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Strain and electronic structure of Ge nanoislands on Si(111)-7×7 surface

Masahiko Suzuki, Ryota Negishi, and Yukichi Shigeta*
Graduate School of Integrated Science, Yokohama City University, Seto, Kanazawa-ku, Yokohama 236-0027, Japan

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To study the relation between the strain and the electronic structure in two-dimensional (2D) Ge nanoislands on the Si(111)-7×7 surface, we calculated the relation based on the density functional theory and measured with the angle resolved ultraviolet photoelectron spectroscopy (ARUPS) and the scanning tunneling microscopy (STM). In the calculation, the dangling-bond state at the strained adatom on the 2D Ge island (S^R_{Ge} state) shifts to lower energy at the rate of -8.2 eV/nm with the height of the adatoms. The ARUPS spectrum shows a characteristic peak corresponding to the S^R_{Ge} state, whose energy depends on the size of the Ge nanoisland. The state appears at -0.7 eV below the Fermi level for the small Ge islands (3.8–5 nm) and at -0.6 eV for the large Ge islands. The height of the Ge islands estimated from the energy difference is consistent with a result of the STM measurement. The strain of Ge islands can be estimated from the electronic structure.

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I. INTRODUCTION

Germanium quantum dots formed on the Si substrate are attractive for their potential applications as Si-based quantum electronic and photoelectronic devices.[1] In such a heteroepitaxial system, the change on the electronic structure due to the strain caused by the lattice mismatch between Si and Ge is a key phenomenon. To control their properties, it is very important to understand the strain and the electronic structure for the system, synthetically.

For the electronic and optical properties of such systems, many works have been done both experimentally and theoretically in connection with their geometric structures.[2–9] The morphological properties of Ge layers thicker than 1 bilayer (1 BL corresponds to 1.57×10^{15} atoms/cm^2) grown on the Si(111) surface have been discussed from their electronic density of empty states measured with x-ray absorption spectroscopy.[7] The surface structure and chemical composition of Ge layers on the Si(111) surface have been studied from their core level and valence band spectra measured with photoelectron spectroscopy.[8]

However, few studies have researched the effect of the strain on the electronic property for the system experimentally in atomic scale because of experimental difficulties. The morphology and electronic property of Ge critical nuclei formed on the Si(111) surface have been studied with scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), but the certain structure of the nuclei remains unclear.[9]

Recently, we reported about studies of the electronic structure of two-dimensional (2D) Si nanoislands formed on the Si(111)-7×7 surface by STS[10,11] and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS).[12] In the nanoislands, rounded islands with a diameter of 3.8 nm (*R* islands) are formed at the initial stage of the homoepitaxial growth as ones of the stable islands.[13–17] The *R* island consists of 162 atoms and the 5×5 dimer-adatom-stacking fault (DAS) structure is constructed on it [see an inset of Fig. 2(b)].

The STS spectra measured on the adatoms on the *R* islands show a large peak at -0.35 eV below the Fermi level.[10] The peak also appears on the ARUPS spectra.[12] The origin of the peak is the dangling-bond (DB) state at adatoms on the *R* islands of Si. The state is created by the geometrical relaxation of the island (we call it the S^R_{Si} state). The peak from the S^R_{Si} state disappears in the ARUPS spectra for the surface composed of large islands. The relaxation occurs so that the edge of the island shrinks inward and the adatoms protrude into the vacuum. The results indicate that the electronic structure is closely related to the strain.

To investigate the atomic geometries of the Si islands, we measured the height profiles on the STM images in the previous studies. However, we needed many supports to estimate adatom geometries by this way, because what the STM images show is the undulation of the charge density on the surface. Moreover, we had to verify the reproducibility of the measurements; even then, the images must be of sufficiently high resolution, because the STM images are dependent on their scanning conditions, for example, the scanning speed and the tip condition.

In the present study, we try to estimate the strain of Ge nanoislands on the Si(111)-7×7 surface through a relation between the relaxation structure and the electronic structure. Since the relaxation structure depends on the size of Ge nanoislands, the electronic structure was investigated for the Ge islands having different sizes on the Si(111) substrate by the ARUPS. To measure the ARUPS for the nanoislands, we optimized the growth condition of the Ge nanoislands whose size becomes uniform. The energy calculation based on the density functional theory was also performed to calibrate the relation between the relaxation of adatom and the electronic structure.

II. ENERGY CALCULATION

We calculated electronic structure to estimate the adatom geometries of the islands. To simplify the calculation, we chose a cluster forming a T_4 site as shown in Fig. 1(a). In the calculation, we fixed the first-layer atoms at the ideal sites of the Si crystal to reproduce the situation on the Si substrate. The energies of the electronic states were calculated for a Si

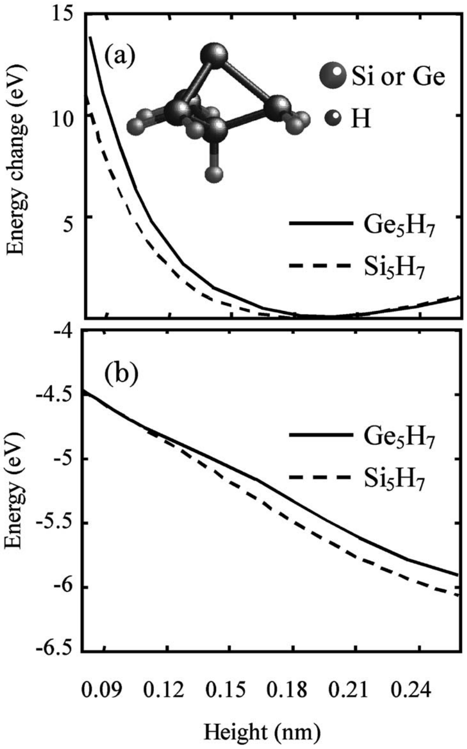

FIG. 1. (a) Model cluster of energy calculation. The cluster forms a T_4 site and all the Si (or Ge) atoms except for the adatom were fixed on the ideal sites of the Si bulk crystal. (b) Relationships between the height of the adatom and the energy of the DB state for the Si and Ge clusters.

and a Ge cluster with an adatom at various heights in the range of 0.08–0.26 nm from the first layer. The energy calculations were performed based on the density functional method within the generalized gradient approximation using the Becke3LYP functional[18,19] and the 6-311G basis functions by GAUSSIAN 03.[20] The relations between the height of the adatom and the energy of the DB state for the Si and Ge cluster are shown in Fig. 1(b).

For any adatom height, the calculated electron density of the highest occupied molecular orbital (HOMO) was preferentially distributed around the adatom. Therefore, the HOMO state is the DB state at the adatom. The energy of the HOMO state decreases with the adatom height almost linearly at the rate of -9.4 eV/nm for the Si cluster and -8.2 eV/nm for the Ge cluster while their total energies reach their minimums at 0.185 nm for the Si and 0.193 nm for the Ge from the first layer, respectively.[21]

For the *R* island of Si, the S_{Si}^{R} state shifts to -0.12 eV compared to the state of center adatom[12] and the adatom height on the *R* island is 0.012 ± 0.005 nm higher than that of the Si(111)-7×7 structure.[10] Since the energy shift is in good agreement with the calculated rate of -9.4 eV/nm for the Si cluster, we will use the linear relation for the Ge cluster to estimate the heights of the strained adatoms on the Ge islands.

In the calculation for the Ge cluster, we did not consider the lateral relaxation of the Ge islands caused by the lattice mismatch between Si and Ge, because the lateral relaxation is not considered to be an essential matter. To estimate the maximum error in the height of the adatom caused by the lateral relaxation, we also performed calculations for an extreme case in which the Ge atoms would recover their ideal positions of the bulk. The rate of the energy shift of the HOMO state becomes -4.8 eV/nm, which is ~40% smaller than that without the lateral relaxation. Therefore, an error in the estimation of the adatom height will not exceed ~40%.

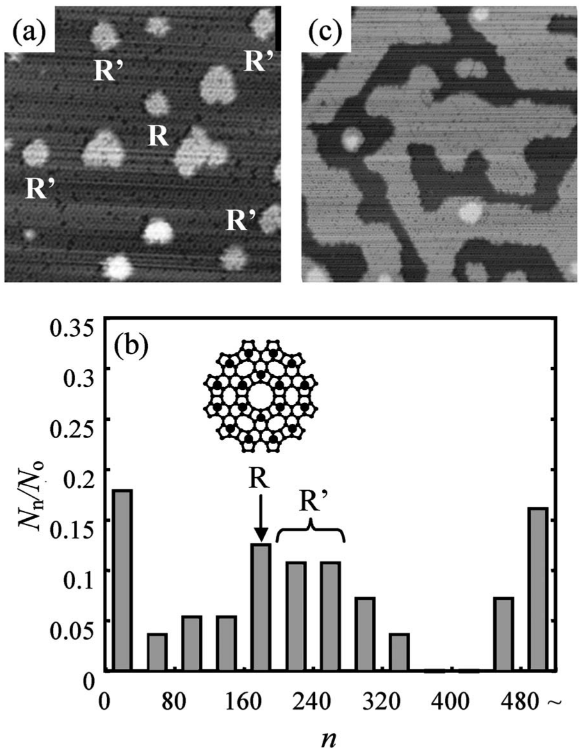

FIG. 2. (a) STM image (45×45 nm^2) of Ge islands on a Si(111)-7×7 substrate deposited at $d = 0.1$ BL, $T_s = 230$ °C and $T_a = 340$ °C. (b) Size distribution of Ge islands of (a). A broad peak in the range of $n = 160$–280 corresponds to the *R* and *R'* islands of Ge. Inset is a structure model of the *R* island. (c) STM image (80×80 nm^2) of Ge islands at $d = 0.5$ BL, $T_s = 230$ °C and $T_a = 340$ °C.

III. EXPERIMENTAL

STM observations were performed in an ultrahigh vacuum (UHV) camber (the base pressure was less than 2×10^{-8} Pa). The UHV chamber was equipped with a STM head, a reflection high-energy electron diffraction (RHEED) optics, an electron-beam evaporation source, a quartz crystal thickness monitor, and a sample transfer system. The STM images in this study were taken in the constant-current mode at room temperature.

The ARUPS measurements were performed by using synchrotron radiation on the beam line BL-7B (Research Centre for Spectrochemistry, the University of Tokyo) at Photon Factory, KEK, Japan. The experimental chamber (the base pressure was less than 6×10^{-8} Pa) was equipped with an angle-resolved photoelectron spectrometer, a low-energy electron diffraction (LEED) optics, an evaporation source, a quartz crystal thickness monitor, and a sample manipulator with a cryostat. The angular and energy resolution were about 1.5° and 0.1 eV, respectively. All the spectra were taken along the $[11\bar{2}]$ azimuth at 120 K. The photon energy was 21.2 eV and the photon incident angle was 45° from the surface normal. The spectra were taken every 1° in the range of emission angles (θ_e) between 7° and 17° from the surface normal.

In the STM and ARUPS experiments, the Ge films were prepared by vacuum evaporation and their coverages were estimated from the frequency shift of the quartz oscillator and confirmed by the STM observation. The substrate temperature (T_s) was measured with an infrared radiation thermometer ($T_s < 800$ °C) and an optical thermometer ($T_s > 800$ °C).

IV. RESULTS AND DISCUSSION

To observe the ARUPS for the nanoislands, it is essential to make the nanoislands the same size. In the initial growth of Ge on the Si(111) surface, the Ge nanoislands showing some characteristic sizes are self-assembled similar to the Si nanoislands. However, in the case of Ge islands, many deformed rounded islands with additional atoms (R' islands) are formed.[22,23] The R' island consists of 162–300 atoms and its shape is disordered by the additional atoms. The size distribution of the R' islands broadened from 3.8 to 5 nm and the occupancy of the R' islands was about 10% at a mean thickness (d) of about 0.04 BL.[23]

Although, in the case of Ge islands, the additional atoms of the R' island decrease with an annealing temperature (T_a) after deposition, they are not completely removed even after annealing at $T_a > 340$ °C because of the small step energy of the Ge islands.[23] Therefore, we optimized a growth condition to form both of the R and the R' islands. After repeated trial and error, we reached an optimum growth condition ($d = 0.1$ BL at $T_s = 230$ °C and $T_a = 340$ °C), under which the density of the R and R' islands increased more than 30%.

A typical STM image of Ge islands grown under the optimum condition is shown in Fig. 2(a), where many R and R' islands of Ge are formed with a few large islands (the number of atoms: $n > 400$) and a few small clusters ($n < 40$). The size distribution of the Ge islands on the surface is plotted in Fig. 2(b), where the number of islands (N_n) composed of n atoms is normalized by the total number of islands (N_o). A broad peak in the range of $n = 160$–280 corresponds to R and R' islands, and the percentages of the N_n for $n < 40$, $n = 160$–280, and $n > 400$ are about 18%, 34%, and 23%, respectively.

When the Ge coverage increases at the same T_s and T_a, the islands coalesce and become large islands. A typical example of the large islands at $d \approx 0.5$ BL is shown in Fig. 2(c), where the surface is covered by large islands showing a shape like a channel and the 5×5 DAS structure is formed on those islands, predominantly. When the Ge coverage reaches to 1 BL, the surface is almost covered with a complete 2D Ge layer, on which the 5×5 DAS structure is also constructed, predominantly. The ARUPS spectra were measured for those surfaces at $d = 0.1$, 0.5, and 1 BL.

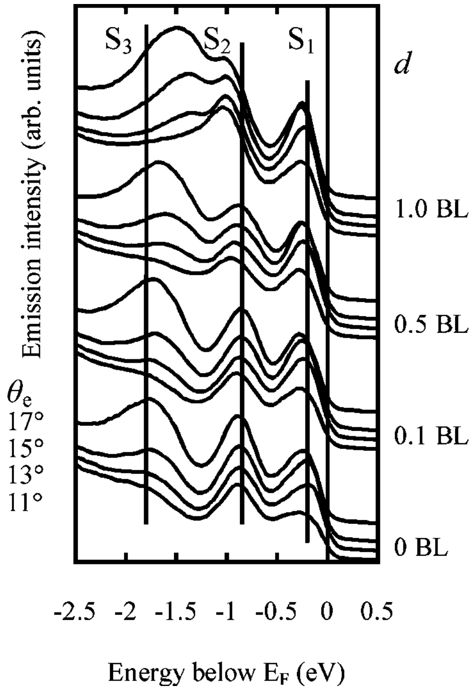

FIG. 3. ARUPS spectra from Ge/Si(111) surfaces at $d = 0$, 0.1, 0.5, and 1 BL along the $[11\bar{2}]$ azimuth. The photon energy and incident angle are 21.2 eV and 45°, respectively. The spectra at $\theta_e = 11°$, 13°, 15°, and 17° are plotted for each Ge coverage. The positions of the S_1, S_2, and S_3 peaks for the Si(111)-7×7 surface[24] are indicated by solid lines.

Figure 3 shows ARUPS spectra from Ge/Si(111) surfaces deposited at $d = 0$, 0.1, 0.5, and 1 BL, where the surface at $d = 0$ BL means the clean Si(111)-7×7 surface. The spectra at $\theta_e = 11°$, 13°, 15°, and 17° are plotted for each Ge coverage, respectively. The spectra from the clean surface show well-known peaks corresponding to three surface states (S_1, S_2, and S_3) of the Si(111)-7×7 surface.[24] The S_1, S_2, and S_3 peaks at $-0.2, -0.8$, and -1.8 eV are assigned to the DB states on the adatom and the rest atom and the back bond state. The change in the spectra with Ge coverage is that the S_1 and S_2 peaks shift to lower energies and the S_3 peak shifts to a higher energy. To make clear the change with Ge coverage, we plot difference spectra between each spectrum and that from a clean surface, as shown in Fig. 4.

The difference spectra show three peaks labeled by B_1, B_2, and B_3, which are increasing with the Ge coverage. These peaks have been reported as the surface states of the Si(111)-5×5 Ge DAS structure in Ref. 24. The B_1 and B_2 peaks at -0.25 and -1.1 eV correspond to the DB states of adatom and rest atom, and the B_3 peak at about -1.3 eV comes from the back bond state. The appearance of those peaks is consistent with the formation of the 5×5 DAS structure on the large Ge islands, predominantly.

We have also observed an additional peak between the B_1 and B_2 peaks. The additional peak appears even at the low coverage of 0.1 BL and has almost same intensity at $d = 0.5$ BL. The peak is hardly observed at $d = 1$ BL, in

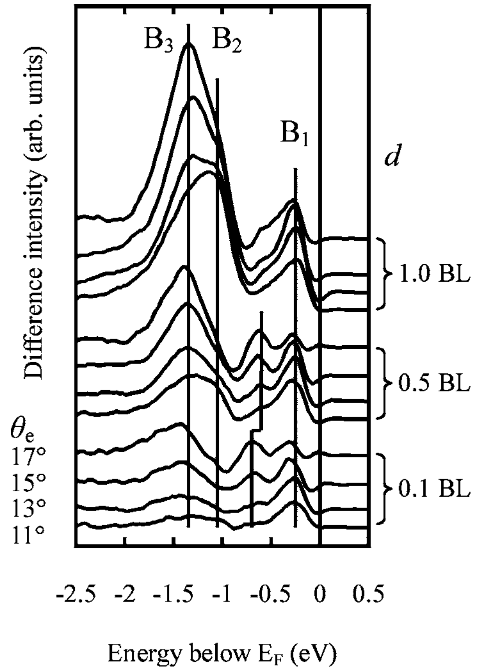

FIG. 4. Difference spectra between each ARUPS spectra (at d=0.1, 0.5, and 1 BL) from that for a clean Si surface. Four spectra at θ_e=11°, 13°, 15°, and 17° are plotted for each Ge coverage. The positions of the B_1,B_2, and B_3 peaks for the Si(111)-5 $\times$5 Ge DAS structure[24] are indicated by solid lines.

contrast to the growth of the B_1,B_2, and B_3 peaks. The additional peak corresponds to the DB state at the strained adatoms on the Ge islands (S_{Ge}^R state), which is created from the B_1 state as a result of the geometrical relaxation of the islands.

The state will be localized near the edges of the islands, because the geometrical relaxation should be smaller and smaller with the distance from the edge of the island. Therefore, if the state is the S_{Ge}^R state, the intensity of the peak should be in proportion to the density of adatoms near the edges of the islands. The densities of the outermost adatoms in the Ge islands are about 0.12 nm^{-2} for d=0.1 BL, 0.15 nm^{-2} for d=0.5 BL, and less than 10^{-2} nm^{-2} for d=1 BL. Since the intensity of this peak is nearly in proportion to the density of the adatoms near the edge of the Ge islands, we judge that the additional peak is emitted from the S_{Ge}^R state.

We should note that the peak position of the S_{Ge}^R state does not depend on the emission angle (no dispersion) but on the Ge coverage. The Ge coverage has a great influence on the islands' size. Since the strain in the large islands can be shared with more constituent atoms of the islands, the strain in the large islands must be smaller than that of the small one. So the peak position reflects the strains of the adatoms on the different sizes. By using the relation between the height of the adatom and the energy of the DB state, the heights of the strained adatoms on the small and the large Ge islands are about 0.05 and 0.04 nm higher than that of the Si(111)-5$\times$5 Ge structure, respectively.

To confirm the size dependence of the adatom height on Ge islands, we measured the height profiles on the STM images directly. The height can be compared within one image to exclude the influence of the scanning conditions. Figure 5(b) shows a typical example of the height profile across the adatoms on the small and the large Ge islands (A-A' line) in Fig. 5(a). It is clear that the adatom height on the small island is higher than the large one. An averaged height profile is shown in Fig. 5(c), where eight profiles from A-A' to B-B' lines are averaged to increase an accuracy. The adatom height on small Ge island is ~0.01 nm higher than that of the large one. The result is in good agreement with the strain estimated from the result of the ARUPS with the energy calibration.

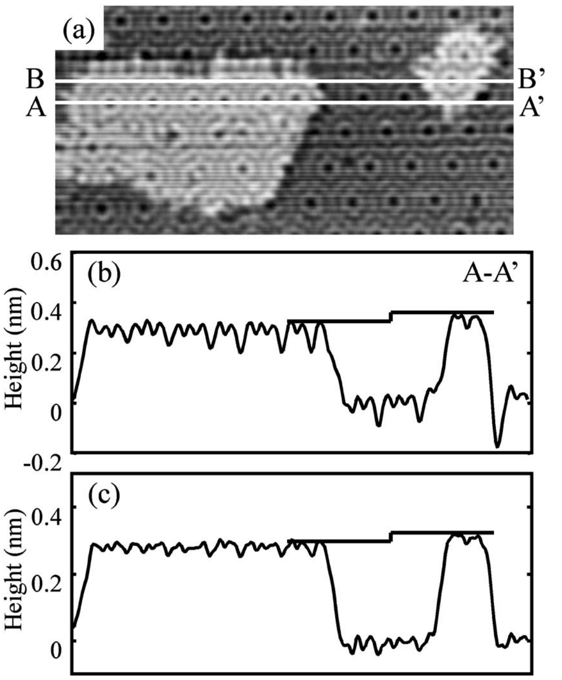

FIG. 5. (a) STM image (50$\times$25 nm^2) of an area including both small and large Ge islands. (b) Height profile across the adatoms on the small and large Ge islands (A-A' line) in (a). (c) Averaged height profile over a width from A-A' to B-B' lines in (a).

Thus the strain in the nanoislands can be estimated from the electronic structure in atomic scale by using the results of the energy calculations for the small cluster, which consists of an adatom and its nearest neighbor atoms. However, we should note that, at the edge of the islands, the dimer atoms also have DBs and are close spatially to the edge adatom. If their energies are very close, the ARUPS spectra from the adatom DB state may be greatly modified by the density of states of the dimer atoms. To know the effect of the dimer DBs, we performed energy calculations for a Ge island composed of 11 atoms including three edge dimers on Si layers. The energy of the adatom DB state was investigated at various adatom heights. We found that the adatom DB energy increases with the height of adatom, even if the dimer DBs are taken into the consideration.

Although, in our calculation, the structural relaxation is not considered, the absolute strain of the adatom should be determined from results of geometry optimizations of Ge islands. The height of the adatoms to the substrate results from not only the shift of the adatoms but also the displacements of their underlying atoms.[25] To determine the adatom geometry due to strain, we should measure the local density of states at adatoms and dimer atoms, respectively, with STM/STS and reconfirm the geometries by comparison with the calculated results.

In conclusion, we found that the energy shift of the adatom DB state of Ge islands on the Si(111) surface, which relates to the shift of the adatom height. From the energy calculations, we found that the adatom DB energy decreases with the adatom height at the rate of $-8.2\ \text{eV/nm}$. From the shift of the peak position, we estimated the height of the adatoms of small Ge islands is about 0.01 nm higher than that of large ones.

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*Author to whom correspondence should be addressed. Electronic address: shigeta@yokohama-cu.ac.jp

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