RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Si(111) (7×7)-Ge and Si(111) (5×5)-Ge surfaces studied by angle-resolved electron-energy-loss spectroscopy

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(Received 26 June 1985; revised manuscript received 3 September 1985)

Very thin Ge layers on Si(111) are investigated with the use of angle-resolved electron-energy-loss spectroscopy and low-energy electron diffraction. Ge-derived (7×7) and (5×5) surfaces are identified by these measurements. New surface one-electron transitions are found at 1.4 eV on the Si(7×7)-Ge surface and at 1.4 and 9 eV on the Si(5×5)-Ge surface. Hydrogen adsorption and desorption measurements on these surfaces indicate that the transitions at 1.4 eV are ascribable to the Ge dangling-bond surface state. The emergence of a 9-eV peak on the Si(5×5)-Ge surface suggests that the Si-Si back-bond surface states are replaced by those of Ge-Ge. We discuss the Ge growth mode on Si(111) in the light of our results and the previously reported results of total-energy calculations on several models.

The initial stages of semiconductor heterostructure formation are important both for theoretical and practical reasons. Because the Si-Ge system is one of the simplest semiconductor heterostructures, several experiments have been performed on it with low-energy electron diffraction (LEED), Auger-electron spectroscopy (AES), Rutherford backscattering (RBS), and reflection high-energy electron diffraction (RHEED). Narusawa and Gibson[1] have studied the interface structure of Ge on Si(111) with RBS and have shown that for Ge deposition at 350 °C the Ge film grows in a layer-by-layer fashion up to a coverage of 3 monolayers (ML) and then Ge islands grow; i.e., the Ge film grows in the Stranski-Krastanov mode. Recently, Gossmann, Feldman, and Gibson[2] studied the system with RBS and reported that beyond room temperature, indiffusion effectively removes additional Ge from the surface region beyond a critical coverage (about 3 ML). Ichikawa and Ino[3] have shown with RHEED that for Ge deposition on Si(111) at temperatures beyond 360 °C, a Ge-incorporated (7×7) superstructure develops first (<1.5 ML), and then a (5×5) superstructure develops (>1.5 ML). The electronic structures of these surfaces are, however, still unknown.

In this paper, we report on a study of the Ge on Si(111) system using angle-resolved electron energy-loss spectra (AR-EELS)[4] combined with LEED, LEED I-V curve, and AES measurements. We identify a Si(7×7)-Ge structure and obtain new information on the Si(7×7)-Ge and Si(5×5)-Ge surface states. The interaction of these surface states with hydrogen is also reported.

A single crystal of n-type silicon with 5-Ω cm resistivity is used as a specimen. The sample surface is covered with a thin oxide layer formed by Henderson's method[5] and mounted in an UHV chamber whose base pressure is below 1×10^{-8} Pa. The sample surface is cleaned by heating to 1200 °C for several minutes. After the heat treatment, only a trace amount of carbon is observed with AES; the peak-to-peak height of the carbon signal is about 10^{-3} of that of the Si LVV signal. The Si(111) surface shows a well-developed (7×7) LEED pattern and the characteristic AR-EEL spectra.[6]

Germanium is deposited from a tungsten spiral filament onto the Si substrate maintained at either room temperature or at 450 °C. The background pressure during Ge deposition is about 8×10^{-8} Pa. The Ge deposition rate is estimated from a plot of the Si LVV AES signal versus the deposition time for the deposition onto the substrate maintained at 450 °C. A break point which is ascribed to the critical coverage (3 ML)[2,7] appears at 12 min, and thus the deposition rate is estimated as 0.25 ML/min.

The Si(111)(7×7)-Ge and the Si(111)(5×5)-Ge surfaces are obtained by annealing at 700 °C after 1.5- and 2-ML depositions at room temperature, respectively. The Si(7×7)-Ge surface is also obtained by annealing the Si(5×5)-Ge surface at 870 °C for 2 min. Our observation is consistent with the report by Ichikawa and Ino.[3]

The LEED I-V curves of the specular reflection are measured by the rotatable electron-energy analyzer, which is also used for the AR-EELS measurements. Figure 1 shows the I-V curves for the surfaces studied. The incident angles are 26° from the surface normal and in the $[1\bar{2}1]$ azimuth. The I-V curve for the Si(7×7)-Ge resembles that of the clean Si(7×7) surface but is distinguished by the intensified peaks of the I-V curve around 70 eV. On the other hand, the Si(5×5)-Ge surface shows quite a different I-V curve. In this study we could easily distinguish the clean Si(7×7), Si(7×7)-Ge, and Si(5×5)-Ge surfaces by the I-V curves. The Si(7×7)-Ge LEED pattern resembles that of the clean Si(7×7).

The I-V curves are also used to choose the primary energy of the AR-EELS measurements. The peak energies around 95 eV for the incident angle used (see Fig. 1) are selected to improve the signal-to-noise ratio and to reduce a distortion of the profile due to diffraction effects.[8] To emphasize the one-electron transitions with small energy losses, the lower energy peaks of the I-V curves around 60 eV (see Fig. 1) are employed.

The negative second derivatives of AR-EEL spectra for the three surfaces are shown in Fig. 2. In each AR-EELS measurement, the exit angles are set 3° apart from the specular angle to the surface-normal side. The loss peaks of the clean Si(7×7) surface are assigned to bulk plasmon $\hbar\omega_p$, surface plasmon $\hbar\omega_s$, bulk interband transitions E_1 and E_2,

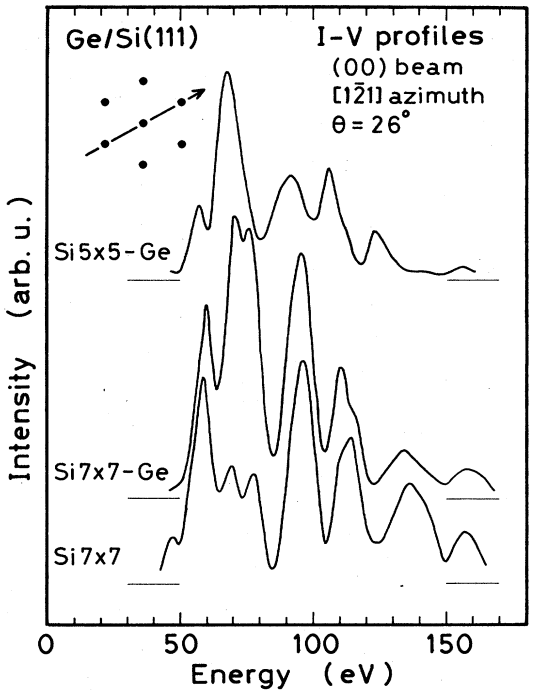

FIG. 1. LEED I-V curves of specular reflection for the Si(7×7), the Si(7×7)-Ge, and the Si(5×5)-Ge surfaces. The incident angles are 26° from the surface normal and in the [1$\bar{2}$1] azimuth.

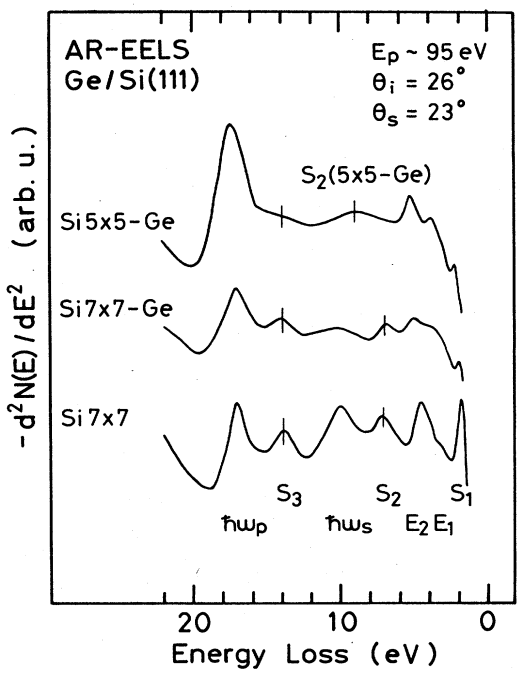

FIG. 2. Negative second derivatives of AR-EELS for the three surfaces. The primary energies are about 95 eV, corresponding to the peak positions of I-V curves in Fig. 1. The incident angles are 26° from the surface normal and in the [1$\bar{2}$1] azimuth. The exit angles are set 3° apart from the specular direction to the surface normal side to resolve the structures near the elastic peak.

and surface one-electron transitions S_1, S_2, and S_3.[9] The initial state of S_1 (1.7 eV) is the dangling-bond surface state and those of S_2 (7.0 eV) and S_3 (14 eV) are back-bond surface states. We have found that the S_2 peak shows a negative and anisotropic dispersion. This will be reported elsewhere.[10]

Figure 3 shows the enlarged AR-EEL $N(E)$ spectra of loss energies from 0 to 4 eV. Both on the Si(7×7)-Ge surface and on the Si(5×5)-Ge surface, the loss peak S_1 on the Si(7×7) disappears and new peaks appear at 1.4 ±0.05 eV. We indicate these peaks by S_1(7×7-Ge) and S_1(5×5-Ge), respectively. As both the S_1(7×7-Ge) and the S_1(5×5-Ge) peaks are located on the energy axis where the peak due to the Ge dangling-bond surface state was found on the clean Ge(111) surface,[11] it is probable that they are due to a Ge dangling bond.

To confirm their origins, adsorption and thermal desorption of atomic hydrogen on these surfaces are studied. Hydrogen molecules are introduced into the UHV chamber through a palladium tube and dissociated by a hot tungsten filament (1700 °C). The result for the Si(7×7) is shown in Fig. 3. On exposure to 1000 L of hydrogen, the S_1, S_1(7×7-Ge), and S_1(5×5-Ge) peaks disappear completely (not shown). By heating to 350 °C for 10 min, the S_1(5×5-Ge) peak partially recovers, but the S_1 peak does not yet appear. By heating to 450 °C for 10 min, the S_1(5×5-Ge) peak completely recovers, while the S_1 peak does so only slightly. It seems necessary to heat to slightly higher than 450 °C for the S_1(7×7-Ge) peak to recover completely. Recovering the S_1 peak completely requires heating the sample up to 530 °C.

Such reversible disappearance and reappearance of the loss peaks due to adsorption and desorption of hydrogen is

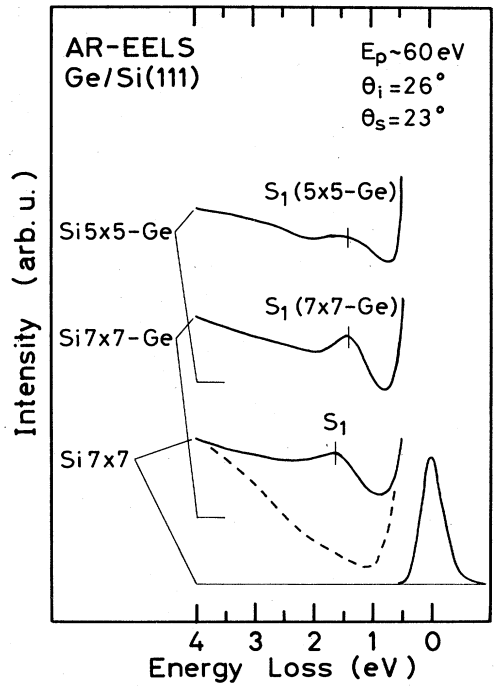

FIG. 3. Expanded AR-EELS $N(E)$ profiles of low-energy-loss part of Fig. 2. The primary energies are about 60 eV and at the peak positions of I-V curves. The incident and exit angles are the same as in Fig. 2. The Si(7×7) profile changes to the dotted curve after exposure to atomic hydrogen.

strong evidence that these peaks are due to surface dangling bonds.[6] The present finding of S_1 reappearance at 530 °C is in agreement with the report by Schulze and Henzler[12] of H_2 thermal desorption on Si(111); i.e., there is one peak around 550 °C which is ascribed to the H on-top position of the Si surface atoms. The measurement of H_2 thermal desorption on Ge(111) by Surnev and Tikhov[13] showed that one desorption peak is observed around 350 °C. This temperature is lower than the present reappearance temperatures of the $S_1(7\times7$-Ge) and $S_1(5\times5$-Ge) peaks. This may reflect modified characteristics of Ge dangling bonds of very thin layers. The AR-EELS measurement of the interaction of hydrogen with the Ge dangling bond of a bulk Ge(111) surface is in progress.

Figure 2 also shows the loss peaks related to the surface transitions due to the back-bond surface states on the three surfaces. In the spectra of the Si(7×7)-Ge, the loss peaks are observed at nearly the same positions on the energy axis as the S_2 and S_3 peaks on the clean Si surface, though weak in intensity. It seems that these peaks are due to the Si-Si back-bond surface states. On the Si(5×5)-Ge, the loss peak S_2 on the Si(7×7) disappears and a new peak appears at 9 eV [hereafter called $S_2(5\times5$-Ge)]. This $S_2(5\times5$-Ge) is nearly the same on the energy axis as the peak due to the back-bond surface state for the clean Ge(111) surface.[11] Therefore, the $S_2(5\times5$-Ge) peak is interpreted as the transition from Ge back-bond surface state. On the Si(5×5)-Ge, a loss peak is observed around 14 eV where the loss peak due to the back-bond surface state is observed on the clean Ge(111) surface.[11]

These results give us a picture of the electronic and atomic structure of the surfaces. On the Si(7×7)-Ge surface, the Ge atoms adsorb just enough to saturate the Si dangling bonds but not enough to release the Si subsurface strain, nor yet to form strained Ge-Ge bonds. The resemblance of the I-V curve of Si(7×7)-Ge to that of the clean Si(7×7) surface also suggests that the Ge atoms adsorb while almost keeping the same arrangement of the substrate atoms. Which sites are occupied by the adsorbed Ge atoms saturating the Si dangling bonds? Zhang, Northrup, and Cohen[14] calculated total energies for several models of Ge adsorption of about 1-ML coverage: the atop site model, the hollow site model, the substitutional model in which Ge atoms replace the topmost Si atoms, and the Seiwatz chain model. They showed that the substitutional model is most favorable when extensive reconstruction is allowed. In the present experiment, we heat the substrate up to 700 °C to form the Si(7×7)-Ge surface. We consider that the substitutional model is correct for the Si(7×7)-Ge surface based on the results that the Si dangling bonds are replaced by those of Ge and that no Ge-Ge back bonds are observed. To get more concrete evidence, however, it is necessary to calculate the Ge dangling bond surface state for the substitutional model.

With increased coverages at the stage of Si(5×5)-Ge, Ge-Ge bonds are likely to form; thus rearrangements of Si-Si bonds occur. The present results for the 5×5 surface are more readily understood on the basis of a layer-by-layer Ge film overgrowth up to 3 ML than on the basis of formation of Ge-Si alloy.[15]

In conclusion, using AR-EELS we find new surface loss peaks on the Si(7×7)-Ge and Si(5×5)-Ge surfaces. On the basis of behavior of these peaks on adsorption and desorption of hydrogen and their sequential changes resulting in the increase of Ge coverage, we propose a model of the initial stages of Ge-Si heterostructure formation.

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