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Atomic structure of the interface between $SrTiO_3$ thin films and Si(001) substrates

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The structure of the $SrTiO_3/Si$ interface is determined by high-angle annular dark field imaging in combination with a recently developed technique based on aberration-corrected high-resolution transmission electron microscopy. At the interface, a monolayer of SrO faces the terminating plane of silicon. In this monolayer, the strontium atoms lie above the face-center of four silicon atoms in the terminating plane, and the oxygen atoms are located directly above the terminating silicon atoms. This structure, which is the dominant type of interface structure observed in this system, agrees with one of the interface structures predicted by first-principles calculations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2981524]

The search for suitable alternative gate dielectric materials to replace SiO_2 in microelectronic devices and to allow miniaturization to continue to follow Moore's law is an active research topic in the materials science community and the silicon-based semiconductor industry.[1,2] $SrTiO_3$ has been touted as a promising candidate for this purpose due to its high dielectric constant ($k=300$) at room temperature and a relatively small lattice mismatch ($\sim 1.7\%$) with the silicon lattice if the $SrTiO_3$ unit cell is rotated by an in-plane rotation of 45° with respect to silicon.[2–4] This good lattice match also makes $SrTiO_3$ an excellent candidate for use as a buffer layer, which could enable various functional oxide thin films, such as ferroelectrics and high-T_c superconductor thin films, to be integrated in epitaxial form into silicon substrates for various device applications. Establishing the electrical properties and stability of the $SrTiO_3/Si$ interface is the key to these applications.[1–9]

$SrTiO_3$ was first epitaxially grown on silicon using an epitaxial SrO buffer layer.[10] McKee *et al.*[11] demonstrated that this SrO layer could be made as thin as a single monolayer. In the latter work, the authors suggested that a Sr-silicide layer formed at the $SrTiO_3/Si$ interface.[2] Since then, the interfacial structure, stoichiometry, and electrical properties between $SrTiO_3$ and silicon have been intensively investigated.[3–9,12] Several structure models of the $SrTiO_3/Si$ interface have been proposed and studied by means of first-principles calculations and density functional theory studies.[3,6,7,12] Significant differences in band offsets among these proposed interfaces arise due to a multiplicity of interfacial structures proposed in theoretical studies. In contrast to the theoretical studies on the interface structure of $SrTiO_3/Si$, the experimental data on the interface structure are far from sufficient for clarifying the atomic structure. In particular, the atomic configuration that includes oxygen at the interfaces is unknown. Although efforts have been made to determine the structure of the interfaces,[2,3,5,8,12] the goal of directly imaging the interface on an atomic level (with respect to all of the atoms including oxygen at the interface) has remained unrealized.

In this work, we investigate the interface structure of $SrTiO_3/Si$ by means of aberration-corrected high-resolution transmission electron microscopy (HRTEM) and high-resolution scanning transmission electron microscopy (STEM). The recently developed negative C_S imaging (NCSI) technique,[13] in particular, allows us to image all types of atoms including chemical elements with a low atomic number such as oxygen. The NCSI technique thus has the potential of determining the full structural arrangement of the interfaces in $SrTiO_3/Si$ systems.

The epitaxial $SrTiO_3$ films were grown on (001) Si by reactive molecular-beam epitaxy using a process described in detail elsewhere.[8,9,14] In brief, half a monolayer (ML=6.8×10^{14} atoms/cm^2) of strontium was deposited on a clean Si(001) surface at a substrate temperature of 700 °C. The wafer was then cooled to near room temperature where an additional $\frac{1}{2}$ ML of strontium was deposited in UHV. Oxygen was then introduced and additional strontium was deposited in the presence of oxygen to form a total of 3 ML of SrO. On top of the 3 ML of crystalline SrO, 2 ML of amorphous TiO_2 was deposited in oxygen with the substrate temperature still near room temperature (under 200 °C). The heterostructure was then annealed in UHV at ~450–550 °C to recrystallize a $SrTiO_3$ layer 2.5 unit cell thick. Further growth of the epitaxial $SrTiO_3$ layer to the desired film thickness was achieved on this recrystallized 2.5 unit-cell-thick $SrTiO_3$ template layer through the repeated codeposition (Sr+Ti+O_2 molecular beams) of an amorphous $SrTiO_3$ layer near room temperature, followed by recrystallization in UHV.

In order to unambiguously determine the interface structure, cross-sectional specimens along both the [100] and [110] crystallographic directions of silicon were prepared using standard TEM sample preparation methods. NCSI of the samples was performed in a Philips CM200 and an FEI

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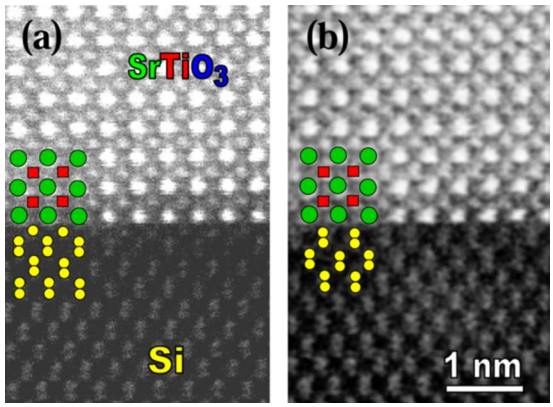

FIG. 1. (Color online) HAADF images of $SrTiO_3/Si$ interfaces along $\langle 110\rangle_{Si}$. The atomic arrangement is denoted by colors: green, Sr; red, Ti; and yellow, Si. (a) A plane of Sr(O) facing a silicon plane with a half dumbbell configuration. (b) A plane of Sr(O) facing a silicon plane with a full dumbbell configuration.

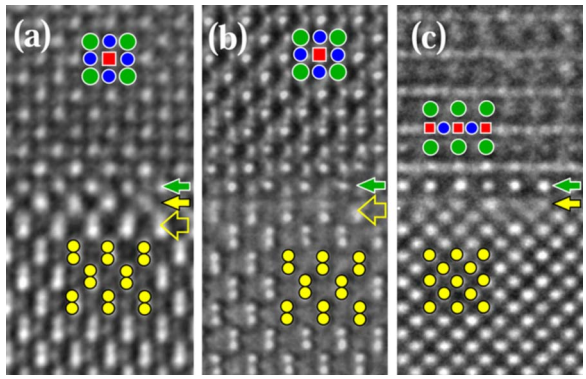

FIG. 2. (Color online) Phase contrast images showing the interfacial structure including oxygen. The atom columns are denoted by color symbols: green, Sr; red, Ti; blue, O; and yellow, Si. (a) A $\langle 110\rangle_{Si}$ image of the interface showing a SrO plane (green arrow) facing a silicon plane with a half dumbbell configuration (thin yellow arrow). (b) A $\langle 110\rangle_{Si}$ image of the interface showing a SrO plane (green arrow) facing a silicon plane with a full dumbbell configuration (thick yellow arrow). (c) A $\langle 100\rangle_{Si}$ image of the interface.

Titan 80–300 microscope equipped with a double-hexapole aberration corrector for the objective lens. The high-angle annular dark field (HAADF) images were recorded on a Titan 80–300 scanning transmission electron microscope equipped with a probe aberration corrector, operated at 300 kV. The probe semiangle was 25 mrad and the inner collection angle of the HAADF detector was 70 mrad. The structural modeling of the $SrTiO_3/Si$ interface and image simulations were carried out by employing the CrystalKit-MacTempas software package.[15] NCSI images were evaluated by comparing the micrographs with the simulated images.

Figures 1(a) and 1(b) show STEM HAADF images of the $SrTiO_3/Si$ interfaces. The bright dots are strontium atoms, the less bright dots represent titanium, and the least bright ones are silicon. The starting atomic plane of $SrTiO_3$ on a silicon surface is the plane containing strontium in both Figs. 1(a) and 1(b). The terminating plane of silicon, however, looks different. In Fig. 1(a), the terminating plane shows a half dumbbell character, while in Fig. 1(b) it exhibits a full dumbbell character. In addition, the atom columns of silicon in the terminating plane are located in the middle below two columns of strontium in the starting plane of the $SrTiO_3$ in Figs. 1(a) and 1(b). These two interface variants were frequently observed in the samples. In some cases, the two variants appeared across a surface step with a height of one quarter of the silicon unit cell. Based on the HAADF image, it can be concluded that $SrTiO_3$ starts with the SrO atomic plane.

In order to solve the oxygen configuration at the interface, HRTEM was performed on the $SrTiO_3/Si$ interface using the NCSI technique. Under our experimental conditions, all atom columns along the viewing direction appear bright in the experimental image. Figure 2(a) shows an interface where the lattice plane directly above the uppermost dumbbell is separated by about 0.138 nm, which matches the (004) plane spacing of silicon very well. Therefore, the atomic plane directly above the uppermost dumbbell can be concluded to be the terminating plane of silicon. The lattice spacing between the $SrTiO_3$ starting layer and the uppermost silicon is about 0.194 nm. The value of the spacing was calibrated using the lattice parameter of Si. We note that in the interface area the contrast for oxygen is visible in the plane (green arrow) directly above the silicon terminating plane (thin yellow arrow). Figure 2(b) shows an interface where SrO is the starting plane of the $SrTiO_3$ film directly above the uppermost dumbbell (thick yellow arrows). The lattice spacing between the starting layer and the uppermost silicon in this interface is also about 0.194 nm, which agrees well with the image in Fig. 2(a). It should be noted that the interface structure in Fig. 2(a) is identical to that in Fig. 1(a) and that Fig. 2(b) shows the same structure as Fig. 1(b).

This interfacial structure was further investigated along the [100] direction of silicon. Figure 2(c) shows an image of the interface recorded along the [100] direction of silicon (the [110] direction of $SrTiO_3$). The stacking of the atomic planes across the interface was determined by checking the atomic arrangement from both the top and bottom of the image of the interface. In Fig. 2(c), the lattice planes down to the SrO plane marked by a green arrow are in the $SrTiO_3$ film, and the planes up to the one marked by a yellow arrow belong to the silicon lattice. A spacing of 0.196 nm was again obtained between the starting SrO plane and the terminating plane of silicon. This result is in excellent agreement with the images viewed along the $\langle 110\rangle$ directions.

Based on the atom arrangement at the interface, the structures of the interfaces shown in Fig. 1 and Fig. 2 can be considered identical. The difference in interface structure observed in the images along the Si $\langle 110\rangle$ was due to the different viewing directions: rotating of the sample images in Figs. 1(a) and 2(a) by 90° around the film normal results in the images in Figs. 1(b) and 2(b). This interfacial structure was confirmed by the image in Fig. 2(c), which is a consequence of rotating the sample from $\langle 110\rangle$ to $\langle 100\rangle$ by 45° around the film normal. It can be concluded that in our $SrTiO_3/Si$ system, the interface consists of a SrO plane connecting to the silicon plane. The strontium atoms are located above the face-center formed by four silicon atoms in the terminating plane. The oxygen atoms are located directly above the terminating silicon atoms. Figure 3 shows the structure model including a SrO monolayer of an $SrTiO_3$ film and part of the silicon substrate, viewed along the $[001]_{Si}$, the $[100]_{Si}$ [as in Fig. 2(c)], the $[110]_{Si}$ [as in Figs.

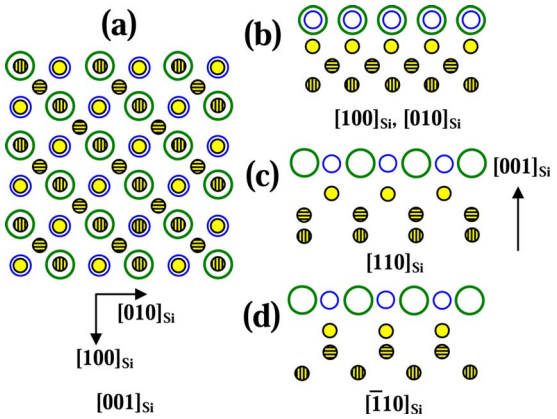

FIG. 3. (Color online) The structure model including a monolayer of SrO and part of the silicon of the interface viewed along (a) the $[001]_{Si}$, (b) the $[100]_{Si}$ and $[010]_{Si}$, (c) the $[110]_{Si}$, and (d) the $[\bar{1}10]_{Si}$ directions, respectively. The atoms are denoted by color circles: green, Sr; blue, O; and yellow, Si.

1(a) and 2(a)], and the $[\bar{1}10]_{Si}$ [as in Figs. 1(b) and 2(b)] directions, respectively.

In addition to the above interfacial structure which is dominant, another interfacial structure was also observed though less frequently. As shown in Fig. 4(a), the atomic plane directly above the uppermost dumbbell (thick arrows) does not belong to the silicon substrate since the atomic configuration does not exist in the silicon structure. In addition, the lattice spacing between the atomic plane and the uppermost silicon layer is about 0.214 nm, which is larger than the 0.196 nm spacing between the first SrO layer and the uppermost silicon of the interface shown in Fig. 3. Figure 4(b) shows another image of the $SrTiO_3/Si$ interface. In this image the atom plane (denoted by a thin yellow arrow) above the dumbbell layer indicated by a thick yellow arrow is separated by about 0.137 nm from the uppermost silicon layer of the dumbbell. This matches the (004) plane spacing of silicon very well. It can be concluded that the atomic plane directly above the uppermost dumbbell is the terminating plane for silicon. The atomic plane above the terminating silicon, indicated by a green horizontal arrow, is separated by about 0.217 nm, which agrees with the measurements from Fig. 4(a). According to the film deposition procedure, a half monolayer of strontium was first deposited to passivate the initial silicon surface. It is reasonable that the starting plane includes strontium. According to the images in Fig. 4, several structure models can be suggested, which differ from that shown in Fig. 3.

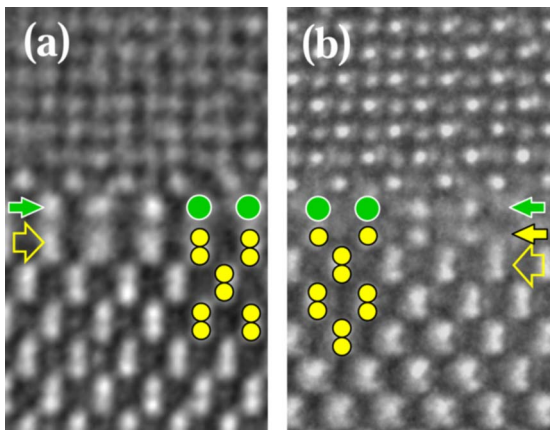

FIG. 4. (Color online) $\langle 110\rangle_{Si}$ images of the interface where the structure differs from that shown in Fig. 3. The interface atoms are denoted by color circles: green, Sr and yellow, Si.

By combining HAADF imaging with the NCSI technique, the interfacial structure of $SrTiO_3/Si$ is determined, which agrees with the interface model with a full monolayer of SrO proposed by calculations based on density functional theory in Ref. 7. This type of interfacial structure was shown to have lower energy in comparison to the structure with a half monolayer of SrO. The observed interfacial structure shows that the $SrTiO_3$ film wets the surface of the silicon substrate better, which results in improved epitaxy. This result agrees with our HRTEM study of the samples in which atomically sharp interfaces were observed. Calculations indicated that the conduction band offset between $SrTiO_3$ and silicon at the dominant interface determined by our study is small,[7] which means that this interface is not suitable for conventional transistors. Nonetheless, it could be interesting for other applications where a negligible band offset is desired, e.g., spin injection structures.

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