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STABLE AMORPHOUS GERMANIUM FILMS PREPARED IN ULTRA HIGH VACUUM AND MEASURED IN-SITU: STRUCTURE AND ELECTRONIC PROPERTIES

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Abstract.- Stable, homogeneous germanium films have been prepared by slow evaporation onto heated sapphire substrates in ultra high vacuum. Their properties do not change on annealing until they crystallise at 250°C (1,2). The structure of these films is characterised by low density, by a shift of the first diffraction peak to higher scattering angle, with respect to the crystal and by the existence of a diffraction pre-peak. The optical absorption edge is relatively sharp, has a shoulder at 0.85 eV, and the low photon energy refractive index has a lower value than for the crystal. The temperature T dependence of the d.c. electrical conductivity σ is characterised by an "S" shaped curve, when plotted as log σ versus T⁻¹. The photoconductivity shows marked long time (t > 10² sec) relaxation effects at 77K and exhibits photoconductivity fatigue at 5K. These results are compared with amorphous germanium (a-Ge) films prepared under different conditions and with other amorphous and glassy materials. Some common trends in the structure and electronic properties are pointed out.

Preparation.- A-Ge films were prepared by slow evaporation (0.1 - 0.5 Å sec⁻¹) at normal incidence (distance between the source and the substrate ~ 50 cm), of high purity germanium (10¹³ cm⁻³ of electrically active impurities) from a tungsten boat (degassed under ultra high vacuum conditions) onto single crystal sapphire substrates held at 400K during the evaporations. The pressure during preparation was kept below 5.10⁻¹⁰ torr. The thickness of the deposited films was varied between two monolayers and one micron to suit various experimental requirements. For comparison, other films were also prepared, with varying rates of depositions (up to 40 Å sec⁻¹) and substrate temperature (down to Ts = 77K). However, unless specifically stated, the properties discussed in the following sections refer to stable films for which the evaporation rate was 0.1 Å/sec and Ts = 400K.

Density and Electron Diffraction measurements.- In-situ density measurements (3) were made on 500 Å, 3000 Å and 10000 Å thick films. In constrast to previous work concerning the density of annealed, stable films, a relatively large density deficit of approximately 16.5% with respect to the crystal was found, somewhat dependent of thickness (4). Of course large density deficits are generally found in bulk, covalent glasses such as a-As, a-SiO₂ and some chalcogenide glasses. It appears to be a general feature of the topology and connectivity of continuous, random networks, which are thought to represent the structure of these materials. The results of high energy electron elastic scattering experiments are summarised in Figure 1. Here the elastically scattered intensity of 40 keV electrons through a 500 Å thick a-Ge film is plotted against scattering angle s = 4θ sin θ. The important new feature is the shift by ca 6% of the first diffraction peak (f) towards a higher scattering angle relative to the crystal. A similar observation was made in a-As (5) and the phenomenon maybe due to the
more molecular nature of stable glasses (6). Further evidence comes from the new finding of a diffraction pre-peak (p) at a scattering angle $s \approx 1.2 \text{ Å sec}^{-1}$. As far as we are aware this has not previously been reported for amorphous films of group IV elements.

**Optical Properties.** The simultaneous measurements of optical reflection and transmission have given an independent determination of both parts of the dielectric response function between 0.45 and 3.0 eV. The results are shown in figures 2 and 3, together with previous results by Paul et al. (7) and Donovan et al. (8).

Main new feature, apart from the shift of $\varepsilon_2$ to higher energies is the value of the refractive index $n$ at low energies $- n (\omega\nu_0) = 3.6$. This is appreciably lower than in the crystal, but again agrees with the general trend of similar observations in a-As, a-SiO$_2$ and some chalcogenide glasses. The "main optical gap" (the intercept of $\omega\varepsilon_2$ with the energy axis) is found to be 1.0 eV, with an absorption shoulder at 0.85 eV (at the values of absorption coefficient $\alpha \approx 10^4 \text{cm}^{-1}$) extending down 0.65 eV. This "minimum optical gap" has also been confirmed from measurements of the spectral response of the photoconductivity. These results differ from those obtained by Paul et al. (7) and Donovan et al. (8), but are in agreement with the work of Elliott (9) on a-Ge films, prepared in ultra high vacuum on cold sapphire substrates ($T_s = 77K$), at high evaporation rates ($\approx 30 \text{ Å sec}^{-1}$), but annealed to 400K. They also agree with measurements by Connell and Pawlik (10) on hydrogenated, sputtered a-Ge (with 2.8% hydrogen). It would seem that both annealing to high enough temperatures or partial hydrogenation of a-Ge films can lead to the same (assymptotically) optical absorption characteristic of the stable, amorphous state of germanium.

**D.C. electrical conductivity.** Measurements of the d.c. electrical conductivity reported earlier (11), have now been extended to lower temperatures (noise current of the order of $5 \times 10^{-16}$ Amps) and to larger film thicknesses (up to one micron). These measurements have confirmed the previously reported high temperature behaviour, and have established the deviation from linearity of the log $\sigma$ versus $T^{-1}$ plot at the lowest temperatures reached (below 40K) (12). A typical result (representing the behaviour of films ranging from 500 Å to one micron) is shown in Figure 4. The curve
Fig. 4: Log of d.c. electrical conductivity $\sigma$ versus temperature $T^{-1}$.

Fig. 5: Log of d.c. electrical conductivity $\sigma$ versus temperature $T^{-1}$: 3- present work, 2- Elliott (9); 5- Lewis (12); 6- Beyer et al. (10).

The conductivity has a strong (on a scale of $kT$) "S" shape, the conductivity deviating downwards at high temperatures and upwards at the lowest temperatures. The conductivity data is replotted in Figure 5 together with the results of other investigations. The most interesting feature in Figure 5 is again that $\alpha$-Ge films prepared under very different preparation conditions, when annealed to high enough temperatures, or hydrogenated (by approx. 2.8% of hydrogen) show qualitatively the same behaviour, as stable UHV prepared film.

Photoconductivity. - The spectral response of the steady state (chopping frequency $\approx 138$ Hz) photoconductivity showed, in agreement with the optical measurements, a cut-off at 0.65 eV, suggesting a relatively sharp optical absorption edge. The temperature dependence of the steady state photoconductivity was measured between 15 K and 300 K, for an excitation radiation of 1.3 eV (low photon flux levels $\approx 0.5 \times 10^{12}$ photons cm$^{-2}$ sec$^{-1}$) and the result is shown in Figure 6, together with the temperature dependence of the dark conductivity in amorphous (present study) and crystalline (n-type; $10^{13}$ donors cm$^{-3}$) germanium. The photoconductivity is almost temperature independent and has a value which is higher or comparable to the values found in hydrogenated germanium (13), silicon (14) and other photoconductive glasses such as As$_2$Te$_2$ (15). The time response of the photocurrent was also measured and a slight decrease of the signal ($\approx$ up to 5%) was detected when the chopping rate of the incident light was increased from 20 to 850 Hz. However, a much more pronounced long duration ($t > 10^3$ sec) strongly temperature dependent effect was observed, when the continuous white light illumination was interrupted by a shutter. Typical results are shown in Figure 7 (77K) and 8 (5.5K).
At 77K, the saturation of the photocurrent was not achieved after $10^3$ sec, and also the decay of the photocurrent was characterised by a long time constant of the order of $10^3$ sec. Cooling the sample to liq. He temperature decreased the absolute value of the photocurrent from appr. $5 \times 10^{-12}$ Amps to appr. $1 \times 10^{-13}$ Amps. However, contrary to the behaviour at 77K, strong fatiguing of the photo-signal was now observed on a time scale of 60 sec., after which a relatively constant "fast" (response and decay times less than 0.1 sec) photo-signal of $6 \times 10^{-14}$ Amps was observed on repeated, aperiodically interrupted illuminations, as shown in Figure 8. These effects are at present being investigated by ex-situ time resolved photoconductivity and photoluminescence experiments.

References: