Thin Solid Films 520 (2012) 3300–3303

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Analysis of buried heterointerfacial hydrogen in highly lattice-mismatched epitaxy on silicon

T. Yamazaki [a,b], H. Asaoka [a,*], T. Taguchi [a], S. Yamamoto [a], D. Yamazaki [a], R. Maruyama [a], M. Takeda [a], S. Shamoto [a]

[a] Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan
[b] Eiko Engineering Co., Ltd., Hitachinaka, Ibaraki 312-0024, Japan

ARTICLE INFO

Available online 29 October 2011

Keywords:
Silicon
Hydrogen
Lattice mismatch
Heterointerface
Neutron reflectivity
Resonant nuclear reaction analysis

ABSTRACT

We realized the epitaxial growth of a Sr layer on Si(111) with an atomically abrupt heterointerface – in spite of its large lattice mismatch (12%) with Si – by introducing a monoatomic layer of H on Si. In order to identify the buried H, we carried out a combination analysis involving neutron reflectometry and resonant nuclear reaction of $^1H(^{15}N,\alpha\gamma)^{12}C$ analysis. We found different neutron reflectivity profiles resulting from a contrast variation between the H and D atoms at the buried heterointerface. Furthermore, the depth γ-ray intensity profiles revealed that the H at the heterointerface acts as an effective buffer layer that enables it to manage the highly mismatched epitaxy on Si.

1. Introduction

Heterostructures with atomic-order thickness can be fabricated by using molecular beam epitaxy methods. Heteroepitaxial growth, however, can be achieved only for limited material combinations because of the lattice mismatch in a large number of material combinations. In many cases, the deposited atoms react with the active dangling bonds on the Si atoms; thus, the existence of these dangling bonds makes it difficult for the growth of an abrupt and strain-free heterointerface. Sr and SrO are well-known templates on Si for the growth of $SrTiO_3$, which is a highly desirable complex oxide for use in next-generation transistor gate dielectric applications. A number of studies have been conducted on the epitaxial growth of SrO layers on Si(100) 2×1 and Si(111) 7×7 surfaces with $SrSi_2$ or SiO_2 interfaces [1–6]. Sr layers on Si(100) 2×1 and Si(111) 7×7 surfaces have amorphous forms that result from a large lattice mismatche (as large as 12%) with Si. If the surface is modified by foreign atoms, both the interaction with the deposited atoms on the modified Si surfaces as well as the growth mode would be totally different. For instance, it is well known that the interdiffuse and the Stranski–Krastanov growth mode of Ge on Si can be suppressed by using As and Sb surfactants [7–9]. In such surfactant-mediated epitaxy (SME), a flat layer grows on Si while the surfactant floats up to the growth front and constantly covers the surface. H is also a well-known surfactant for use in SME, and several materials have been grown on H-modified Si surfaces [10–14]. However, these heterostructures have strained lattices or amorphous forms at their interface.

By introducing a monoatomic layer of H on Si, we realized the epitaxial growth of a Sr layer on Si(111) with an atomically abrupt interface [15–17]. By using the *in situ* reflection high-energy electron diffraction (RHEED) method, we found that the initial growth stage of the Sr layer with its bulk lattice constant begins after the onset of the second atomic layer deposition. The first interfacial Sr atomic layer forms an original structure that is different from its bulk structure but has the same lateral atomic interval as the Si(111) 1×1 surface [18]. When H resides at the buried heterointerface, the interfacial monoatomic layer of H, together with the first one atomic layer of Sr, acts as an effective buffer layer. Furthermore, *in situ* FTIR method shows the interaction between the Sr and H at the interface [19]. However, it is somewhat mysterious as to how H manages this large mismatch. Methods such as X-ray photoelectron spectroscopy and RHEED are not very effective in elucidating the buried interfacial H structure, because these methods do not directly show the H atoms. Probing into such interfacial H structures is essential for revealing the crystal growth mechanism in highly lattice-mismatched epitaxy on Si. Neutron reflectometry and resonant nuclear reaction of $^1H(^{15}N,\alpha\gamma)^{12}C$ analysis will enable us to directly detect buried H with depth resolution.

In this study, we have carried out a combination analysis involving neutron reflectometry and resonant nuclear reaction analysis in order to understand the behavior of buried H. We have found distinct neutron reflectivity profiles resulting from a sharp contrast between the scattering lengths of H and D atoms. Furthermore, γ-ray intensity profiles as a function of the incident ^{15}N beam energy enable us to distinguish between the surface and buried interface H. These results indicate that the H at the heterointerface acts as an effective buffer layer that enables it to manage this highly mismatched system.

---

* Corresponding author.
E-mail address: asaoka.hidehito@jaea.go.jp (H. Asaoka).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.10.081

2. Experimental procedures

Epitaxial growth was conducted in an ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-8} Pa. H-terminated and deuterium (D)-terminated Si substrates were chemically treated before being introduced into the UHV system in the following manner. In order to terminate the surface with H, we boiled the substrate in a solution of H_2SO_4 and H_2O_2 (H_2SO_4:H_2O_2 = 3:1) for 10 min and treated it in a 1% HF solution for 5 min. After this process, the substrate was dipped in a hot 40% NH_4F solution for 30 s [20,21]. In order to terminate the surface with D, we boiled the substrate in a solution of H_2SO_4 and H_2O_2 (H_2SO_4:H_2O_2 = 3:1) for 10 min and treated it in a 40% KF/D_2O solution for 90 min [22,23]. We used Auger electron spectroscopy to confirm that the surfaces were devoid of contamination. The thickness of the layers and the growth rate were monitored by a quartz crystal oscillator that was placed close to the substrate. The thickness monitor was calibrated *ex situ* by using X-ray reflectometry. Sr (99.99%) was evaporated from a Knudsen effusion cell at a typical rate of 0.05–0.5 Å/s. The substrate temperatures were between 300 K and 350 K during the layer growth and the oxidation procedures. They were measured by using a thermocouple inserted into the back of the substrates. The crystallinity and orientation of the layers were observed by using the *in situ* RHEED method with an incident energy of 15 keV. The neutron reflectivity was measured by the neutron reflectometer, JRR-3 SUIREN, at JAEA. The depth γ-ray intensity profile as a function of the incident ^{15}N beam energy for the sample was obtained by using the ion accelerator, TIARA, at JAEA.

3. Results and discussion

In situ RHEED measurement shows sharp and bright 1 × 1 patterns with low background in both the H-terminated (Fig. 1(a)) and D-terminated Si(111) surfaces. Fig. 1(b)–(d) shows the evolving RHEED patterns during Sr deposition on the H–Si(111) surface from a thickness of one to three atomic layers. As the deposited amount of Sr increases, the intensity of the streaks originating from Si becomes weak. At the same time, new vertical straight streaks originating from the bulk Sr lattice appear abruptly, with lines parallel to the Si streaks. The superposed peak positions from the Sr structure remain constant during the growth. These diffraction streaks of Si and Sr appear without lattice strain or amorphous form. Judging from the RHEED patterns from several azimuths, we can ascribe the new streaks to a hexagonal Sr lattice with an epitaxial orientation relationship of Sr(111)//Si(111) and Sr[$1\bar{1}\bar{2}$]//Si[$1\bar{1}\bar{2}$]. In spite of a large lattice mismatch of 12%, the evolving RHEED profiles prove that Sr grows heteroepitaxially on both H–Si(111) and D–Si(111) surfaces with abrupt interfaces.

The monoatomic layer of H on the Si surface causes the epitaxial growth of the Sr layer with good crystallinity, in spite of the large lattice mismatch. It could be interesting to see how the interfacial layer can accommodate the lattice mismatch. Neutron reflectometry is one of the best techniques to reveal the role of H in crystal growth. Fig. 2(a) shows the reflectivity profile of the chemically treated monoatomic H–Si(111) and D–Si(111) substrates before Sr deposition. The experimental data corresponding to H–Si and D–Si surfaces are plotted as solid and open circles, respectively, and the fitted

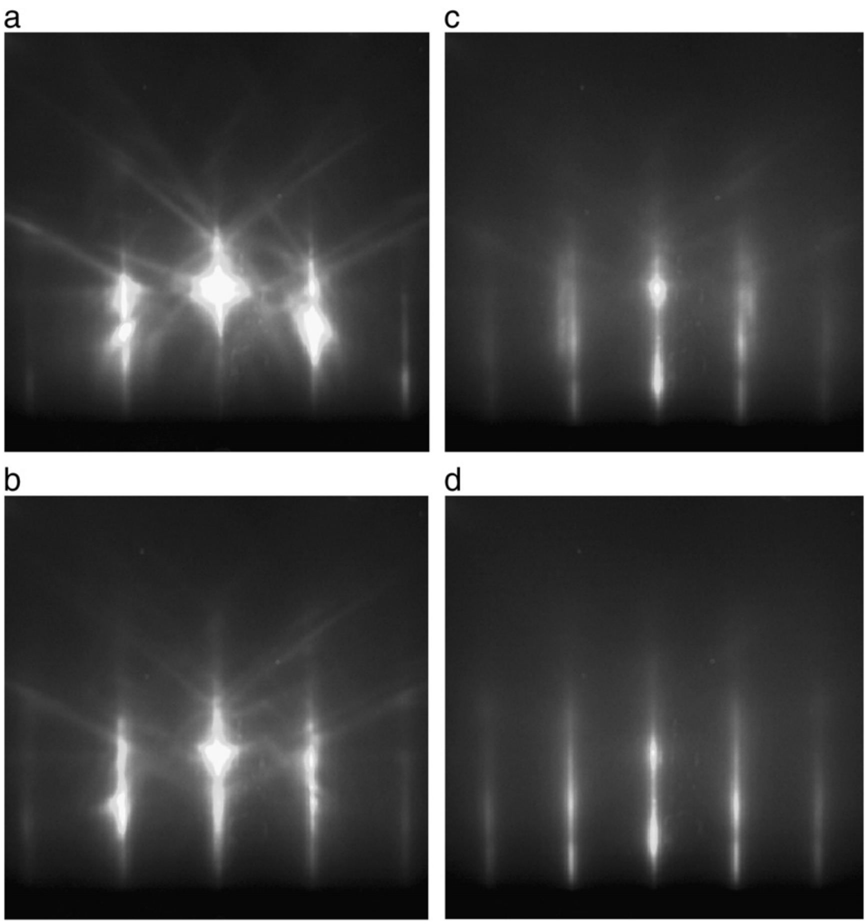

Fig. 1. Evolution of the RHEED patterns during Sr deposition on (a) the H–Si(111) surface. The thickness of the deposition layer in panels (b), (c), and (d) is one, two, and three atomic layers, respectively. The orientation of the incident electron is parallel to the [$1\bar{1}\bar{2}$] azimuth of the Si surface.