Optical properties of tetragonal germanium nanocrystals deposited by the cluster-beam evaporation technique: New light emitting material for future

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Abstract. The germanium (Ge) nanocrystals were deposited on substrates whose temperature was kept at room or liquid nitrogen (LN₂) temperature by the cluster-beam evaporation technique. The deposited films are found to consist of the tetragonal crystalline structure rather than the diamond structure of bulk Ge. Such a phase-transition has been theoretically predicted for sizes smaller than 4 nm, which agrees with the size measured by the transmission electron microscopy (TEM). The tetragonal Ge is expected to have a direct band gap of 1.47 eV. Furthermore, the Ge film deposited at LN₂ temperature exhibits unique properties, such as photo-oxidation and blue-light emission. The Ge-nanocrystal films deposited by the cluster-beam evaporation technique are attractive materials for application to light emitting devices in future.

Keywords. Germanium; nanocrystal; crystal structure; ST-12; photo-oxidation; blue-light emission.

1. Introduction

It is interesting to study the crystalline structure of germanium (Ge) nanocrystals. Saito (1979) 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 (ST-12). It was theoretically pointed out that nanoparticles 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 (1987), for example, predicted a possible phase transition of silicon (Si) nanocrystals from the diamond to body centred cubic (bcc) structure for sizes of $10^2 \sim 10^3$ atoms.

Among the high-pressure forms of Ge, the ST-12 structure is the most attractive for device application. Joannopoulos and Cohen (1973) made a theoretical calculation, using the empirical-pseudopotential method, and predicted that the ST-12 structure of Ge was a semiconductor with a direct band gap of 1.47 eV. The diamond structure of Ge has been regarded as a less interesting material for device application because of its small and indirect band gap, while the ST-12 structure of Ge could become an important material for future electronics.

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

2. Experimental

Figure 1 shows an apparatus of the cluster-beam evaporation technique equipped with a crucible machined from a carbon rod. 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 ($\sim 40 \Omega \text{ cm}$) 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 at room or liquid nitrogen temperature. The typical film thickness was 100 nm after 60 min deposition. The classical nucleation theory predicts that the sizes of Ge nanocrystals formed by the cluster-beam evaporation technique would be much smaller than those by the gas-evaporation technique, which is conventionally used to deposit metal or semiconductor nanocrystals.

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 carried out 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 band-pass 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.

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3. Results and discussion

Typical Raman spectra of the Ge films deposited at 77 and 300 K are shown in figure 2, where the Raman spectra of an undoped Ge wafer (*c*-Ge) (curve a of figure 2) and a high-pressure form of Ge (ST-12) (curve d of figure 2) are also shown for comparison. The Raman spectra of both Ge films deposited at 77 (curve c of figure 2) and 300 K (curve b of figure 2) indicate that their structure is not the ordinary diamond structure but the tetragonal structure, for which Kobliska *et al* (1972) reported peaks at $273 \pm 3 \text{ cm}^{-1}$ (Γ_5) and $246 \pm 3 \text{ cm}^{-1}$ (Γ_3). The double peak observed for both Ge films by the cluster-beam evaporation technique resembles those obtained by Kobliska *et al* (1972). Sato *et al* (1995)

reported that in TEM micrographs, the Ge film deposited at 300 K appeared smooth and uniform, while that deposited at 77 K was nonuniform and consisted of nanocrystals with diameters ranging from 4 to 40 nm. However, even a larger nanocrystal may be agglomeration of smaller nanocrystals.

Near-infrared to near-ultraviolet optical absorption spectra of the Ge films deposited at 300 and 77 K are shown in figure 3 (curves a and b). In the figure, the absorption edge of the film deposited at 300 K is estimated to be 1.5 eV. However, it is difficult to estimate the absorption edge of the film deposited at 77 K from the spectrum because of no sharp rise in the spectrum. The optical band gap of the Ge film deposited at 300 K is larger than that of bulk Ge (0.66 eV, indirect) and close to that of ST-12, predicted by Joannopoulos and Cohen (1973).

All the above results support the presence of the ST-12 structure of Ge in the Ge films deposited by the cluster-beam evaporation technique. The detailed study on the crystal structure of the Ge nanocrystals was reported by Sato *et al* (1998).

Although the ST-12 structure of Ge is known to be metastable and therefore not stable at high temperature, Nozaki *et al* (1996) earlier reported the thermally stable ST-12 structure of Ge present in the Ge-nanocrystal films deposited by the cluster-beam evaporation technique. The Raman spectra showed the presence of the tetragonal

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

Figure 2. Raman spectra of the Ge films deposited at 300 K and 77 K (curves b and c, respectively). The Raman spectra of bulk Ge and ST-12 structure of Ge are also shown for comparison (curves a and d, respectively).

structure of Ge nanocrystals even after annealing at 800°C.

The ESCA spectra of the surfaces of the Ge films deposited at 77 K and 300 K are shown in figure 4 by the curves a and b, respectively. The solid and broken curves are the spectra of the as-deposited samples and those of the samples after exposure to 313 nm line of UV light with a power of $20 \mu\text{W}/\text{mm}^2$ for 30 min, respectively. It is observed 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 level inside the Ge nanocrystal for a prolonged exposure. With decreasing the size of Ge core, the apparent band gap of a Ge nanocrystal increases due to the quantum-size effect. An increase in the optical band gap of the Ge film deposited at 77 K after photo-oxidation, as shown in figure 3, curve c evidences the quantum-size effect. The detailed study on photo-oxidation was reported elsewhere by Sato *et al* (1997).

The observed difference in photo-oxidation of Ge films deposited at 300 and 77 K cannot be, however, explained merely by a difference in the size. Both sizes are small enough to confine the carriers three-dimensionally. Unlike the film deposited at 77 K, the film deposited at 300 K is hard to become naturally oxidized and keeps its surface free of oxide, as shown in figure 4. The film deposited at 77 K is more subject to natural oxidation perhaps 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 the film deposited at 300 K cannot be confined in a nanocrystal. A nanocrystal in the Ge-film deposited at 300 K consisting of several tetragonal-Ge unit cells resembles a grain of a polycrystal. In contrast, a nanocrystal in the Ge film deposited at 77 K 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 (1988), 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 the Ge film deposited at 77 K shows rapid photo-oxidation but not the film deposited at 300 K, because the conduction band offset at the interface between the Ge core and the surrounding oxide in the former film is significantly reduced by the three-dimensional carrier confinement. 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.

The photoluminescence (PL) spectra of the Ge film deposited at 77 K after 0, 15, and 30 min exposures to the UV light are shown in figure 5. The solid curve is a Gaussian curve which is fitted to the experimental

Figure 3. Optical absorption spectra of the Ge films deposited at 300 K and 77 K (curves a and b, respectively). The curve c is for the Ge film deposited at 77 K after exposure to 313 nm line of UV light with a power of $20 \mu\text{W}/\text{mm}^2$ for 30 min.

Figure 4. Ge-3d ESCA spectra of the surface of the Ge films deposited at 77 K and 300 K (curves a and b, respectively). The solid and broken spectra are for those before and after UV exposure, respectively.

data. The PL peak energy is 2.8 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 GeO_x .

An effect of anneal on the luminescence characteristic of the Ge film is more complex. The Ge films deposited at 77 K were annealed in argon atmosphere at 500°C for 60 min. The sequence of photo-oxidation and annealing treatments affects the PL spectrum. A typical PL spectrum of the Ge film after 60 min UV exposure is shown in figure 6. The PL with a peak energy at 2.8 eV was associated with radiative centres in GeO_x , as discussed earlier. The PL spectrum of the Ge film which went through treatments of the 60 min photo-oxidation and the 60 min 500°C-anneal in that order shows a broader peak with at a PL peak intensity one third of the peak intensity of the photo-oxidized Ge film (curve b of figure 6).

The Ge film which went through the treatments of the photo-oxidation and the anneal in that order shows detectable PL immediately after exposure to the UV light, while the Ge film without the photo-oxidation treatment before the anneal requires a prolonged exposure to the UV light for detectable PL. The PL spectrum of the latter is not much different from that of the photo-

oxidized Ge film without the anneal and shows a peak at 2.8 eV. Their PL spectra show a constant peak energy and a peak intensity increasing with increasing the UV-exposure time. The effect of the photo-oxidation on the PL spectra overrides that of the anneal.

The above effects of the photo-oxidation and the anneal on the PL are not easily understood. As mentioned earlier, the photo-oxidation of Ge nanocrystals forms GeO_x , where radiative recombination centres are present. The PL with a peak energy at 2.8 eV, which contributes to blue-light emission, is attributed to these radiative centres. However, the anneal converts some GeO_x into GeO_2 and Ge. This process grows Ge nanocrystals and decreases the apparent band gap determined by the three-dimensional quantum confinement effect. The PL peak of the Ge film which went through the photo-oxidation and annealing treatments in that order appears to consist of several peaks including one at 2.8 eV. The other peaks may be associated with the Ge/ GeO_2 interface or GeO_2 . The peak at 2.8 eV is attributed to radiative centres in the remaining GeO_x .

4. 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 77 K is found to consist of nanocrystals

Figure 5. PL spectra of the Ge films deposited at 77 K after exposure to the UV light for 0, 15 and 30 min.

Figure 6. PL spectra of the Ge film deposited at 77 K after exposure to the UV light for 60 min (curve a), and the Ge film deposited at 77 K after exposure to the UV light for 60 min and subsequent anneal at 500°C for 60 min (curve b). The PL spectrum of the latter was normalized so that the PL peak intensity becomes equal to that of the former. The actual intensity of the latter is one third of that of the former.

with diameters from 4 to 40 nm, while that deposited at 300 K appears to consist of much smaller nanocrystals. Even a larger-size nanocrystal in the Ge film deposited at 77 K may be an agglomeration of smaller-size nanocrystals. 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 77 K is oxidized by the UV exposure and consequently exhibits blue light emission. The blue light emission was attributed to defect centres in Ge oxide formed by photo-oxidation. Although the Ge film deposited at 300 K is not luminescent in the visible range, it may emit infrared light efficiently, because the ST-12 structure of Ge, which is present in it, is predicted to have a direct band gap of 1.47 eV. Therefore, both Ge-nanocrystal films deposited at 300 and 77 K by the cluster-beam evaporation technique are new attractive materials for light emitting device application.

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