Interface structure and thermal stability of epitaxial SrTiO3 thin films on Si (001)

L. V. Goncharova and D. G. Starodub
Department of Physics and Astronomy, and Laboratory for Surface Modification, Rutgers University, Piscataway, New Jersey 08854

E. Garfunkel
Department of Chemistry and Chemical Biology, and Laboratory for Surface Modification, Rutgers University, Piscataway, New Jersey 08854

T. Gustafsson
Department of Physics and Astronomy, and Laboratory for Surface Modification, Rutgers University, Piscataway, New Jersey 08854

V. Vaithyanathan, J. Lettieri, and D. G. Schlom
Department of Material Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 9 January 2006; accepted 9 March 2006; published online 14 July 2006)

We have used medium energy ion scattering, temperature programmed desorption, and atomic force microscopy to study the interface composition and thermal stability of epitaxial strontium titanate thin films grown by molecular-beam epitaxy on Si (001). The composition of the interface between the film and the substrate was found to be very sensitive to the recrystallization temperature used during growth, varying from a strontium silicate phase when the recrystallization temperature is low to a Ti-rich phase for a higher recrystallization temperature. The films are stable towards annealing in vacuum up to ~550 °C, where SrO desorption begins and the initially flat film starts to roughen. Significant film disintegration occurs at 850 °C, and is accompanied by SiO and SrO desorption, pinhole formation, and finally titanium diffusion into the silicon bulk. © 2006 American Institute of Physics. [DOI: 10.1063/1.2206710]

I. INTRODUCTION

It is only recently that relatively defect-free epitaxial oxide films have been successfully grown on silicon, with particular attention focused on the perovskite strontium titanate (SrTiO3).1–7 Contemporary interest has focused on the use of this class of epitaxial oxides as high-κ gate dielectrics because of its potential of providing a higher uniformity, lower defect density, lower leakage current alternative to polycrystalline SiO2 films less than 10 Å thick.1,2,4 Subsequent theoretical8,9 and experimental10 estimates of conduction band offsets have raised serious questions about the possibility of using SrTiO3 as a substitute for SiO2 in transistors. Another reason for interest in epitaxial SrTiO3 is its potential use as a thin buffer layer, as its lattice structure permits epitaxial integration of other functional transition metal oxides into heterostructures.11–17 Such structures would enable the integration of a range of oxides with silicon or germanium. As a result, significant effort has been made in growing “single crystal” SrTiO3 films with ideal interface properties.1,3–7,18 Although epitaxial structures of SrTiO3 on silicon show less than 2% lattice mismatch, the two materials are intrinsically thermodynamically unstable next to each other, with some reduction of the SrTiO3 and oxidation of the silicon expected.19 Thus, any ideal epitaxial SrTiO3/Si structures are metastable at best, and the kinetic properties of the growth and postprocessing will be of central importance.

Several different models have been proposed to describe the interfacial structure between epitaxial SrTiO3 and the underlying silicon it is grown upon. These include amorphous SiO2 interfaces,1–18 reduced amorphous silicon oxide, or amorphous or crystalline (depending on the temperature) silicates,19 crystalline monolayers consisting of strontium, silicon, and likely oxygen,9,21 Sr1−xBa xO/SrSi2 layers,1,4 etc. These models were based on x-ray photoemission spectroscopy (XPS) and/or high-resolution transmission electron microscopy (HRTEM) measurements, or were postulated from considering the initial growth sequence. Two crucial issues need to be addressed to better understand these systems. First, as film growth involves recrystallization at elevated temperatures,15,7,22 it is not obvious that the final structure is that of the initial growth sequence. Second, and related, is how does the elemental composition of the interface and epitaxial film itself change during annealing treatments that might be used in the semiconductor industry (postdeposition reducing, oxidizing, or dopant-activation anneals).1,25 So far only a limited number of studies have addressed these questions. Using Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis, and XPS, Shutthanandan et al.24 investigated the evolution of 20–1000 Å thick SrTiO3 films on silicon. Growth of interfacial SiO2 layers was found both
in the case of annealing in ultrahigh vacuum (UHV) and in \( \text{O}_2 \). They concluded that the oxygen atoms removed from the SrTiO\(_3\) film most probably migrated to the interface and are responsible for the formation or growth of interfacial SiO\(_2\) layers. A detailed study of the interface structure was not possible due to the lack of depth resolution in RBS (\( \sim 100 \text{ Å} \)).

The aim of our work is to examine the structure and composition at the interface between epitaxial SrTiO\(_3\) and silicon using a high-resolution elemental depth profiling technique—medium energy ion scattering (MEIS). We show how the initial structure and composition of the interface as well as additional postgrowth annealing affects the final structure and composition of the multilayer stack. We find that the structural integrity of the SrTiO\(_3\) film can be maintained over a wide range of conditions or even improved, although heating to temperatures above 900 °C inevitably leads to degradation and eventually to full decomposition.

II. EXPERIMENT

Epitaxial SrTiO\(_3\) films on Si (001) were grown by molecular-beam epitaxy (MBE) system (EPI 930) modified for the growth of oxides on silicon.\(^{26,27}\) A quartz crystal microbalance was used to measure the fluxes of the elemental species to be deposited and in situ reflection high-energy electron diffraction (RHEED) was used to monitor the growth of the oxide film. Molecular beam of strontium (flux \( J_{\text{Sr}} \approx 3 \times 10^{13} \text{ at.}/\text{cm}^2 \text{s} \)) from a conventional effusion cell, titanium (flux \( J_{\text{Ti}} \approx 4 \times 10^{13} \text{ at.}/\text{cm}^2 \text{s} \)) supplied by a titanium sublimation pump (Ti-Ball),\(^{27}\) and molecular oxygen were used as the elemental sources for SrTiO\(_3\) deposition. The base pressure in the growth chamber was \( \sim 2 \times 10^{-9} \text{ Torr} \). The substrates were 50 mm diameter epiready commercial Si (001) wafers cut with an accuracy of \( \pm 0.1 \text{°} \). Prior to loading the silicon substrates into the MBE system, the surface organics were removed by ozone cleaning for 20 min.

The growth process is described in detail elsewhere,\(^{32,22}\) but in brief it consisted of the following steps. A SiO\(_2\)-free silicon surface, identified by a sharp double-domain 2 \( \times \) 1 Si (001) RHEED pattern, was obtained by heating in UHV to \( \sim 980 \text{ °C} \). Upon the clean Si (001) surface at a substrate temperature of 700 °C (measured by an optical pyrometer), a strontium dose of \( 3.4 \times 10^{14} \text{ at.}/\text{cm}^2 \) [1/2 ML (monolayer)]\(^{28}\) of strontium was deposited from a strontium MBE source. This formed an interfacial strontium silicide layer\(^{1,4}\) that functions to protect the underlying silicon from oxidation and thus preserve an epitaxial template for epitaxial oxide overgrowth.\(^{29}\)

The wafer was then cooled to near room temperature (under 200 °C), where in UHV an additional 1/2 ML (\( 3.4 \times 10^{14} \text{ at.}/\text{cm}^2 \)) of strontium was deposited. Unlike the strontium deposited at high temperature, which forms strontium silicide,\(^{1,4}\) this strontium deposited at low temperature remains metallic and enables moving a little farther away from the interface before exposing the wafer to oxygen. This helps to avoid oxidizing the underlying silicon.

With the substrate still near room temperature (under 200 °C), oxygen was then introduced to a background pressure of \( 4 \times 10^{-8} \text{ Torr} \) and additional strontium was deposited in the presence of the oxygen to form a total of 3 ML of epitaxial SrO. The 1/2 ML of metallic strontium deposited prior to the oxygen exposure also gets oxidized during this step and becomes an integral part of the epitaxial SrO on silicon. The thickness of the epitaxial SrO layer on silicon is limited to its critical thickness value of \( \sim 3 \text{ ML} \) (based on observations of the RHEED patterns), due to the 5% lattice mismatch between SrO and silicon. On top of the 3 ML of crystalline SrO, 2 ML of amorphous TiO\(_2\) was deposited in an oxygen background pressure of \( 3 \times 10^{-7} \text{ Torr} \), with the substrate temperature still near room temperature (under 200 °C).

The oxygen was then turned off and the heterostructure was annealed in UHV at \( \sim 450–550 \text{ °C} \) to recrystallize a SrTiO\(_3\) layer. 2.5 unit cells thick through a topotactic reaction between the TiO\(_2\) and the underlying SrO. In this topotactic reaction the TiO\(_2\) diffuses into the crystalline SrO layer, transforming it into SrTiO\(_3\), while maintaining its orientation relationship with the underlying silicon substrate.\(^{22}\) The extent of diffusion of TiO\(_2\) into the underlying SrO layer during the recrystallization depends on the recrystallization temperature and time. At \( \sim 450 \text{ °C} \) the recrystallization time is \( \sim 1 \text{ h} \); at 550 °C it is \( \sim 30 \text{ min} \). The intensity of the specular spot (along the [100] SrTiO\(_3\) or equivalently [110] Si azimuth) and the half-order signature of a SrO-rich surface atop SrTiO\(_3\) in the RHEED pattern (along the [110] SrTiO\(_3\) or equivalently [100] Si azimuth)\(^{30}\) during the recrystallization were used to qualitatively monitor the extent of TiO\(_2\) indiffusion. These observations are confirmed by the MEIS measurements described in this paper.

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 \((\text{Sr}+\text{Ti}+\text{O}_2\) molecular beams) of an amorphous SrTiO\(_3\) layer near room temperature (under 200 °C), followed by recrystallization at \( \sim 450–550 \text{ °C} \) in UHV. Such film growth is analogous to the “periodic annealing” method developed by Cho\(^{31}\) to grow GaAs by MBE. Based on in situ RHEED and ex situ x-ray characterization, it was found that the smooth and relatively high structural quality epitaxial SrTiO\(_3\) films were obtained when the SrTiO\(_3\) deposited and recrystallized in each step was three to five unit cells thick.\(^{22}\)

The annealing experiments were carried out in two different ultrahigh (UHV) chambers. Films were annealed in the main scattering MEIS chamber (base pressure <3 \( \times 10^{-10} \text{ mbar} \)) followed by MEIS measurements. Prior to MEIS analyses all the samples were degassed thoroughly at \( T<300 \text{ °C} \). The temperature was measured by an optical pyrometer calibrated with a thermocouple. Thermal desorption spectroscopy (TDS) data were acquired using an Inficon Quadrex 200 quadrupole mass spectrometer. An additional aperture was installed between the sample and the ionization region to insure that only the central part of the heated sample was in direct line of sight with the mass spectrometer.

MEIS is a low energy, high-resolution version of conventional Rutherford backscattering. By using an electrostatic ion energy analyzer,\(^{32,33}\) it is possible to obtain subma-
nometer depth resolution. The experiments were performed using 98–130 keV H⁺ beams. Analysis of the top surface termination was done in a double aligned geometry in the ⟨110⟩ scattering plane, in which the incoming beam was aligned with the SrTiO₃ film [111] channeling direction, and the detector axis with the [111] film crystallographic axis. For the depth profile analysis, the incident beam was aligned normal to the surface and the backscattered ions were detected along the [011] direction of the SrTiO₃ film. To ascertain the difference in ion straggling between channeling and random directions, additional measurements were conducted at −10° off axis. The MEIS beam size at the sample was ~1×0.1 mm²; the spectra cannot give direct information about possible lateral inhomogeneities in the sample on a scale smaller than the beam size.

Ex situ atomic force microscope (AFM) measurements under ambient conditions were carried out using a JEOL JSPM 4210 in the “tapping” mode.

III. RESULTS

MEIS depth profiles for 35 Å thick (nine unit cells) SrTiO₃ films recrystallized at 450 and 550 °C are presented in Fig. 1(a). The degree of crystallinity of the films is determined by taking the ratio of the yield in the channeling geometry to a (calculated) random direction yield (“the maximum yield”). These ratios for thicker films (>70 Å), where the signals from a film’s surface, bulk, and interface are well separated, range from 1% to 4%, thus the films appear to be quite well ordered. Distinct peaks of strontium, titanium, and oxygen can be observed corresponding to the top surface layer of the SrTiO₃ film. In addition, interface peaks of the same elements are also observed slightly lower in energy.

As we are using a channeling and blocking configuration, we do not detect subsurface atoms in lattice positions. Atoms in an amorphous region of the sample, however, or those in a crystalline region, but in positions that are situated away from the rows of atoms positioned “above” them in the film, will be visible to the ion beam. Furthermore, due to the proton energy loss inside the film the scattering from interface species will likely be separated from the surface signal. Figure 1(b) presents the results for a somewhat thicker (78 Å) SrTiO₃ film (recrystallized at 550 °C), where the separation between surface and interface peaks is correspondingly larger.

Quantitatively, the spectrum in Fig. 1(b) can be modeled by a ~78 Å crystalline SrTiO₃ film on top of a ~2 Å partially visible SrO layer, a TiSi₂O₅ layer, and a TiSi₂ layer or islands extending deeper into bulk silicon [Fig. 2(a)]. This composition clearly deviates from the initial deposition sequence: the first and crucial step in the film growth involves depositing a small number of strontium atoms on the substrate, forming a SrO enriched interface. The fractional (0.4–0.7) number of atoms visible to the ion beam in the interfacial region indicates that the interfacial layer is crystalline.

Perovskite SrTiO₃ structures can be considered as consisting of alternating SrO and TiO₂ layers. MEIS measurements in the (110) SrTiO₃ scattering plane allow us to determine the surface termination. If the incident beam is aligned with the [111] SrTiO₃ direction (54.74° off normal) and the detector is positioned along the [111] axis, two distinct situations are possible. If the top surface is a SrO layer [Fig. 3(a), SrO termination], every titanium atom in the second layer will be within the shadow cone of a strontium atom and the measured titanium yield will be much smaller than that of strontium. Calculated angular distributions for strontium and titanium assuming such a SrO termination are shown in Fig. 3(a). For the semiquantitative analysis we assume the bulk terminated surface. The other alternative is TiO₂ termination, where every strontium atom is shadowed by a titanium atom. The simulated ion yields for this case are presented in Fig. 3(b). The simulations clearly imply that the surface is predominantly SrO terminated. A numerically better fit is obtained by assuming ~80% SrO and 20% TiO₂ termination [Fig. 3(c)]. We conclude that the surface is predominantly SrO terminated. The SrO termination is also confirmed by measuring the energy shifts between leading edges of Sr and Ti peaks in the energy spectra.

Control over the interfacial region composition can be
achieved by carefully varying the recrystallization temperature during growth. By comparing the area of the interface peaks, we conclude that the number of strontium and titanium atoms detected in this region (aligned away from ideal overlayer lattice sites) is approximately the same, and slightly smaller than that of oxygen. For high recrystallization temperatures, the titanium interface peak extends to lower energy, most likely indicating TiSi₂ formation. TiSi₂ precipitates have been identified by HRTEM studies on similar SrTiO₃/Si (001) films prepared using an ~550 °C recrystallization temperature. The data for the film recrystallized at 450 °C [Fig. 1(a)] show a narrower titanium peak, indicating that in this case titanium is not moving deeper into the substrate. The interface composition can be modeled as a SrSi₂O₄ crystalline layer for this sample [Fig. 2(b)].

After heating the low recrystallization temperature sample in vacuum, the sample composition and structure changes gradually (Fig. 4). At 650 °C, there is first an improvement of the film crystallinity, as indicated by a small reduction of the titanium interface peak. After annealing to 780 °C we see an increase in the strontium, silicon, and oxygen interface peaks, indicative of the onset of disorder of the strontium and oxygen sublattices, or alternatively an increase in the interfacial Sr–Si–Oₓ layer at this temperature.

There are no significant changes at higher temperatures until partial film disintegration starts at 850 °C. The Sr peak area as well as yields of other elements (Ti, Si, and O) increase in channeling geometry. Whereas the reduction of the Sr peak area in the random geometry assumes removal of Sr into the gas phase, presumably in the form of SrO. Above 850 °C, we observe an onset of titanium diffusion into the silicon bulk, accompanied by the appearance of a surface silicon peak in both channeling and random geometries. This shows that silicon atoms now exist at the surface and implies the appearance of lateral discontinuities or/and silicate formation in the film. SrTiO₃ film decomposition is complete at 950 °C, where only titanium and silicon surface peaks are observed (not shown).

The decomposition process occurring during film annealing in vacuum was monitored using TDS in the temperature range of RT-1000 °C (Fig. 5). Several mass channels were monitored simultaneously corresponding to O (m=16), O₂ (m=32), SiO or CO₂ (m=44), Ti (m=48), Sr (m=88), and SrO (m=104) desorption species. The only volatile form of strontium and titanium found to desorb was SrO, starting at ~500 °C. The amount of desorbed material is relatively small, possibly representing the decomposition of surface layers only. The bulk decomposition of SrTiO₃ starts at ~900 °C as indicated by the loss of oxygen-, silicon-, and strontium-containing species from the surface, implying the complete decomposition of the film.

An AFM image of the surface topography of the as-grown film [Fig. 6(a)] shows flat terraces with neither detectable roughness nor signs of microvoids or grains. After annealing to the highest temperatures, a fraction of the surface is covered with 50–100 Å high islands [Fig. 6(b)]. According to MEIS these islands are titanium silicide, presumably partially oxidized after exposure to air.
annealing temperature:

position and interface structure of an ideal SrTiO3 /Si hetero-

device applications. There is still debate about what the com-

facial region, which would likely be detrimental for most

serve the formation of a titanium silicide phase in the inter-

facial layer. For higher recrystallization temperatures we ob-

junction should be. For certain applications, a very thin low-

a flat surface. Low temperature annealing

950 °C.

FIG. 6. Temperature desorption spectra for a 35 Å thick SrTiO3 fi l mo nS i

termination. SrO desorption was also observed by Shin

minor surface disordering associated with some SrO loss and

layer changes from predominantly SrO termination to TiO2

relieve strain in the system.

Our results show that the initial films are crystalline with

flat surface. Low temperature annealing (<650 °C) causes

minor surface disordering associated with some SrO loss and

desorption of the carbon-containing species. In MEIS we see

carbon loss desorption of the carbon-containing species. In MEIS we see

FIG. 5. AFM images (300 × 300 nm²) of the SrTiO3 surface depending on

annealing temperature: (a) before annealing and (b) after annealing to

950 °C.

IV. DISCUSSION

Our results indicate that high quality epitaxial SrTiO3 film growth can be achieved with a very thin Sr–SiO2 inter-

face. For higher recrystallization temperatures we observe the formation of a titanium silicide phase in the inter-

facial region, which would likely be detrimental for most device applications. There is still debate about what the com-

position and interface structure of an ideal SrTiO3/Si hetero-

junction should be. For certain applications, a very thin low-

Sr (SiO2 or silicate) layer may actually be desirable to (i)

passivate the interface (minimizing the number of interface trap states), (ii) change the band alignment (epitaxial

SrTiO3/Si is thought to have a very low offset),8–10 and/or

(iii) relieve strain in the system.

Our results show that the initial films are crystalline with

a flat surface. Low temperature annealing (<650 °C) causes

minor surface disordering associated with some SrO loss and

desorption of the carbon-containing species. In MEIS we see

carbon loss desorption of the carbon-containing species. In MEIS we see

FIG. 6. Temperature desorption spectra for a 35 Å thick SrTiO3 film on Si

(001) recorded for selected mass channels and a heating rate of 1.5 K s⁻¹.