Initial growth stage of a highly mismatched strontium film on a hydrogen-terminated silicon (111) surface

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We report the formation of an atomically abrupt interface without strain in a strontium film using a hydrogen buffer layer on silicon, in spite of large lattice mismatch such as 12%. The onset of the initial growth stage of strontium film with its bulk lattice constant occurs with one atomic layer deposition. The interfacial monoatomic layer of hydrogen together with the first one atomic layer of strontium acts as an effective buffer layer. Our results provide microscopic evidence of heteroepitaxial growth of the strain-free film with the atomically abrupt interface in a highly mismatched system. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2205160]

Heterostructures with atomic order thickness are fabricated for devices by molecular beam epitaxy (MBE) methods. Since the advent of integrated circuits, electronic technology has been successively implemented to maintain the pace of reduction in the microelectronic 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 and strain-free heterointerface. On the other hand, the van der Waals epitaxy method developed by Koma and co-workers[1,2] enabled initiation of atom, deposit using the relatively weak force between the layered materials, without dangling bonds on their clean surfaces. These layered films need not have good lattice match with cleaved surfaces of other layered 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 heterointerfaces on Si.

Strontium and SrO are well-known templates on Si for $SrTiO_3$ which is a highly desirable complex oxide for future generation transistor gate dielectric applications. The epitaxial growth of SrO films on Si(100) 2×1 and (111) 7×7 surfaces with $SrSi_2$ or SiO_2 interfaces were studied well.[4–9] While Sr films on Si(100) 2×1 and (111) 7×7 surfaces had amorphous form resulting from a lattice mismatch as large as 12% with Si. If the surface is modified by foreign atoms, the interaction of deposited atoms on Si is strongly affected. One of the most popular species for this purpose is hydrogen, and several materials were grown on hydrogen modified Si surfaces.[10–14] However, these heterostructures had strained lattices or amorphous form at their interfaces. We introduced an interfacial hydrogen layer between the growing Sr film and the Si substrate. It made the surface stable, and at the same time made the chemical bonds to the growing film weak.[15,16] Here, we will report an achievement of an atomically abrupt interface without strain in a Sr film on a hydrogen-terminated Si(111) surface. Based on *in situ* reflection high-energy electron diffraction (RHEED) method, we have found that the onset of the initial growth stage of Sr crystal occurs with only one atomic layer deposition. These results demonstrate that the interfacial hydrogen layer together with the first one atomic layer of Sr acts as an effective buffer layer in the highly mismatched system.

In situ RHEED measurement was performed in an ultrahigh vacuum (UHV) system with a based pressure of 1×10^{-8} Pa. Antimony doped Si(111) substrates were cleaned by *in situ* thermal treatments at 1200 °C for 30 s and then exposed to atomic hydrogen by dissociation of hydrogen gas. After the above treatment, a complete transformation of the surface occurred from the 7×7 to the 1×1 structure. The RHEED measurement showed a sharp and bright 1×1 pattern with low background in this surface. Strontium atoms were deposited on this modified Si(111) surface at room temperature.

Figure 1(a) shows the evolving horizontal line profile of RHEED patterns comprising a specula reflection and diffraction streaks during Sr growth. As the deposit amount increases, the intensity of streaks originating from the Si becomes weak. At the same time, other 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 ranging from one to three Sr atomic layer deposition. Judging from RHEED patterns from several azimuths, these streaks can be ascribed to a hexagonal Sr lattice with an epitaxial orientation relationship of $Sr(111)\|Si(111)$ and $Sr[11\bar{2}]\|Si[11\bar{2}]$. In spite of a lattice mismatch as large as 12%, the evolving RHEED profile proves that Sr grows heteroepitaxialy on the regular hydrogen 1×1 surface with an abrupt interface. Figure 1(b) shows sequential horizontal line profile of RHEED patterns and their fitting profiles for Sr and Si diffraction streaks in the thickness range of 1.0–2.0 atomic layer deposition. In-plane lattice constants observed from the streak interval originating from Sr and Si, respectively, are plotted

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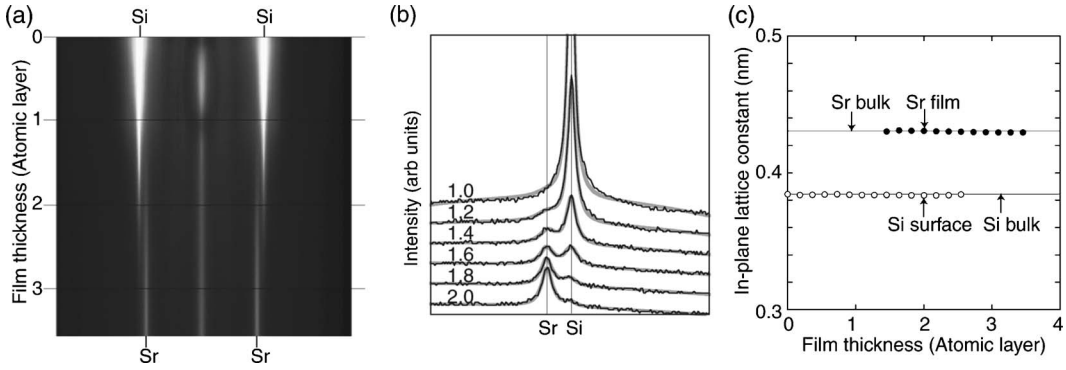

FIG. 1. (a) Horizontal line profile of RHEED patterns comprising Si and Sr streaks. (b) Sequential horizontal line profile of RHEED patterns and their fitting profiles (solid and gray lines, respectively) for Sr and Si streaks in the thickness range of 1.0–2.0. (c) In-plane lattice constants of Sr film and Si surface. The orientation of incident electron beam is parallel to the $[11\bar{2}]$ azimuth of Si(111) substrate.

as a function of the film thickness [Fig. 1(c)]. Error bars indicating deviation from the fitting curve for the streak are smaller than the size of each circle. The streaks of Sr and Si coexist in that thickness range. Furthermore, both peak positions show no change from the initial state, within the experimental error of the RHEED measurement ($\sim 1\%$) as shown in Fig. 1(c). *In situ* RHEED measurement reveals that the Sr film with its bulk lattice constant (0.430 nm) grows abruptly without layer strain on the modified Si surface with lattice constant (0.384 nm).

The evolution of growing crystal can be characterized using diffraction streak intensity and the width in RHEED patterns. The integrated intensity is proportional to the amount of epitaxial Sr film in the initial growth stage. After the onset of Sr crystal formation, the intensity increases linearly with the deposited amount as shown in Fig. 2(a). To our surprise, the onset of the initial growth stage of Sr crystal occurs with one atomic layer deposition, as determined by extrapolation of the linear function to zero intensity. The grain size on the surface can be observed from the full width at the half maximum intensity in the RHEED pattern from Si and Sr crystals as shown in Fig. 2(b). At the beginning of adsorption of deposited Sr atoms, the streaks from the Si surface become broad, indicating that the ordered Si 1×1 surface area becomes narrow during Sr adsorption. The initial dependence of grain size is followed by grain growth incorporating adsorbed Sr atoms on the surface. At the same time, the in-plane lattice parameter remains the same as the interval of Si 1×1 until one atomic Sr layer deposition before the Sr bulk structure begins to form. This observation suggests that the interfacial Sr monolayer forms an original structure different from its bulk structure but with the same lateral atomic interval as the Si 1×1 surface. The thickness of the interface layer is inferred to be one atomic layer from Fig. 2(a). On the interfacial Sr layer, the strain-free Sr grains begin to grow proportionally to the square root of the deposited amount as shown in Fig. 2(b), which shows that the number of formed nuclei on the Sr interface remains the same from the initial stage. This suggests that the grain growth must be a dominant mechanism for the film growth in order to keep its own lattice parameter. During Sr crystal growth with its bulk structure, slight oscillations owing to layer-by-layer variations are observed in both Figs. 2(a) and 2(b).

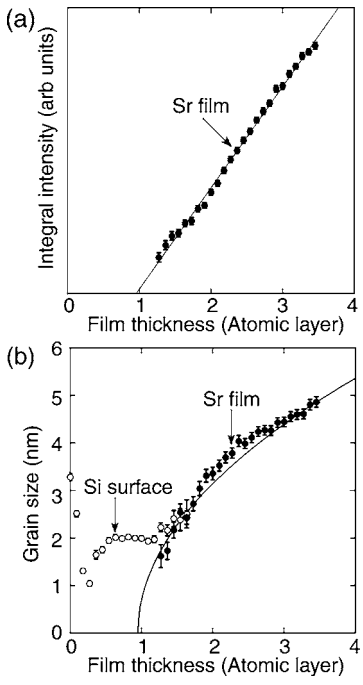

FIG. 2. (a) Integrated intensity of streaks from Sr film. (b) Grain size at Si surface and Sr film. The orientation of incident electron beam is parallel to the $[11\bar{2}]$ azimuth of Si(111) substrate.

The initial deposited Sr atoms on the hydrogen surface are expected to occupy positions on the hydrogen atom triangular lattice plane like the SrH_2 crystal structure.[17] Positional parameters for SrH_2 structure are close to those for CaH_2 (Ref. 18) and BaH_2 (Ref. 19) and for halides such as $PbCl_2$. Hydrogen atoms approximate the triangular lattice network in the downward projection of the SrH_2 structure [010]. The deposited initial Sr atoms will be in the center of the H triangle plane and on the apex of triangular prisms with H triangle plane as shown in Fig. 3. The Sr atoms in the center of the H triangle plane will expand its plane to have a side of 0.4321 nm, as long as the SrH_2 crystal structure. The Sr with its bulk lattice constant of 0.4303 nm can nucleate the triangle side to have the best matching with lattice mismatch of 0.5%.

The chemical bonds between Sr and SrH_2 at the surface must be weak, since the nuclei can grow with its own lattice parameter. The interfacial hydrogen monolayer together with the Sr monolayer acts as an effective buffer layer. The hydrogen atom, with only single bond order, is expected to provide a stable unreconstructed 1×1 surface and weak

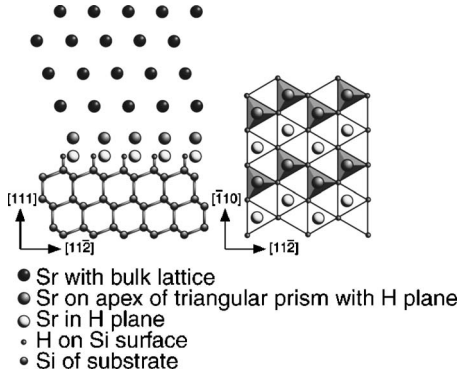

FIG. 3. Schematic atomic structure of Sr/Si(111) interface. Left, view of Sr(111) on a Si surface terminated by hydrogen atoms along the [$\bar{1}$10] direction. Right, view of the interface with the initial one atomic layer of Sr.

chemical bond to the growing film appropriate for this purpose. Strontium monolayer, however, also plays an important role for this heteroepitaxial growth. We have found that the strontium-hydrogen interface makes it possible for heteroepitaxial growth with large lattice mismatch such as 12%. It is expected that strain-free three-dimensional material can be grown even with large lattice mismatch. It is also expected that an abrupt interface with small amount of defects can be fabricated because of the nonexistence of active dangling bonds. This structure has opened up a way to grow strain-free heteroepitaxial films on silicon with the atomically abrupt interfaces, and fabricate heterostructures in highly mismatched systems.

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