Morphological Evaluation of Ge Nanoclusters by Spot Shape of Surface Electron Diffraction*

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Nanoclusters of Ge, such as hut clusters and pyramidal clusters, were grown on Si(001) substrates and evaluated by surface electron diffraction methods such as reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED). Observations of the same sample by both RHEED and LEED were carried out for the first time. The diffraction spots had a characteristic shape and intensity distribution depending on the morphology of the clusters. The spot shapes in RHEED and LEED were simulated by kinematic calculations, which reproduced the experimental results fairly well. It was confirmed that the characteristic spot shapes can be explained by refraction effects and Laue function of diffraction intensity. [DOI: 10.1380/ejssnt.2012.18]

Keywords: Reflection high-energy electron diffraction (RHEED); Low-energy electron diffraction (LEED); Ge; Si(001)

I. INTRODUCTION

Recently, nanocluster-containing materials for optoelectronic devices [1] and single-electron transistors [2] have been actively investigated. In order to clarify whether the formed nanoclusters are intended ones, the morphological evaluation method is important as well as the forming technology of such materials. Until now, real space observation methods such as scanning electron microscopy (SEM), scanning probe microscopy (SPM), and transmission electron microscopy (TEM) have mainly been used for the morphological evaluation; however, these are all ex situ observation methods. If an electron diffraction method, in which in situ observation is possible, could acquire morphological information on nanoclusters, it would be very useful. In order to investigate the possibility of morphological information acquisition, the spot shapes of RHEED and LEED were observed for Ge nanoclusters grown on clean Si(001) 2×1 surfaces. The experimentally obtained spot shapes were simulated based on kinematic calculations.

II. EXPERIMENTAL

A new system combining RHEED and LEED was used in this study. RHEED is a well-known in situ observation technique, in which a grazing-incidence electron beam can produce the transmission pattern for a nanocluster. In LEED, on the other hand, the incident electron beam is normal to the sample substrate, and the reflection pattern is always observed. A side view obtained by RHEED and a top view obtained by LEED may be helpful to investigate the morphology of the nanoclusters. The base pressure of the apparatus was an ultra-high vacuum (UHV) of 2×10⁻⁹ Torr. The substrate Si(001) wafer was cut to 3×14×0.5 mm³ and cleaned by direct current heating to 1200°C several times in the UHV chamber. Ge nanoclusters were grown on a clean Si(001) 2×1 substrate surface, which was kept at about 400°C, while RHEED was monitored. Ge was evaporated by a simple handmade evaporator, in which a piece of Ge crystal was wound by a W wire of φ0.15 for heating, and the evaporation rate was controlled by the electric current passing through the wire.

III. NANOCLUSTER MORPHOLOGY

The growth process of Ge on a clean Si(001) 2×1 substrate surface at 400-500°C is well understood. [3] In the initial stage, up to about 4 ML, Ge grows in a layer by layer mode, but then it shifts to an island growth mode. This is due to the competition between the surface energy and the accumulated lattice distortion energy that arises from the 4% lattice mismatch between Ge and Si. STM observation by Tomitori et al. [4] indicated that Ge nanoclusters, which are called “hut clusters”, are densely formed on the whole substrate surface during the initial stage of the island growth. Later, the clusters shift to “pyramidal clusters”, which are sometimes called “giant clusters”. The hut cluster and the pyramidal cluster are surrounded by {105} and {113} facet planes, respectively. The two types of clusters have an azimuthal relationship which is 45° rotated from each other, and have different slope angles of the facet planes. According to STM observations, [4] the mean size of hut and pyramidal cluster are about 10 nm and a few tens of nm, in the length of their bottom edges, respectively. For the calculation of RHEED and LEED patterns, the hut cluster and the pyramidal cluster shown in Fig. 1 were used. The basal planes of the two types of nanoclusters were assumed to be square. The bottom edge length was 10 nm for the hut cluster and 13 nm for the pyramidal cluster, and the number of included Ge atoms was n = 1750 and n = 7436, respectively. In these clusters, Ge atoms were arranged as a diamond crystal lattice. For simplicity, the superstructure of Ge atoms on the facet surfaces and substrate Si lattice was not considered.

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IV. KINEMATIC CALCULATION

The trajectory of the incident electron wave passing through the nanocluster toward a fluorescent screen was considered, as shown in Fig. 2(a). This involved three processes: refraction at the entrance plane, scattering at an internal Ge atom, and refraction at the exit plane. The electron wave intensity at any given point on the screen was calculated as the square of the summation of all transmitted electron wave function as follows, [5]

\[ I = \sum_{i=1}^{n} \alpha_i f(s) \exp(2\pi i s \cdot r_i) \exp(-M) \]

The RHEED pattern could be obtained by performing this calculation for all points on the screen. The scattering vector \( s \) was defined as \( s = k_2 - k_1 \). The atomic scattering factor \( f(s) \) [6] and the Debye-Waller factor \( \exp(-M) \) [7] were also considered. For the absorption coefficient \( \alpha_i \) of an incident electron passing through the nanocluster, the empirical formula \( \alpha_i = \exp(-l/\Lambda) \) was adopted using the mean free path \( \Lambda \) and path length \( l \) of the incident electron. Based on the experimental results of Seah et al. [8], the mean free path of a 10 keV electron was assumed to be \( \Lambda = 5 \) nm. Due to the refraction effect at the entrance plane of the nanocluster, the wave vector \( k_1 \) that enters the cluster was obtained by the following equation [9] using the incident wave vector \( K_1 \) in vacuum, the averaged inner potential \( V_0 = 15.6 \) eV [6] in the cluster, and the normal vector \( n_1 \) to the entrance plane.

\[ k_1 = K_1 + \left( \sqrt{(K_1 \cdot n_1)^2 + \frac{2me}{\hbar^2}V_0 - K_1 \cdot n_1} \right) n_1. \]

For refraction at the exit plane of the cluster, a similar relation was established. In the case of RHEED at [110] incidence, the trajectories of the incident electrons were considered to be as shown by arrows A – C in Fig. 2(b) for the hut cluster, and as arrows A – E in Fig. 2(c) for the pyramidal cluster. In Figs. 2(b) and 2(c), the black and white arrows show electron trajectories outside and inside of the clusters, respectively, and the white and black dots denote entrance and exit points on the facet planes, respectively.

V. RESULTS AND DISCUSSION

A. Growth process of Ge on an Si(001)2×1 surface

The results of RHEED observations of the growth of Ge on a Si(001)2×1 surface at about 400°C are shown in Fig. 3. The incident 10 keV electron beam was adjusted to the [110] azimuth of the Si(001) substrate, at a glancing angle of about 2°. Figure 3(a) shows a RHEED pattern from the clean Si(001)2×1 substrate surface with Si dimer rows. After about 1 ML of Ge deposition, the RHEED pattern changed, as shown in Fig. 3(b), and the diffraction spots became streaky. Additional streaks at a slightly narrower interval than those of the Si substrate were also observed. The streak interval was considered to correspond to the lattice constant of Ge, and suggested the growth of a Ge(001) layer. After about 3 ML of Ge deposition, intensity modulation appeared along the streaks as shown in Fig. 3(c). This indicates that the Ge began to shift from layered growth toward three-dimensional growth. After about 5 ML of deposition, the RHEED pattern changed to the spotty transmission pattern, as shown in Fig. 3(d). This suggests the growth of nanoclusters. The extended
FIG. 3: Growth process of Ge nanoclusters on Si(001), as observed by RHEED.

photograph is shown in Fig. 4(a). Two kinds of whisker-like intensity distributions appeared in the vicinity of the spots. One was a whisker pair with a narrow cross angle of 16° and is indicated by arrows labeled “A” (“type A” whiskers), and the other had a wider cross angle of 50° and is indicated by arrows labeled “B” (“type B” whiskers) in Fig. 4(a). Furthermore, weak half-order streaks indicated by arrows labeled “S” were also observed, and were probably due to the double period of the Ge atoms on the facet surfaces. After further deposition of about 7 ML, the type A whiskers disappeared, and only type B whiskers remained, as shown in Fig. 3(e).

B. Comparison between experimental and calculated RHEED patterns

Figure 4(b) shows a calculated RHEED pattern based on one hut cluster of Fig 1(a) and one pyramidal cluster of Fig. 1(b). The calculations indicated that the type A and type B whiskers originated from the hut cluster and pyramidal cluster, respectively. The calculated pattern of Fig. 4(b) can reproduce the experimental pattern of Fig. 4(a) fairly well, even if it is not optimized. Thus, it was confirmed that the nanocluster sample of Fig. 4(a) consisted of both hut and pyramidal clusters. Further deposition of Ge transformed the cluster morphology from hut to pyramidal, as shown in Fig. 3(e).

The inclinations of these whiskers can be explained as follows. The 16° cross angle of the type A whiskers corresponds to that of the [1 1 0] and [1 1 10] directions perpendicular to both side ridges of the hut cluster as viewed along the [1 1 0] azimuth, as shown in Fig. 1(a). On the other hand, the 50° cross angle of the type B whiskers corresponds to that of the [1 1 3] and [1 1 3] directions normal to the side facet planes of the pyramidal cluster, as viewed along the [1 1 0] azimuth, as shown in

FIG. 4: (a) experimental and (b) calculated RHEED patterns for sample surface containing both hut and pyramidal clusters.

C. Comparison between experimental and calculated LEED patterns

Figures 5(b) and 5(d) show experimental LEED patterns at incident electron energies of $E = 40$ eV and $E = 50$ eV, respectively. The patterns were obtained from a sample surface covered mainly with Ge hut clusters, which gave rise to mainly type A whiskers in the RHEED pattern, corresponding to just before the growth stage shown in Fig. 3(d). Half-order superspots indicated by arrows labeled S appeared in the LEED patterns, and were also observed in the RHEED pattern of Fig. 4(a). These superspots were most likely due to the existence of a superstructure on the facet planes of the hut clusters. Here, we focus on the fundamental (integer) spots denoted by 1 0 and 1 1 indices. These integer spots split in four-fold directions, like a four-leaf clover, and were surrounded by white circles. The shape of the fundamental spots was based on the morphology of the hut cluster, and the four-fold symmetry of the splitting arose from the symmetry of the hut cluster. The degree of splitting of the 1 0 and 1 1 spots depended on the incident beam energy. The splitting of the 1 1 spot at $E = 40$ eV converged to a point at $E = 50$ eV, and this point was very close to the three-dimensional reciprocal lattice point of
FIG. 5: Calculated and experimental LEED patterns at $E = 40$ eV and $E = 50$ eV for a sample surface covered with Ge hut clusters.

206. On the other hand, the 10 spot was very weak and widely split at $E = 40$ eV, but became more intense and smaller at $E = 50$ eV. Calculated LEED patterns, such as those shown in Figs. 5(a) and 5(c) based on the hut cluster of Fig. 1(a), can reproduce the experimentally observed features of the LEED spots fairly well. The splitting of the spots can be explained by reciprocal rod’s inclination toward isotropic four-fold directions which are perpendicular to the corresponding {105} facet planes. [10] In this case, the splitting direction should be normal to the facet. It can be judged by the splitting direction of a spot whether hut clusters or pyramidal clusters are present. Because the two kinds of nanoclusters have a 45° rotational relationship with each other. The other additional spots were considered to originate from the splitting of half-order spots. The details will be analyzed in future.

VI. CONCLUSION

Nanoclusters of Ge, such as hut and pyramidal clusters, grown on a clean Si(001)2×1 surface were observed by both RHEED and LEED. The characteristic shapes of the diffraction spots, whisker-like shape in RHEED and four-leaf clover-like shape in LEED, were successfully reproduced by kinematic calculations based on nanocluster models consisting of a diamond lattice with thousands of Ge atoms in each cluster. In RHEED, the cross angles of type A and type B whiskers, 16° and 50°, respectively, originate from the slopes of ridges on the hut cluster and facet planes of the pyramidal cluster. In LEED, the four-fold splitting of the spots originates from four-fold inclined facets. This work has demonstrated that RHEED and LEED observations are useful for characterizing the morphology of nanoclusters by viewing from the side and top directions.

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