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Crystal Structure and Particle Size of Ge-Nanoparticles Depending on the Flowing Gas Evaporation Conditions

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Germanium nanoparticles were formed by the flowing gas evaporation method. Depending on the experimental conditions, the amorphous, diamond and tetragonal nanoparticles were formed. A new tetragonal structure with the lattice parameters of a=5.38 and c=8.79 Å was found to form in a restricted He gas condition. Particle size correlates strongly with the crystal structure, as the following order that the amorphous particles are smaller than 10nm, tetragonal ones are between 16 to 30nm, and diamond ones range from 30 to 200nm. Formation of Ge-nanoparticles with three kinds of structure may be due to the particle size and the cooling rate of them during nucleation and growth.

Key words: Ge, Nanoparticle, Tetragonal structure, Particle size, FGE-method

1. INTRODUCTION

The three crystal structures are known in Germanium. The first one is the diamond structure, which is stable in the bulk Ge. The second one is the amorphous structure, which is formed in vacuum evaporated thin films on the room temperature substrate, in general [1,2]. The third one is the tetragonal structure, which was found at first in high-pressure form [3-5] and later similar structure with different lattice spacing was found in nanoparticles prepared by the gas evaporation technique [6,7] and nanocrystalline in the thin films deposited by the cluster-beam evaporation [8] and plasma enhanced CVD [9].

Recently, optical properties of Ge-nanoparticles have been studied from the interest of quantum confinement [10,11]. In these studies the particle size selection is quite difficult, but is the most important technique in sample preparation. In the present experiments the formation of size-selected Ge-nanoparticles has been demonstrated by using the flowing gas evaporation (FGE) method [12,13]. It is found that Ge-nanoparticles with structures of diamond, amorphous and tetragonal can be formed individually depending on the FGE conditions. In this paper the preparation of Ge-nanoparticles and the structure analysis of them by X-ray diffraction (XRD) method and transmission electron microscopy (TEM) are described.

2. EXPERIMENTAL

Figure 1 shows a schematic diagram of FGE apparatus. A steady flow of carrier gas was made

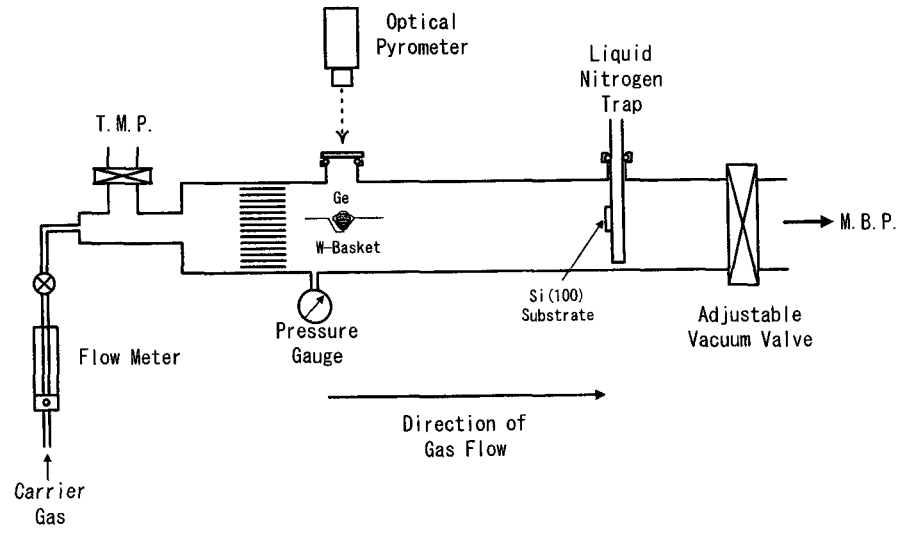

Fig. 1 Schematic diagram of FGE apparatus.

by introducing He gas continuously to the cylindrical chamber through a flow meter and evacuating the chamber by a mechanical buster pump. The gas velocity and the gas pressure were separately controlled by changing the flow rate and adjusting the valve installed in the front of mechanical buster pump. The gas velocity and the gas pressure were from 0.17 to 36m/s and from 0.5 to 8.0Torr, respectively. The temperature of evaporation source during the evaporation was measured by an optical pyrometer.

XRD measurement and TEM observation were carried out for the specimens collected on a Si(100) substrate for XRD and on an electron microscope grid covered with an amorphous carbon film for TEM.

The distance from the evaporation source to the collection position was 0.40m.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The typical XRD patterns of Ge-nanoparticles are shown in Fig. 2(a), (b) and (c). The amorphous nanoparticles shown in (a) were produced under the He gas condition of 0.3Torr in gas pressure and 36m/s in gas velocity. Here, the gas velocity v is derived experimentally from the following equation:

$$v = \frac{P_0 \cdot Q}{P \cdot S}, \qquad (1)$$

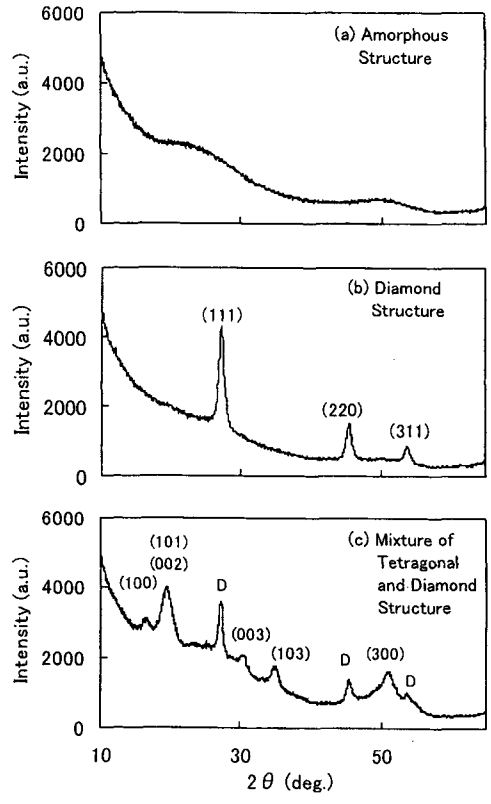

Fig. 2 Typical XRD patterns of Ge-nanoparticles. Miller indices in (b) represent of diamond structure and in (c) of tetragonal one, respectively.

where P_0 is the atmospheric pressure, Q the flow rate of He gas, P the gas pressure, S the cross sectional area of the cylindrical chamber, respectively. The sample shown in (b) was prepared under the He gas condition of 0.3Torr in gas pressure and 3.6m/s in gas velocity, and showed diamond structure which was the most dominant phase in the present study. In addition to the diamond structure, a new tetragonal structure was detected in XRD pattern of the sample formed under the He gas condition of 1.9Torr in gas pressure and 3.5m/s in gas velocity as shown in (c). The lattice parameters can be derived from the XRD to be a=5.38 and c=8.79Å, these are different from those of the same structure as already reported [3-9].

Figure 3 represents the diagram of the crystal structure of Ge-nanoparticles in relation to the He gas pressure and the gas velocity. The three structures: amorphous, diamond and tetragonal, can be roughly located in three zones as shown in the diagram. It is considered that the zoning (in Fig. 3) for the crystal structure is closely related to the cooling rate of nanopaticles in the particle

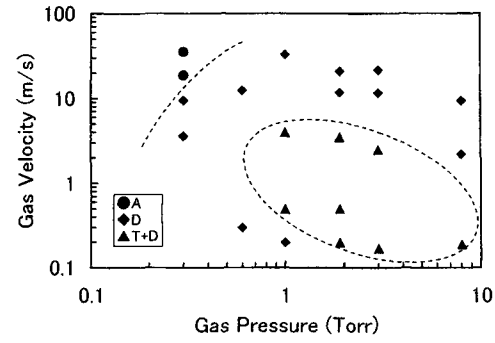

Fig. 3 Diagram of the crystal structure of Ge-nanoparticles in relation to the He gas pressure and the gas velocity. A, D and T in the graph represent particles of amorphous, diamond and tetragonal structure, respectively.

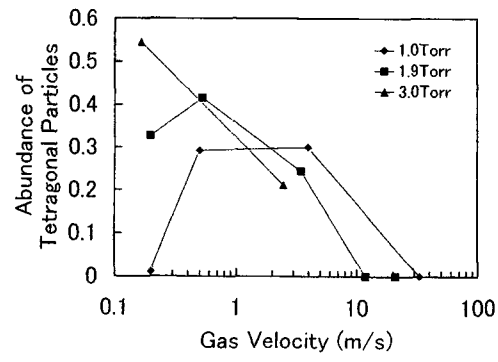

Fig. 4 Abundance of tetragonal particles vs. He gas velocity.

growth region of FGE apparatus. Especially in the formation of the amorphous particles it might be due to the large cooling rate. The cooling rate is determined by the temperature difference between the evaporated Ge vapor and the surrounding He gas, the temperature of which elevates in accordance with the heat transfer from the evaporation source. In the case of low pressure and a high gas velocity, the heat transfer from the hot evaporation source to the surrounding gas is small, then, a large cooling rate is achieved. The same explanation was successfully done for the formation of amorphous Sb-particles formed by the FGE method [12].

To see the effect of gas velocity for the formation of tetragonal particles, the abundance of tetragonal particles is plotted against He gas velocity in Fig. 4. From three curves the formation of tetragonal particles is found to be influenced significantly with He gas velocity. The abundance in this case was estimated from the intensity ratio of tetragonal (103) to diamond (111) peak in the XRD pattern.

It is well known that the evaporation temperature is one of the important factors to decide the nucleation rate and the initial size of nuclei even at a constant He gas condition. Then,

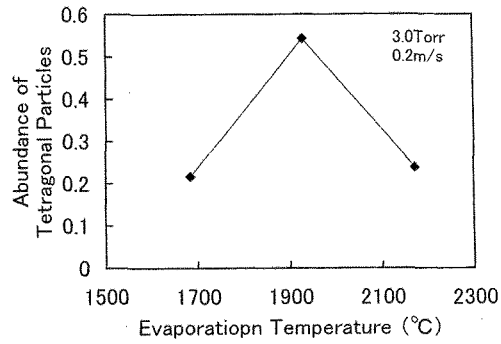

Fig. 5 Abundance of tetragonal particles vs. the evaporation temperature.

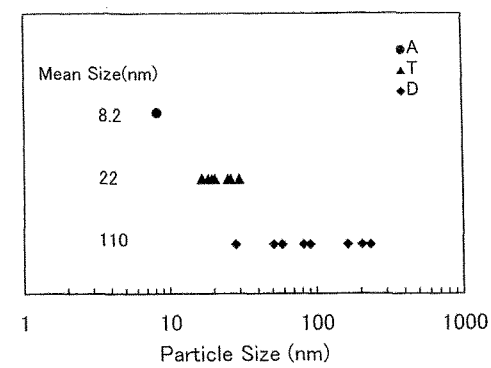

Fig. 6 Particle size plotted for three structures. A, T and D in the graph represent particles of amorphous, tetragonal and diamond structure, respectively.

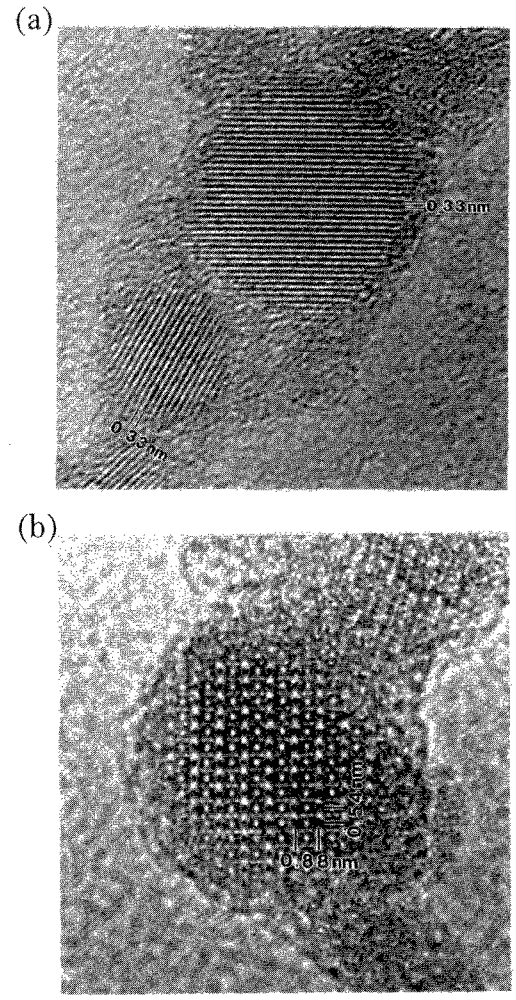

Fig. 7 Electron micrographs of Ge-nanoparticles of diamond structure (a) and tetragonal structure (b).

Ge was evaporated from the different source temperatures under the constant gas conditions of 3.0Torr in He gas pressure and 0.2m/s in the gas velocity. In the curve of the abundance of tetragonal particles vs. the evaporation temperature in Fig. 5, the maximum is obtained at 1930℃.

The particle size was derived from XRD profiles using Scherrer's formula for crystalline particles and from TEM observation for the amorphous specimen. The particle size of all the specimens in the present study are plotted in Fig. 6, where the following features are found, (1) the crystal structure depends on the particles size, (2) the amorphous particles are the smallest among them and the diamond particles are lager than the tetragonal ones.

3.2 TEM Observation

The TEM images are shown in Fig. 7(a) and (b), where Ge-nanoparticles with diamond structure are identified from (111) lattice spacing in the former, and the tetragonal structure from [100] zone axis is clearly seen in the latter.

4. SUMMARY

Ge-nanoparticles with the mean particle size from 8.2nm to 110nm were produced by FGE method using He as a cooling gas. Mean particle size and the crystal structures of amorphous, tetragonal and diamond thus produced depend on three factors in FGE method, gas pressure, gas velocity and evaporation temperature. The factors affect strongly the cooling rate during nucleation and growth stage of nanoparticles. It is considered that the difference of the cooling rate reflects the structure and the particle size of Ge-nanoparticles. A new tetragonal structure, which is considered as a meta-stable one, is identified to have the lattice parameters of a=5.38 and c=8.79Å from XRD analysis.

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