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Germanium nanoislands formation on silicon oxide surface by molecular beam epitaxy

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Abstract

The discussion deals with experimental data on the process of formation of self-organized Ge islands on the oxidized atomically pure Si(1 0 0) surface. Unlike the Stranski–Krastanow mechanism, which is characteristic of Ge growth on the pure silicon surface, the Volmer–Weber growth mechanism is observed on the oxidized silicon surface. The growth process is accompanied by a considerable change (up to 7%) in the surface unit cell of Ge relative to the parameters of Si. The elastically strained nanoislands are less than 10 nm in base size and more than $2 \times 10^{12}\,\mathrm{cm}^{-2}$ at the Ge film not thicker than 5 monolayers. Bimodal size and density distribution of islands is observed on the oxidized Si(1 0 0) surface at germanium film thickness of more than 5 monolayers.

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Keywords: Epitaxy; Si; Ge; Diffraction

1. Introduction

The process of self-organization of nanosized islands, intensively studied in recent years, has become practically attractive due to the presence of dislocation-free germanium islands (10–100 nm in size) that are generated on the Si(1 0 0) surface after a Ge-wetting layer has grown [1]. The islands can be minimized in size to provide appearance of the size quantization effects at as low as room temperature [2]. The optoelectronic applications of the silicon structures with germanium quantum dots cover the regions from IR [3] through the wavelengths used in fiber-optic communications [4]. In order to reduce the size but increase the density of the islands, they can be grown on a pre-oxidized silicon surface [4].

The islands can be downsized when germanium is deposited at a lower temperature. The smallest germanium islands grown on the pure silicon surface are 15 nm in size. They can be reduced in size when grown on the oxidized atomically pure surface prepared in situ in the molecular beam epitaxy (MBE) growth chamber. It has been known for long that the oxide layer can be generated on the silicon surface under vacuum conditions. The possibility of choosing regimes of etching and growth of the oxide film depending on oxygen pressure and temperature has been demonstrated for the first time elsewhere [5]. Growth of germanium islands on the pre-oxidized silicon surface (oxide thickness of 1–3 monolayers) allows the islands to be decreased considerably in size at a higher density. The islands grown on the oxidized Si(1 1 1) surface are shown [6,7] to be 10 nm in lateral size at density greater than $10^{12}\,\mathrm{cm}^{-2}$.

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The authors [4] used TEM data to suppose that this is the case of local deoxidation of silicon by germanium accompanied by desorption of germanium monoxide. Germanium nanoislands conjugated coherently with silicon are nucleated in these sites.

The oxidation conditions not only considerably affect the process of germanium island nucleation, but they also are of critical importance for further growth of a silicon layer over the islands. When the silica layer is thick enough, the defectiveness of the epitaxial Si layer becomes inappropriate. High-energy electron diffraction is the most practicable controlling tool in MBE facilities; it allows both oxidation [8] and the further growth of germanium and silicon to be controlled layer-by-layer.

2. Experimental

An MBE installation Katun-C equipped with two electron beam evaporators for Si and Ge was used for material synthesis. Analytical equipment of the chamber included a quadrupole mass spectrometer, a quartz thickness monitor and a reflection high-energy electron (20 kV) diffractometer (RHEED). Diffraction patterns were monitored at a rate of 10 frames/s during the growth using a CCD camera on line with a PC. Ge grew at a rate of 10 monolayers/min; temperature was varied between 300 and 700 °C. Silicon wafers (1 0 0) misoriented by less than 0.5° were used as substrates. Before a Ge film started growing, the substrate was annealed and a buffer Si layer was grown at 600 °C. An MBE installation was used for oxidation at oxygen supply up to 10^{-4} Pa and the substrate temperature was 400–500 °C. Then Ge was deposited on the oxidized surface.

3. Results and discussion

Variations in the intensities of reflections in RHEED patterns were monitored during the oxidation process. Most informative are variations in the specular reflection intensity. Fig. 1 shows intensity variations of specular and superstructure (2×1) reflections during oxidation of Si(1 0 0) surface at 400 °C in oxygen fed to a pressure of 2×10^{-5} Pa to the chamber. The minimum intensity in the specular reflection relates to the maximum surface roughness that indicates 0.5 oxide monolayer coverage. The intensity decreases later on to tend to some stationary value. Formation of the second and further layers results in no variation in the intensity of the specular reflection because the surface morphology does not alter. The superstructure reflection almost fades at a coverage equal to ~0.5 monolayers.

The process of Ge film growth was controlled using RHEED patterns by registering both qualitative

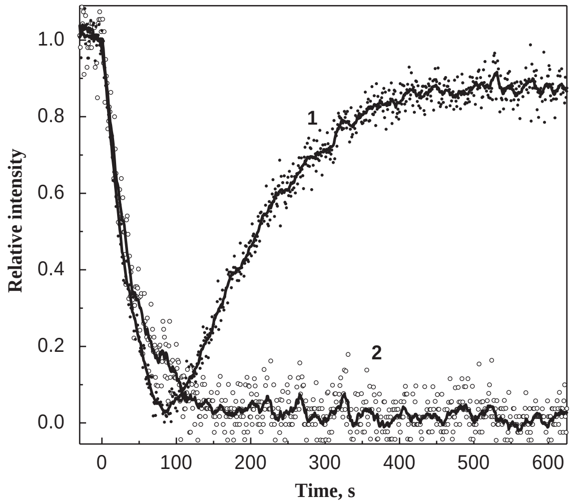

Fig. 1. Relative intensity variations of specular (1) and superstructure (2) spots during Si(1 0 0) oxidation at 400 °C and oxygen pressure 2×10^{-5} Pa.

changes in the structure and morphology of the growing film and quantitative information about elastic deformation of the surface unit cell [9]. The initial stage of germanium film growth on the oxidized Si surface was analyzed by registering variations in the intensities of specular reflection and three-dimensional diffraction reflection (3D-reflection). These values were very sensitive to variations in the surface roughness, while the appearance of 3D-reflection indicated the presence of 3D objects on the surface under study. The occurrence of intensity oscillations of the specular reflection during growth on the pure surface, extinction of the reflection and appearance of 3D-reflection at germanium film thickness of more than 4 monolayers argue for 2D growth of the wetting layer followed by formation of 3D islands. As to the Ge film growth on the oxidized surface, the reflection intensities are only varied after deposition of 1 monolayer and the specular reflection intensity does not oscillate (Fig. 2). These observations indicate the absence of the stage of wetting layer formation. While the first monolayer is deposited on the SiO_2 surface, an adsorbed Ge layer is formed which is transformed into 3D islands during the growth of the second and next monolayers. Therefore, germanium film growth on the oxidized silicon surface by the Volmer–Weber mechanism, but not by the Stranski–Krastanow mechanism, is characteristic of the growth of a pure Si surface.

Deformations of germanium lattice were studied by measuring in-plane lattice constant $a_{||}$ of the surface 2D unit cell. For this purpose, variations in the distance between reflections corresponding to the $a_{||}$ parameter were registered in the diffraction pattern. The film growth results in changes of in-plane lattice constant of

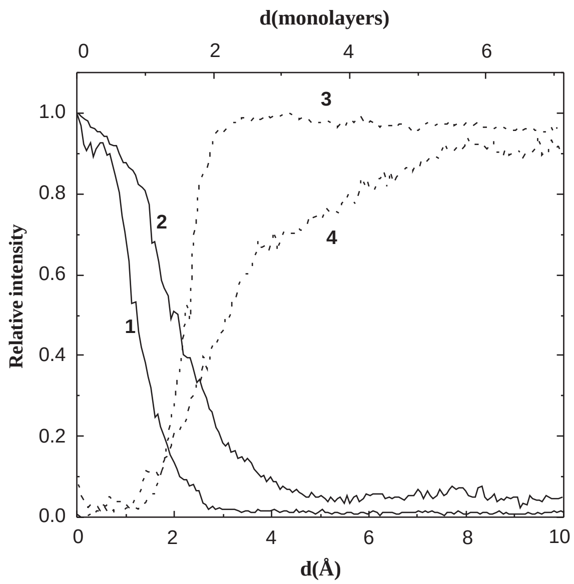

Fig. 2. Relative intensity variations of specular (solid line) and 3D reflections (dashed line) during growth of Ge film on oxidized Si(1 0 0) surface at different substrate temperatures: 1,2–$T_s = 550\,°C$, 3,4–$T_s = 450\,°C$.

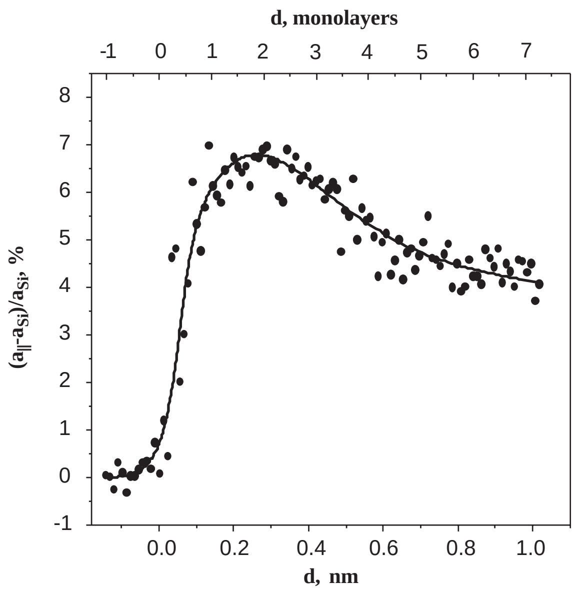

Fig. 3. Variations of in-plane lattice constant $a_{||}$ during growth of Ge film.

Ge layer against the constant of Si lattice which remains constant (Fig. 3). The difference may reach 7% as reported for the growth on pure Si(1 0 0) surface [9]. Elastically strained islands grow first; then, $a_{||}$ decreases to the value characteristic of bulk germanium that indicates complete plastic relaxation of the islands. The mode of parameter $a_{||}$ variations is similar to that observed during germanium heteroepitaxy on the pure Si(1 0 0) surface, except in the considerably smaller region of existence of strained Ge islands; as a result the maximal constant of the surface 2D unit cell is characteristic of 3D islands formed after deposition of one germanium layer. Hence, the maximal elastic deformation already occurs in the 3D island nuclei. Plastic relaxation of the islands becomes detectable upon deposition of 3 or 4 germanium monolayers and is practically completed after 6 or 7 monolayers. Hence, the elastically strained islands occur in a considerably narrower region (no more than 2–3 germanium monolayers) than those grown on the pure silicon surface.

Depending on the thickness of the deposited germanium layer, the islands differ in size and density. In a film not thicker than 5 monolayers, the islands are less than 10 nm in base size at a density greater than $2 \times 10^{12}\,cm^{-2}$. Fig. 4 is an STM image ex situ of an array of Ge islands on the silica surface obtained after deposition of 0.3 and 0.7 nm germanium at the substrate temperature of 650 °C. An increase in the effective thickness of deposited germanium results in the formation, along with small-sized islands, of islands with size larger by an order of magnitude at a considerably lower density. Their lateral size reaches 200 nm at a density equal to $1.5 \times 10^{9}\,cm^{-2}$. If we consider variations in the in-plane lattice constant (see Fig. 3), it is reasonable to conclude that the germanium islands larger in size are relaxed and their lattice constant equals that of bulk germanium. This conclusion is also supported by the presence of Moire fringes in the electron micrographs. It should be noticed that the islands are not pronouncedly faceted but are almost spherical in shape. A similar island shape was observed [6] during in situ STM analysis of germanium islands on Si(1 1 1) surface. It appears as though like the island shape depends on the occurrence of an oxide layer but not on the layer thickness or substrate orientation. Only minor variations in size and density are observed in small-size islands upon covering, when large islands appear, and they all co-exist (Fig. 4b). Therefore, bimodal size and density distribution of islands is observed on the oxidized Si(1 0 0) surface at germanium film thickness more than 1 nm. Electron microscopic studies also support this conclusion (Fig. 5).

In conclusion, we have observed bimodal size and density distribution of islands on the oxidized Si(1 0 0) surface at germanium film thickness of more than 5 monolayers. The elastically strained nanoislands are less than 10 nm in base size and more than $2 \times 10^{12}\ cm^{-2}$ at Ge film not thicker than 5 monolayers. An increase in the effective thickness of deposited germanium results in formation, along with small-sized islands, of fully relaxed islands with the lateral size up to 200 nm at a density of $1.5 \times 10^{9}\ cm^{-2}$. The region of existence of

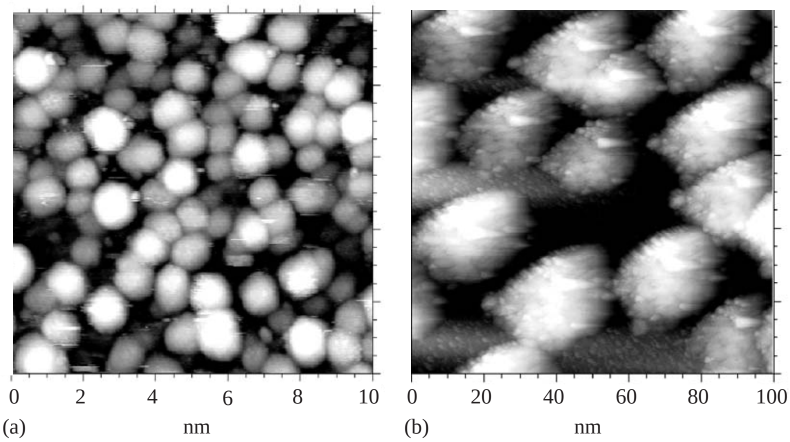

Fig. 4. STM micrograph of an array of Ge islands on silicon oxide surface: $d_{Ge} = 0.3$ nm (a); $d_{Ge} = 0.7$ nm (b).

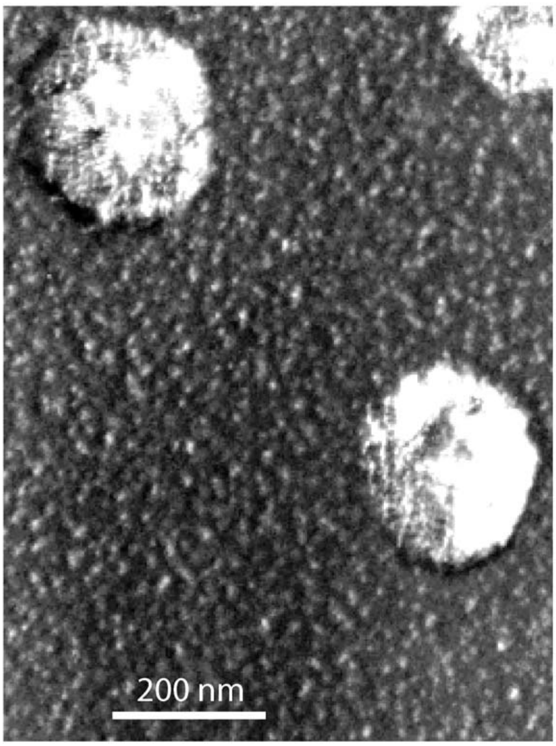

Fig. 5. TEM micrograph of an array of Ge islands on silicon oxide surface: $d_{Ge} = 0.7$ nm.

elastically relaxed small-size islands is 2–4 monolayers of deposited germanium.

Acknowledgements

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