High-pressure structural behavior of nanocrystalline germanium

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Abstract

The equation of state and the I–II transition of nanocrystalline Ge with crystallite sizes 13, 49 and 100 nm have been studied using X-ray diffraction and synchrotron radiation. Whereas the percentage volume collapse at the transition is constant, values of the bulk modulus and the transition pressure increase with decreasing particle size. A model for the structural high-pressure behavior is presented. Since a large fraction of the atoms reside in the grain boundaries, the interface structure plays a significant role in affecting the physical properties of nanocrystalline Ge.

Introduction

The bulk modulus and possible transition pressures for nanocrystalline materials have been extensively investigated in the past decade in order to improve our understanding of the crystal stability and the mechanical properties of nanocrystals. Previous high-pressure studies have indicated correlations between bulk modulus, transition pressure and the crystal size. However, the grain-size effect on e.g. the transition pressure can be of either sign, depending on the system under investigation, as discussed by Jiang (2004) in a recent review paper. The general case seems to be the smaller the crystallites, the higher the transformation pressure, as as exemplified by ZnS, PbS and ZnO (Jiang et al. 1999a, 2000a, 2000b), but there are exceptions from the rule. It was recently found that for AlN (Wang et al., 2004a), CeO$_2$ (Rekhi et al., 2001b; Wang et al., 2001a, b), $\alpha$-Fe (Jiang et al., 2001b) and $\gamma$-Fe$_2$O$_3$ (Jiang et al., 1998), the transition pressures are significantly lower for the nanocrystalline materials than for the corresponding bulk materials. In contrast, no particle-size effect on the transition pressure was observed for SnO$_2$ (Jiang et al., 2001a).
Similarly, the bulk modulus was found to decrease with decreasing grain size for Fe and Cu (Jiang et al., 1999b), Al₂O₃ (Chen et al., 2002; Zhao et al., 2001) and PbS (Qadri et al., 1996). No appreciable change in the value of bulk modulus was found for Ni (Rekhi et al., 2001a), ε-Fe (Chen et al., 2001) and CuO (Wang et al., 2002). On the other hand, the bulk modulus is found to increase with decreasing grain size for nanocrystalline TiO₂ (Swamy et al., 2003), AlN (Wang et al., 2004a), CeO₂ (Wang et al., 2004b), ZnS:Eu (Pan et al., 2001) and γ-Fe₂O₃ (Jiang et al., 1998).

At ambient conditions, Ge crystallizes in the cubic diamond-type structure with space group \( Fd\overline{3}m \) (227). At about 10 GPa it undergoes a semiconductor-to-metal transition, \( \text{I} \rightarrow \text{II} \). The Ge-II modification has a tetragonal structure of the \( \beta \)-Sn type with space group \( I4_1/amd \) (141). Although nanocrystalline germanium is an important semiconductor, little is known about its high-pressure structural behavior and stability. In the present work, we have measured the bulk modulus of Ge-I and studied the pressure-induced Ge-I \( \rightarrow \) Ge-II transition for nanocrystalline Ge with crystallite sizes 13, 49 and 100 nm.

**Experimental**

Nanocrystalline samples were prepared by evaporation in helium atmosphere, using germanium of 99.999 % purity. The evaporated Ge condensed in the form of a fine-grain powder, accumulated on the surface of a cold finger. The material was then stripped off and compacted in vacuum (\( 10^{-3} \) Pa) under a uniaxial pressure of 1 GPa. The average grain size of the as-prepared Ge sample was 13 nm, as determined from X-ray diffraction (XRD) line broadening, using Cu K\( \alpha \) radiation. Samples with average grain size of 49 nm and 100 nm, were obtained by annealing the as-prepared Ge pellets in vacuum (\( 10^{-3} \) Pa) at 473 K for 1h and 10 h, respectively.

![Fig. 1. XRD spectra; e = escape peaks.](image)
In situ high-pressure, energy-dispersive XRD spectra up to a maximum pressure of about 35 GPa were recorded at Station F3 of HASYLAB in Hamburg, Germany. These experiments were performed at ambient temperature using a Syassen-Holzapfel type diamond-anvil cell. The powder samples were placed in a 300 μm diameter hole of an inconel gasket, using a 4:1 methanol:ethanol mixture as the pressure transmitting medium. The actual pressure was measured by the ruby fluorescence method, using the non-linear pressure scale of Mao et al. (1986). The Bragg angle for each run was determined from a zero-pressure diffraction pattern of NaCl, situated in the pressure cell.

**Results and discussion**

XRD spectra recorded at different pressures during a compression run for 100 nm Ge are shown in Fig. 1. The Ge-I → Ge-II transition at about 10 GPa is clearly seen. The indices of the most prominent diffraction peaks of Ge-I and Ge-II are given in the figure. From the observed diffraction spectra, lattice parameters and unit-cell volumes have been derived and refined by standard crystallographic techniques. The experimental pressure-volume data can then be described by the Birch-Murnaghan equation of state (Birch, 1938; 1947):

\[
P = \frac{2}{3} B_0 (x^{-7/3} - x^{-5/3}) \left\{ 1 + \frac{3}{4} (B_0' - 4)(x^{-2/3} - 1) \right\},
\]

where \( x = V/V_0 \), \( V \) is the volume at pressure \( P \), \( V_0 \) is the volume at zero pressure, and \( B_0 \) and \( B_0' \) are the isothermal bulk modulus and its pressure derivative, both parameters evaluated at zero pressure.

![Fig. 2. Compression curves. Left: Ge-I. Right: Ge-I and -II, showing volume collapse at the transition.](image)

Fig. 2 shows the compression curves. Values of \( B_0 \) and \( B_0' \) have been obtained from a least-squares fit of Eqn. (1) to the experimental pressure-volume points for Ge-I (left figure). It is seen (right figure) that the volume change, \(-\Delta V/V\), at the phase transition is about 17%.
The value of the transition pressure, \( P_{tr} \), for each particle size has been determined by plotting the intensity ratio:

\[
\frac{[I(200) + I(101)]_{\text{Ge-II}}}{[I(111) + I(220)]_{\text{Ge-I}}}
\]  

(2)

and extrapolating the steep part of the curve to zero intensity as shown in Fig. 3.

![Fig. 3. Intensity ratio versus pressure](image)

Table 1 summarizes the experimental results. The bulk modulus and the transition pressure are strongly affected by the crystal size, whereas the lattice constant is only slightly affected, and the volume change, \( \Delta V/V \), at the Ge I → Ge II transition is practically size-independent. Moreover, it should be noticed that the differences between the 100 and 49 nm samples are small, but the size-dependence is enhanced for the 13 nm sample. Several authors have reported a critical size around 20 nm (Villain et al., 2002; Shen et al., 1995; Zhou et al., 2003), below which interface contributions become significant.

Table 1. Summary of experimental results. \( a_0 \) is zero-pressure lattice constant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a_0 ) (Å)</th>
<th>( B_0 ) (GPa)</th>
<th>( P_{tr} ) (GPa)</th>
<th>( -\Delta V/V ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>5.6576(^a)</td>
<td>75(^b)</td>
<td>8.0(5)(^c) – 10.5(2)(^d)</td>
<td>19.4(9)(^c)</td>
</tr>
<tr>
<td>100 nm</td>
<td>5.660(2)</td>
<td>88(3)</td>
<td>11.5(3)</td>
<td>17.5(3)</td>
</tr>
<tr>
<td>49 nm</td>
<td>5.659(3)</td>
<td>92(3)</td>
<td>12.4(3)</td>
<td>17.3(3)</td>
</tr>
<tr>
<td>13 nm</td>
<td>5.645(5)</td>
<td>112(3)</td>
<td>16.4(3)</td>
<td>17.3(3)</td>
</tr>
</tbody>
</table>

\(^a\)PDF#5-545; \(^b\)McSkimmin and Andreatch, 1963; \(^c\)Baublitz and Ruoff, 1982; \(^d\)Qadri et al., 1983.
The Stillinger-Weber (1985) two-body interatomic potential can be written:

\[ u = 2\varepsilon A [B \left( \frac{r}{\sigma} \right)^{-4} - 1] \exp \left[ \left( \frac{r}{\sigma} - 1.8 \right)^{-1} \right] \]  

(3)

where \( r \), the spacing of nearby atoms, is the one and only parameter determining \( u \). Values of the parameters \( \varepsilon, \sigma, A \) and \( B \) for Ge are given by Ding and Andersen (1986).

![Diagram](a) ![Diagram](b)

Figure 4. (a) A given spherical region with diameter \( D_{0s} \) in an infinite volume; (b) The corresponding free particle with diameter \( D_s \). The diameter \( D_{0s} \) is shown by the broken circle.

First, we will focus on the grain size effect on surface energy. Consider a spherical region with diameter \( D_{0s} \) and lattice parameter of \( a_0 \) in an infinite volume of Ge, as shown in Fig. 4(a). The total potential energy of the sphere is given by

\[ U_{0s} = 8 \frac{4\pi}{3} \left( \frac{D_{0s}}{2} \right)^{3} u_{0} = \frac{4\pi}{3} \left( \frac{D_{0s}}{a_0} \right)^{3} u_{0} \]  

(4)

where \( u_{0} \) is the average potential energy per atom and can be derived from Eqn. (2). If we separate this sphere from the infinite volume, surface energy will change the potential energy and the interatomic distance. As a result, also the diameter of the sphere will change. For a nanometer sized particle one can show that the following relation is valid:

\[ \frac{1}{4} a_{0,n}^{2} \gamma_{n} = \frac{1}{4} a_{0,B}^{2} \gamma_{B} + \frac{D_{s}}{3a_{0,n}} (u_{B} - u_{n}) \]  

(5)

where indices \( B \) and \( n \) refer to bulk and nanocrystals, respectively. For bulk Ge-I one has the surface energy \( \gamma_{B} = 589 \text{ mJ/m}^{2} \) (CRC Handbook of Chemistry and Physics, 1988–89). The corresponding energies, \( \gamma_{n} \), for the 49 and 13 nm samples can now be calculated as 589 and 585 mJ/m\(^2\), respectively. Thus, grain size has only a minor influence on the surface energy of the low-pressure phase.

As suggested by Jiang (2004), the effect of grain size on the transition pressure is governed by three factors: (i) the volume collapse at the transformation pressure, (ii) the surface
energy difference, and (iii) the internal energy difference between the phases involved. The equation can be written

\[ P_n - P_B = P_B \left( \frac{\Delta V_B(P_B)}{\Delta V_n(P_n)} - 1 \right) + \frac{U_{\text{surf}}(2, P_n) - U_{\text{surf}}(1, P_n)}{\Delta V_n(P_n)} + \frac{(U_B(1, P_B) - U_B(1, P_n)) - (U_B(2, P_B) - U_B(2, P_n))}{\Delta V_n(P_n)} \]

(6)

where indices \( B \) and \( n \) refer to bulk and nanocrystals, respectively. \( P \) is the transition pressure, and \( \Delta V \) is the volume change at the transition. \( U \) and \( U_{\text{surf}} \) are the internal energies of core and interface, respectively. The numbers 1 and 2 indicate the low- and high-pressure phases, respectively. The last term of Eqn. (5) can be calculated by the integral:

\[ U_B(i, P_B) - U_B(i, P_n) = -\int P dV ; i = 1, 2, \]

(7)

using the experimental pressure-volume data. \( U_{\text{surf}} = \gamma A N \), where \( \gamma \) is the average surface energy, \( A \) is the surface area of the crystal, and \( N \) is the number of the crystals per mole. The results of the calculations are listed in Table 2. The experiments have shown (Table 1) that the volume collapse is practically independent of the grain size. Thus, Term 1 is small, as seen in Table 2. Term 3 is found to be small and negative. It follows from Term 2 that the surface energy difference between Ge-I and Ge-II is the main factor that determines the enhancement of the transition pressure. The surface energy of Ge-II is found to be size dependent and about four times larger than that of Ge-I.

In Eq. (5), the volume-pressure relationship is assumed to be similar for bulk and nanophase material. However, as shown in Fig. 2, the compressibility depends on grain size. Thus, Eq. (6) needs to be modified as

\[ U_B(k, P_B) - U_B(k, P_n) = U_B(k, P = 0) - \int P(k, B) dV \bigg|_{P=0}^{P_B} - (U_a(k, P = 0) - \int P(k, n) dV \bigg|_{P=0}^{P_n}) \]

\[ \text{for } k = 1, 2. \]

(8)

If \( U_B(k, P = 0) \) and \( (U_a(k, P = 0) \) – the internal energies of bulk and nanocrystalline Ge at zero pressure – are equal, then the revised version of Eq. (5) can be simplified as

\[ P_n - P_B = P_B \left( \frac{\Delta V_B(P_B)}{\Delta V_n(P_n)} - 1 \right) + \frac{U_{\text{surf}}(2, P_n) - U_{\text{surf}}(1, P_n)}{\Delta V_n(P_n)} \]

\[ + \left( \int P(1, n) dV \bigg|_{P=0}^{P_n} - \int P(1, B) dV \bigg|_{P=0}^{P_B} \right) - \left( \int P(2, n) dV \bigg|_{P=0}^{P_n} - \int P(2, B) dV \bigg|_{P=0}^{P_B} \right) \]

\[ \Delta V_n(P_n) \]

(9)

The results of these calculations are summarized in Table 2.
Table 2. Detailed parameters in calculations of surface energies for the high pressure Ge-II phase

<table>
<thead>
<tr>
<th>Sample</th>
<th>Term 1 (GPa)</th>
<th>Term 2 (GPa)</th>
<th>Term 3 (GPa)</th>
<th>γ (Ge-I) J/m²</th>
<th>γ (Ge-II) J/m²</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>49 nm</td>
<td>0.14</td>
<td>0.99</td>
<td>-0.23</td>
<td>0.589</td>
<td>1.99</td>
<td>(6)</td>
</tr>
<tr>
<td>49 nm</td>
<td>0.14</td>
<td>1.10</td>
<td>-0.34</td>
<td>0.589</td>
<td>2.14</td>
<td>(9)</td>
</tr>
<tr>
<td>13 nm</td>
<td>0.23</td>
<td>6.14</td>
<td>-1.47</td>
<td>0.585</td>
<td>2.88</td>
<td>(6)</td>
</tr>
<tr>
<td>13 nm</td>
<td>0.23</td>
<td>5.69</td>
<td>-1.29</td>
<td>0.585</td>
<td>2.81</td>
<td>(9)</td>
</tr>
</tbody>
</table>

It should be noticed that the XRD signal originates from the coherent core region of the grains. Grain boundaries most likely contain defects and to be highly disordered in nanostructured materials (Gleiter, 2000). Thus, lattice parameters and the unit-cell volumes estimated from the XRD measurements refer to the coherent regions of the grains. The bulk modulus in the present work is deduced from the cell volume vs. pressure relationship, which might be different from that of the true sample volume vs. pressure. Strain gradients are strong near interfaces. Thus, the lattice parameter might be varying in the grain, and the bulk modulus should be considered a weighted mean value of the whole grain.

In our Ge samples there are about 43 and 11 atomic layers for the 49 and 13 nm grain sizes, respectively. Two models for the lattice parameter distribution in a grain are suggested here: (1) the lattice parameter changes linearly from the core to the boundary in a grain, and (2) the lattice parameter is different in the outermost layer only, while it is the same as for bulk Ge in the interior of the grain.

In model (1), the change of the lattice constant between the adjacent layers was estimated as 0.0000314 and 0.00174 Å for 49 and 13 nm Ge, respectively. In model (2), the lattice parameters in outermost layer differ by 0.01484 and 0.06280 Å as compared to the bulk for 49 and 13 nm Ge, respectively. For both models, the bulk modulus is found to increase with decreasing grain size. However, the differences between the experimental values and the estimated theoretical ones are still large.

The bulk modulus is closely linked with the spacing of nearby atoms. In contrast to most other elements, tetrahedral Ge-I shrinks when it melts (Glazov et al., 1969). It has been reported that the structures of the highly-constrained grain boundaries, triple lines and point grain junctions in nanocrystalline Si are highly disordered and similar to the structure of amorphous Si (Keblinski et al., 1997a, b). The structure of Ge might be similar to the one of Si. Thus, the density of the grain boundary regions should be larger than the density of the crystalline material, as shown by molecular dynamics simulations (Keblinski et al., 1997a). This may cause a compression force on the core of the grain, resulting in a decrease of the lattice parameter, which is consistent with the experimental observations (cf. Table 1).
Consequently, the compressibility of a grain decreases, i.e. the bulk modulus increases, with decreasing grain size. More studies are needed, however, in order to arrive at a quantitative explanation of the enhancement of the bulk modulus for nanocrystalline Ge.

Conclusions

We have studied the equation of state and the I→II transition of nanocrystalline Ge with crystallite sizes 13, 49 and 100 nm. It is found that the smaller the particles, the higher the bulk modulus and the transition pressure. The influence on the transition pressure and bulk modulus is particularly strong when the grain size is below a critical value of about 20 nm. Surface energy differences between the phases involved can explain the increase of the transition pressure for the nanocrystalline material. The enhancement of the bulk modulus is attributed to compression effects due to the amorphous grain boundary regions in the nanophase material.

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