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ELECTRONIC PROPERTIES OF FLASH-EVAPORATED AMORPHOUS GaSb FILMS

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Abstract. - The optical and transport properties of flash-evaporated amorphous GaSb thin films are described as a function of preparation conditions. The results for nearly-stoichiometric samples are discussed in relation with the presence of defects. The influence of Sb excess is also considered.

1. Introduction. - GaSb is one of the less ionic III-V compound semiconductors: \( f_i = 0.261 \) according to Phillips' scale (1). This may favour the existence of chemical disorder in amorphous GaSb samples, especially if they are deposited from the vapour. Wrong bonds (bonds between like-atoms) are expected to produce detectable effects, in particular on the optical properties, since the Sb-Sb covalent bonding is weaker than the Ga-Sb heteropolar bonding. We present here the results of optical and transport measurements performed on flash-evaporated amorphous GaSb thin films as a function of preparation conditions. Attention is focused on nearly-stoichiometric (N.S.) samples but the influence of Sb excess is also considered.

2. Sample preparation and characterization. - Thin (200-1000 \( \mu \)m) films of amorphous GaSb are deposited under ultra-high vacuum by flash-evaporation of crystalline powder onto supersmooth silica substrates maintained at different temperatures between 100 and 390 K. They can be annealed in situ under control by resistance measurements. The crystallization temperature ranges from 430 to 470 K. The average film composition is determined by \( \alpha \)-particle back-scattering with a few % accuracy. Nearly stoichiometric samples (within a few %) have been obtained with powder grain size in the 125-160 \( \mu \)m range, and crucible temperatures of the order of 1500° C. Higher crucible temperatures result in films with increasing Sb excess.

The film thickness is determined with 1 % accuracy by an X-ray interference technique (2). The complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + ik)^2 \) is deduced from reflectance and transmittance measurements performed in air between 0.5 and 6.2 eV, using exact thin film formula (3); a Kramers-Kronig analysis of reflectance data is also used for opaque films. The electrical d.c. conductivity is measured in situ versus temperature with a Keithley electrometer.

The film structure is investigated by electron diffraction and microscopy. For N.S. samples, the diffraction diagrams are typical of tetrahedrally-coordinated amorphous semiconductors (4), but the first diffuse ring is slightly shifted with respect to the crystalline (111) peak. Increasing the Sb content produces a gradual modification of these diagrams; there is no evidence for microcrystallites of metallic Sb. These data will be analysed in order to characterize the changes in average local structure.

3. Properties of nearly stoichiometric (N.S.) films. - Figure 1 presents the \( \varepsilon_1 \) and \( \varepsilon_2 \) spectra for N.S. amorphous GaSb films deposited at 100 K and annealed at 300 and 420 K; the results for crystalline GaSb (5) are given for comparison. The amorphous data look roughly similar to those previously reported for flash-evaporated samples
In our case the $\varepsilon_2$ maximum is shifted to higher energies and the $\varepsilon_1$ values in the infrared are lower.

The effects of increasing the substrate temperature during deposition and of annealing are qualitatively similar to those already observed for amorphous Ge (7) and for the other amorphous Ga compounds (8). One can see in figure 1 that, even after annealing, the $\varepsilon_1$ values in the infrared remain significantly higher than the corresponding crystalline values (5, 9). This indicates an appreciable decrease of the Penn gap, thus of the average bonding strength, which is difficult to explain by structural disorder and defects of the dangling-bond-type only, and suggests the presence of a certain proportion of wrong bonds.

The optical gap $E_o$, determined through the empirical law: $(\hbar\omega)^2 \cdot \varepsilon_1 \alpha (\hbar\omega - E_o)^2$, is equal to 0.64 eV for NS films deposited or annealed at room temperature, in agreement with previous results on flash-evaporated films (10). It increases to 0.74 eV after high-temperature annealing, i.e. a value very close to the crystalline minimum gap. Moderate absorption tails are observed below $E_o$. The slope of the absorption edge is only slightly increased by annealing (figure 2).
Figure 3 shows the conductivity $\sigma$ versus reciprocal temperature for the same films as in Figures 1 and 2. After room temperature annealing, the $\sigma$ behaviour over the whole temperature range is best represented by $\sigma = C \exp \left[ -\left( \frac{T}{T_0} \right)^{1/2} \right]$; this suggests transport by hopping in localized states in the pseudo-gap away from the Fermi level. After high-temperature annealing, the data can be fitted with a sum of two exponentials:

$$
\sigma = \sigma_o \exp \left( -\frac{E_o}{kT} \right) + \sigma'_o \exp \left( -\frac{E'_o}{kT} \right),
$$

with $E_o = 0.55 \text{ eV}$, $\sigma_o = 4 \cdot 10^6 \Omega^{-1} \text{ cm}^{-1}$,

$E'_o = 0.31 \text{ eV}$, $\sigma'_o = 90 \Omega^{-1} \text{ cm}^{-1}$.

This indicates two parallel transport mechanisms. Above room temperature, conduction occurs in extended states beyond the mobility edge. In contradiction with the case of amorphous Ge(11) or amorphous GaAs (8), the activation energy is significantly larger than half the optical gap (0.55 eV compared to 0.37 eV). This means, either a strong temperature dependence of the gap width, or a shift of the Fermi level due to localized states related to some specific defects. Below room temperature, the observed activated behaviour, again in contradiction with amorphous Ge or GaAs, suggests transport by hopping following excitation in tail states at the band edge. It is remarkable that variable-range hopping conduction in states near the Fermi level is not observed, either before or after annealing, although numerous defects are obviously present in the films.

4. Influence of Sb excess. - As the film Sb content is increased, the optical and transport properties are gradually modified. For a given composition, a material with well-defined properties is obtained, and it undergoes similar annealing effects as the nearly stoichiometric samples. For the same deposition conditions and increasing Sb excess, the $\varepsilon_2$ values in the infrared increase and the $\varepsilon_2$ spectrum is shifted to lower energies, the optical gap decreases (figure 4). The absorption tails are not significantly enhanced. The room temperature conductivity is first little affected, then increases. The $\sigma$ behaviour below room temperature is modified and tends to follow a $T^{-1/4}$ law for non-annealed films with high Sb content (Ga/Sb = 0.5); for annealed films, an activated behaviour is no more observed. Above room temperature, conduction is still activated, with an activation energy remaining larger than half the optical gap.

![Figure 3: Conductivity $\sigma$ versus reciprocal temperature $T^{-1/2}$ for the same films as in Figs. 1 and 2.](image)

![Figure 4: Plots of $\Pi \omega \sqrt{\varepsilon_2}$ versus energy $\Pi \omega$ showing the decrease of the optical gap with increasing Sb excess: (a) Ga$_{0.44}$Sb$_{0.56}$, (b) Ga$_{0.31}$Sb$_{0.69}$.](image)
5. Conclusion. - In spite of an overall similarity, the properties of flash-evaporated amorphous GaSb films present significant differences with those of the other amorphous Ga compounds. The observed large decrease of average bonding strength with respect to the crystal suggests the presence of a certain proportion of wrong bonds. The defects, both structural and chemical, do not give rise to large absorption tails and to conduction by variable-range hopping in localized states near the Fermi level. More experiments are under way in order to determine the nature of these defects. The gradual changes of the properties due to increasing Sb excess suggest that Sb in excess is incorporated into the network in a self-compensated or alloying mode (12).

References