Direct Observation of Intermixing at Ge/Si(001) Interfaces by High-Resolution Rutherford Backscattering Spectroscopy

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The initial stage of Ge/Si(001) epitaxial growth is studied with high-resolution Rutherford backscattering spectroscopy. In contrast to the generally accepted picture, intermixing of Ge and Si begins before the first layer is completed at the growth temperature of 500 °C. If the layer is deposited at room temperature, intermixing takes place during annealing at 300–800 °C. These observations are in reasonable agreement with a recent theoretical study based on generalized gradient approximation density functional calculations [Y. Yoshimoto and M. Tsukada, Surf. Sci. **423**, 32 (1999)].

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Ge on Si(001) is a model system for investigation of heteroepitaxy. It has been extensively studied from the viewpoint of fundamental physics and because of its technological importance. The growth mode is known to be the Stranski-Krastanov with a critical thickness of three monolayers (ML) [1]. In the sub-ML coverage region, investigations with low-energy electron microscopy [2] and surface stress-induced optical deflection [3] provide a picture of dispersive adsorption, with Ge displacing Si from terraces. This is followed by full Ge termination at 1 ML, because the Ge dangling-bond energy is lower than the Si dangling-bond energy [4]. Above 1 ML coverage, an intermixing phase has been observed. The first evidence of the intermixing layer was reported by Copel *et al.* with medium energy ion scattering (MEIS) [5]. They found intermixing at coverages larger than 2 ML at a growth temperature of 500 °C, while intermixing was not detected at 1 ML. Similar results were also reported at 400 °C using extended x-ray absorption fine structure: substantial intermixing was observed at 2 ML, while no intermixing was detected at 1 ML [6].

In a recent study, however, significant intermixing at 1 ML was reported by Sasaki *et al.* using the Auger electron diffraction (AED) technique [7]. They found that more than half of the deposited Ge atoms are distributed in the subsurface region even at 1 ML, when the Ge/Si(001) is annealed at 350–600 °C after room-temperature (RT) deposition. The best fit between the observed and simulated AED patterns was obtained with a Ge distribution over the first to the fifth layers with a concentration ratio of 4:1:1:1:1, although quantitative analysis is rather difficult in AED [7]. The same result was obtained by the deposition of 1 ML Ge at 400–600 °C. Formation of a stable phase was concluded [8]. More recently, Ikeda *et al.* studied the intermixing at the Ge/Si(001) interfaces prepared by the deposition of 0.15 and 1 ML Ge at 400 °C by means of surface energy loss spectroscopy of MEIS (SELS-MEIS) [9]. The observed mean energy loss of the scattered ions from the surface Ge atoms can be explained by a Ge distribution with a concentration ratio of 4:3:1 or 4:2:2 both at 0.15 and 1 ML assuming an adequate surface stopping power. Although neither AED nor SELS-MEIS provides an accurate Ge distribution, these results disagree qualitatively with the generally accepted picture of the full Ge termination at 1 ML.

Because the intermixing affects considerably the Si/Ge heterostructure properties (optical, electronic, and so on), it is important in the semiconductor industry to solve this controversy. In order to address the intermixing mechanism in the sub-ML region, more accurate measurement of the Ge profile is required. Recently, we have demonstrated that monolayer resolution can be achieved in Rutherford backscattering spectroscopy (RBS) using a high-resolution spectrometer and a grazing angle technique [10]. This new technique, called high-resolution RBS (HRBS), is a powerful tool in surface studies [11]. Here we report on the direct measurement of the Ge distribution in the initial stage of the Ge/Si(001) epitaxial growth with HRBS. Existence of an intermixing layer at sub-ML coverages is confirmed by the direct measurement of the Ge profile.

The measurement of HRBS was performed in a UHV scattering chamber (base pressure 9×10^{-11} Torr), which was connected to a 300 kV tandem-type accelerator (Shimazu, MIG-300) via a differential pumping system. A clean Si(001) surface was prepared *in situ* by dc-resistive heating of a Si(001) wafer at ~1200 °C. A Si buffer layer with thickness about 50 nm was deposited at 650 °C with an electron beam evaporator to prepare a flat and clean surface. Deposition of Ge was done with a W wire basket at a rate of ~0.5 ML/min at RT as well as at 500 °C. The layer deposited at RT was annealed *in vacuo* at 300, 400, 500, 600, 700, and 800 °C for 3 min at each temperature. The temperature of the Si wafer was measured with an infrared radiation thermometer.

A beam of 400 keV He^+ ions from the accelerator was collimated to 3×3 mm^2 by a series of apertures. A typical beam current was about 10 nA. The ions scattered

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at 30° from the Ge/Si(001) were energy analyzed by a 90° sector magnetic spectrometer. The exit angle θ_e was 2° with respect to the surface plane. The energy resolution of the system was about 0.9 keV, which was mainly determined by the energy spread of the incident beam. A typical dose for one HRBS measurement was about 20 μC.

Figure 1(a) displays an example of the observed HRBS spectrum for the Ge/Si(001) prepared by the deposition of 0.4 ML Ge at RT together with the HRBS spectrum for the virgin Si(001). There is a sharp peak at ~393.5 keV, which corresponds to the Ge atoms in the topmost atomic layer. In order to analyze the HRBS spectrum, we have developed a simulation code to calculate the HRBS spectrum. The simulation includes the energy loss straggling and the reduction of the scattering cross section from the Rutherford formula due to screening effects. The solid curve shows the best-fit result of the simulation. The dotted curve presents the Ge contribution in each atomic layer. The concentrations C_i of Ge are found to be 32.5%, 3.5%, 0.5%, and 1% ± 0.5% for the first, second, third, and fourth atomic layers, respectively. These concentrations are close to the calculated result (33%, 6%, 1%, and 0.1%) for the simultaneous multilayer growth mode [12], suggesting that surface diffusion is suppressed at RT.

Upon annealing at 300 °C for 3 min, a notable change can be seen in the HRBS spectrum as shown in Fig. 1(b). The height of the Ge peak decreases, while the total amount of Ge does not change, indicating that intermixing of Ge and Si takes place. Although formation of Ge islands by annealing may explain the observed change, the observed reflection high energy electron diffraction (RHEED) pattern did not show any bulk spots, indicating that there were no islands detectable by RHEED. This is consistent with scanning tunneling microscopy (STM) observations, which showed no Ge island higher than one atomic height [8]. Thus the observed change can be ascribed to the intermixing of Ge and Si. The best-fit result of the spectral simulation is shown by the solid and dotted curves. The obtained Ge concentrations of the first four atomic layers are 26%, 6%, 1%, and 1.5% ± 0.5%, respectively. The HRBS spectra calculated with the concentration ratios reported by Sasaki *et al.* and Ikeda *et al.* are also shown for comparison [Fig. 1(b)]. These curves do not agree with the present results.

In our simulations, the surface was assumed to be atomically flat. If the surface step density is comparable or larger than $\sin\theta_e/d$, where d is the surface step height, the interpretation of the result would change substantially. In order to see the effect of the surface roughness, HRBS measurements at various θ_e ($= 2°, 3°, 4°, 6°$) were performed. The obtained Ge concentrations hardly depend on θ_e, indicating that the surface step density is low enough not to affect the present interpretation. This

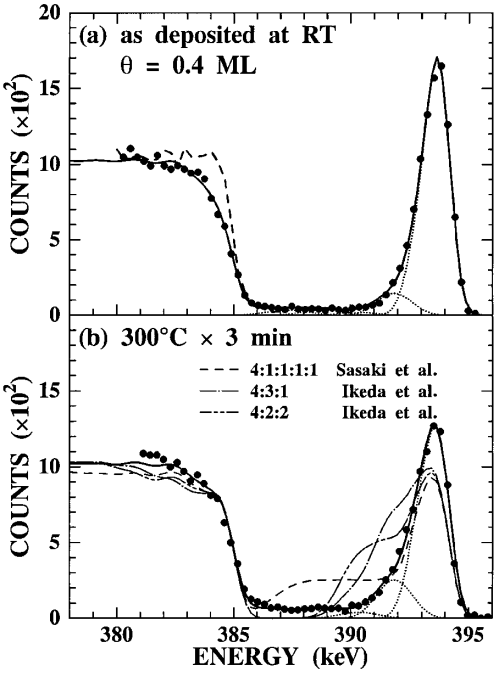

FIG. 1. (a) HRBS spectrum of Ge/Si(001) prepared by deposition of 0.4 ML Ge onto Si(001) at RT. The dashed curve shows the spectrum of the virgin Si(001). The best-fit simulation result is shown by the solid curve. The dotted curves show the contribution of Ge for individual atomic layers. (b) Postannealed (300 °C × 3 min) result. The calculated spectra with Ge distributions proposed by Sasaki *et al.* [7] and Ikeda *et al.* [9] are also shown for comparison.

is also supported by the STM observation of the Si(001) obtained from the same wafer and prepared by the same procedure as the present preparation. The observed step density was about 0.05 nm^{-1}.

A series of anneals at 400, 500, 600, 700, and 800 °C for 3 min each was applied to the Ge/Si(001) sample after the 300 °C anneal. The change in the Ge concentration is shown in Fig. 2(a). The concentration C_i of each layer normalized to that of the first layer (C_1) is also shown in Fig. 2(b) to see clearly the small change. After the decrease at 300 °C mentioned above, C_1 is almost constant up to 600 °C and then decreases rapidly at 800 °C. The behavior of C_2 is characteristic: C_2 shows a maximum at 400 °C, while the concentrations of deeper layers show monotonic increases. The bulk diffusion coefficients estimated from the high temperature data (a preexponential factor 0.35 cm^2/s and an activation energy 3.93 eV [13]) are 9.5×10^{-36}, 1.3×10^{-30}, 7.2×10^{-24}, and 1.2×10^{-19} cm^2/s at 300, 400, 600, and 800 °C, respectively. These values are too small to explain the observed intermixing, except at 800 °C.

The present results can be qualitatively understood by the following scenario. The migration energy in the surface region is usually smaller than the bulk value. The observed intermixing at 300 °C indicates that the height of the energy barrier E_{12} for Ge migration from the first layer to the second layer is much smaller than the

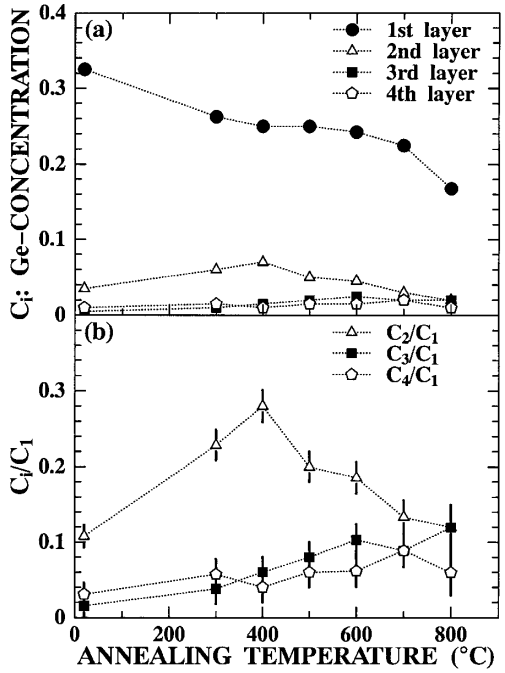

FIG. 2. (a) Change of the measured Ge concentrations in the first four atomic layers as a function of temperature for the last annealing step. (b) Concentrations relative to the first layer.

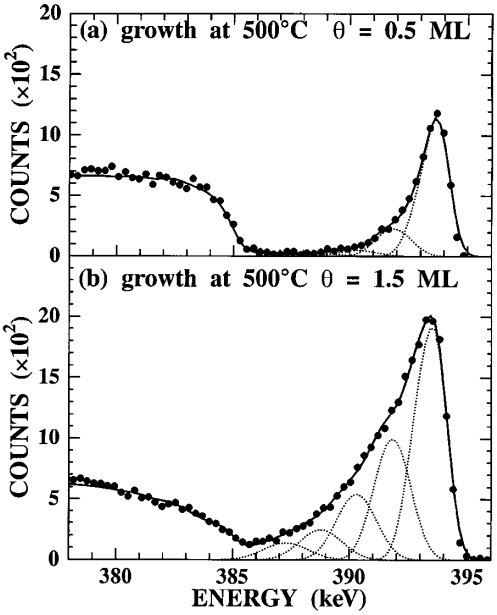

FIG. 3. HRBS spectra of Ge/Si(001) prepared by deposition at 500 °C. Best-fit simulation results are shown by curves. Significant intermixing can be seen at 1.5 ML.

bulk migration energy. At 500 °C, C_2 starts to decrease, indicating that Ge atoms migrate into the third layer. This means that the energy barrier E_{23} for Ge migration from the second layer to the third layer is larger than E_{12}, but still smaller than the bulk value.

The mechanism of the intermixing of Ge and Si is often discussed in terms of the stress induced by surface dimers [8,14–16]. There are atomic sites under tensile stress in the third and fourth layers between the surface dimers. These sites favor Ge occupation, because Ge atoms reduce the tensile stress with their larger atomic size. Nevertheless, our results show no accumulation of Ge in the third and fourth layers. This is consistent with a recent theoretical study based on a generalized gradient approximation density functional calculation, which predicted no anomaly in the Ge concentration in the third or fourth layers [17]. The slightly larger occupation probability at the between-dimer-row sites is canceled out by the lower occupation probability at the under-dimer-row site, which is compressed by the dimer row. The calculated ratios for 0.4 ML under thermodynamical equilibrium at 600 °C are $C_2/C_1 = 0.067$, $C_3/C_1 = 0.06$, and $C_4/C_1 = 0.05$. These are of the same order as our results, although the observed Ge concentration decreases somewhat more rapidly with depth than the calculated results. This suggests that full thermodynamical equilibrium is not reached at 600 °C in our experiments.

Figure 3 shows the HRBS spectra observed during the initial stage of the Ge growth at 500 °C. The amount of the deposited Ge was 0.5 ML for Fig. 3(a) and 1.5 ML for Fig. 3(b). The obtained Ge concentrations in the first four layers are 34%, 8.5%, 2%, and 1% ± 0.5% at 0.5 ML, and 64.5%, 38%, 22.5%, and 11% ± 1% at 1.5 ML. Based on simple surface energy considerations, after the complete occupation of 1 ML Ge in the first layer, the Ge atoms start to occupy up to 0.5 ML at the fourth-layer tensile sites [16]. The present result, however, does not show any anomaly in the Ge concentration in the fourth layer, and the concentration in the first layer is not 100% but about 65% at 1.5 ML. This clearly indicates that simple surface energy considerations are not sufficient.

In the present study, the energy spectrum of the backscattered He^+ ions was measured. If the charge state distribution depends on the atomic species and/or depth from which the ion scattered, the Ge distribution deduced from the He^+ spectrum does not represent the true distribution. Figure 4 shows examples of He^+ and He^{2+} spectra for Ge/Si(001) prepared by the deposition of 0.5 ML Ge at 500 °C, together with the ratio of the He^+ yield to the He^{2+} yield (filled circles). The He^+/He^{2+} ratio is almost constant, indicating that charge state distribution does not depend on the atomic species or depth [18]. This allows quantitative analysis in HRBS without measuring all charge states.

During the HRBS measurements, radiation damage may cause so-called *ion beam mixing*. The defect distribution in Si(001) generated by the irradiation of 400 keV He ions was estimated using the TRIM95 code. The calculated concentration of vacancies produced by one HRBS measurement (irradiation of 6.5×10^{14} ions/cm^2) is about 0.7% in the surface region. This is low enough to neglect the effects of the radiation damage. In order to confirm this, the same HRBS measurement was repeated

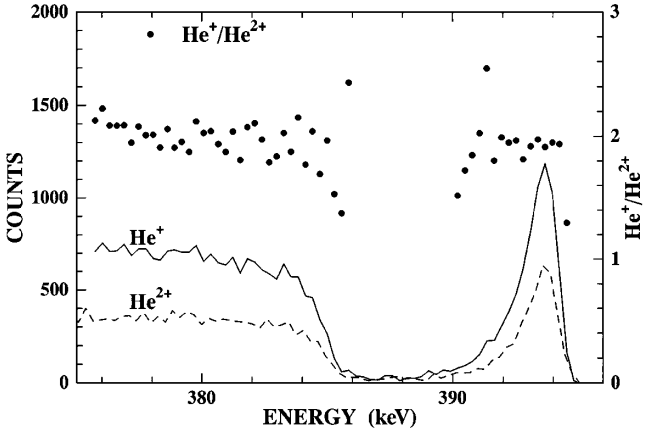

FIG. 4. HRBS spectra of the scattered He^+ and He^{2+} ions for Ge/Si(001) prepared by deposition of 0.5 ML Ge onto Si(001) at 500 °C. The ratio of the He^+ yield to the He^{2+} yield is also shown by filled circles. The charge state distribution does not depend on the atomic species or depth.

after the irradiation of 3×10^{15} ions/cm^2, which corresponds to the dose of five HRBS measurements. There was no detectable change in the HRBS spectrum, indicating that the effect of the radiation damage induced by the HRBS measurements is negligibly small.

In summary, HRBS was successfully used to study the initial stage of Ge/Si(001) epitaxial growth. The distribution of Ge was directly measured with monolayer resolution. Substantial Ge concentration in the second atomic layer (about one-fourth of the first layer concentration) was found at submonolayer coverages, either upon 300 °C annealing after RT deposition, after deposition at 500 °C. These results are in reasonable agreement with recent first principles calculations based on a generalized gradient approximation density functional method [17].

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