Interface Characterization of SrTiO₃/Sr/Si Heterostructure through X-ray Reflectivity

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**Abstract.** The growth of hetero-epitaxial strontium titanate (SrTiO₃) on single-crystal silicon (Si) substrate is of considerable scientific interest because of its wide range application. Unlike other hetero-epitaxial systems, there exists a fairly large lattice mismatch between SrTiO₃ and Si. This leads to the possibility of strain in SrTiO₃ thin film. In order to prevent the formation of amorphous SiO₂ phase and interdiffusion of component atoms at the interface, an ultrathin strontium (Sr) layer is deposited on the underlying Si-substrate. The X-ray diffraction (XRD) is used for characterization of hetero-structures. In this paper, we report the characterization of SrTiO₃ thin film on Si (100) substrate with Sr interlayer by a variety of X-ray measurements. Based on the data obtained from SrTiO₃ thin film, the growth characteristics of the sample is objectively appreciated. The sample is prepared by laser molecular beam epitaxy (L-MBE) under optimized conditions of substrate temperature and oxygen pressure. 2θ/ω scan indicates a high crystallization quality and epitaxial grown of SrTiO₃ thin film in the nanometre scale. Φ-scans have further revealed the in-plane orientation relationship between SrTiO₃ and Si. The α- and c- lattice parameters of the SrTiO₃ thin film are found to be 0.3898, and 0.3901 nm, respectively, which suggests a slight elastic distortion. More detailed investigations by X-ray reflectivity have therefore been carried out, in order to get better understanding to the effect of the buried heterointerface.

**Keywords.** strontium titanate (SrTiO₃), Sr termination, X-ray diffraction (XRD), X-ray reflectivity (XRR)

1. Introduction
Strontium titanate (SrTiO₃) is an incipient ferroelectric material in perovskite structure, which has been extensively studied for its application in tunable microwave devices for having a large and variable dielectric constant. SrTiO₃(STO) is also a perfect prototype to investigate phase transition, especially to understand the surface and interface structural configuration for the perovskite films.
grown on it. STO thin film on Si has potential application\textsuperscript{1,2}. STO thin film on Sr terminated (100) Si substrate has been achieved.

In this paper, we report the characterization of STO thin film on Si (100) substrate with Sr interlayer by X-ray measurements. Phase determination, thin film reflectivity, orientation relationship, lattice strain and texture are discussed. The growth characteristic of the sample is objectively appreciated.

2. Experimental procedure
Approximately 10-nm-thick STO films were deposited by laser molecular beam epitaxy (laser-MBE) on (100)-oriented, silicon wafer. Ceramics of STO was used as target. In the fabrication process, the wafers were ultrasonically cleaned in acetone, followed by dipping into a 10% HF solution for 5 mins to remove the surface oxide layer. The wafer was heated by a hot plate at 850°C for 15 mins to clean the surface free of the hydrogen. In order to prevent the formation of amorphous SiO\textsubscript{2} phase and interdiffusion of component atoms at the interface, an ultrathin strontium (Sr) layer was deposited on the wafer by Laser-MBE at 650°C and followed by a thermal treatment. The Sr buffer layer acting as seed for STO nucleation can be considered as a “sacrificial” epitaxial template. The required minimum thickness of Sr for the epitaxial growth of STO can be less than 2 nm. The termination of the Si (100) surface by ultrathin Sr drastically improves the growth behavior of STO films. Fig. 1 is the flow diagram of sample preparation mentioned above.

![Figure 1. The flow diagram of sample preparation for the STO/Sr/ Si heterostructure.](image)

The greatest use of XRD is for characterization of heterostructures. To check the the STO/Sr/ Si heterostructure, the crystal structure and orientation of STO thin film is identified using the Bede D1 four-circle X-ray diffractometer (Cu K\textsubscript{a}, \(\lambda=0.1541874\text{nm}\)) by wide (2\(\theta\)-\(\omega\)) scanning, specular reflective curve\textsuperscript{3}, pole figure and \(\Phi\)-scan analysis\textsuperscript{4}. 

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3. Measurement of lattice constants

Strain field in STO thin film on large mismatched Si (100) substrate is determined by the spatial distribution of lattice constants and, in principle, can be deduced from X-ray diffraction measurements. Fig.2 (a) and (b) illustrate the symmetric and asymmetric diffraction patterns of STO thin film, respectively. Notice that there is only the STO (00l) reflection in addition to that from the substrate (Fig.2 (a)). The full width at half maximum (FWHM) for STO (002) rocking curve (ω scan) is 0.31° (not shown here), indicating comparable structural quality to STO grown on Sr terminated (100) Si substrate. The profile refinement of all STO thin film peaks determines a tetragonal structure with a=b=0.3898 nm and c=0.3901 nm, revealing a slight elastic distortion. The cause of strain is primarily the larger lattice mismatch between the film and the substrate, which achieves the mismatch about 7%.

![Figure 2. Symmetric 2θ/ω scan of STO (a) and asymmetric 2θ/ω scan of STO (b).](image-url)
4. Measurement of $\Phi$-scan and texture

The STO thin film is purposely grown with a lattice mismatch so that the in-plane orientation of the film and substrate is established by X-ray pole figure and $\Phi$-scan. Fig. 3 gives the 360° $\Phi$-scan on the STO (101) and Si (202) reflections, and it shows that the two groups of reflections are separated by 45°, consistent with the $\chi$ value ($\chi=45^\circ$). It implies that the STO thin film is also epitaxial, and the in-plane epitaxial relation is [100] STO // [110] Si. This plus (001) STO // (001)Si from Fig.1(a) completely determine the epitaxial relation between the film and the substrate.

Fig. 4 shows the measured X-ray pole figure of STO (110). Clearly there is a strong preferred alignment of these STO grain. Especially note that the four poles corresponding to the (110) reflection in film are elongated along the Chi ($\chi$) direction, which is related to deviation of orientation distribution. This phenomenon is normal since the competition between the elastic restore for STO unit cell and the lattice mismatch between STO film and silicon substrate may result in the elongation of the four poles corresponding to the (110) plane in film.

High quality texture on the STO thin film is needed. Fig.4 shows the measured X-ray pole figure of STO (110). Clearly there is a strong preferred alignment of these STO grain. Especially note that the four poles corresponding to the (110) reflection in film are elongated along the Chi ($\chi$) direction, which is related to deviation of orientation distribution. This phenomenon is normal since the competition between the elastic restore for STO unit cell and the lattice mismatch between STO film and silicon substrate may result in the elongation of the four poles corresponding to the (110) plane in film.

Figure 3. $\Phi$-scan over SrTiO3 (101) (top) and Si (202) (bottom) reflections.

Figure 4. Pole figures of (110) STO thin film.
5. Measurement of X-ray reflectivity curves

X-ray reflectivity can provide microscopic information about the thickness, the interfacial roughness and the electron density within the ultra-thin film. Here we briefly introduce our investigation carried out for the STO/Sr/Si heterostructure. Fig. 5 is the specular X-ray reflectivity curves. The black solid lines represent the experiment data and the red dotted lines represent the fitted data. Obviously, the match between experimental data and calculated data is pretty good. Here note that the interference oscillations, called “Kiessig fringes”, can obviously be observed in the reflectivity profile. This means that the densities of thin films are different from that of the substrate. The thickness of STO overlayer is given as follows,

\[ 2t(\sin \theta_{i+1} - \sin \theta_i) = \lambda \]

where, \( t \) is the thickness of the film, \( \lambda \) is the wave length of X-ray, \( \theta_{i+1} \) and \( \theta_i \) are the angles of the angles of the \((i+1)\)th and the \(i\)th peaks of the oscillations in the reflectivity profile, respectively. By cross-sectional high-resolution transmission electron microscopy (HRTEM) characterization, we found that the film has a sharp interface (see Fig. 6). In fact, the structural parameters, such as thickness of films and interface and surface roughness, are obtained by simulating the X-ray reflectivity curve. To simulate the measured reflectivity curve by dynamical diffraction theory, we have already been contiously trying to apply different structure model. According to our study, the structure model in Fig. 7 is very reliable. By using a non-linear least-squares curve-fitting technique, we obtained the structural parameters of the sample, which are listed in Table 1.

| Table 1. The structural parameters ascertained from XRR |
|--------------------------------------------------------|
| Fitted thickness (Å) | Fitted density (%) | Root-mean-square surface and interface roughness (Å) |
| dSTO | dSr | ρSTO | ρSr | σSTO | σSTO/Sr | σSr/Si |
| 100.12 | 18.72 | 90.04 | 80.53 | 1.77 | 1.01 | 2.00 |

Figure 5. X-ray reflectivity spectra for STO/Sr/Si heterostructure. The black solid lines represent the experiment data and the red dotted lines represent the fitted data.
STO Epitaxial film
Sr Buffer layer
Si Substrate

Figure 7. Schematic diagram of sample structure model.

6. Summary
Sr-terminated Si(100) surface provides a sacrificial epitaxial template for STO thin film. The (001) epitaxial growth of STO films on the template is achieved by an in-situ laser-MBE. The X-ray measurement technique used here gives us a convenient way to investigate the required microstructure information for STO /Sr/ Si heterostructure. We have demonstrated that STO film has a slightly different lattice parameter compared with bulk STO. The XRR experimental results confirm that the STO/Sr/Si interface of the sample appeared to be very abrupt and STO film was very dense. The thickness of STO film is approximately 10 nm, which is in good agreement with cross-sectional HRTEM.

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