substrate. The result confirms a highly epitaxial STO film grown directly on the Si substrate. An intermediate layer approximately 2.6 nm thick is visible, which grew epitaxially from the Si plane. Periodic array of misfit dislocations can be observed in the interface area as marked with arrow heads in the TEM image, revealing that lattice strain and interdiffusion at the interface may occur. Also, it is worth noting that there is no blurred diffusing ring pattern in the fast Fourier transforms of the intermediate layer, which is characteristic for amorphous structure in TEM analysis. The observation of a crystalline transition across the STO/Si has provided convincing evidence to exclude the formation of an amorphous interfacial layer, which is commonly found at the STO/Si interface grown by various techniques.[9,23] From the TEM image of Fig. 2, it is visible that a considerable miscut of around 8° was introduced in the Si substrate. Earlier studies revealed that a miscut of the substrate has a strong effect on the microstructure of the film.[24–26] It seems possible that the STO epitaxial orientation in this work has also been influenced by the Si substrate miscut. Furthermore, we speculate that the intermediate phase layer is very crucial to the subsequent epitaxy growth of the STO film. For certain Si(001) miscut angles and direction, the highly epitaxial film indicates that there may be a coincident site lattice at the interface between Si and the intermediate phase and/or the STO film that helps to stabilize STO in the epitaxial orientation reported here.

In order to confirm the absence of amorphous silicon oxide in the STO(110)/Si heterostructure, we examined the changes in XPS core levels of Si 2*p* and O 1*s* of the STO/Si interface as shown in Fig. 3. Apart from the Si 2*p* peak at 99.6 eV for pure Si, a broad peak centered about 102.6 eV formed. On the other hand, the binding energy of O 1*s* of the STO/Si interface was found to be 531.5 eV. It is known that the binding energies of Si 2*p* and O 1*s* peak for SiO_2 are at 103.6 and 532.5 eV, respectively. Consequently, no peak corresponding to the binding energy of amorphous SiO_2 was found at the interface, which agrees well with the TEM observation shown in Fig. 2. The lower binding energy of the Si 2*p* and O 1*s* lines of the STO/Si interface than that of SiO_2 may be explained on the basis of two possible mechanisms. The first mechanism is associated with the oxygen loss for SiO_2 layer. The second mechanism for the peak shift may be attributed to the formation of silicate.[27–29]

To distinguish between those two possibilities and clarify the interfacial chemical state, the XPS depth profile of the Sr 3*d* spectrum was investigated. As shown in Fig. 4, the Sr $3d_{5/2}$ and Sr $3d_{3/2}$ lines shift towards higher binding energy when the probing depth approaches to the STO/Si interface. It indicates that the chemical state of Sr has changed throughout the region of STO/Si interface. This finding excludes the possibility of the existence of a reduced SiO_2 compound. In that case, the chemical state of Sr should remain the same throughout the STO/Si system. Furthermore, the peaks of Si 2*p*, O 1*s*, and Sr 3*d* core-level spectra at the interface shown in Fig. 3 and 4 are in agreement with earlier reported values in silicates.[16,27–31] Thus, we could conclude that an interfacial Sr-silicate compound was formed at the

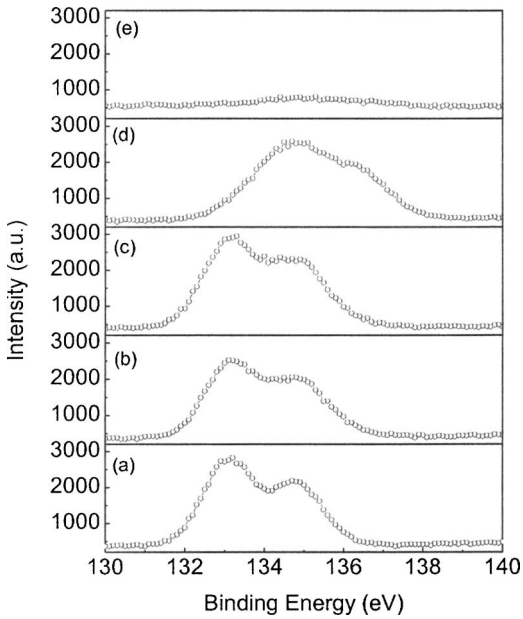

FIG. 4. XPS depth profile of Sr 3*d* core-level spectra for epitaxial STO (110) film on Si: (a) film surface, (b) after a 168 s sputtering, (c) after a 336 s sputtering, (d) after a 420 s sputtering, and (e) after a 487 s sputtering.

STO/Si interface. Our results are similar to those of STO (100) films grown under relatively high temperature growth conditions by MBE.[16,27]

The (110)-oriented STO structure is useful for practical applications such as the preparation of ferroelectric-insulator-semiconductor devices.[4] Most recently, Mukunoki *et al.* further proposed that (110)-oriented STO multilayer growth may provide a broad solution to the generic problem of polarity discontinuities at perovskite heterointerfaces.[32] Earlier work indicated that the use of a single buffer layer like $Ce_{0.12}Zr_{0.88}O_2$ or double buffer layer like CeO_2/YSZ is necessary to prepare high-quality STO (110) films on Si (100) substrates.[4,13] Our successful growth of epitaxial STO (110) films without any buffer layer is thus unexpected. Moreover, direct epitaxy of STO on Si was commonly regarded as quite difficult due to the thermodynamic problem of interfaces. Therefore, the complicated and precise growth process for the epitaxy of STO thin films on Si has been presented in previous work.[11,15,33,34] Comparatively, our process for the epitaxial growth is simpler and easier to handle. In our experiments, the conditions for achieving epitaxial STO thin films on Si were limited to deposition conditions such as deposition temperature and oxygen pressure as well as specific growth sequences. It is likely that the silicate interfacial layer was formed initially at the early stage of film growth in our deposition. The interfacial layer could terminate the Si surface prior to the establishment of epitaxy of STO thin films. This reflects the fact that the Sr-silicate/Si interface may be more stable than the STO/Si interface.

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