Proposal of Hexagonal Structure for Ge-Nanoparticles

Kei Tanaka, Takashi Saka and Saburo Iwama

Daido Institute of Technology, 10-3, Takiharu-cho, Minami-ku, Nagoya, 457-8530, Japan

Fax: 81-052-612-5623, e-mail: kei@daido-it.ac.jp

The unidentified structure was obtained from germanium nanoparticles formed by the flowing gas evaporation method. At first, we considered that this structure is the tetragonal one with the lattice parameters of a_0=5.38 and c_0=8.79 Å. However, it was revealed by more precise analysis of XRD pattern that the hexagonal structure is much more acceptable than the tetragonal structure. The lattice parameters of hexagonal structure are a_0=6.21 and c_0=8.79 Å.

Key words: Ge, Nanoparticle, Hexagonal structure, FGE-method

1. INTRODUCTION

Three structures have been reported 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 found in thin films evaporated in vacuum at room temperature [1,2]. The third one is the tetragonal structure, which was found at first in high-pressure phase [3-5]. Recently, this structure with different lattice spacing has been found in nanoparticles prepared by gas evaporation technique [6,7], nanocrystalline in thin films deposited by cluster-beam evaporation [8] and plasma enhanced CVD [9]. The present authors (K.T. and S.I.) also reported that Ge nanopartcles formed by flowing gas evaporation method have the tetragonal structure by the X-ray diffraction analysis [10]. However, it was revealed by more precise analyses that the tetragonal structure is not probable and a hexagonal structure is much more acceptable. In the present report, it is shown that the intensities of X-ray diffraction pattern indicate a hexagonal structure.

2. EXPERIMENTAL

For the following discussion, the previous experimental results are summarized here. A thin film of few hundred nm thickness was deposited on a Si (100) substrate by flowing gas evaporation method and X-ray diffraction patterns from the film were observed. Among diffraction peaks due to the ordinary diamond structure, some new peaks were observed. From these peak positions, it was concluded that the film consists of are constructed with nanoparticles with tetragonal structure, the lattice constants being 5.38 and 8.79 Å.

In the previous analyses, as the film was so thin, only the peak positions were taken into account and the intensities of the respect peaks were out of consideration. In the present experiment, nanoparticles were deposited ten times on the respect substrates by the same manner. Then these were compacted on a single Si plate so that a relatively thick film was formed. Then, X-ray diffraction patterns were observed using the CuK α characteristic rays and the diffraction patterns were analyzed.

3. ANALYSIS AND DISCUSSION

The observed result is shown in Fig.1, where the background of the profile has been subtracted by a computer treatment. In Fig.1(a), the peak positions are shown by the solid lines assuming that Ge has the tetragonal structure determined previously and by the dotted lines assuming the ordinary diamond structure. The peak positions assigned well explain the observed pattern. However, a close attention should be paid to the diffraction peak at 50.88° . This peak is assigned to the (300) reflection in the tetragonal structure. The intensity is very strong though the diffraction angle is large. This is the reason why we notice that the intensities of the peaks should be analyzed in further detail. This peak can be assigned to the (114) and the (300) reflections as these peaks are very close each other, if we assume a hexagonal structure whose lattice constants a_0 and c_0 are 6.21 and 8.79 Å , respectively as shown in Fig.1(b). In Fig.1(b), other possible peaks are also shown assuming the hexagonal structure.

In the followings, we attempt to determine which structure is more acceptable by comparing the observed intensities with the calculated ones. The scattered intensity of X-ray I is given by

$$ I = |F|^2 p \left(\frac{1+\cos^2 2\theta}{2\sin^2 \theta \cos \theta} \right) \frac{1}{2\mu}, \qquad (1) $$

where F is the structure factor, p the multiplicity

factor, 2θ the diffraction angle, μ the absorption coefficient. The term in the bracket is the Lorentz polarization (LP) factor. The factor due to the absorption is derived assuming the samples are thick enough. This factor is omitted henceforth as this is independent of the scattering angle and therefore is independent of the reflections.

The structures of the Ge nanoparticles affect the diffraction intensities through the structure factors as follow,

$$F_{hkl} = f\sum_{j=1}^{N} e^{2\pi i(hu_j + kv_j + lw_j)}, \qquad (2)$$

where f is the atom scattering factor of Ge, h, k and l the Miller indices, N the number of atoms in the unit cell, u_j, v_j and w_j three components of the position vector of the j-th atom. The temperature factor is omitted in the equation (2).

Now, the intensity at $2\theta =50.88°$ is compared with that at $2\theta =16.49°$ assuming that these peaks are due to the (300) reflection and the (100) reflection, respectively. The respective intensities are denoted as $I_{(300)}$ and $I_{(100)}$. The numerical values for these reflections and the observed intensities (a.u.) are summarized in Table 1. Inserting these values into eq.(1), the relation

$$\frac{\left|\sum_{j=1}^{N} e^{2\pi i 3u_j}\right|^2}{\left|\sum_{j=1}^{N} e^{2\pi i u_j}\right|^2} = 82, \qquad (3)$$

is obtained. From eq.(3), the number of atoms and the positions of the respective atoms in the unit cell are estimated.

We first notice that the (200) reflection cannot be observed. From this experimental result, the 3-fold stacking of atomic planes along a-axis is not acceptable. The another important result is that the diffraction intensity by the (300) reflections is stronger than that by the (100) reflections. From this result, the 2-fold stacking as well as the 4-fold stacking is not acceptable. Therefore, it is considered that the atom positions in the unit cell are probably formed by the 6-fold stacking along the a-axis. By applying eq. (2) to the (h00) plane, the exponential terms in F_{hkl} can be written by the following equation for (100) plane,

$$\sum_{j=1}^{N} e^{2\pi i u_j} = N_A + \frac{1}{2}N_B - \frac{1}{2}N_C - N_D - \frac{1}{2}N_E + \frac{1}{2}N_F$$

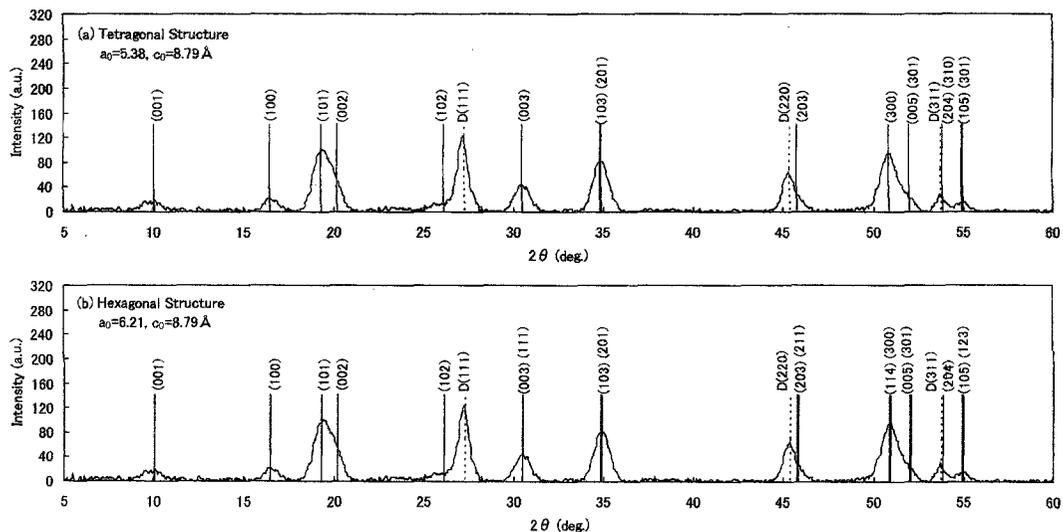$$+ \frac{\sqrt{3}}{2}i(N_B + N_C - N_E - N_F), \qquad (4)$$

Fig. 1   XRD peaks assigned by a tetragonal structure (a) and a hexagonal one (b).

Table I.   Observed XRD intensities for two planes and numerical values for the corresponding planes.

Plane	X-ray Intensity (Experiment)	f	L_P	p
(100)	21.9	29.8	47.3	4
(300)	93.2	22.8	4.2	4

In the same manner, for (200) plane, the following equation is derived,

$$\sum_{j=1}^{N} e^{2\pi i 2 u_j} = N_A - \frac{1}{2}N_B - \frac{1}{2}N_C + N_D - \frac{1}{2}N_E - \frac{1}{2}N_F$$

$$+ \frac{\sqrt{3}}{2} i(N_B - N_C + N_E - N_F) \quad , \quad (5)$$

and for (300) plane, the equation

$$\sum_{j=1}^{N} e^{2\pi i 3 u_j} = N_A - N_B + N_C$$

$$- N_D + N_E - N_F , \qquad (6)$$

is derived. In eqs.(4) ~ (6), N_A, N_B, N_C, N_D, N_E and N_F are the number of atoms in respective stacking planes.

It is impossible to solve eqs. (4), (5) and (6) uniquely, because the number of unknown parameters is larger than that of equations. However, the following results of the diffraction intensities are useful. One is that the (200) reflection is forbidden and another is that the intensity of the (300) reflection is strong. From the former, the relation

$$N_A + N_D = N_B + N_E = N_C + N_F, \qquad (7)$$

is obtained. Then, the eq. (6) is reduced to the following form,

$$\sum_{j=1}^{N} e^{2\pi i 3 u_j} = 3N_A + N_D - 2(N_B + N_F). \quad (8)$$

From the latter, we may assume that

$$N_B = N_F = 0, \qquad (9)$$

Then, the following equations are also derived,

$$N_C = N_E, \qquad (10)$$

$$N_C = N_A + N_D. \qquad (11)$$

Using eqs. (9), (10) and (11), the eqs. (4), (5) and (6) are rewritten as follows,

$$\sum_{j=1}^{N} e^{2\pi i 1 u_j} = -2N_D, \qquad (12)$$

$$\sum_{j=1}^{N} e^{2\pi i 2 u_j} = 0, \qquad (13)$$

$$\sum_{j=1}^{N} e^{2\pi i 3 u_j} = 3N_A + N_D. \qquad (14)$$

From the facts that the intensity of the (100) reflection is not zero and that of the (300) reflection is much stronger than that of the (100) reflection, we can assume that $N_D = 1$. Then, eq. (3) is simplified for only one unknown parameter N_A as follows,

$$\frac{(3N_A + 1)^2}{(-2 \cdot 1)^2} = 82. \qquad (15)$$

From eq (15), the most probable number of 6 is derived for N_A. Then the total number of atoms in the unit cell becomes 21, which is too large and this structure will not be acceptable.

Now, we assume that the diffraction peak at $2\theta = 50.88°$ consists of the (300) reflection and the (114) reflection of the hexagonal structure whose lattice constants are 6.21A and 8.79A. Here, the structure of 6-fold stacking along a-axis is again employed. As we have no information on the distribution of the atoms on each stack, the intensity of the (114) reflection can not be estimated. Therefore, we assume that the intensity of the (114) reflection is stronger twice than that of the (300) reflection, as the multiplicity factor for the former is twice of that of the latter. Then, eq. (15) is replaced by the following equation,

Table II.   Number of atoms, density and filling rate for the diamond structure and those for calculated to the tetragonal and the hexagonal structure.

Crystal Structure	Number of Atoms in the Unit Cell	Density (kg/m^3)	Filling Rate (%)
Diamond	8	5320	33.7
Tetragonal	21	9949	62.8
Hexagonal	12	4926	31.1

$$\frac{\left|\sum_{j=1}^{N} e^{2\pi i 3u_j}\right|^2}{\left|\sum_{j=1}^{N} e^{2\pi i u_j}\right|^2} = 27, \qquad (16)$$

and the most probable number of 3 is derived for N_A. In the present case, the total number of atoms in the unit cell becomes 12.

In deriving eq. (15), we used assumptions that are not justified experimentally. Therefore, other possibilities of combinations of $N_A \sim N_B$ which may explain the observed diffraction intensities. However, the present result leads to the smallest number of the atoms in the tetragonal unit cell. Furthermore, in deriving that N_A =3 in the hexagonal unit cell, we employed the same procedure used for the tetragonal structure. In the case of the hexagonal structure, the intensities of the (003) reflection will not be much stronger than that of the (001) reflection and therefore, other distributions may be probable. However, in this stage, the further discussion on the other possibilities will not lead to any results that are much more reliable as the experimental data are not enough.

The density and filling rate of this structure are calculated for the present tetragonal and hexagonal structures and the results are shown in Table 2. It is shown that the density of the tetragonal structure is about twice of that of

diamond structure, which is not realistic. On the other hand, in the case of the hexagonal structure, this becomes nearly equal. Consequently, it is concluded that the hexagonal structure is strongly suggested from the intensities of X-ray diffraction patterns for the present Ge-nanoparticles.

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