Germanium Nanostructures Deposited by the Cluster-beam Evaporation Technique

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Abstract

The Ge nanostructures were deposited on substrates whose temperature was kept at room or liquid nitrogen (LN_2) temperature by the cluster-beam evaporation technique. The deposited film is found to consist of the tetragonal crystalline structure, not the diamond structure in bulk Ge. Such a phase-transition is theoretically predicted for sizes smaller than 4 nm, which agrees with the size measured by the transmission electron microscopy (TEM). The Ge film deposited at LN_2 temperature exhibits unique properties such as photo-oxidation and blue-light emission.

Introduction

It is interesting to study the crystalline structure of Ge nanostructures. Saito reported that the crystalline structures of Ge ultrafine particles whose diameters were less than 20 nm were a mixture of the diamond and the tetragonal structures [1]. It was theoretically pointed out that nano-particles with the diamond structure exhibit a phase transition in order to reduce the surface energy when the size becomes smaller than a threshold value. Tomanek and Schluter, for example, predicted a possible phase transition of Si clusters from the diamond to body centered cubic (bcc) structure for sizes of $10^2 \sim 10^3$ atoms [2]. The phase transition of the crystalline structure of Si clusters has never been experimentally observed.

In this study, Ge nanostructures were deposited by the cluster beam evaporation technique, and their structure and optical properties were studied.

Experimental

Figure 1 shows an apparatus of the cluster-beam evaporation technique equipped with a crucible machined from a carbon rod [3]. The cap of the crucible is 1 mm thick and has a nozzle hole with a diameter of 1 mm. The crucible loaded with small pieces of undoped Ge (~40Ω cm) was heated by electron bombardment. During the deposition, the temperature of the crucible was kept at 2000 K, and the pressure in the chamber was fixed at 5×10^{-6} torr. The substrate temperature was either room or liquid nitrogen temperature. The typical film thickness was 100 nm after 60 min deposition. The classical nucleation theory [4] predicts that the sizes of Ge nanostructures formed by the cluster-beam evaporation technique would be much smaller than those

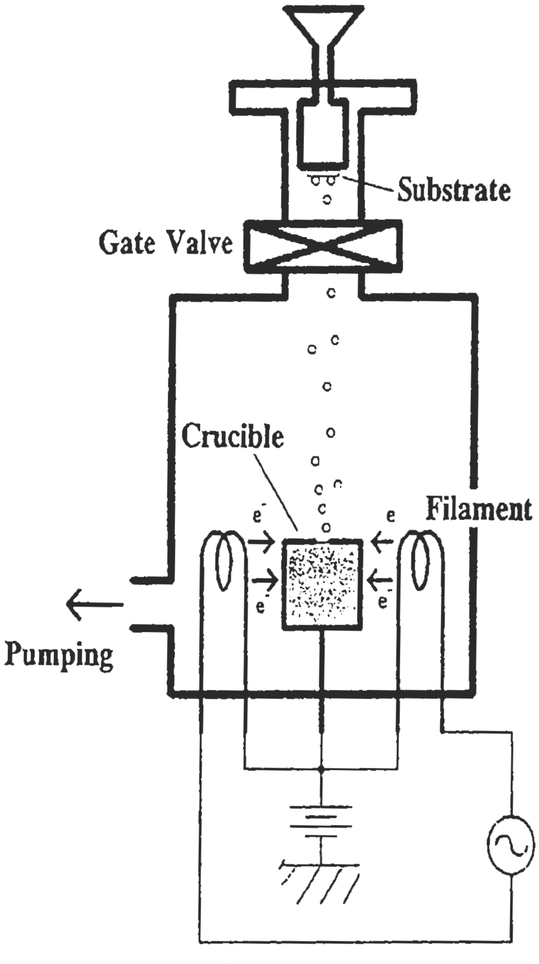

Fig.1 Apparatus of the cluster-beam evaporation technique.

by the gas-evaporation technique, which is conventionally used to deposit metal or semiconductor nanostructures.

P-type (100) Si substrates were used for Raman spectroscopy, electron spectroscopy for chemical analysis (ESCA) and photoluminescence (PL) measurements, while quartz substrates were used for optical absorption measurements. The Raman study was made by using the 514.5 nm line of argon (Ar) ion laser with an intensity of 400 mW. The 313 nm line of a mercury lamp selected with an optical bandpass filter, whose full width at half maximum (FWHM) was 10 nm, was used as an irradiation light and an excitation source for PL measurements. PL and Raman measurements were carried out in the air at room temperature.

Results and Discussion

Typical Raman spectra of the Ge films deposited at 77 and 300 K are shown in Fig. 2, where the Raman spectra of an undoped Ge wafer (c-Ge) and a high-pressure form of Ge (ST-12) [5] are also shown for comparison. The Raman spectra of both Ge films deposited at 77 and 300 K indicate that their structure is not the ordinary diamond structure but the tetragonal structure, for which Kobliska et al. reported peaks at 273±3 (Γ_5) and 246±3 cm^{-1} (Γ_3). The double peak observed for both Ge films by the cluster-beam evaporation technique resembles that obtained by Kobliska et al. Tomanek and Schluter estimated that the phase transition of Si nanostructures from the diamond to the bcc structure, a high-pressure form of Si occurred when the number of atoms in a nanostructure becomes $10^2 \sim 10^3$ [2]. In TEM micrographs, the Ge film deposited at 300 K appears smooth and uniform, while that deposited at 77 K consists of nanostructures with diameters from 4 to 40 nm [3]. However, the Ge film deposited at 300 K may consist of much smaller nanostructures.

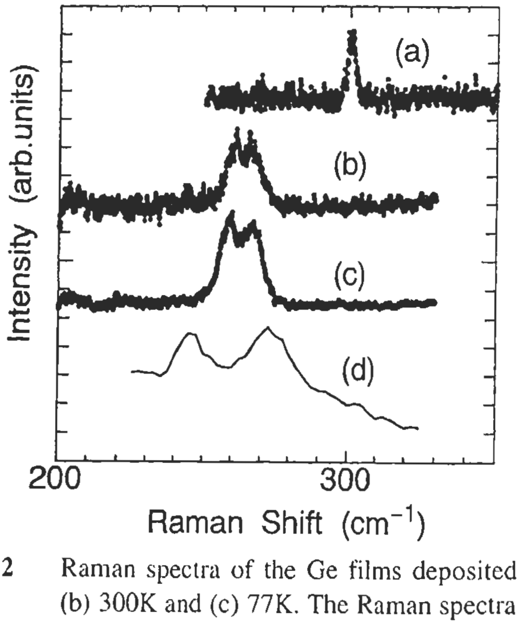

Fig.2 Raman spectra of the Ge films deposited at (b) 300K and (c) 77K. The Raman spectra of (a) bulk Ge and (d) a high-pressure form of Ge are also shown for comparison.

Figure 3 shows the ESCA spectra of the surfaces of the Ge films deposited at 300 and 77K. The solid and broken curves are the spectra of the as-deposited samples and those of the samples after exposure to the 313 nm line of UV light with a power of 20 μW/mm^2 for 30 min, respectively. It is found that the Ge film deposited at 300 K is hardly oxidized as expected, while the Ge film deposited at 77 K, which is partially oxidized even before exposure to the UV light, is photo-oxidized rapidly. The photo-oxidation is found to proceed to a deeper inside the Ge nanostructure for a prolonged exposure. With decreasing the size of a Ge core, the apparent bandgap of a Ge nanostructure increases due to the quantum-size effect. An increase in the optical bandgap of the Ge film deposited at 77K after photo-

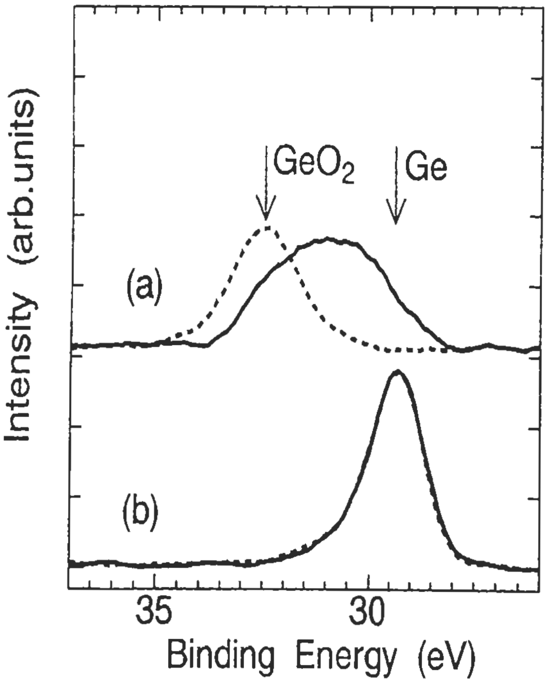

Fig.3 Ge3d ESCA spectra of the surfaces of (a) the Ge film deposited at 77 K and (b) that deposited at 300 K. Solid and broken curves are those for before and after UV irradiation, respectively. The samples are exposed to 20 μ W/mm^2 UV light with a wavelength of 313 nm for 30 min.

oxidation evidences the quantum-size effect.

The observed difference in photo-oxidation of Ge-RT and Ge-LNT cannot be, however, explained simply by a difference in the size. Both sizes are small enough to confine the carriers three-dimensionally. Unlike Ge-LNT, Ge-RT is hard to become naturally oxidized and keeps the surface free of oxide, as shown in Fig. 3. Ge-LNT is more subject to natural oxidation probably because a larger distance between nanocrystals allows more surface area to be exposed to oxygen. Since the nanocrystals are physically in contact with each other, the carriers in Ge-RT cannot be confined in a nanocrystal. A nanocrystal of Ge-RT consiting of several tetragonal-Ge unit cells resembles a grain of a polycrystal. In contrast, a nanocrystal of Ge-LNT is isolated from the adjacent nanocrystals by the surface oxide barrier. In this case, the carriers are confined three-dimensionally, and the quantum-size effect is expected. According to the model of photonically stimulated oxidation enhancement of Si proposed by Young [6], the rate-determination step of the oxidation is the dissociation of molecular oxygen into its atoms. In his model, electrons in Si need to be excited to the conduction band of SiO_2 in order to dissociate molecular oxygen. Thus, it is quite reasonable to consider that Ge-LNT shows rapid photo-oxidation but not Ge-RT, because the conduction band offset at the interface between the Ge core and the surrounding oxide in Ge-LNT is significantly reduced by the three-dimensional carrier confinement. Detailed experimental results and discussion on the photo-oxidation are published elsewhere [7]. It is also predicted from the photo-oxidation model that the final size of Ge cores is determined by the incident photon energy, and that the size of Ge cores becomes more uniform for prolonged photo-oxidation.

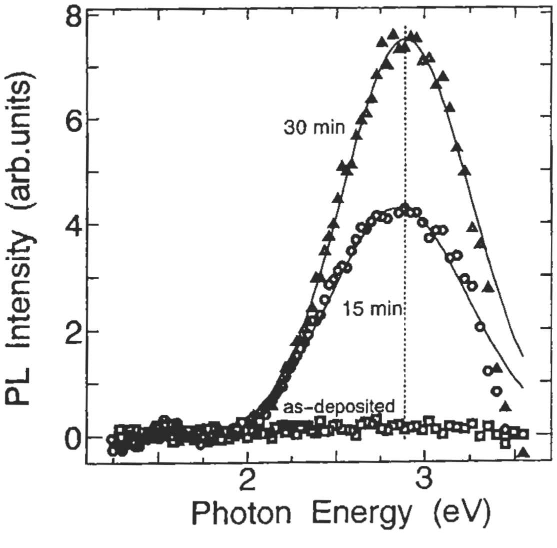

Fig.4 Typical PL spectra of the as-deposited and UV-irradiated Ge films. Solid curves are the Gaussian curves fitted to experimental data. The sample was exposed to 20 μW/mm² UV light with a wavelength of 313 nm. The irradiation periods are shown in the figure.

The PL spectra of the Ge film deposited at 77 K after 0, 15, and 30 min-exposures to the UV light are shown in Fig. 4. The solid curve is a Gaussian curve which is fitted to the experimental data. The PL peak energy is 2.9 eV, independent of the exposure time.The blue light emission is strong enough to be recognized with the naked eye even under room light. It should be noted that the Ge film deposited at 77 K shows no detectable luminescence before exposure to the UV light, and that the Ge film deposited at 300 K is not luminescent either before or after exposure to the UV light. Since the PL peak energy is independent of the degree of photo-oxidation, and its intensity correlates with the degree of photo-oxidation, we attribute the blue-light PL to defects in GeOx.

Conclusions

Ge films were deposited on substrates whose temperatures were kept at room and liquid nitrogen temperatures by the cluster-beam evaporation technique. The Ge film deposited at 77K is found to consist of nanostructures with diameters from 4 to 40 nm, while that deposited at 300K appears to consist of much smaller nanostructures. Even a larger-size nanostructure in the Ge film deposited at 77K may be an agglomeration of smaller-size nanostructures. Both Ge films are found to consist of the tetragonal crystalline structure, not the ordinary diamond one. Such a phase transition to a close-packed structure was theoretically expected in order to reduce the surface energy when the size becomes smaller than a critical size. It is also found that the Ge film deposited at 77K becomes oxidized by the UV exposure and exhibits blue light emission. The blue light emission was attributed to defect centers in Ge oxide formed by photo-oxidation.

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References

1. Y. Saito, J. Crystal Growth **47**, 61 (1979).
2. D. Tomanek and M. A. Schluter, Phys. Rev. B **36**, 1208 (1987).
3. S. Sato, S. Nozaki, H. Morisaki and M. Iwase, Appl. Phys. Lett. **66**, 3176 (1995).
4. T. Takagi, Ionized-Cluster Beam Deposition and Epitaxy, Chapter 3, Noyes Publications, Park Ridge, NJ, USA, 1988.
5. R. J. Kobliska, S. A. Solin, M. Selders, R. K. Chang, R. Alben, M. F. Thorpe and D. Weaire, Phys. Rev. Lett. **29**, 725 (1972).
6. E. M. Young, Appl. Phys. A **47**, 259 (1988).
7. S. Sato, S. Nozaki and H. Morisaki, J. Appl. Phys. **81**(3), 1518 (1997).