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In situ monitoring of nucleation and evolution of Ge nanodots on faintly oxidized Si(1 1 1) surfaces

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ABSTRACT

We have investigated the nucleation and evolution of germanium (Ge) nanodot (ND)s taking place while depositing Ge onto the silicon (Si) (1 1 1) surfaces with ultra-thin Si oxide films by using ultra-high vacuum *in situ* high-resolution transmission electron microscopy in the profile-imaging geometry. Various types of growth phenomena such as nucleation, growth and coalescence of Ge NDs have successfully been observed. The results show that the growth phenomena of the Ge NDs are dramatically rapid after their size reaches the size of the critical nucleus. The critical nucleus size estimated from a model using the cohesive energy of the Ge NDs has been consistent with observed one.

1. Introduction

The self-organization of germanium (Ge) nanodot (ND)s on silicon (Si) surfaces is of great interest because of their potential applications as Si-based optoelectronics. One of the critical issues to the success of such applications is that the island size and density are carefully controlled; in order to use the quantum confinement phenomena, the dots must be approximately 10 nm or smaller and the dot density must be as high as possible [1–3]. However, the typical size of self-organized Ge islands was usually larger than 30 nm and they exhibit broad distributions. Recently, it was reported that Ge NDs with a typical size of ~7 nm and an ultra-high density were formed on Si surfaces covered with 0.3-nm thick SiO_2 films [4,5]. This result is also very interesting as the self-organization process for applications of Si-based optoelectronics. Their studies are, however, based on only *ex situ* observations or experiments in the reciprocal space. For further understanding of the growth mechanism, real space and *in situ* observations of the growth phenomena of Ge NDs are necessary.

In the present work, we investigate reaction processes taking place while depositing Ge onto slightly oxidized Si(1 1 1) surfaces by using ultra-high vacuum *in situ* high-resolution transmission electron microscopy in the profile-imaging geometry (UHV *in situ* HR-profile TEM), which enables us to observe various types of growth phenomena such as nucleation, growth and coalescence of Ge NDs on surfaces in the real space at the atomic level and in a time-resolution of 1/30 s. The results show that the growth features of the Ge NDs are different before and after the size of critical nucleus. We also discuss the critical nucleus size estimated from a model using the cohesive energy of the Ge NDs, which is consistent with observed one.

2. Experimental detail

The present experiments were carried out in an UHV *in situ* HRTEM equipped with a bakable stainless-steel specimen chamber, in which two MBE units are attached [6]. The ultimate base pressure in the chamber was less than 2×10^{-10} Torr, and the pressure during Ge evaporation was below 1×10^{-9} Torr. This system enables characterization of microstructures and growth phenomena on the surface without any contamination in air. Samples for a profile observation were prepared by crushing of an n-type Si(0 0 1) wafer with an agate mortar and pestling under purified ethanol. The resulting fragmentary TEM specimen, Si crystal grains with size from 1 to 100 μm were then mounted onto a holey carbon film supported on a molybdenum microgrid. The TEM specimen was mounted in a holder and preheated at ~973 K for 1 h. Next, to prepare the Si(1 1 1)-(7 × 7) surface, we tried the method of heating and electron-beam irradiation reported by Yokota et al. [7] as follows: The TEM specimen was maintained at ~773 K and then an electron-beam focused onto the Si fragmentary. A large number of Si daughter crystals exploded out and deposited onto the carbon films. Most of the deposited Si daughter crystals are sphere-close polyhedral shapes with size range of 10–200 μm. The polyhedral shapes resulted from cooling of molten

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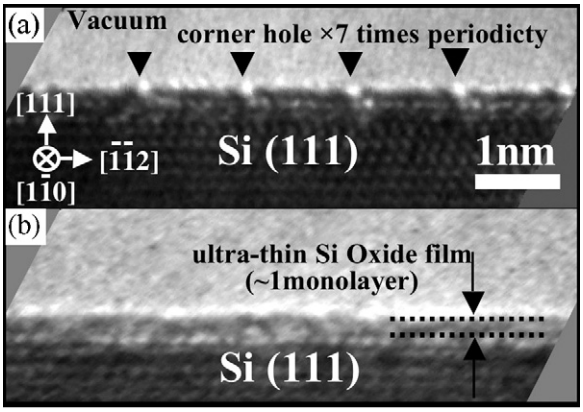

Fig. 1. HR-profile TEM image of the (a) Si(1 1 1)-(7 × 7) structure prepared in the present TEM and (b) Si(1 1 1) surface with ultra-thin Si oxide films.

droplets, and had the facets of low index planes such as {1 1 1}, {0 0 1} and {1 1 0}. We selected the Si particles that have a well-defined surface structure of the Si (1 1 1)-(7 × 7) in their particles using HR-profile TEM as shown in Fig. 1(a). After confirming the (7 × 7) structure, the specimen temperature raised from room temperature to 913 K for 10 min after oxygen had been introduced at a pressure of 2×10^{-6} Torr. Such treated Si surfaces formed ultra-thin Si oxide films (Fig. 1(b)), which are similar to those reported by Ichikawa group [4,5]. Then Ge depositions were performed at 723 K and at a rate of 2.0×10^{14} at. cm^{-2} min^{-1} (1–3×10^3 nm/s) by MBE. The HR-profile TEM observation was carried out at 200 kV using a very small beam current density of ~1 A cm^{-2} on a video tape recorder (Gatan 622SC). The temperature was kept at 723 K.

3. Results and discussion

Fig. 2(a)–(d) shows a time-series of HR-profile TEM images taken during Ge deposition on the Si(1 1 1) surface with the ultra-thin oxide films at 723 K. In these images, numbers at right top represent the Ge deposition duration time in minute. When Ge is deposited on the Si surfaces formed ultra-thin Si oxide films, the thickness of the oxide films was decreased through the reaction $SiO_2(s) + Ge(ad) \rightarrow SiO(g) + GeO(g)$ [4,5], and voids with bare Si created there [8–11]. Shklyaev et al. [4,5] reported on the role of these voids as follows: Epitaxial Ge NDs were contacted with the Si substrates through voids formed in the ultra-thin SiO_2 films during the initial stages of Ge deposition at higher than ~703 K. Ge deposition at temperatures below ~703 K, however, formed nonepitaxial Ge NDs were separated from the Si substrate by the ultra-thin SiO_2 films because the formation of voids in the ultra-thin SiO_2 films is not sufficient at such low temperatures. Therefore, these areas with the voids in the ultra-thin SiO_2 films provided conditions for the epitaxial growth of three-dimensional Ge NDs. HRTEM [8,9] and C_S-corrected scanning TEM [10,11] observations also confirmed the existence of voids through the ultra-thin SiO_2 films beneath the epitaxial Ge NDs. Recently, Nakamura et al. [12] reported that the single-electron discharging is caused by the electron wave packet propagation from epitaxial Ge quantum dots to the Si substrate by a tunneling effect of passing through voids in the ultra-thin SiO_2 films. More experimental, as well as theoretical, research on the voids behavior is expected. After Ge deposition of ~30 min, a new lattice fringe image of Ge, as a nucleation of Ge NDs appears on the Si(1 1 1) surface as shown in Fig. 2(a) and indicated by two black arrows. The direction of these lattice fringes is equal to {1 1 1} lattice fringes of the Si substrate. The number of the constituent atoms in the nuclei is 8–10. After Ge

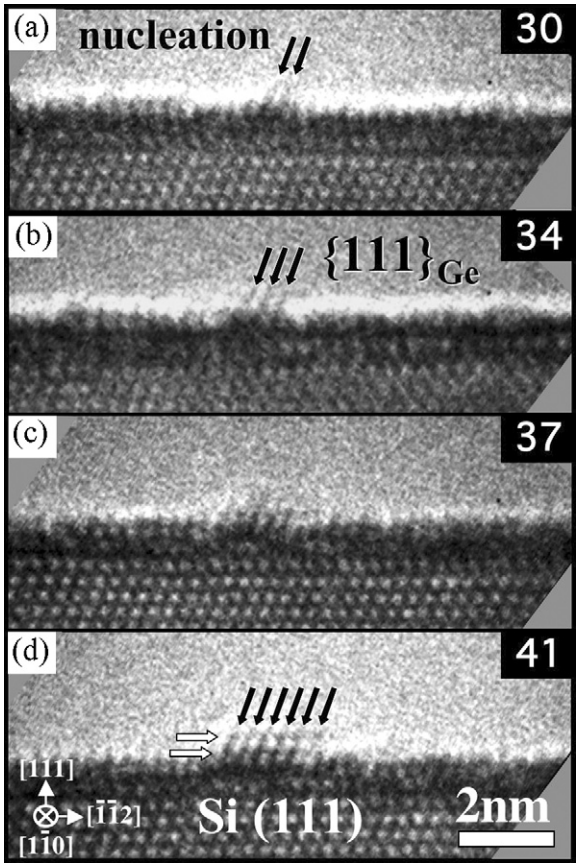

Fig. 2. Time series of HR-profile TEM images taken during Ge deposition on the Si(1 1 1)surface with the ultra-thin oxide films at 723 K.

deposition of 34 min (Fig. 2(b)), these lattice fringes grow from 2 rows to 3 rows, the number of lattice fringes increases further after 37 min passes (Fig. 2(c)), and a new atomic row aligned parallel to the Si(1 1 1) plane was observed as shown in Fig. 2(d) marked with two white arrows. This means that the Ge NDs are epitaxially grown on the Si(1 1 1) at the beginning of the nucleation.

Fig. 3(a)–(d) shows a time-series of HR-profile TEM images taken during growth of Ge NDs after the nucleation of Ge NDs. Numbers at right top represent the Ge deposition duration time in minute. The first frame (Fig. 3(a)), after Ge deposition of ~45 min, Ge NDs (the right side labeled by ND_L in Fig. 3(a)) had a dome shape with a diameter of ~3.0 nm and a height of ~1.2 nm. The Ge NDs after 47 min and 52 min from the Ge deposition time are diameters of ~6.0 nm and ~7.3 nm, and heights of ~1.8 nm and ~3.3 nm, respectively. Moreover, when size of Ge NDs increases to more than ~8.0 nm, coalescence of neighboring Ge NDs occurred frequently. Furthermore, single crystalline Ge NDs grow up without containing a defect during the growth. The aspect ratio (height-to-width) of the Ge NDs is nearly constant during growth, about 0.4. This aspect ratio will be used to evaluate the critical nucleus described later. Next, Fig. 3(e) shows the number (volume) of the constituent atoms in the Ge NDs in Figs. 2(a)–(d) and 3(a)–(d) as a function of Ge deposition time. The growth phenomena of the Ge NDs represent two stages. First, the initial growth rate after forming the nucleus of Ge NDs is rather slow. Second, the slowly grown Ge NDs begin to very rapidly grow in the critical nucleus size (200–300 atoms). The critical nucleus size and the above growth phenomena will be described in detail later.

Fig. 4(a) shows a typical HR-profile TEM image of a single-crystal Ge NDs. The incident electron-beam is in the ⟨1 1 0⟩ direction of the Si substrate. The Ge NDs has a dome shape with a