

Strained Ge overlayer on a Si(001)-(2×1) surface

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The epitaxial growth behavior and the strain distribution of Ge overlayer grown on Si(001)-(2×1) surface were studied with medium energy ion scattering spectroscopy and scanning tunneling microscopy. We were able to grow flat Ge overlayers up to ten monolayers, thicker than the known critical thickness of Stranski-Krastanov growth mode, with hydrogen surfactant, as suggested by recent theories. By comparing the dips of Ge overlayer and Si bulk in the angular scan of ion blocking, we found that the flat Ge overlayer is uniformly strained in the direction perpendicular to a surface while the overlayer with three-dimensional islands is fully relaxed at the thickness of ten monolayers.

I. INTRODUCTION

For real device applications, the growth of flat overlayers with an abrupt interface is highly demanded in heteroepitaxial systems. There is even a prediction that Ge-Si heterostructure may have the direct band gap between a conduction and a valence band due to a zone-folding effect.¹ These possible applications of the heterostructure in fast and optoelectronic devices provide motivations for the growth of Ge on Si substrate. Because of the 4.2% lattice mismatch between them, Ge on Si substrate is a typical Stranski-Krastanov growth system. Up to the critical thickness of three monolayers (ML), Ge overlayer grows layer-by-layer, followed by three-dimensional (3D) islands. Recent studies showed that 3D islands can be classified into three types. Two of them are strained while the third is relaxed. Strained islands initially have the hut cluster shape with four {105} facets² and transform to the dome cluster shape to maximize the strain relieving effect.³⁻⁵ Eventually they become mesoscopically relaxed islands with the introduction of dislocations at the interface,⁶ while the dislocations degrade the electronic transport property of the grown layers.

It is well known that one can suppress the growth of 3D islands by using a surfactant.^{7,8} In the growth process, the surfactant continuously floats on a surface and terminates the reactive dangling bond of Ge, resulting in an energetically stable surface. The surfactant also contributes to decrease the surface diffusivity of Ge adatoms and kinetically prevents the formation of 3D islands. Mostly group-V elements (As, Sb, Bi, etc.) have been used as a surfactant in the Ge growth. However, those elements can cause detrimental effects to the grown layers like unwanted doping. It was also reported that group-II elements cannot play the role of surfactant.⁹

In chemical vapor deposition processes, the gas sources of

germane and silane are dynamically dosed to a substrate at an elevated temperatures of >300 °C. The molecules are thermally dissociated at the temperature, producing Ge (Si) atoms as well as some reaction by-products. The growth process can be expected to be more complicated than that with solid sources. Recently, it was reported that the precursor state with a tetramer structure is formed on Si(001)-(2×1) whose chemical composition was suggested to be SiH₂.^{10,11} It was reported that hydrogen (H) atoms are coadsorbed on the growth surface. Adsorbed H can stabilize the growth surface by terminating the dangling bonds of top-layer atoms. In an *ex situ* transmission electron microscopy (TEM) study, H was backfilled into a growth chamber to suppress the 3D island formation.¹² Reaction pathways for Si (Ge) on H-terminated Si(001)-(2×1) surface were studied with first-principles calculations, suggesting the surfactant effect of H.^{13,14}

A recent scanning tunneling microscopy (STM) study showed that the atomic H flux can be a prospective surfactant in the Ge growth.¹⁵ It reveals that the adsorption and diffusion behaviors show excellent agreement with the theories and that the atomic H flux can suppress the growth of 3D hut cluster islands. While STM is suitable to study the growth kinetics in atomic scale and the nanoscopic structure of grown overlayers, medium energy ion scattering spectroscopy (MEIS) can reveal short range information such as the elastic strain and the atomic registry of an overlayer. It is also powerful for indepth composition analysis.

In this paper, we study the epitaxial growth behavior and the strain distribution of Ge overlayers grown on Si(001)-(2×1) with MEIS and STM. Flat Ge overlayers could be grown up to 10.0 ML with H surfactant. By measuring the angular dips of ion blocking as a function of depth, we found that elastic strain is uniformly distributed

over the overlayer in the direction perpendicular to the surface for the flat Ge overlayer of 10.0 ML.

II. EXPERIMENT

MEIS and STM experiments were performed in two separate chambers^{16,17} with the base pressures of 4×10^{-10} and 1×10^{-10} Torr, respectively. The growth and characterization were done *in situ* in each chamber, separately. An As-doped Si wafer (resistivity of $\sim 1 \Omega\text{-cm}$) was outgassed and flash-cleaned in ultrahigh vacuum condition. The Si(001)-(2 \times 1) surface was obtained without any noticeable trace of impurity. Ge was deposited with a Knudsen cell at a rate of ~ 1 ML/min. The growth temperature of Ge was $\sim 350^\circ\text{C}$. H surfactant was dynamically dosed through a 1/16 in diameter tube with a hot cracking filament ($>1600^\circ\text{C}$) to a Si sample by a precision peak valve. MEIS measurements were performed at room temperature using a primary proton beam accelerated at 97.3 keV. The random direction for ion beam incidence was chosen by rotating 11° along a polar angle direction from [111] incidence. The secondary ions scattered from Si and Ge atoms were detected along [111] direction with a toroidal electrostatic analyzer with the scattering angle of $\sim 70^\circ$. The blocking dips around the $\langle 111 \rangle$ direction were measured in a single alignment condition, with an incident ion beam at 2.5° from (001) direction, to improve counting statistics. The angular resolution, determined mainly by an incident ion beam divergence and a position sensitive detector, was estimated to be better than 0.1° . Other experimental details of MEIS can be found elsewhere.¹⁸

III. RESULT AND DISCUSSION

A. Layer-by-layer growth

Rutherford backscattering spectroscopy (RBS) with a high energy ($\sim \text{MeV}$) primary ion beam is a well-established technique to study thin film growth.¹⁹ MEIS spectra can be interpreted in the same way as for RBS, simply bearing in mind that the energy scale of MEIS is one order of magnitude lower (~ 100 keV) than that of high energy RBS. The chemical composition of the surface and near surface region can be uniquely determined by the incident energy, the atomic masses of the target and the projectile, and the scattering angle. With the 97.3-keV proton beam, the energies of backscattered ions for Si (mass 28) and Ge (mass 72) targets are 92.8 and 95.5 keV, respectively. When the primary ion beam is aligned along the channeling directions of a crystal, the atoms in the string are shadowed by the uppermost atom so that a backscattering yield is highly sensitive to the surface atoms, showing the surface peak. On the other hand, if a primary ion beam is incident along nonspecific (random) directions, ions can penetrate deeply into the bulk and be backscattered by inner layer atoms as well as surface atoms. Channeling spectra are frequently used to probe the crystallinity of a film, while random spectra are for the in-depth analysis of the composition and the structure.

The structure of a Ge overlayer grown without *H* has been well understood.²⁻⁶ Up to ~ 3 ML, the wetting layers of Ge dimers are formed with dimer vacancy lines, showing (2 \times *n*) reconstruction. At ~ 3 ML, 3D hut cluster islands begin

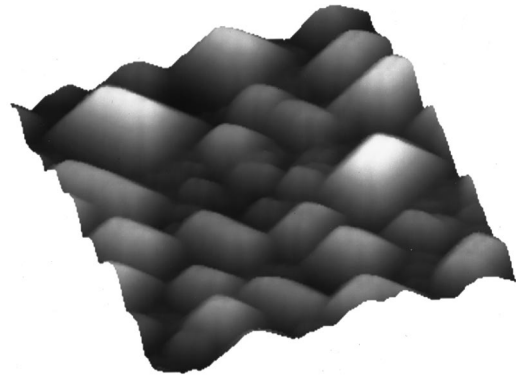


FIG. 1. Three-dimensional view of STM image for a 5.6-ML Ge overlayer grown without hydrogen. $850 \times 850 \text{ \AA}^2$. Whole range of height variation is $\sim 50 \text{ \AA}$.

to appear. Figure 1 shows a 3D view of an STM image with hut clusters. They reveal pyramidal shapes with four {105} facets. Figure 2(a) shows the scattered ion spectra for Ge overlayers grown on a Si(100)-(2 \times 1) without H, along the random incidence. As stated above, the peak at 95.5 keV is the scattered ion yield from surface Ge, and the plateau below 92.8 keV is from the Si substrate at the coverage < 3 ML. In Fig. 2(a), the height of Ge peaks increases up to ~ 3 ML and the Ge peaks remain narrow. The background with the energy range less than 95 keV begins to increase at 4 ML. This can be understood that the coverage of Ge wetting layers increases layer-by-layer up to ~ 3 ML at which 3D islands begin to appear, showing Stranski-Krastanov growth mode as illustrated in Fig. 2(b).

A previous STM study and first principles calculations showed that the surface diffusivity of Ge adatom is much

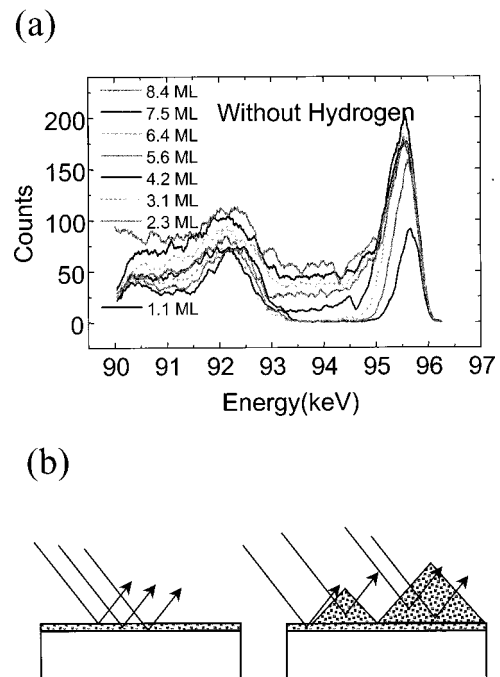


FIG. 2. (a) Energy spectra of scattered ion yield in random incidence for Ge overlayers grown on Si(001) surface without hydrogen at 350°C and (b) an illustration of scattering with Stranski-Krastanov growth mode.

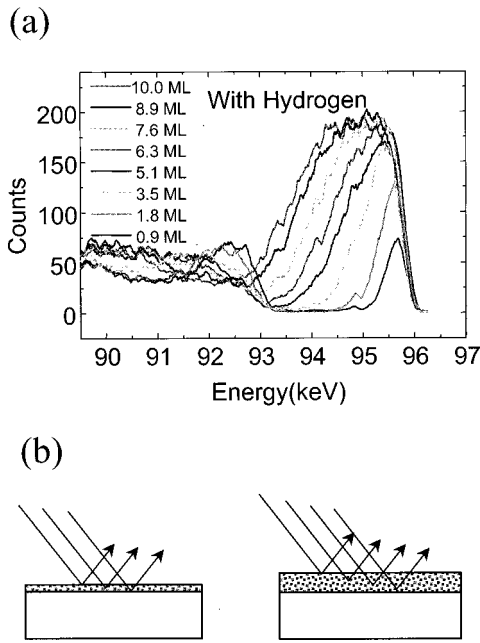


FIG. 3. (a) Energy spectra of scattered ion yield in random incidence for Ge overlayers grown on Si(001) surface with atomic hydrogen flux of 2 ML/s at 350 °C and (b) an illustration of scattering with layer-by-layer growth mode.

reduced with *H*-surfactant so that the growth of 3D island can be kinetically suppressed.^{13–15} Figure 3(a) shows the scattered ion spectra for Ge overlayers grown on a Si(100)-(2×1) with H surfactant along the random incidence. The broad enhancement around 92.0 keV is caused by a focusing effect.²⁰ Up to ~3 ML, in Fig. 3(a), the heights of Ge peaks increase with the same behavior as Fig. 2(a). But, at >3 ML, there is a big difference between the spectra from the overlayers grown with and without H. In Fig. 3(a), the Ge peak becomes wider and wider, suggesting a layer-by-layer growth with flat overlayers, as illustrated in Fig. 3(a). A 3D view STM image is shown in Fig. 4(a) for a 5.6-ML Ge overlayer grown with H surfactant. The surface of the overlayer is flat without any 3D island, consistent with MEIS spectra. The surface is composed of 2D patches with mono-atomic height. The typical widths of the 2D patches are ~60

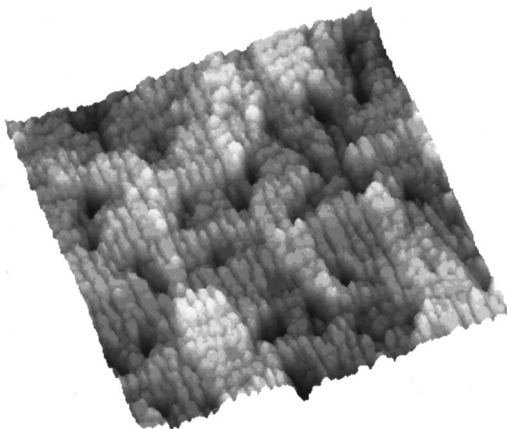


FIG. 4. Three-dimensional view of STM image for a 5.6-ML Ge overlayer grown with hydrogen. $1700 \times 1700 \text{ \AA}^2$. Whole range of height variation is ~8 Å.

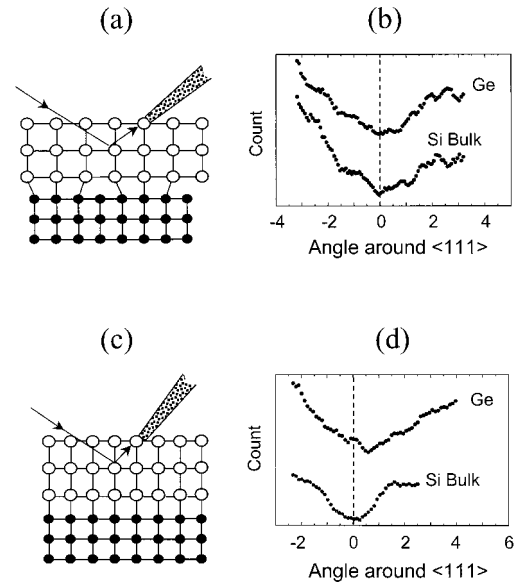


FIG. 5. Ball and stick model of (a) relaxed and (c) strained Ge overlayer on Si substrate with the illustration of angular blocking cones, and (b), (d) corresponding blocking dips.

Å. The average distance between two neighboring patches is ~15 Å. The basic building blocks of the patch are Ge dimers and dimer row. Other featured structures are pin holes distributed over the surface. We confirmed that the growth behavior is continued up to 10.0 ML.

B. Strain distribution

The origin of Stranski-Krastanov growth mode is the lattice mismatch between Ge and Si. Up to the critical thickness, flat wetting layers are pseudomorphically grown with elastic strain. Beyond the critical thickness, the elastic strain energy is too large to have pseudomorphic layers and the 3D islands are formed to relax the strain through the local deformation of a lattice. In a recent x-ray diffraction study, the lattice constant of Ge at the interface is nearly the same as that of Si, but the lattice constant of Ge at the top of a hut cluster is close to that of bulk Ge.²¹ In the previous section, we showed that the flat overlayers can be grown with H surfactant. A natural question that can be made is how the elastic strain can be relieved without the 3D islands. It may also be wondered if the flat overlayer is still strained. To understand this problem, we measured ion blocking dips for the Ge overlayers of 10.0 ML.

The concept of ion blocking can be found elsewhere,¹⁹ but, will be described briefly. The cross section for an atomic target is so small that a backscattered ion reaching a detector has undergone only a single collision with an atom. If a target atom is located beneath a surface layer, the backscattered ion may be scattered on its way out by another atom and thereby can be blocked, as illustrated in Figs. 5(a) and 5(c). Therefore, within a certain solid angle (blocking cone), a backscattering yield is reduced relative to other angles, showing the angular blocking dip as shown in Figs. 5(b) and 5(d). It should be noted that the position of an angular blocking dip depends on the angular configuration among neighboring atoms. The position of an angular blocking dip for a relaxed Ge overlayer would coincide with that of a bulk Si

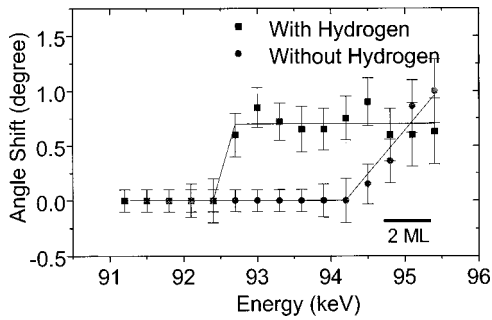


FIG. 6. The angular shift of Ge blocking dips from Si one as a function of depth for a 10.0-ML Ge overlayer grown on Si(001) surface with and without atomic hydrogen.

substrate as shown in Fig. 5(b), because they have the same atomic structure despite of their different lattice constants. However, the position of an angular blocking dip for a strained Ge overlayer would not coincide with that of a bulk Si substrate as shown in Fig. 5(d). There must be some angular shift $\Delta\theta$ due to a tetragonal distortion which can be correlated to the misfit as (in pseudomorphic growth with biaxial stress by simple trigonometry)

$$\frac{\Delta\theta}{\sin\theta\cos\theta} = \frac{1+\nu}{1-\nu} \frac{a_s - a_f}{a_f},$$

where $a_s(a_f)$ is the Si(Ge) lattice spacing, 5.43 Å (5.66 Å), θ is the angle of a bulk axis with respect to a surface plane, and ν is the Poisson's ratio, 0.272. In our experimental geometry, $\Delta\theta$ is expected to be 2° with fully strained Ge overlayer.

In order to examine the strain distribution in the direction perpendicular to a surface, we analyzed blocking dips at various backscattering energies with the Ge overlayers of 10.0 ML. Since a backscattering energy corresponds to the depth of a target atom from a surface, blocking dips at the energy range lower (higher) than 92.8 keV show the strain distributions of the Si substrate (Ge overlayer). The examples of the blocking dips are shown in Figs. 5(b) and 5(d). Their good χ_{\min} (minimum yield) and shapes imply good crystallinity. The angular shift of the Ge blocking dips with respect to that of Si bulk is plotted as a function of depth for 10.0-ML Ge overlayers in Fig. 6. For the overlayer grown without H, the angular shift of a blocking dip is absent near the interface, suggesting fully relaxed 3D islands with a bulklike lattice structure. Some shifts near the surface of Ge overlayer can be explained with strained wetting layers in Stranski-Krastanov growth mode. For the overlayer grown with H, the blocking dip for the Ge layer is shifted by $\sim 0.7^\circ$, nearly

constant from the interface to the top of the Ge overlayer, implying the uniform strain distribution. The shift at the interface is quite abrupt probably due to the sharp interface.

As stated above, if a Ge overlayer is fully strained, the shift of blocking dips should be 2° , but the observed value is $\sim 0.7^\circ$. There are two possible scenarios to explain the difference. First, the overlayer is under low strain due to the alloy formation of Ge and Si. The intermixing was proposed in recent studies.²² In this case, the $\sim 0.7^\circ$ shift can be caused by a lattice mismatch of 1.4%, suggesting the alloy layer of $\text{Si}_{0.7}\text{Ge}_{0.3}$. In our channeling spectra (not shown here), the amount of Si on the first layer of epitaxial film at the coverage >3 ML is never more than 10 at. %. Moreover, the random spectra of Fig. 3(a) cannot be explained with alloying of Si and Ge with the Si composition larger than 25 at. %. Second, the Ge overlayer is partially pseudomorphic. The strain can be locally relieved by the formation of dislocations at the interface. With As surfactant, it was previously reported on the basis of TEM experiments that Ge films are pseudomorphic up to 8 ML and that shaped defects are formed at 12 ML. In the STM image (Fig. 4), we have seen the distribution of pin holes on the overlayer. It is hard for us to say that the pin hole is exactly the same structure as V-shaped defect because of their different growth temperatures, $\sim 350^\circ\text{C}$ and 500°C , respectively. But, they may have same origin to relieve elastic strain. Both of them are homogeneously distributed over the film. V-shaped defect cannot relieve the elastic strain completely because of their high-formation energy and work as a seed for the dislocation, which might occur to pin holes.

IV. CONCLUSIONS

Agreeing well with previous reports on H surfactant effect, we observed layer-by-layer growth of Ge on Si(100)(2×1) with atomic H. By analyzing the angular positions of ion blocking dips for 10.0-ML Ge overlayers as a function of depth we found that the overlayer grown with H surfactant is uniformly strained in the direction perpendicular a surface, while the overlayer grown without H is relaxed. A sharp interface is expected from the abrupt shift of blocking dips at the interface for the overlayer grown with H.

ACKNOWLEDGMENTS

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