

Epitaxial growth of SrTiO₃ thin film on Si by laser molecular beam epitaxy

X. Y. Zhou, J. Miao, J. Y. Dai, H. L. W. Chan, C. L. Choy, and Y. Wang^{a)}
*Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR,
 China and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong SAR, China*

Q. Li
Department of Physics, The Chinese University of Hong Kong, Hong Kong SAR, China

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SrTiO₃ thin films have been deposited on Si (001) wafers by laser molecular beam epitaxy using an ultrathin Sr layer as the template. X-ray diffraction measurements indicated that SrTiO₃ was well crystallized and epitaxially aligned with Si. Cross-sectional observations in a transmission electron microscope revealed that the SrTiO₃/Si interface was sharp, smooth, and fully crystallized. The thickness of the Sr template was found to be a critical factor that influenced the quality of SrTiO₃ and the interfacial structure. Electrical measurements revealed that the SrTiO₃ film was highly resistive. © 2007 American Institute of Physics. [DOI: 10.1063/1.2430407]

The epitaxial growth of SrTiO₃ (STO) thin film on silicon has attracted extensive interest in recent years.^{1,2} The STO/Si heterostructure not only provides an ideal model structure for the study of growth dynamics and kinetics of perovskite-structured oxides on silicon^{3–8} but is also a useful substrate for various microelectronic devices, such as silicon complementary metal oxide semiconductor devices, random access memory, and microelectromechanical systems.^{9–11} Good crystallinity, epitaxial alignment, and clean interface are the major requirements of STO and the STO/Si heterostructure. Several thin film deposition techniques, including molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), have been adopted for the synthesis of STO.^{2,12} While the processing conditions and thin film growth mechanisms are significantly different in these deposition processes, it is noted that the use of strontium (or strontium oxide) template has become a common and—to a certain extent—“standard” procedure in the latest literature reports. The major purpose of introducing such a template is to suppress the formation of an amorphous silicon oxide layer on the Si surface and assist the growth of STO.^{5,8,9,12–14} Under optimal conditions, it has been reported that high quality STO films have been deposited (by MBE and MOCVD) on Si.^{2,12}

In this letter, we report on the epitaxial growth of STO on Si by laser molecular beam epitaxy (laser MBE) using a SrTiO₃ ceramic target. Compared with many other thin film deposition methods (such as magnetron sputtering and MBE), the laser-MBE technique has the advantage of precise composition control. The possible disadvantage of this technique, however, is that the use of a ceramic target may make it more difficult to obtain a clean interface between STO and Si. This is because the plume (generated by the irradiation of the ceramic surface by a pulsed laser beam) may contain quite a number of oxygen atoms and ions which can react with silicon, leading to the formation of an amorphous silicon oxide layer on the substrate surface. Thus how to suppress or prevent the oxidizing reactions is the major problem to be tackled in this work.

The deposition was conducted via a three-step procedure: (1) Wet cleaning, a (001) Si wafer was treated by standard chemical cleaning procedures followed by HF etching. The freshly cleaned wafer, together with two targets (high-purity Sr and SrTiO₃), was then installed in the vacuum chamber of the laser-MBE system. After the target installation, the chamber was immediately evacuated by using a mechanical pump and a turbomolecular pump. (2) Dry cleaning, when the pressure in the chamber was lower than 1×10^{-6} Torr, the Si wafer was heated up to 850 °C and kept at this temperature for 15 min, with the aim of removing the residual hydrogen on the Si surface. Then the temperature was lowered to a temperature T_d and a very thin layer of strontium was deposited by irradiating the Sr target with a pulsed KrF excimer laser beam. This step aimed to remove the SiO₂ layer that had been freshly formed during the processing.^{15,16} (3) Deposition, following the deposition of the Sr layer a STO layer was deposited using the same laser. Initially a relatively low substrate temperature (~ 650 °C) and low oxygen pressure (0.02 Pa) were used, while at a later stage the temperature and oxygen pressure were increased to ~ 800 °C and 50 Pa, respectively.

Crystallographic characterizations of the samples were performed in a Bruker AXS D8 Discover x-ray diffractometer. The surface morphology of the STO thin film was observed in an atomic force microscope (AFM) (Digital Instrument Nanoscope IV) working in the tapping mode. A JEOL JEM-2011 transmission electron microscopy (TEM) operating at 200 kV was used to observe the crystal structure and interfaces at the atomic level. The high resolution scanning transmission electron microscopy image was taken using a high angle annular dark field detector in a scanning transmission electron microscope (STEM) (Tecnai G2 FEG). The electron energy loss (EEL) spectroscopy was performed in the STEM line scan mode, using a Gatan imaging filtering system attached to the same microscope. The electron probe size was maintained at 0.3 nm. Gold dot electrodes (200 μm in diameter) were deposited on top of the film by magnetron sputtering, and the current-voltage (I - V) characteristics of the Au/STO/Si capacitor (metal oxide semiconductor structure) were measured using an Advantest TR8652 digital electrometer.

^{a)} Author to whom correspondence should be addressed; electronic mail: apywang@inet.polyu.edu.hk

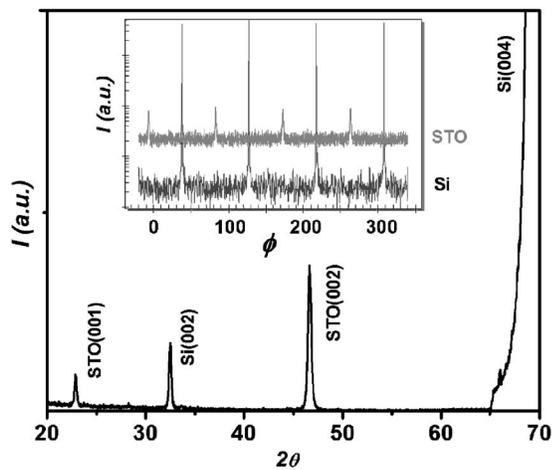


FIG. 1. X-ray diffraction patterns of STO/Si. The inset shows the offset ϕ -scan results of the sample.

The structures of the STO-film and STO/Si interface were found to be very sensitive to the processing parameters, including the deposition temperature, atmosphere and pressure, and laser energy and pulse rate. This observation is consistent with literature reports.^{2,4,17} Among these parameters, however, the parameters that have the most critical influence are the thickness of the Sr template t_{Sr} and the deposition temperature for the Sr template T_d . Samples prepared under optimized processing conditions ($T_d \approx 650 \pm 50$ °C and $t_{Sr} \approx 1.2 \pm 0.4$ nm) tend to be of high quality and have a sharp and clean (free of amorphous material) STO/Si interface, while samples prepared under conditions outside the above range either have a rough and sawlike interface (when the deposition temperature is too high and/or the Sr template is too thick) or a thick amorphous layer (when the deposition temperature is too low and/or the Sr template is too thin). This processing-structure relationship, we believe, is closely related to the reaction $\text{SiO}_2 \rightarrow \text{Si} + 2\text{O}$ and the role that Sr plays in the reaction. SiO_2 in the above chemical equation corresponds to the amorphous SiO_2 layer that forms on the fresh Si surface during its contact with air (i.e., in the time interval after the chemical cleaning and before the achievement of high vacuum in the chamber) and exposure to the plume (in the first few seconds of STO deposition). The rate of the decomposition of SiO_2 at high temperatures could be enhanced by the catalyst Sr, as suggested in the literature. It is reasonable to assume that, under optimized conditions, the SiO_2 layer could be completely removed, so the surface of the Si substrate would become very clean.

In the following we will show the typical structure of the sample prepared under optimized conditions. Figure 1 shows the x-ray diffraction (XRD) $\theta/2\theta$ scan of the sample. The STO thin film has a pure perovskite phase with lattices highly oriented along the (00 l) direction. The in-plane alignment of the STO thin film with respect to the major axes of the (001) Si substrate was also investigated by XRD off-axis ϕ scans and the results are shown in the inset of Fig. 1. Based on the XRD data, it is concluded that the crystal structures of STO and Si have the relationship of $(100)_{\text{STO}} \parallel (100)_{\text{Si}}$ and $\langle 100 \rangle_{\text{STO}} \parallel \langle 110 \rangle_{\text{Si}}$, which is consistent with results reported in the literature.^{10,18} The surface morphology of the STO thin film was observed in an AFM (picture not shown). The average grain size was in the range of

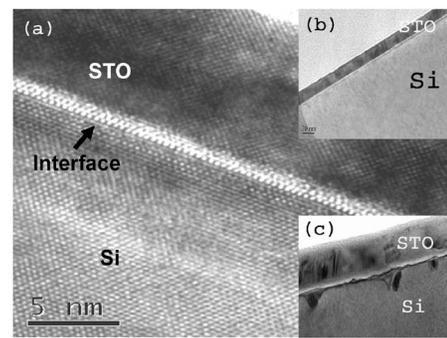


FIG. 2. Cross-sectional observation of STO/Si samples under TEM. (a) High resolution image and (b) conventional resolution image of a sample prepared under optimized conditions and thus having a clean and sharp interface. (c) Conventional resolution image of a sample with a poor interfacial structure. The sample was prepared with processing conditions of $T_d \sim 750$ °C and $t_{Sr} \sim 3.6$ nm.

40–50 nm and the root-mean-square roughness was about 1.0 nm over a $1 \times 1 \mu\text{m}^2$ area, which suggests that STO has a fairly flat film surface.

The cross-sectional structures of the STO/Si observed in a TEM are shown in Figs. 2(a) and 2(b) (high resolution and conventional resolution images, respectively). The STO layer was found to be well crystallized and epitaxially aligned. The crystallographic relationship of STO and Si, determined by means of selected area electron diffraction (patterns not shown), was found to be consistent with the XRD observations. Between the STO and Si layers, a clean, sharp, and fully crystallized interface layer was observed. The thickness of the interface layer is about 1.2 nm. No misfit dislocations were found at the interface, implying that there is only a slight elastic distortion in the STO lattice along the in-plane direction due to the lattice mismatch between the STO and Si layers (the lattice spacings along STO [100] and Si [110] are 0.390 and 0.385 nm, respectively, and the mismatch between them is $\sim 1.4\%$). As a comparison, the cross-sectional view of a STO/Si sample with a rough and sawlike interface structure (prepared under conditions of $T_d \sim 750$ °C and $t_{Sr} \sim 3.6$ nm) is shown in Fig. 2(c).

A more detailed microstructure of the STO-film/Si-substrate interface was disclosed by the high resolution STEM, as shown in Fig. 3. A Sr-deficient layer with a thickness of 1–2 ML was found in-between the Si and the STO film. This observation suggests that strontium deposited in the step of dry etching of the fabrication process had actually evaporated from the Si surface after the reaction of SiO_2

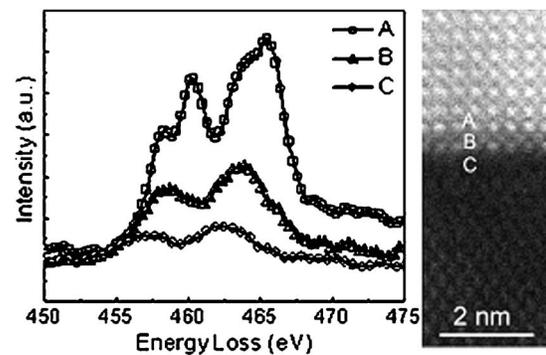


FIG. 3. Electron energy loss spectra taken at the Ti L edge from locations A, B, and C, as indicated in the high resolution scanning transmission electron microscopy image.

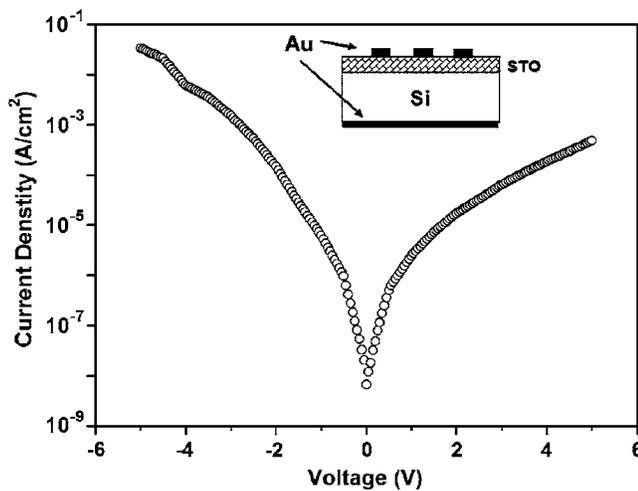


FIG. 4. Leakage current density as a function of applied voltage of the STO/Si structure.

→Si+2O. The EEL spectra taken at the Ti *L* edge from locations A, B, and C (as marked in the STEM image) reveal a valence decrease of the Ti, as the electron probe moves from the film interior to the interface. One can see that the EEL spectrum taken from location A has a double peak splitting feature, which is characteristic of the Ti⁴⁺. The peak splitting disappears with peak center redshifting in the EEL spectrum taken from location B. This is the signature of Ti³⁺. The double peak further shifts to lower energy at location C before the Ti signal completely vanishes, suggesting a further decrease in the Ti valence. The variation of Ti valence is obviously the result of the change of the atmosphere in the step of STO deposition. The results exclude firstly the possible formation of interfacial SiO₂ layer when one should not obtain any signal from the Ti, and secondly the existence of interfacial TiSi₂, when one should expect valence increase in Ti instead of decrease. Such interfacial configuration is different from the previous literature reports, and interesting enough, it also leads to epitaxial growth of STO on Si. Further study on the interface structure is still in progress.

The electrical properties of the STO thin film were also determined. Figure 4 shows the *I-V* measurement results. The film was found to be electrically highly resistive. When the test voltage=1 V, for example, the leakage current density of the STO film (200 nm thick) is $\sim 5 \times 10^{-6}$ A/cm². Apart from the structural and electrical characterizations, we have developed a heterostructure of NBCO/STO/Si (NBCO stands for the superconducting oxide with a nominal composition of NdBa₂Cu₃O₇) to demonstrate the application of STO/Si as a substrate. The deposition conditions for the NBCO film were very much similar to that for STO. X-ray diffraction measurements revealed that the NBCO was well crystallized and epitaxially aligned with STO (picture not shown). The electric measurements indicated that the electri-

cal resistivity of NBCO decreased as the temperature decreased and dropped very quickly when the temperature was below 90 K, a behavior very much analog to the NBCO films grown on SrTiO₃ single crystal substrates.¹⁹

In summary, high quality SrTiO₃ thin films have been deposited on Si wafer through laser molecular beam epitaxy. Prepared under optimal conditions, STO thin films were found to be well crystallized and epitaxially aligned. The interface between STO and Si was clean and sharp. The electrical measurements indicated that the STO film was highly resistive. Future work will include the further optimization of the laser-MBE processing and investigation of the interface structure.

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