Improvement of laser molecular beam epitaxy grown $SrTiO_3$ thin film properties by temperature gradient modulation growth

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Oxygen diffusion at the $SrTiO_3$/Si interface was analyzed. A method called temperature gradient modulation growth was introduced to control oxygen diffusion at the interface of $SrTiO_3$/Si. Nanoscale multilayers were grown at different temperatures at the initial growing stage of films. Continuous growth of $SrTiO_3$ films was followed to deposit on the grown sacrificial layers. The interface and crystallinity of $SrTiO_3$/Si were investigated by *in situ* reflection high energy electron diffraction and x-ray diffraction measurements. It has been shown that the modulated multilayers may help suppress the interfacial diffusion, and therefore improve $SrTiO_3$ thin film properties.
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Many efforts have been devoted to the study of crystalline oxide thin films on silicon (Si) since the unique properties of those oxides may be combined with Si-based integrated circuits.[1,2] $SrTiO_3$ (STO) is a cubic perovskite structure and has a lattice constant closely matched to a large number of other perovskite oxides. Thus, the STO/Si system can be used as a growth substrate for the preparation of many functional oxides. However, the union of oxides and Si presents potentially the significant challenge to the basic study of growth, due to serious complications concerning reactivity between the oxide and Si as well as bonding changes from covalent bond in Si to ionic in the oxide.[3] The main problem is the formation of an amorphous oxide over Si surface due to oxygen diffusion, which may prevent STO film from crystal growth. Therefore, those STO films grown directly on Si were usually polycrystalline with randomly oriented grains.[4–6] Extensive research has been carried out on the finding of a solution to the problem. Up to know, the study mainly focuses on the introduction of additional materials, i.e., various single or double buffer layers between STO and Si.[7–9] Typical work includes the growth of $SrSi_2$ submonolayer as a buffer layer by molecular beam epitaxy (MBE), which was reported by McKee *et al.*[10] There are a few reports on the growth of STO directly on Si.[11,12] In this letter, we have grown (100)-oriented STO thin films on silicon without any buffer layer by controlling oxygen diffusion at the STO/Si interface by laser MBE. The growth mode and structure of STO/Si were verified using a variety of measurements.

STO thin films were deposited directly on *p*-type Si substrates by laser MBE. The laser used in this study was KrF ($\lambda = 248$ nm) excimer laser. The laser energy density was 6 J/cm^2 in a repetition rate of 3 Hz. A single crystal target of STO was employed in the experiments. The (100)-oriented Si substrates were first chemically cleaned, then dipped into a buffered solution with 4% HF for 60 s to remove the amorphous SiO_2 layer from the surface of the Si, leaving a hydrogen-terminated surface. The substrates were mounted on a commonly used resistive heater block made of heating wire. During the film growth, the *in situ* reflection high energy electron diffraction (RHEED) was used to investigate the formation of interface and structure of films grown at different temperatures. The microstructures were also studied using x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) measurements.

As shown in left inset of Fig. 1(a), the RHEED patterns of the Si (100) have clear bright 1×1 streaks, indicating that substrates have an atomic flatness without any formation of the amorphous layers. STO films were grown directly on Si (100) substrates at the temperature of 600 °C. As the deposition of STO films started, the RHEED patterns disappeared immediately, which indicated that an amorphous layer was formed, as shown in right inset of Fig. 1(a). No spotty or streaky RHEED pattern was observed until the end of the deposition, suggesting that nonsingle crystal films formed under the condition. As shown in Fig. 1(a), polycrystalline STO films with random orientations were obtained from the XRD patterns. When the growth temperature was increased to 700 °C, similar results with random orientations were observed in Fig. 1(b). Combining the XRD and RHEED results, we could speculate that the Si surface was oxidated at the initial growing stage of STO deposition. Oxygen diffusion at the STO/Si interface may lead to the formation of an amorphous layer, resulted in the subsequent polycrystalline growth. This is commonly found at the STO/Si interface grown by various techniques.[4–6,13,14]

In order to examine behaviors of oxygen diffusion and amorphous layer in the STO/Si system, we have measured the changes in XPS core levels of Si 2*p* at the STO/Si interface grown within relatively low temperature ranges from 300 to 500 °C. Figure 2 shows that a broad peak centered about 102.4 eV formed besides for the Si 2*p* peak from pure Si. The broad peak was possibly associated with the binding energy of reduced SiO_2 (SiO_x). With increasing the growth temperature, the intensity of the peak relative to the signal

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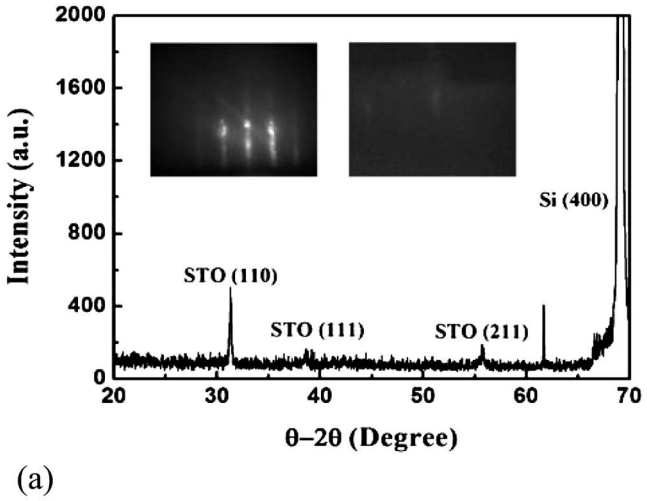

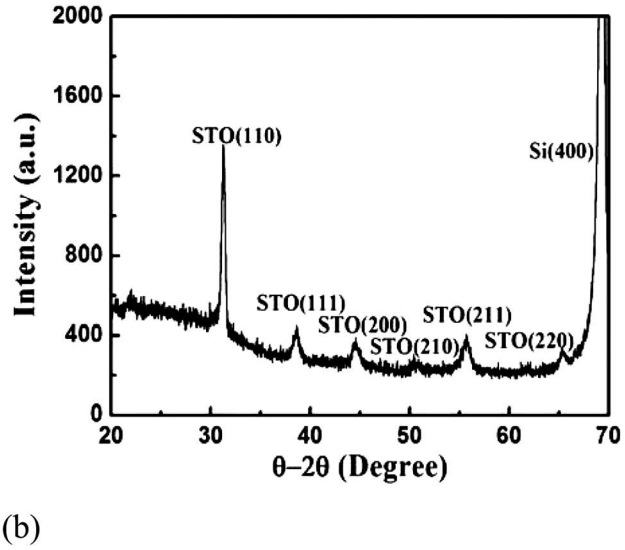

FIG. 1. XRD patterns of STO films grown directly on silicon at different temperatures. (a) 600 °C and (b) 700 °C. The left inset of (a) is a RHEED pattern of Si substrates, and the right inset is a RHEED pattern of STO film.

from pure Si increases. It indicates that the oxygen diffusion increases, and then the Si atoms can be more oxidized. The observation agrees well with other researchers' results.[15,16]

In the case of oxide/Si interface diffusion, both growth temperature and film thickness have great influence on the interface and structures of thin films. Therefore, it is possible to control the oxygen diffusion and structure of STO/Si through manipulating the growth temperature and film thickness. A method called temperature gradient modulation growth (TGMG) has been proposed and carried out. At the initial growing stage, STO films as nanoscale multilayered structures were deposited on Si at different temperatures with various thicknesses. The growth parameters were carefully managed to control the layer thickness at different stages as follows: at 100 °C of growth temperature with 2 nm of thickness, then at 300 °C of growth temperature with thickness of 4 nm, and at 400 °C of growth temperature with 10 nm of thickness. Afterward, further continuous growth of STO films was followed to deposit on the grown sacrificial layers at the temperature of 600 °C.

During the whole growth processes of nanoscaled multilayers of STO films, the initial RHEED patterns with clear

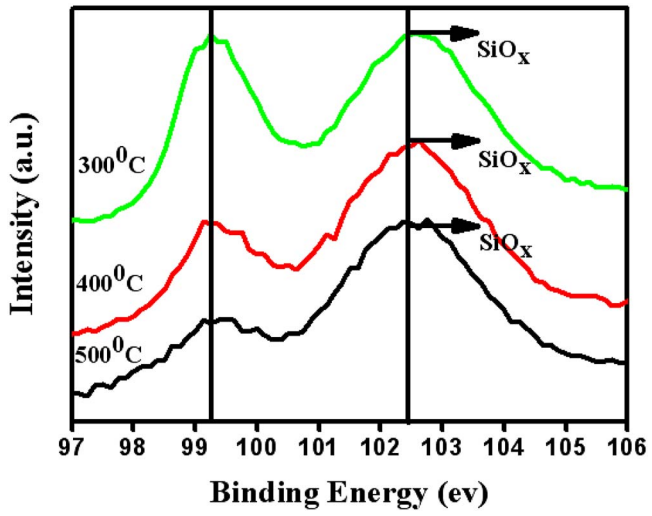

FIG. 2. (Color online) XPS spectra of Si 2*p* of STO/Si for different temperatures.

bright 1×1 streaks from Si substrates became gradually diffused and disappeared eventually, as shown in Figs. 3(a) and 3(b). When the subsequent STO films were grown on those former sacrificial layers, the streaky patterns were observed, as shown in Fig. 3(c). Also, no arc or ring pattern associated with the polycrystalline pattern appeared. According to extensive studies in our earlier work,[17–20] Fig. 3(c) demonstrates that the growth switches to good crystalline growth with highly orientation in two-dimensional layer-by-layer growth. On the other hand, the streaky RHEED pattern of the as-grown STO films grown on Si in Fig. 3(c) looks dim compared with the bright streaky patterns from our previous observation in homoepitaxial STO films.[17] XRD measurement has been performed to reveal the crystal structure of as-grown STO films. Figure 4 shows the highly (*h*00) orientation of STO films, indicated the formation of high-quality STO thin films with good crystallization. In comparison with the polycrystalline STO films in Fig. 1, no extra XRD peaks from other crystalline orientations of the STO films exist in the measured 2θ range, suggesting that the STO thin films have a pure perovskite phase with lattices highly oriented along the (*h*00) direction, although the films possess some defects detected by RHEED. Based on these results and recent literatures,[21,22] it could be speculated that the initial modulated nanoscale multilayers consisted of many defects and/or nanoscale second phase, which may help to suppress the interface diffusion between STO and Si. Furthermore, the crystalline STO films have been promoted by the former sacrificial layers at the interface. Actually, some gradient growth techniques, e.g., oxygen relaxation techniques, had been carried out to deposit STO and $Sr_xBa_{1-x}Nb_2O_6$ thin films by

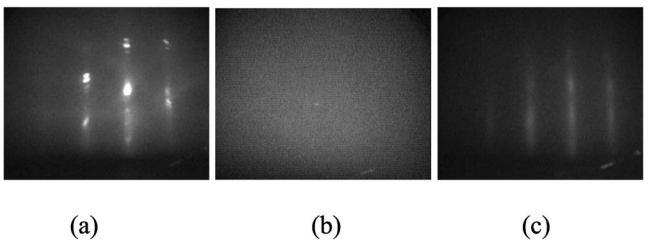

FIG. 3. RHEED patterns of (a) Si substrate, (b) as-grown nanoscale sacrificial layers, and (c) subsequent STO films.

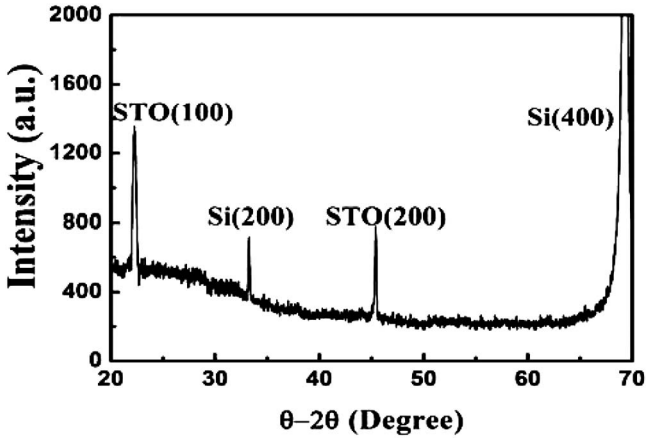

FIG. 4. XRD θ-2θ scan of the STO/Si system grown by TGMG method.

other research groups toward improvements of crystalline qualities, electrical properties, and the microstructure of ferroelectric thin films.[23,24] However, there is no report on the system of STO/Si by gradient growth. It is well-known that randomly oriented polycrystalline films have certain limitations in various applications. Formation of various grain sizes and growth orientations and coexistence of secondary phase may cause low performance of the integrated devices. The technique reported in our work makes it possible to fabricate well-ordered interface for STO/Si heterostructures. Moreover, the reported technique may be expected to extend to the fabrication of other perovskite titanate heterostructures. In principle, it is possible to improve the crystallinity degree of the as-grown sample through postannealing process. Our previous results showed that the formation of STO crystalline phase processed by rapid thermal annealing was strongly dependent on the postannealing temperature, and the increase of annealing temperature led to an improvement in the crystalline quality of STO thin films grown on Si.[25] Further study on the optimization of postannealing process is in progress.

In summary, we demonstrate a TGMG technique to control oxygen diffusion at the interface of STO grown directly on Si. It suggests that the initial modulated STO nanoscale multilayers may have many defects and/or second phase, which may act to suppress the interface diffusion between STO and Si, and induce later crystalline growth of STO. Improved properties of STO thin film were found.

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