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QUENCHABLE HIGH-PRESSURE PHASES FROM NON-CRYSTALLINE GERMANIUM

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Quenchable products from high-pressure experiments (up to 140 kbar) on non-crystalline Ge of varying density ($\rho = 4.8-6.0 \text{ g/cm}^3$), yield widely different results, depending on the density of the starting non-crystalline materials.

1. Introduction

The resistivity of non-crystalline Ge prepared by three different methods has been measured as a function of hydrostatic pressure to 28 kbar [1].

A pressure-induced semiconductor-metal transition has been reported for non-crystalline Ge [2-3]. It occurs at a lower pressure than the semiconductor-metal transition in crystalline Ge [4]. The metallic conduction found for the non-crystalline material between 60 and 100 kbar was ascribed to a new non-crystalline phase which, on further pressurization above 100 kbar, was thought to crystallize to the β -Sn-type structure. A similar phase has been reported for non-crystalline InSb [5]. The densification of non-crystalline Ge having a starting density lower than that of crystalline Ge, has been studied to 20 kbar; no crystallization of Ge I was found over this pressure range [6].

The phase diagram of crystalline Ge remains uncertain. Substantial differences exist between results obtained for samples quenched after long runs [7,8] and most other results [9,10].

It was decided to perform high-pressure quenching experiments on samples of non-crystalline Ge having a range in density, all prepared by sputtering techniques. The present experiments were not made to determine the position of any phase

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boundaries, but rather to illustrate differences in behavior between crystalline Ge and non-crystalline Ge of different starting densities.

2. Experimental

The non-crystalline Ge used was prepared using a turbo-pumped Ultek 3140-65 sputtering device. The hot-pressed Ge target had a purity of 99.9996%. The films (thickness 15–30 μm) were deposited on glass microscope slides in a 20 μm Ar atmosphere with a target to substrate distance of 52 mm. The high-density films were prepared with the substrate biased, so that $\approx 20\%$ of the RF voltage applied to the target was applied to the substrate. Densities were determined using a weight geometry technique with an accuracy of $\pm 0.3 \text{ g/cm}^3$. Film thickness was determined using a broken edge under an optical microscope.

Prior to the high-pressure experiments the non-crystalline Ge was scraped off the glass substrate and ground. The low and average density non-crystalline Ge films remained non-crystalline after this treatment. However, the high-density non-crystalline Ge showed slight crystallization of Ge I after grinding (fig. 1), but the bulk of the material remained clearly non-crystalline.

Pressure was generated in opposed anvil devices. The experimental technique has been described elsewhere [7]. Anvils with a working face diameter of 6.35 and 4.76 mm were used. The samples were contained in nickel rings and covered with discs of platinum 10% rhodium foil. At all times care was taken to ensure favorable diameter/thickness ratios [11]. Temperatures were obtained using split furnaces, and temperature was measured using chromel/alumel thermocouples wrapped around the sample position but not pinched by the anvils. The products were examined using X-ray diffraction techniques. The quenching procedure was to drop temperature while

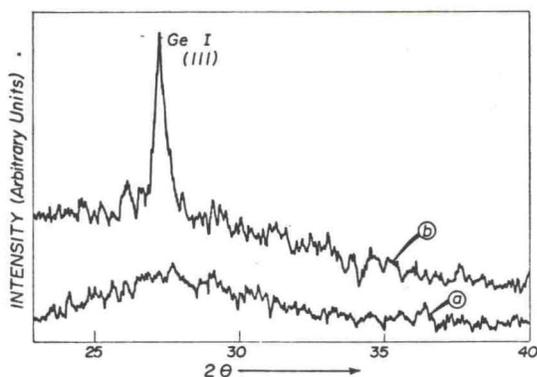


Fig. 1. Portions of X-ray diffraction traces made using $\text{CuK}\alpha$ radiation to illustrate the partial crystallization of high-density non-crystalline Ge by grinding. (a) Prior to grinding, (b) after grinding.

holding pressure constant, using an air blast to cool the sample-anvil composite. When room temperature was reached the pressure was released quickly. No shear was used during any of the present experiments. Run times were a minimum of 24 h and a maximum of 150 h.

3. Results

The results obtained depend strongly on which density the non-crystalline Ge had prior to the run. Runs made on low ($4.8 \pm 0.3 \text{ g/cm}^3$) and average ($5.3 \pm 0.3 \text{ g/cm}^4$) density non-crystalline Ge yielded similar results. These results are shown in fig. 2. The solid lines are the proposed phase boundaries from ref. [8].

From fig. 2 the following trends are evident. The application of pressure at room temperature was sufficient to produce firstly crystallization of Ge I and subsequently Ge III in increasing yields at higher pressures. However, the yields of Ge III are

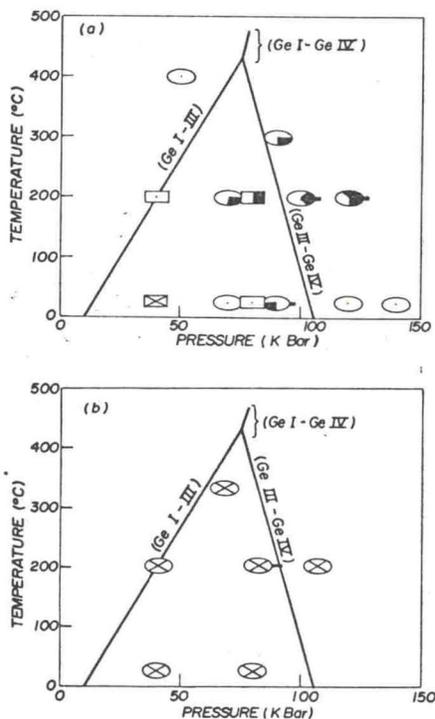


Fig. 2. Present results obtained for non-crystalline Ge of various densities. Phase boundaries from ref. [8]. (a) Average density: ○ Ge I; ● Ge III; ○— Ge IV. Low density: □ Ge I; ⊗ starting materials + small growth Ge I; ■ Ge III. (b) High density: ⊗ no change; ⊙ Ge IV + slight amount Ge I + non-crystalline Ge.

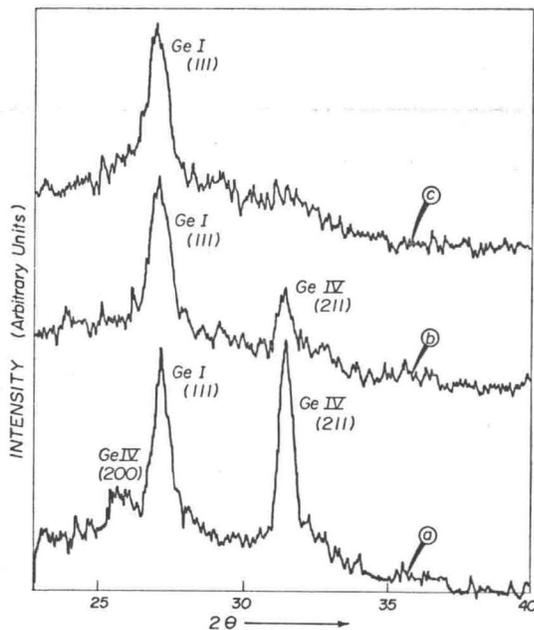


Fig. 3. Portions of X-ray diffraction traces made using $\text{CuK}\alpha$ radiation illustrating the transformation from Ge IV to a non-crystalline product. Note that the Ge I peak does not increase in intensity, whereas the broad non-crystalline background does. (a) immediately after run, (b) after ≈ 48 h at ambient conditions, (c) after ≈ 150 h at ambient conditions.

substantially lower than those obtained for crystalline Ge when subjected to the same conditions [7,8]. Small amounts of Ge IV were detected after treatment at 90 kbar and room temperature.

Fig. 2 also shows the results obtained at higher temperatures at various pressures. These experiments essentially produced higher yields of Ge III in the lower pressure region, and these results agree with the earlier results obtained for crystalline Ge [7,8]. However, Ge III and Ge I were also found well into what was thought to be the stability field of Ge IV [8]. Ge IV was only found in very low concentrations.

Previously [8] Ge IV was reported to transform at atmospheric pressure to an amorphous product over a period of 3 h. Bates [8] used a dry-ice cooling technique to prevent this transformation. In the present work this transformation was confirmed, but no special cooling was used as this transformation was spread out over a number of days. Fig. 3 illustrates the process.

The products obtained when using a high-density ($6.0 \pm 0.3 \text{ g/cm}^3$) non-crystalline Ge are substantially different. Table 1 lists the results obtained and fig. 2 shows them in relation to the boundaries obtained for crystalline Ge. The most significant feature is that Ge III was never obtained in any run done on the high-density non-crystalline Ge. After treatment at room temperature and up to 80 kbar, no increase in Ge I con-

Table 1
Products obtained with the use of non-crystalline Ge.

Pressure (kbar)	Temperature (°C)	Run time (h)	Product after quenching
<i>High density</i>			
40	25	96	no change
80	25	96	no change
40	200	150	no change
80	200	72	no change
80	200	96	Ge IV + slight Ge I + non-crystalline Ge
106	200	24	no change
68	330	24	no change
<i>Average density</i>			
50	400	24	Ge I
70	25	53	Ge I
70	200	24	Ge I + Ge III
90	25	24	Ge I + Ge III and Ge IV
90	300	24	Ge I + Ge III
100	100	53	Ge I + Ge III
100	200	53	Ge I + Ge III + Ge IV
120	25	24	Ge I + Ge III
120	200	24	Ge I + Ge III + Ge IV
140	25	53	Ge III + Ge I
<i>Low density</i>			
40	25	96	Starting material + small growth Ge I
40	200	96	Ge I
80	25	96	Ge I
80	200	96	Ge III + Ge I

centration was found beyond that formed by the grinding process prior to the runs. The non-crystalline nature persists even after treatment at 106 kbar, 200°C for 24 h, or after treatment at 68 kbar, 300°C for 24 h. The phase Ge IV was encountered in certain run products but was not consistent in its appearance.

4. Discussion

The present results on low and average density non-crystalline Ge are in essential agreement. These results are also generally consistent with earlier work [2,3,6-8] on crystalline and non-crystalline Ge in the low-pressure region.

Ge IV is known to be very slow in forming and previously at least 48 h were required for it to form from crystalline Ge. The present experiments, although being of the same duration or somewhat longer, did not utilize the special dry-ice quenching technique. Perhaps partly for this reason and partly for the fact that any crystal-

lization for non-crystalline material can be a very sluggish process, as evidenced by the behavior of the high-density starting material, Ge IV was inconsistent in its appearance in this work. The proposed Ge III–IV boundary [8] was based on a large number of experiments and the present experiments on non-crystalline material can hardly confirm or disprove the previously proposed boundary. However, the very appearance of Ge III and Ge IV in the present work supports their presence, if not their precise placement, in the phase diagram. The stability field of Ge IV requires further study, especially its relationship with that of Ge II; an earlier proposal [8] placed Ge II metastable to Ge IV over a wide pressure range. Clearly in situ X-ray diffraction measurements after significantly long times at high pressure and low to high temperatures would be of value, but kinetic barriers at low temperatures could well resist the dictates of thermodynamics.

The results obtained for the high-density ($6.0 \pm 0.3 \text{ g/cm}^3$) non-crystalline Ge seem to be a direct consequence of the high starting density. Table 2 shows the densities of all possible high-pressure phases, and it is evident that the density of the starting material is higher than or equal to that of Ge III or Ge IV, within the experimental errors involved in the determination of the density of the non-crystalline Ge.

From the present results it appears that the following processes variously affect the behavior of non-crystalline Ge: mechanical grinding involving friction between particles and causing within particles fractures and shears that are coarse or sparse on an atomic scale; internal compaction under high pressures creating fractures and shears that are very extensive on an atomic scale. Mechanical grinding apparently releases sufficient strain energy to initiate partial crystallization of Ge I from the high-density, non-crystalline Ge. The low-density, non-crystalline Ge probably has less strain energy related to it, and hence when it is ground no crystallization occurs. However, upon compression, continuous microscopic strains occur on an atomic scale within the low-density non-crystalline Ge, resulting in an increase in its density [6], and the $P dV$ energy related to this over $\approx 100 \text{ kbar}$ would be $\approx 4.8 \text{ kcal/mol}$. This energy is apparently sufficient to overcome the activation energy related to the formation of Ge III or the new metallic non-crystalline form [2,3]. For the high-

Table 2
Densities of high-pressure phases of crystalline Ge and non-crystalline Ge.

Phase	Density (g/cm^3)	Remarks
Ge I	5.325	—
Ge II	7.51	from in situ crystallographic data [12]
Ge III	5.89	from crystallographic data on quenched phase
Ge IV	5.846	from crystallographic data on quenched phase
low-density non-crystalline Ge	4.8 ± 0.3	from weight geometry measurements
average density non-crystalline Ge	5.3 ± 0.3	from weight geometry measurements
high-density non-crystalline Ge	6.0 ± 0.3	from weight geometry measurements

density Ge no such change occurs as the $P dV$ energy obtained upon compression is probably far less due to the initial high density.

The structural features of the high-density non-crystalline Ge are not yet known.

Two other possible sources of a high-density non-crystalline Ge exist. Firstly the metallic form thought to exist between 60 and 100 kbar [2,3]. Resistivity measurements on the present material confirm that the high-density, non-crystalline Ge is semiconducting and so these two forms are not compatible. Secondly, Ge IV transforms to an amorphous product at ambient conditions. It would be of interest to compare the structural features in the present materials with the aforementioned to obtain an understanding of the mechanism for increasing the density above that of Ge I, and how this is achieved in the sputtering process.

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