# Pseudomorphic Structure at the Interface of Ge on Si(111) Studied by High-Energy-Ion Scattering

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(Received 19 June 1981)

Megaelectronvolt ion scattering is applied to a study of the initial stage of heteroepitaxy of the Ge/Si(111) system and it is shown that the interface is uniform and pseudomorphic at first, after which island formation takes place and strains are introduced at the interface. This change occurs after deposition of a threshold film thickness of ~3 monolayers. More than 10 monolayers are distorted at the interface after deposition of about 30 monolayers of germanium.

PACS numbers: 68.55.+b, 61.80.Mk, 68.20.+t

The initial stage of epitaxial film growth has been studied so far by using conventional surface methods such as electron microscopy, electron diffraction, electron and ion-mass spectroscopies, etc. These methods are well suited to study the first few monolayers (ML); however, as a result of their surface sensitivity, they could not be applied to practical interface problems between a relatively thick film and a substrate without destroying the surface layer. Therefore, since most previous studies were limited to the structure analysis of very thin films on single-crystal substrates or the composition analysis of the interface transient layer, the atomic structure at solid-solid interface has never been solved. In a particular case of Ge deposition on a Si substrate, the electron and optical microscopies and reflection high-energy–electron diffraction studies[1,2] have shown that the movements of steps on the Ge film are accelerated at a critical thickness of ~10 Å followed by the growth of parallel oriented microcrystalline particles, and then Ge growth centers (islands) are formed with gradually increasing sizes. The recent UHV electron microscopic study[3] has also revealed the fairly good heteroepitaxy in this system with some misorientation in the Ge film.

We report in this paper an application of megaelectronvolt $He^+$-ion channeling/backscattering to probe the interface structure of the Ge-on-Si(111) system. Our measurements have shown the initial growth of the pseudomorphic Ge film up to an average film thickness of ~3 ML. In this stage the Ge atoms are stacked layer by layer in the same way as the Si crystal would grow on the substrate Si. When the film thickness exceeds this threshold, substantial strains are introduced into the interface causing displacements of both Si- and Ge-lattice atoms. Our first-order estimates about the strained interface conclude that ~4 ML of Si and ~10 ML or more of Ge are displaced by more than ~0.2 Å in the final stage studied.

The clean Si(111) surfaces were prepared by heating the crystal up to ~1100 °C for several minutes in UHV. We found no significant impurities by Auger-electron spectroscopy and backscattering, and the electron diffraction showed a sharp 7 × 7 pattern characteristic of the clean Si(111) surface. Germanium was deposited on the clean surface by sublimation from a tungsten basket. The deposition rate was ~0.5 ML/min, where we define the average Ge film thickness of 1 ML as the Ge atomic density equal to the theoretical Si atomic density in a (111) Si plane, i.e., $7.8 \times 10^{14}$ atoms/cm$^2$. The aligned and random backscattering spectra were measured at several stages of Ge deposition by use of a surface-barrier–type Si detector located in the grazing exit-angle geometry, and the surface peak (SP) intensities of Si and Ge were evaluated. We define the minimum yield, $\chi_{min}$, for Ge as the ratio of the peak areal intensity in the aligned spectrum to that in the random spectrum (Fig. 1). These experimental results were compared to a computer simulation of the nuclear encounter probability in which the paths of charged particles were traced in a stepwise manner assuming the binary collision approximation.[4] Measurements were done for depositions at room temperature and 620, 720, and 870 K. The background pressure in the target chamber did not exceed $1 \times 10^{-9}$ Torr during deposition and measurements.

We found no decrease in $\chi_{min}$ for Ge with the film thickness in the case of room-temperature deposition. This is an indication of amorphous film formation. The ⟨111⟩ SP intensity of Si at 1 MeV increased by a small amount (~0.2 atoms/row) at the initial stage of deposition correspond-

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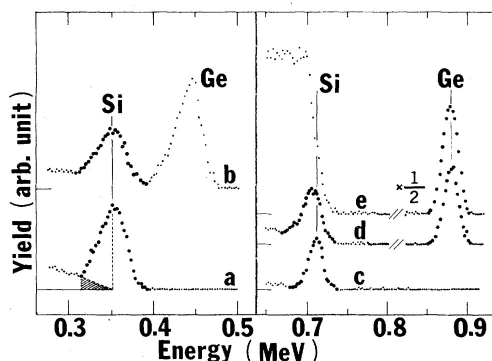


FIG. 1. Typical backscattering spectra at 0.5 MeV curves ($a$ and $b$) and 1 MeV curves ($c$, $d$, and $e$). Curves $a$ and $c$ ⟨111⟩ aligned spectra from the clean Si(111) – 7× 7 surface. Curve $b$ ⟨111⟩ aligned spectrum after the deposition of ~ 2.3 ML Ge film. Curve $d$ ⟨111⟩ aligned spectrum after the deposition of ~ 11 ML Ge film. Curve $e$, random spectrum after the deposition of ~ 11 ML Ge film. The Ge films were deposited at 620 K, and scattering measurements were carried out after cooling the Si substrate down to room temperature. The SP intensities were evaluated as the total integrated counts (the area under heavy dots) minus the background. The background subtraction method is shown schematically in spectrum $a$.

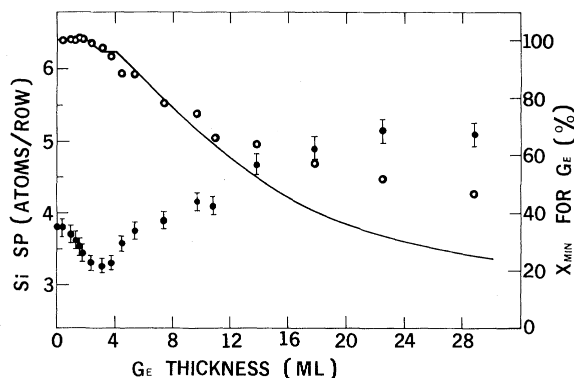


FIG. 2. Variation of ⟨111⟩ surface peak intensity of Si (closed circles) and minimum yield of Ge (open circles) at 1 MeV as a function of average Ge-overlayer thickness. Experimental plots are collected from three runs. The error bars indicate the uncertainty of ±3% in relative measurements of the SP intensity. The uncertainty in relative measurements of $\chi_{min}$ is estimated to be less. The solid curve shows the result of computer simulation for $\chi_{min}$, in which bulklike structure and dynamics are assumed for the Ge film.

ing to a coverage of ~2 ML, and thereafter continued to increase very slowly.[5] The latter slow increase can be attributed to the multiple scattering of projectiles passing through the overlayer and agrees well with a model calculation.[4] The initial increase suggests a small structure distortion in the Si surface layer which may result from the Ge-Si interaction through the dangling bonds. In the case of deposition at the highest temperatures (720 and 870 K), the widths of Si and Ge peaks were broadened and the minimum yield of Si, which is defined as the scattering yield behind the SP of Si, increased considerably. These are indications of Si-Ge intermixing at the interface. Better epitaxial films can be formed on such a mixed interfacial layer as studied previously[1,2]; however, we present here details of a case of epitaxial growth without intermixing (620-K deposition), which is particularly important in gaining an understanding of the formation, structure, and properties of heterogeneous bicrystal interfaces.

Figure 1 shows typical spectra obtained from the clean Si(111)-7×7 surface and after the Ge deposition at the substrate temperature of 620 K. Figure 2 shows variation of the ⟨111⟩ SP intensity of Si and $\chi_{min}$ for Ge at 1 MeV with respect to the average thickness of the Ge overlayer. The *in situ* electron-diffraction measurements showed a gradual change of the 7×7 pattern to a blurred Ge(111)-1×1 pattern with the increase of the thickness. The SP intensity of Si decreases at first until it reaches the minimum point at ~3 ML coverage. This is a direct indication of shadowing of underlying Si atoms by the deposited Ge atoms and cannot be attributed to relaxation of the displacements of surface atoms in contrast to the H-saturated or Au-deposited Si(100) case.[6] Measurements of the angular distribution of the ⟨111⟩ SP intensity at 0.5 MeV support this conclusion. As shown in Fig. 3, the 7×7 surface yields slightly higher SP intensities than the model calculation of a bulklike atomic structure without any enhancement in the surface thermal vibration (curve ***a***). Since, in the first-order approximation, the increase in the ⟨111⟩ SP intensity by 1 atom/row corresponds to displacements of 3 ML of Si from the lattice site, the excess SP intensity measured from the 7×7 surface suggests either that this surface is accompanied by lateral displacements (≲0.15 Å) of the Si atoms in the first one to two monolayers or that the surface thermal vibration amplitude is enhanced by a factor of ~4. These are in a good agreement with detailed measurements by Culbertson, Feldman, and Silverman.[7] In any case, the decrease of the SP intensity due to the Ge deposition to an even lower level than curve ***a*** strongly indicates that this decrease is mainly caused by the shadowing effect. If the as

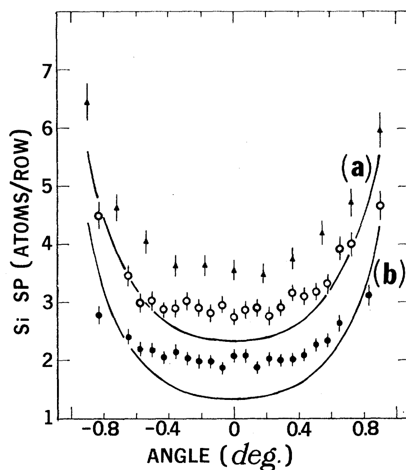


FIG. 3. Angular dependence of ⟨111⟩ Si surface peak intensity at 0.5 MeV. Open circles, the 7× 7 surface; closed circles, after the deposition of ~ 2.3 ML of Ge; triangles, after the deposition of ~ 13 ML of Ge. The exact ⟨111⟩ direction (0 deg) was determined from simultaneous measurements of the bulk Si scattering yields. Computer simulation (curve *a*) assumes bulklike structure and dynamics for the 7× 7 surface. Curve *b* assumes 2 ML of Ge atoms located at on-top positions in addition to curve *a*.

yet undetermined factors that lead to deviation between the clean Si(111) SP intensity and that calculated for an idealized surface (bulk lattice, no enhanced vibration) continue to exist at the interface, then the shadowing due to Ge is perfect. Even if these factors are completely removed, the shadowing is substantial indicating the pseudomorphic growth.

A computer simulation similar to that described by Kinoshita, Narusawa, and Gibson[4] showed that the shadowing effect is maximized if the Ge atom is located exactly on top of the Si-atomic string, it decreases steeply with the misfit distance between the Ge atom and the axis of the string, and it can be neglected if the distance is larger than ~0.25 Å. Results of our SP intensity measurements at both 0.5 and 1 MeV as a function of the average Ge-film thickness are consistent with the conclusion that the Ge atoms of up to ~3 ML are located within 0.1 Å of the axis of the Si string. The $\chi_{min}$ for Ge measured at this stage agrees well with the model calculation justifying the stacking model described above.

The $\chi_{min}$ for Ge stays at 100% in the initial stage indicating that the overlayer is uniform in thickness, or there exists no appreciable buildup of three-dimensional nuclei at this stage. The $\chi_{min}$ starts to decrease with the average film thickness after about 2 ML coverage. The solid curve in Fig. 2 is the result of computer simulation, in which we assumed layer-by-layer growth of the perfect crystalline Ge film with the bulklike structure and dynamics. According to the stacking law in the ⟨111⟩ direction of an ideal diamond structure we assumed that the third layer deposits on top of the second layer. The experimental $\chi_{min}$ indicates that the overlap of layers starts after completion of ~2 ML coverage, and thus supports our assumption on stacking. The value of $\chi_{min}$ lower than the calculation at about 4 ML coverage suggests the onset of island formation. We found no appreciable energy shift in the Si backscattering spectrum after deposition of ~30 ML of Ge. This absence of an energy shift also supports the island formation. The rate of decrease in $\chi_{min}$ after ~4 ML coverage is slightly lower than the calculation and suggests development of imperfections in the film.

The increase in the SP intensity of Si after ~3 ML coverage indicates a change of structure of the Ge overlayer film all the way down to the interface, i.e., the Ge atoms that had been effectively shadowing Si strings shift away from alignment with the underlying Si strings. This is consistent with the slower rate of decrease in $\chi_{min}$ for Ge, which, as noticed above, indicates the formation of strains at the interface. The apparent saturated SP intensity of Si at $\gtrsim$ 20 ML coverage is higher than the clean surface value by ~ 1.3 atoms/row. This is expected if the top ~ 4 ML of Si are displaced by as much as ~0.2 Å. The $\chi_{min}$ for Ge is also higher than the calculation at these stages. For instance, the $\chi_{min}$ at ~29 ML coverage is about the same value as calculated for ~15 ML coverage suggesting that on the average ~14 ML of Ge are not stacked properly.

In summary we have measured the SP intensity of Si and the minimum yield for Ge in the course of Ge deposition on clean Si(111) surfaces. Both of these structure-sensitive quantities showed that the Ge film grows in the layer-by-layer fashion up to ~3 ML coverage, after which the results are consistent with island formation in agreement with other studies.[1,2] This is the so-called Stranski-Krastanov mode.[8] In the initial phase, the Ge film is registered to the substrate Si; however, stress builds up at the interface due to the lattice misfit of ~4%, and at ~3 ML coverage the pseudomorphic structure is collapsed with attendant introduction of strains in both the film and the substrate structure. Furth-

er growth of the crystalline Ge overlayer is undoubtedly affected by the presence of stacking faults and other extended defects resulting from contraction of the overlayer. After growth of ~20 ML of Ge the interface appears stable with ~4 ML of strain on the substrate side and with considerable strain and extended defects in the epitaxial Ge overlayer. These results not only confirm previous electron-microscopic observation but also provide definitive new information on the interface atomic structure which is initially pseudomorphic and layer by layer with a structural phase transition at a critical coverage (~3 ML) leading to a strained and defected interface.

This work was supported by the U. S. Office of Naval Research under Contract No. N00014-78-C-0616.

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# Critical Behavior of a Microemulsion

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(Received 13 July 1981)

Dynamic light-scattering techniques have been employed to study the nature of phase transition in a single-phase microemulsion system near the cloud-point temperature. Critical opalescence and the critical slowing down of the composition fluctuations were observed near the transition temperature. It is further observed that there exists a close parallelism between the critical phenomena and the cloud-point transition in microemulsions.

PACS numbers: 64.70.Ja, 64.60.Fr, 64.75.+g, 82.70.Kj

A microemulsion is defined to be a thermodynamically stable, homogeneous single-phase liquid that contains two immiscible fluids such as hydrocarbon and water, and one or more surface active agents called surfactants. Surfactant molecules are composed of a hydrophilic moiety (water-loving component) at one end, and a hydrophobic moiety at the other. This type of molecule feels most at home at a water-oil interface. When oil is mixed with a small amount of surfactant, one could imagine that the surfactant molecules would aggregate, hiding their hydrophilic end in the center of the cluster away from the oil phase while the hydrophobic ends dissolve in the oil. Obviously, the reverse situation can also happen with water as the continuous phase and surfactant aggregates are formed with the hydrophilic ends sticking out. These surfactant aggregates are called micelles and the fluids containing micelles are called micellar solutions. Now, if we should add a small amout of water to the hydrocarbon micellar solution, the otherwise immiscible water molecules could go to the hydrophilic center of the micelles (traditionally, micelles of this type are called inverted micelles) and swell the micellar aggregates. This water is said to be "solubilized" by the surfactants. A microemulsion containing these swollen micelles (typically 50–100 Å in radius) dissolved in the oil phase resembles a macromolecular solution.

It is possible to formulate microemulsions to coexist with both oil and water simultaneously.[1] One of the more interesting properties of this system is that the interfacial tensions between the microemulsion/oil interface as well as the microemulsion/water interface can be extremely low, of the order of $10^{-3}$ dyn/cm. As a result, microemulsions are thought to be excellent agents for mobilizing the residual oil trapped in watered-out reservoirs.[2]

Our three-component microemulsion contains 3% (wt./vol.) sodium di-2-ethylhexylsulfosuccinate (molecular weight 444.5), a surfactant commonly known as AOT, and 4.76% (vol./vol.) wa-



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