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CRYSTALLIZATION OF AMORPHOUS GERMANIUM INVESTIGATED BY X-RAY ABSORPTION SPECTROSCOPY

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Amorphous and partially crystallized Ge films were investigated by X-ray absorption spectroscopy (XAS). The aim of the investigation was threefold. On the one hand we wanted to study the structure of amorphous Ge and the reasons for the reduced density observed in a-Ge. Furthermore, we wanted to investigate the influence of the method of production, of the substrate and of the substrate temperature on the structure and degree of crystallization of the Ge films. Finally, we wanted to find out how accurately interatomic distances and coordination numbers can be determined by means of EXAFS.

In this paper we have investigated Ge films which were produced by evaporation of high purity Ge (99.999 %) and by plasma decomposition of GeH₄. The substrates used were Al, anodically oxidized Al (called Al₂O₃ in the following) and Kapton. All substrates had a thickness of 25 μm and were free of pinholes or cracks. The temperature of the substrates could be varied between 20 °C and 450 °C. The evaporation rate was 40 Å/sec. The evaporation time was always 30 minutes resulting in film thicknesses of 7 to 8 μm. Details of the sample preparation are given in reference /1/. All samples were investigated by X-ray diffraction using CuKα radiation. In a-Ge two broad peaks were observed out of which grew at higher substrate temperatures the reflections Ge(lll), (220) and (311). Above 220 °C the reflections Ge(400), (331) and (422) are also observed in the angular range investigated. From the width of the Bragg peaks we have deduced a mean diameter of the crystallites of 190 Å at Tₛ = 230 °C and of 330 Å at Tₛ = 273 °C in a-Ge deposited on Al₂O₃. In the fully crystallized samples (Tₛ = 442 °C) the mean diameter of the crystallites was 640 Å. It is noteworthy that the crystallites have immediately a relatively large size (190 Å) as soon as they can be observed in diffraction. This confirms earlier observations /2,3/. The volume fraction of crystallized material could not be deduced from the area under the reflections due to the strong texture of the evaporated films. Thus we have evaluated the intensity of the amorphous background in those angular ranges where no Bragg peaks show up. Figure 1 gives the volume fraction γ of crystallized Ge in films evaporated on Al₂O₃. Crystallization starts in this case at 220 °C and ends at 290 °C. The better heat conductivity of Al as substrate shifts the crystallization by 9 °C to higher temperatures compared to Al₂O₃. Evangelisti et al /3/ investigated 1 μm thick Ge films on glass. They observed crystallization between 240 and 290 °C.
Figure 1:
Volume fraction $\gamma$ of crystallized Ge evaporated on $\text{Al}_2\text{O}_3$ at substrate temperatures $T_s$ deduced from X-ray diffraction (+) from $\text{N}_2$ (v), $\text{N}_3$ ($\Delta$), from $\delta\sigma_1(0)$ and from the Ge K edge (○).

The X-ray absorption measurements were carried out at the ROEMO beam line of the Hamburger Synchrotronstrahlungs labor with a Si(311) double crystal monochromator and an energy resolution of 1.9 eV FWHM at the Ge K edge. Higher harmonics were eliminated by detuning the two crystals in the monochromator. The temperature of the samples was 77 K for all measurements.

Figure 2:
Fourier transforms of the EXAFS $\chi \cdot k^2$ for c-Ge ($T_s = 442 \, ^\circ\text{C}$) and a-Ge ($T_s = 25 \, ^\circ\text{C}$). Figure 2 shows the Fourier transform of $\chi \cdot k^2$ for c-Ge ($T_s = 442 \, ^\circ\text{C}$) and a-Ge ($T_s = 25 \, ^\circ\text{C}$). In c-Ge the first 12 shells are visible. In a-Ge only the first one contributes to the signal. Note the reduced amplitude of the first shell in a-Ge. We have fitted the signal of a-Ge by means of the phases and amplitudes deduced from c-Ge.

A total of 29 amorphous samples have been measured in order to determine the influence of systematic errors in the sample preparation, the data collection and data analysis. The results are summarized in table 1.
Table 1: Interatomic distance $r_1$, coordination number $N_1$ and Debye-Waller factor for the first shell in a-Ge.

<table>
<thead>
<tr>
<th></th>
<th>c-Ge (77 K)</th>
<th>a-Ge (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1 (\AA)$</td>
<td>2.447</td>
<td>2.448 ± 0.003</td>
</tr>
<tr>
<td>$N_1$</td>
<td>4</td>
<td>4.00 ± 0.04</td>
</tr>
<tr>
<td>$\delta r_1^2 (\AA^2)$</td>
<td>0</td>
<td>0.00180 ± 0.00015</td>
</tr>
</tbody>
</table>

These results allow the following conclusions:

i) It is possible to achieve an accuracy of 0.1 % in the determination of interatomic distances and of 1 % for coordination numbers by means of EXAFS. The usual accuracies achieved in $N_1$ are more like 10 %. The only other publication in which an accuracy of 1 % in the determination of $N_1$ was achieved is that of Stern et al. /4/, also for a-Ge. This accuracy can only be achieved when great care is taken in avoiding systematic errors. Good quality data need low harmonic content in the monochromized beam, samples of optimum thickness ($\mu d = 1$, for concentrated systems) and samples homogeneous in composition and thickness. Pinholes and cracks are especially worrying. In the case of amorphous Ge, crystalline Ge is an excellent model compound from which excellent amplitudes and phases can be deduced. This reduces systematic errors in the data analysis.

ii) From the data quoted in table 1 the following conclusions concerning the structure of a-Ge (produced by evaporation and by plasma decomposition) can be drawn:

The values of $r_1$ and $N_1$ in a-Ge being within 0.1 % and 1 %, respectively, identical with those in c-Ge, the concentration of vacancies in a-Ge cannot exceed 1 % and that of divacancies cannot exceed 0.5 % in a-Ge. Therefore, vacancies and divacancies cannot be responsible for the reduced density of a-Ge (typically 9 % for $T_s = 20$ °C) as was suggested by Cargill /5/ on the basis of small angle X-ray scattering. When the density reduction is real, voids of larger than atomic size must be present. We have estimated the minimum radius of the voids to be 14 Å. This is in contrast to the data by Paul et al /6/, but not to those of Cargill /5/. On the other hand, Cargill found too low a density of voids. More systematic density data and further small angle scattering data on a-Ge are needed.

The fact that the second coordination shell is not visible in the EXAFS of a-Ge (figure 2) allows one to determine the minimum smearing in the tetrahedral bond angle /7/. We have deduced a value of 9° r.m.s. compared to 7° found by Exafs /7/ and to 10° found in X-ray diffraction /6/.

It turned out that the crystallization of amorphous Ge films depends very sensitively on the method of preparation of the films, on the type of substrate and on the substrate temperature. For 25 μm Kapton foils crystallization is already completed at 220 °C. For Al and Al$_2$O$_3$ (each 25 μm thick) the films are still completely amorphous. Here crystallization occurs between 220 and 300 °C. This holds for evaporated films. Films produced by plasma decomposition of GeH$_4$/H$_2$ mixtures on Al are still completely amorphous at 350 °C. In the following we will confine ourselves to films deposited by evaporation on Al and Al$_2$O$_3$. Figure 2 shows the Fourier transforms of $\chi \cdot k^2$ for 6 Ge films with substrate temperatures between 25 and 442 °C. It is noteworthy that as soon as the second and third shells are visible all higher shells (up to the 12th) show also up. This supports the result obtained in X-ray diffraction mentioned above that the crystallized regions have a rather
large size as soon as they appear. We have deduced four quantities from the absorption spectra which show the degree of crystallization. These are the effective number of neighbors for the second and third shell, the Debye-Waller factor of the first shell and the shape of the Ge K-edge. As shown by Parsons and Balluffi /2/ and by Stern et al /4/ the crystallized material forms islands of crystalline Ge in an amorphous matrix. The amorphous matrix gives no contribution to the second and third shell. The effective coordination numbers of the second and third shells in figure 2 can therefore be written as 12 times the volume fraction $\gamma$ of crystallized material (the coordination numbers $N_2 = N_3 = 12$ in c-Ge).

Figure 1 gives the volume fraction $\gamma$ deduced from the second and third neighbor contributions. The values for the distances of the second and third neighbors agree within 0.15% with those of c-Ge. The volume fraction of crystallized material can also be deduced from the Debye-Waller factor of the first shell. For a-Ge $\delta q^2_\text{eff} = 0.00180 \, \text{Å}^2$ (table 1). For c-Ge $\delta q^2_\text{eff} = 0$. Using the approximation

$$
\delta q^2_\text{eff}(T_s) = (1 - \gamma(T_s)) \, \delta q^2_1 \alpha
$$

we have obtained the values $\gamma$ given in figure 1.

As shown by Proietti et al /8/ disorder in the Ge lattice changes the shape of the Ge K-edge. An increasing spread in $r_2$ and $r_3$ smears out the shoulder at the high energy side of the edge. This effect can be used to determine $\gamma$. The data are again plotted in figure 1. The accuracy achieved is 5%. Note the excellent agreement in $\gamma$ determined by the four different methods explained above. Crystallization of Ge films evaporated on Al and Al$_2$O$_3$ occurs between 220 and 300 °C. The better heat conductivity of Al shifts the crystallization upwards by 8 °C compared to Al$_2$O$_3$, a value very similar to that found in X-ray diffraction. Note also the great similarity in the dependence of $\gamma$ on $T_s$ found in X-ray diffraction and in X-ray absorption. This is further evidence showing that the crystallized area have a rather large extension (190 Å) right from the beginning of their formation.

REFERENCES


