

Buried H Monolayer at Hetero-Interface between Highly Mismatched Sr Films and Si Substrates

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We succeeded in epitaxial growth of Sr film on Si(111) with an atomically abrupt hetero-interface in spite of the large lattice mismatch of 12%, by introducing a H monolayer on Si. In order to identify the buried H layer, we have carried out combination analysis by neutron reflectometry, multiple-internal-reflection fourier-transform infrared spectroscopy (MIR-FTIR), and transmission electron microscopy (TEM). We have found different neutron reflectivity profiles using the contrast variation between H and D atoms. Furthermore, IR peaks indicating the chemical state of the Si-H bond shift to the lower frequencies during Sr deposition, due to static interaction between the Sr and buried H atoms. These results suggest the existence of buried H layer at the hetero-interface acting as an effective buffer layer to manage the highly mismatched system.

Key words: hydrogen, hetero-interface, neutron, reflectivity, FTIR,

1. INTRODUCTION

Electronic technology has been successively implemented to maintain the pace of reduction in the device size. However, the increasing level of integration of transistor with materials used heretofore is approaching fundamental limits. The projected miniaturization of transistors requires an alternate material with an atomically well-defined heterostructure. The heteroepitaxial growth, however, is possible only for limited material combinations, and the quality of the films is affected strongly by the interfacial strain resulting from lattice mismatch. In many cases, adsorption of deposited atoms causes a strong interaction with active dangling bonds on Si atoms, and thus the existence of dangling bonds makes it difficult to grow an abrupt hetero-interface. On the other hand, the van der Waals epitaxy method developed by Koma *et al.*^[1,2] enabled initiation of atom deposit using the relatively weak force between the layered materials, without dangling bonds. These films need not have good lattice match with surfaces of other substrates. Furthermore, the films exhibit abrupt structures with their bulk lattice constants.^[3] However, up to now, it has been difficult to form metal or semiconductor films with atomically abrupt and strain-free hetero-interfaces on Si.

Strontium and Strontium Oxide are well-known templates on Si for SrTiO₃ which is a highly desirable complex oxide for future

generation transistor gate dielectric applications. The epitaxial growth of SrO films on Si(100) 2x1 and (111) 7x7 surfaces with SrSi₂ or SiO₂ interfaces have been studied well.^[4-9] While Sr films on Si(100) 2x1 and (111) 7x7 surfaces have amorphous form resulting from a large lattice mismatch as 12% with Si. If the surface is modified by foreign atoms, the interaction of depositing atoms on modified Si surfaces must be totally different. One of the most popular species for this purpose is H, and several materials were grown on H modified Si surfaces.^[10-14] However, these heterostructures have strained lattices or amorphous form at their interfaces.

By introducing a H monolayer on Si, we succeeded in epitaxial growth of Sr film on Si(111) with the atomically abrupt interface without strain.^[15-17] Based on *in situ* reflection high-energy electron diffraction (RHEED) method, we found that the onset of the initial stage of crystal Sr growth occurs with only one atomic layer deposition.^[18] However, it is somewhat mysterious how the H monolayer behaves to manage this large mismatch. The methods like X-ray photoelectron spectroscopy (XPS) and RHEED are not so effective to elucidate the buried interfacial H structure because these methods do not directly see the H atoms. The probing such an interfacial H layer is essential to reveal the new mechanism of crystal growth. Neutron reflectometry can be an indispensable technique for investigating the buried H monolayer at

the hetero-interface. The shape of the neutron reflectivity curve provides the depth profile of the scattering length density from the surface, while X-ray reflectivity reveals the electron density profile, and can be used to accurately calculate material density if the atomic composition is known.

In this paper we have carried out combination analysis by neutron reflectometry and multiple-internal-reflection fourier-transform infrared spectroscopy (MIR-FTIR) in order to identify behavior of the buried H monolayer. We have found clear different neutron reflectivity profiles using the large contrast between scattering lengths of H and D atoms. Furthermore, IR peaks indicating the chemical state of the Si-H bond shift to the lower frequencies during Sr deposition, due to static interaction between the Sr and buried H bonded to the Si. These results suggest the existence of H layer at the hetero-interface acting as an effective buffer layer to manage this highly mismatched system.

2. EXPERIMENTAL PROCEDURES

The epitaxial growth was conducted in an ultrahigh vacuum (UHV) system consisting of growth and analysis chambers connected to each other. The based pressure was 1×10^{-8} Pa in both chambers. H or D-terminated Si(111) substrates were chemically treated before introduction into the UHV system in the following way. To terminate the surface with H, the substrate was boiled in a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ for 10 min and treated in a 1% HF solution for 1 min. After this process, it was dipped in a hot 40% NH_4F aqueous solution for 30s.^[19,20] To terminate the surface with D, the substrate was boiled in a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ for 10 min and was treated in a 40% $\text{KF}/\text{D}_2\text{O}$ solution for 90 min.^[21,22] They were checked with Auger electron spectroscopy (AES) to see that no contamination remains on the surfaces. The thickness of the films and the growth rate were monitored by a quartz crystal oscillator located close to substrate position. The thickness monitor was calibrated *ex situ* with multiple beam interferometry method. Strontium (99.99%) was evaporated from a Knudsen effusion cell at the typical rate of 0.01~0.05 nm/s. An O_2 gas was introduced through a stainless steel tube with an inner diameter of 1 mm and was sprayed onto the substrate. The gas pressure was maintained at 1×10^{-6} Pa to oxidize the Sr films. The substrates were kept at room temperature during film growth in the present experiment. *In situ* observation of crystallinity and orientation of the films was studied by RHEED method with an incident energy of 15keV. The incident electron beam was usually parallel to the [112] or [110] direction of the Si(111) substrate. Microstructure observation of the interface was conducted with a transmission electron microscopy (TEM) operated at 200 kV. Focused ion beam processing was used to prepare thin foil specimens for TEM observation. *In situ* observation of the chemical

state of H-chemisorbed Si(111) surface was monitored by MIR-FTIR. The p-polarized IR beam from a FTIR spectrometer was directed into the UHV chamber through a CaF_2 viewing port onto a bevel of the sample edges and penetrated through the Si substrate. The number of internal reflections was 30 in the present MIR geometry. The multiple-internal reflected IR beam was focused onto a mercury cadmium telluride (MCT) detector outside the chamber. Neutron reflectivity was measured at the neutron reflectometer SUIREN of JRR-3 at Japan Atomic Energy Agency (JAEA) and PORE at High Energy Accelerator Research Organization (KEK).^[23] A sample was vertically mounted in an Al can filled with He gas or in an evacuated one.

3. RESULTS AND DISCUSSION

In situ RHEED measurement shows sharp and bright 1×1 patterns with low background in both H- and D-terminated Si(111) surfaces. Strontium atoms are deposited on this modified Si(111) surface. As the deposit amount increases, the intensity of streaks originating from the Si becomes weak. At the same time, new vertical straight streaks at positions originating from bulk Sr lattice appear abruptly with lines parallel to the Si streaks. The superposed peak positions from Sr structure remain the same during growth. These diffraction streaks of Si and Sr appear without lattice strain or amorphous form. Judging from RHEED patterns from several azimuths, new streaks can be ascribed to a hexagonal Sr lattice with an epitaxial orientation relationship of $\text{Sr}(111)//\text{Si}(111)$ and $\text{Sr}[11\bar{2}]/\text{Si}[11\bar{2}]$. In spite of a lattice mismatch as large as 12%, the evolving RHEED profiles prove that Sr grows heteroepitaxially on both regular H and D 1×1 surfaces with abrupt interfaces.

TEM microphotograph of the interface is shown in Fig. 1. The lattice distance of Sr layer evaluated from TEM images is approximately 1.1 times larger than that of Si layer. The TEM observation indicates that no amorphous region

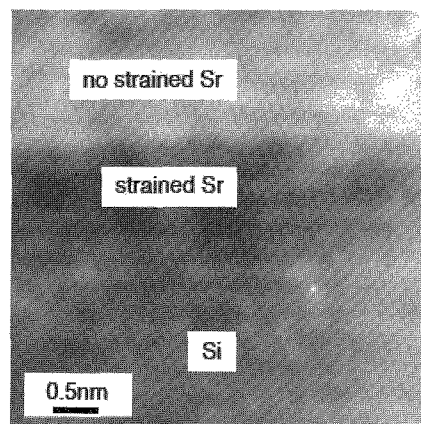


Fig. 1 TEM microphotograph of a interface between epitaxial Sr (which has large lattice mismatch with Si: 12%) layers and a Si substrate.

exists in the interface between Si and Sr layers. This result leads to the formation of the atomic ordered interface in the film, in spite of the large lattice mismatch. The dark strain contrast is observed in three Sr atomic layers on Si substrate. On the other hand, no strain contrast is observed from three Sr atomic layers. This result of the TEM observation is consistent with the previous stress study that stress-free Sr layers are grown epitaxially from three Sr atomic layers.^[16]

MIR-FTIR is used to provide direct information on the buried hetero-interface of Sr grown on Si(111) 1x1: monohydride. Fig. 2 displays evolution of the infrared spectra, in the frequency region of the Si-H stretching mode, before and during Sr deposition. Atomically flat H-terminated Si(111) surfaces are characterized by sharp Si-H stretching mode at 2083.7cm^{-1} .^[19] We should notice that the intensity of Si-H stretching mode at 2083.7cm^{-1} is from both Si sides, top side under Sr deposition and the bottom side remaining H-termination intact without Sr deposition. The frequency is affected by electronegativity of its environment.^[24] At the beginning of Sr growth on the H-Si(111) surface, the IR peak shift to the lower frequencies, due to the interaction between the Sr and the H bonded to the Si first layer. In the initial state at 0.03 AL Sr deposition, part of the Si-H stretching mode is shifted to lower frequency (peak (a): 2082.5 and peak (b): 2080.5cm^{-1}). The larger shift of peak (b) than that of (a) should be originated from stronger interaction between the Sr and the H bonded. The peak (a) shows the maximum intensity at 0.06 AL Sr deposition, while the peak (b) shows the maximum intensity at larger deposition amount (0.4 AL) as shown in Fig. 3. The largest shift of peaks (c): 2078 and (d):

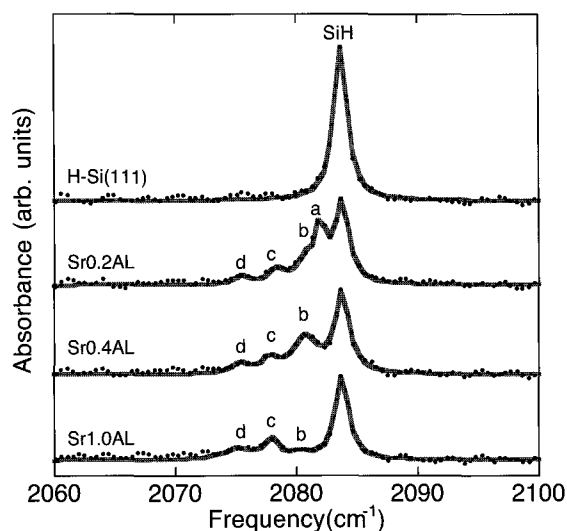


Fig. 2 Polarised infrared absorption spectra of the H-terminated Si(111), in the $2060\text{--}2100\text{cm}^{-1}$ frequency range, during initial Sr deposition. Spectra have been recorded with an instrumental resolution of 1cm^{-1} .

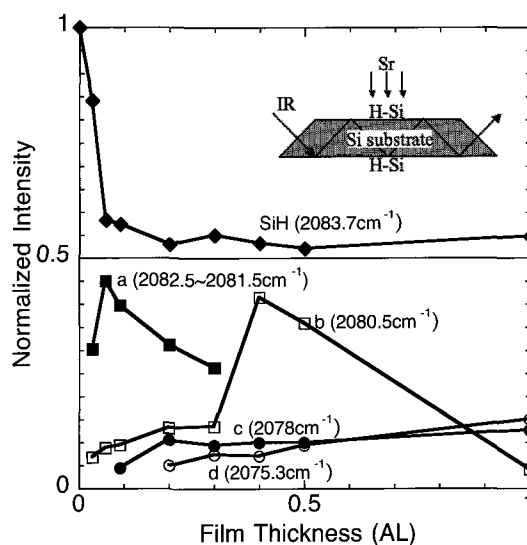


Fig. 3 Intensity of polarised infrared absorption spectra of the H-terminated Si(111) during Sr deposition on the Si surface. The intensity of Si-H stretching mode at 2083.7cm^{-1} is the sum of that of Si-H bands at the top side under Sr deposition and at the bottom side remaining H-termination intact without Sr deposition.

2075.3cm^{-1} in the $2060\text{--}2100\text{cm}^{-1}$ frequency range is appeared as Sr depositing sites increase. Judging from the evolution of Si-H bonding features during Sr growth, buried H monolayer on Si suffers with the first one atomic layer of Sr and acts as an effective buffer layer to manage the highly mismatched epitaxial system.

We observed neutron reflectivity of the films on both H- and D- terminated Si (111) substrates

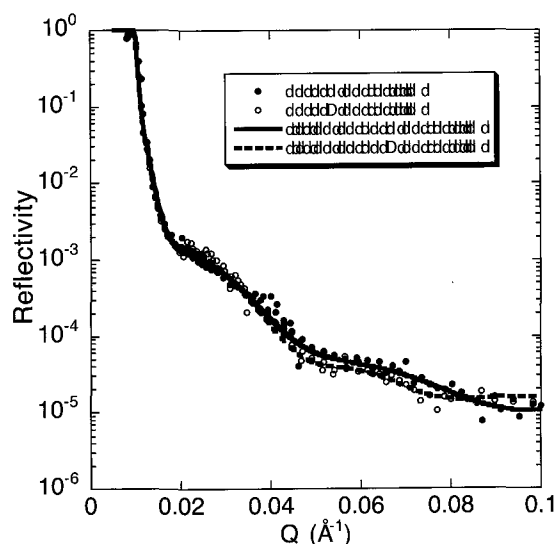


Fig. 4 Neutron reflectivity profile of SrO/Sr epitaxial films on H- and D-terminated Si(111) substrates.

Table 1 Fitting parameters of 3 layer models: SrO/SrO_{1-x}/H/Si and SrO/SrO_{1-x}/D/Si

		films on H/Si	films on D/Si
SrO	thickness (Å)	33.6	29.7
	roughness (Å)	90.7	60.8
SrO _{1-x}	thickness (Å)	177.9	119.5
	roughness (Å)	16.2	11.6
H or D	thickness (Å)	1.3	1.3
	roughness (Å)	0(fixed)	0(fixed)
total thickness (Å)		212.8	150.5
R(%)		2.3	6.3

using PORE. We prepared SrO_{1-x} films instead of Sr ones to prevent the surface from an abrupt deterioration accompanied with roughening when the samples are transferred from the UHV chamber to the Al can in which the sample was mounted during the reflectivity measurements. The films were grown by an alternate supply of Sr metal and O₂ gas in the UHV chamber. The results are shown in Fig. 4. The experimental data of SrO_{1-x}/H/Si and SrO_{1-x}/D/Si are plotted as solid and open circles, and solid and broken lines are the fitting results using a 3 layer model (SrO/SrO_{1-x}/H/Si and SrO/SrO_{1-x}/D/Si), respectively. The fitting parameters are summarized in Table 1. The difference of the both films clearly appears in the reflectivity profiles in the vicinity of 0.05 Å⁻¹ where the difference between the H and D interfaces is most enhanced in simulation of the reflectivity curves of SrO/SrO_{1-x}/H and SrO/SrO_{1-x}/D with the same thickness of the SrO/SrO_{1-x} layer. Although the thickness of these two samples is not exactly the same, these results suggest that the H or D layer still exist at hetero-interface even after the epitaxial growth of SrO_{1-x}.

CONCLUSION

We have carried out by neutron reflectometry as well as MIR-FTIR to investigate the buried hetero-interface of Sr and SrO grown on H- and D-Si(111) 1x1. We have found different neutron reflectivity profiles using the contrast variation between H and D atoms. Furthermore, Si-H IR peaks shift to the lower frequencies during Sr deposition, due to static interaction between the Sr and buried H atoms. These results suggest the existence of H layer at the hetero-interface acting as an effective buffer layer to manage the large lattice mismatch of 12%.

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