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EXAFS INVESTIGATION OF AMORPHOUS-TO-CRYSTAL TRANSITION IN Ge

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The structure of a-Ge as a function of the deposition temperature T_s has been studied by the EXAFS technique for the first time. The results demonstrate the sensitivity of EXAFS to structural differences in the medium range. The data provide strong evidence for a continuous transition from the amorphous to the crystalline phase over a temperature interval from 130°C to 300°C. The analysis of the data is in line with the microcrystal model of amorphous Ge films and allows an estimate of the average grain size for the lower range of T_s used.

It is customary to assume that Si and Ge films, grown below a critical temperature T_c, are virtually amorphous. As a matter of fact, the radial distribution function, as determined by X-ray or electron diffraction analys s, does not show any systematic variation with the method of preparation nor with such parameters as substrate temperature, rate of deposition, pressure, etc. /1/. However, diffraction techniques do not allow direct and reliable detection of structural differences over distances less than 15÷20 Å. As a consequence, although the localization and coordination of the nearest neighbours are well known, it has proven a difficult task to ascertain how, from this local structure, one arrives at the long range disorder characteristic of amorphous materials. The understanding of what could be called the medium-range structure (i.e. over distances larger than the tetrahedral unit but less that about 20 Å) is therefore at a rather primitive level /2/. The above mentioned features render the study of the transition from amorphous to crystalline material as a function of deposition temperature T_s rather difficult. Although several investigations have been made in the past using a variety of techniques /3/, the results concerning the temperature of crystallization T_c and the nature of the transition process are often contradictory.

In the present letter we report the first investigation of amorphous Ge films as a function of T_s by analysis of the Extended X-ray Absorption Fine Structure (EXAFS). Applicability of the EXAFS technique to crystalline and amorphous Ge has been shown feasible by other investigators /4/. The aim of the work is twofold. First, we want to verify that EXAFS is more sensitive than diffraction techniques to differences in the medium-range structure. Second, if this is the case, we intend to follow in detail the amorphous to polycrystal transition in order to establish whether there is a continuous structural change as a function of T_s or rather an abrupt transition at a given temperature T_c. A possible interpretation of the experimental findings is briefly outlined, while a thorough discussion is left to a more extended paper to be published separately.

The Ge films have been grown by thermal evaporation of Ge single crystals in vacuum of 10^{-6} Torr on < 111 > Si substrates. The range of

uncertainty in the deposition temperature was $\pm$ 10°C. The sample thickness ranged from 4 to 7 μ m, with a deposition rate of about 5 μ m/hr. In such conditions phase diagrams for epitaxial deposition of Ge which point to a crystallization temperature T_c =250°C have been obtained in the past using electron diffraction /5/. All EXAFS measurements have been performed at liquid nitrogen temperature at the PULS X-ray acility of the ADONE storage ring of the Frascati Laboratories. Details of the experimental setup and data processing have been published elsewhere /6/.

Structural information can be obtained from the oscillatory part of the X-ray absorption coefficient $\mu(k)$ above the K-edge /7/ by subtracting the smoothly varying contribution $\mu_o(k)$ and by defining the normalized interference term $\chi(k) = (\mu(k) - \mu_o(k))/\mu_o(k)$ which is the EXAFS. Neglecting multiple-scattering effects between atoms, $\chi(k)$ can be expressed as /7/

$$\chi(k) = \frac{m_e}{4\pi^2 \hbar^2 k} \sum_j t_j(2k) .$$

$$\int \cdot \frac{e^{-\frac{2r_j}{\lambda}}}{r_j^2} \sin(2kr_j + \delta_j(k))p(r_j)dr_j \qquad (1)$$

where k and λ are respectively, the wave vector and the mean free path of the ejected photoelectron, $t_j(2k)$ is the backscattering amplitude from the j-th atom, $\delta_j(k)$ is the phase shift which is the sum of the contributions of the absorbing and the backscattering atoms. The sum is over all atoms in a shell at distance r_j from the absorbing atom and over all shells. Due to disorder and lattice vibrations there is a distribution $p(r_j)$ of atoms around the mean distance R_j of the j-th shell. Informations concerning $p(r_j)$ can be obtained by the Fourier transform of the experimental $\chi(k)$. As can be inferred from eq. (1), each shell, whose distribution function is sufficiently narrow, shows up as a peak in the magnitude of the Fourier transform.

The Fourier transforms of $\chi(k)$ for some of the measured Ge samples grown at different T_s are shown in Fig. 1. All EXAFS spectra have been transformed over the same interval of k using a Gaussian window; no correction has been introduced to account for the k dependence of phase shift because the exact determination of the peak position is not relevant to the present discussion. The major peak in each spectrum is the contribution of the first nearest neighbors and its linewidth is mainly determined by the finite transformation range. For $T_s \leq$ 130°C the peak of the first nearest neighbors is the only one present in the spectrum. Upon increasing T_s, peaks related to the second and followir shells become gradually more apparent, providin, clearcut evidence for the increasing order inside the

material. Finally, at T_s =390°C, as a many as seven shells are present and the spectrum is not discernible from that of a crystalline Ge. It is worth mentioning here that the radial distribution function derived from X-ray scattering measurements hardly shows any difference for samples up to T_s =350°C /8/. Although the data are not yet fully analyzed to extract all possible informations, we believe that Fig. 1 is a
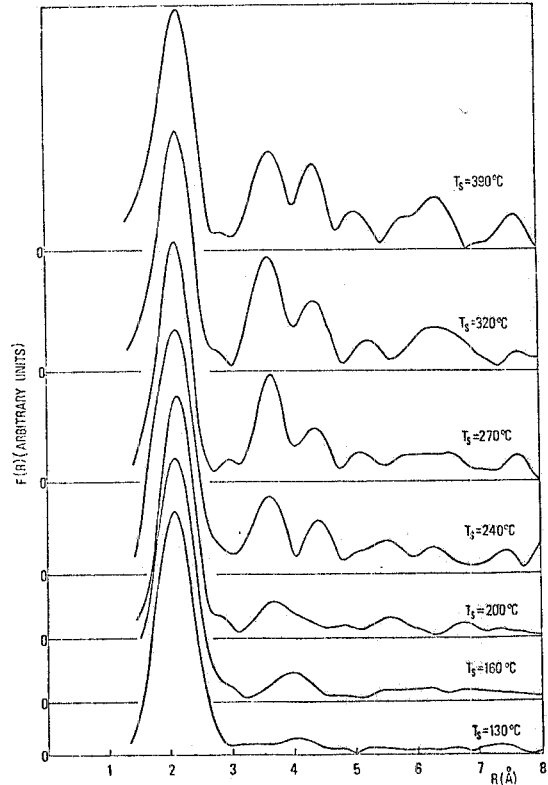

Fig.-1 Magnitude of Fourier transforms of the EXAFS of the Ge K-shell absorption for different deposition temperatures T_s. The scale of R is not corrected for the k-dependence of phase shifts.

strong proof of the power of EXAFS in the study of the medium-range order in amorphous structures. The most immediate conclusion that can be drawn from the present data is that the transition from the amorphous to crystalline state is a continuous process so that no transition temperature T_c can be defined, opposite to what is usually assumed in the literature. This can be easily seen in Fig. 2, where the strengths of the second and third shell contribution are shown as a function of T_s. The values for crystalline Ge are reported on the right. The gradual structural evolution occuring in the range from 130 to 300°C accounts for the continuous change of some macroscopic properties observed in this temperature interval, for example the variation in the refractive index /9/.

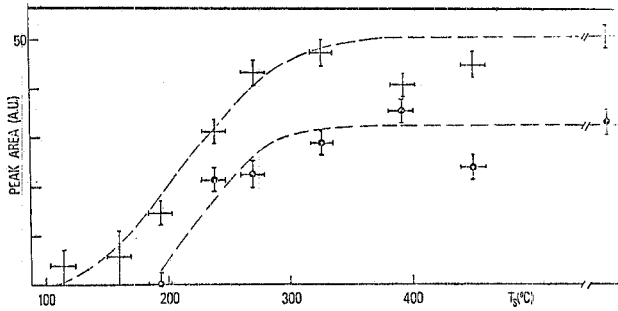The analysis of our results is simplified by

Fig.-2 Strength of the second (crosses) and third (circles) shell versus deposition temperature T_s. Values for crystalline Ge are reported on the right. The dashed lines are drawn as a visual aid.

the circumstance that EXAFS spectra of the same monoatomic substance are compared and only effects related to structural disorder are of interest. Assuming the mean free path λ as independent of deposition temperature T_s, the structural difference among the samples affects the EXAFS spectra through the distribution function $p(r_j)$ only. In germanium one can assume /10/:

$$p(r_j) \alpha \exp(-r_j - R_j)^2/2\sigma_j^2)$$

where R_j is the distance, from the absorbing atom, of the j-th shell in the crystal; σ_j is related to the disorder and is determined by a thermal contribution σ_{Tj}^2 and a structural contribution σ_{Sj}^2, so that $\sigma_j^2 = \sigma_{Tj}^2 + \sigma_{Sj}^2$. Because the structural disorder contribution is the result of a statistical average over all atomic distances, the σ_{Sj} are not independent among themselves but are a function of σ_{S1}. However, due to the fact that even in the crystal the atoms in each shell do not line up with those of the previous shell, σ_{Sj} is not simply the product of σ_{S1} times j and such dependence is not easy to calculate.

The data are consistent with two alternative explanations that will be outlined below together with the arguments which, in our opinion, render the second explanation more satisfactory. In the first scheme the data can be interpreted assuming that the σ_{Sj} decrease with increasing T_s. Preliminary computer simulations of EXAFS spectra using eq. (1) and the phases $\delta_j(k)$ given by Teo et al. /11/ have shown that this can indeed be the case. The above explanation is consistent with a "continuous random network" where the disorder decreases as a function of increasing deposition temperature. The ultimate test of this interpretation is the determination of the σ_{Sj} from the experimental results, a complex task which we have undertaken. The above explanation, on the other hand, faces the following objection: it is hard to conceive that the topological disorder peculiar to a random network can smoothly evolve as a whole to the order of a crystalline structure. Therefore we

tend to prefer the alternative assumption that the data give evidence of ordered micro-structures at medium-range level. If this is the case, a-Ge evaporated at $T_s > 130°C$ is composed by two coexisting phases: a more ordered phase A corresponding to nucleation of islands in the growth process and a more disordered phase B which acts as a connective tissue. This two-phase model has been recently gaining support as the structure which is most compatible with several macroscopic properties of tetrahedral-ly-bonded amorphous semiconductors, e.g. electrical transport in a-Si:H /12/. Obviously, if phase A is composed of fully ordered grains, the model is nothing else but the microcrystal approach earlier proposed to describe the actual structure of an amorphous semiconductor /13/. The presence of microcrystals in a-Ge was suggested in the past by Rudee and Howie /14/ to explain the fringe-like structures in their high resolution electron micrographs. However, their interpretation was later questioned on grounds that similar effects could be observed without a direct relationship to the arrangement of the atoms. More recent high resolution transmission electron microscopy measurements /15/ do confirm the microcrystal approach.

In this model, the distribution function which enters eq. (1) should be:

$$p(r_j) = p_A \exp(-(r_j - R_j)^2/2\sigma_{Aj}^2) +$$

$$+ p_B \exp(-(r_j - R_j)^2/2\sigma_{Bj}^2)$$

where p_A and p_B are proportional to the number of atoms belonging respectively to phases A and B. Assuming that the connective tissue is a minor fraction of the total material, the ratio of the area of j-th peak to the area of the corresponding peak for crystalline material gives directly the percentage of atoms surrounded by an ordered j-th shell. Combining this information for all peaks appearing in each sample, it is possible to evaluate the average grain diameter < D > in phase A. We get < D > ≃ 11 A for $T_s = 200°C$, < D > ≃ 9 A for $T_s = 160°C$ and establish an upper limit of 8 A, i.e. grains composed of two shells, for $T_s = 130°C$.

In conclusion this work has shown for the first time that:
a) EXAFS technique can be very useful in the study of medium-range structure in amorphous materials;
b) the structure of a-Ge evolves continuously to greater order as the deposition temperature T_s increases in the interval from 130°C to 300°C and no transition temperature T_c can be defined;
c) a microcrystal approach seems more promising in the explanation of the experimental results as opposed to a continuous random network. In this model the average grain size has been determined for the lowest range of the deposition temperature used.

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