CRYSTALLIZATION PROCESS AND CHEMICAL DISORDER IN FLASH EVAPORATED AMORPHOUS GALLIUM ANTIMONIDE FILMS

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ABSTRACT

In this work we describe a flash evaporation system specially built to produce amorphous films of III-V compounds and characterize GaSb films using optical, electrical and X-Ray diffraction measurements. Changes in the composition of the GaSb samples were obtained by the use of different crucible temperatures. In such samples, consequently, the optical absorption edge and the DC electrical conductivity were modified. The departure from stoichiometry in GaSb films is analyzed on the basis of these results which can be used as an evidence of the chemical disorder. This kind of disorder is represented by either wrong bonds or sites with different coordination.

Thermal annealing with a sequence of increasing temperatures first induced detectable variations in the optical absorption edge and in the vibrational properties of the amorphous GaSb. These variations are compatible with the GaSb local ordering and were observed by Raman scattering and infrared absorption spectra. The annealing at higher temperatures allowed the crystallization of the material confirmed by X-Ray diffraction. From these experimental results a crystallization mechanism based on the segregation of Sb excess coming from the crystallized regions toward the amorphous tissue is proposed.

INTRODUCTION

In the crystallization of bulk GaSb from the melt, when the thermodynamic equilibrium is practically attained, there is a strong tendency to the formation of stoichiometric material[1]. Differently, stoichiometry in amorphous GaSb films prepared by evaporation is a difficult task[2,3,4]. Even if the amorphous material is stoichiometric some degree of chemical disorder is present besides the structural disorder. The combined effects of these two kinds of disorder on the physical properties of the materials are not well understood at present. In this work we describe some experiments related to the chemical and structural disorder in the amorphous semiconductor GaSb, and the results are used to qualitatively check some recently developed models[5,6].

EXPERIMENTAL PROCEDURE

A set of a-$Ga_{1-x}Sb_x$ films with different concentrations ($0.50 \leq x \leq 0.59$) and thicknesses ranging from 200 to 1200 nm were prepared on silica glass and crystalline silicon substrates using a specially designed flash evaporation system (fig.1). The evaporation assembly consists of a high

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vacuum chamber, with a feeder (F), a crucible (C) and a substrate holder (S).

The feeder is able to continuously supply the hot crucible with crystalline GaSb powder first kept in the reservoir (R) until the beginning of the evaporation process. At this time the powder is continuously supplied to the hot crucible by an externally rotated worm-gear(W-G). The rotation speed determines the film deposition rate. The gear which provides vibration (VG) to the feeder, and the tube (T) which mechanically guides the steel cable are important in order to get constant feeding rates.

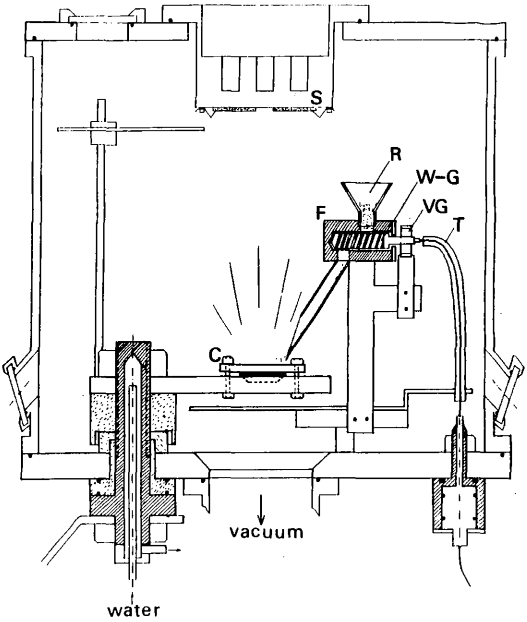

Fig.1 Cross section of the flash evaporation system described in the text.

As the vapor pressure of antimony is at least four orders of magnitude higher than that of gallium at common evaporation temperatures, the control of the film composition is not easy[2,3], even if the flash process is used. The relevant parameters in this respect are the crucible temperature, the powder grain size, the deposition rate, and the substrate temperature. We were able to get materials with variable composition by controlling the crucible temperature and by keeping the other parameters constants. a-Ga$_{1-x}$Sb$_x$ films with x varying between 0.50 (stoichiometric) and 0.59 were obtained using crucible temperatures between 1070 and 990°C. The raw material was a 30μm powder obtained from a pure crystalline GaSb rod, with an acceptor concentration of 1.5x10^{17}cm^{-3}. A feeding rate of 0.3*grams/min.* resulted in deposition rates of approximately 3*nm/s*. The substrates (silicon (100) and silica glass) stayed at room temperature during all the depositions.

The compositions of the samples were measured[7] by a combination of XPS and AES techniques. No contaminant, specially oxygen, carbon, tungsten or iron were detected in the films after standard cleaning of the surface with argon ions.

The films were optically characterized using transmittance and reflectance measurements at normal incidence in a wide spectral region (50000 to 180cm^{-1}). These data were used to determine the optical constants by fitting and iterative[8] computer routines based in thin film optical theory.

Nearly stoichiometric films were submitted to thermal annealings at different temperatures(180, 210, 250 and 400°*C*). No detectable changes were observed below 180°*C*. These annealings were performed for 20 minutes in a pure nitrogen atmosphere in order to prevent surface contaminations. After each annealing, X-ray diffraction, UV-Vis., infrared absorption and Raman scattering measurements were performed in order to characterize the structural changes which had occurred.

RESULTS

Fig.2 shows the absorption coefficient vs. photon energies for the various compositions, calculated using the reflectance and transmittance data. In this figure it is included the absorption coefficient of a sample (7B) grown during the final stage of a standard evaporation (not flash evaporation). One can observe that the absorption edges for the materials with compositions nearly stoichiometric (*X* = 0.50, 0.51, 0.52) display similar behavior, while highly unbalanced samples (*X* = 0.59 and 7B) are different showing less steep absorption edges and higher absorption at low energies.

Fig.3 presents the absorption coefficient as a function of the photon energies, calculated for a nearly stoichiometric (*X* = 0.51) sample thermally annealed at various temperatures. One can verify that the annealing at 180°*C* causes a lowering of the absorption relative to the as grown condition, and a slight lowering of the Urbach[9] energy. These changes are compatible with a

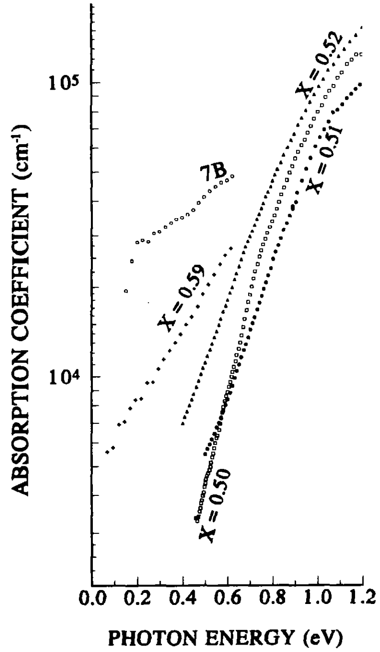

Fig.2 Absorption coefficient vs. photon energy of a-$Ga_{1-X}Sb_X$.

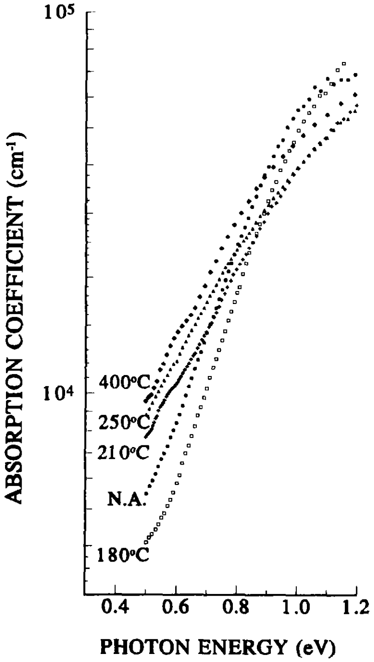

Fig.3 Absorption coefficient vs. photon energy of thermally annealed a-$Ga_{0.49}Sb_{0.51}$. The absorption edge for the not annealed (N.A.) condition was also included.

reduction of the potential fluctuations (in an atomic scale) and consequently with an increasing degree of the local order in the material^{10,9}. A completely different feature occurs when the annealing temperature is 210°*C* or higher. In these cases the absorption edges become less steep. These changes are associated with the increase of disorder as will be discussed later on.

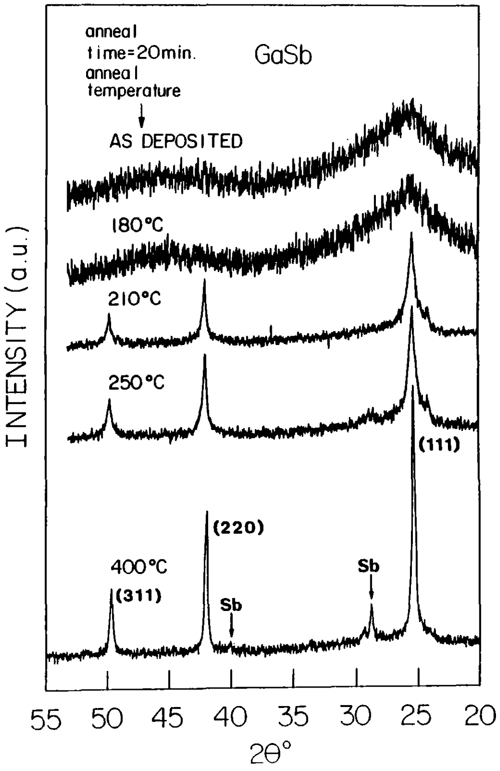

Fig.4 X-Ray pattern measuremets of a nearly stoichiometric material (X = 0.51) submitted to thermal annealings.

Fig.4 shows the X-Ray pattern measurements of a nearly stoichiometric sample (X = 0.51) following the thermal annealing. It is clear from this figure, and from the UV-Vis. reflectance spectra^{7} that the annealing at 180°*C* did not induce appreciable long range ordering. On the other hand, the subsequent pattern (210°*C*) displays a clear set of peaks, the positions and intensity ratios of which coincide with that of crystalline GaSb. The annealing at 250°C is responsible for the raise of the crystallized material fraction, due to the increasing number of crystallites. In this case, a growth of the crystallite size (≃ 220 Å) is not expected since the diffraction peak widths are unchanged. A bump at $2\theta \simeq 29^\circ$ appears as a consequence of this annealing, and develops into two new peaks in the next annealing. At 400°C, the small peak observed at 29.26° corresponds to the planes (200) in crystalline GaSb, while the peak at 28.75 is related to the planes (102) of the crystalline Sb. The other small peak at $2\theta = 40.07^\circ$ is associated to the planes (014) of c-Sb. Therefore the annealing at 400°C guarantees the formation of Sb crystallites inside the GaSb matrix.

DISCUSSION

In order to explain the previous results we will use two hypotheses. The first one is that the Sb excess is homogeneously distributed into the network of the amorphous material. The second hypothesis is that the main electronic effect of the excess atoms in the network is to increase the number of triply coordinated (C_3) atomic centers, which is also the main defect of the stoichiometric amorphous GaSb. The first hypothesis is based on experimental data[3,11,12], while the second is based on theoretical calculations of the electronic structure of amorphous III-V materials, specially a-GaAs[6,5].

Using these hypotheses we can explain the disorder effects observed in the unbalanced material as due to the bond angle fluctuations, that are enhanced with the Sb excess in the materials. According to the molecular dynamics calculations[5] the Sb-C_3 centers have trigonal symmetry, introducing large bond angle deviations in the material.

On the thermally annealed material (180°*C*) one can observe the effect of ordering in the absorption edge, also confirmed by infrared and Raman scattering results that will be published in a forthcoming paper. This ordering effect is probably due to small atomic arrangements, which in some way are able to reduce the bond angle distortions and eliminate part of the C_3 centers and part of the existent wrong bonds. On the other hand, annealings at higher temperatures, which are responsible for crystallite formation, may introduce a large amount of under coordinated centers (both Sb-C_3 and Ga-C_3) in the grain boundaries. Furthermore, the amorphous region that remains among the crystallites may receive the excess Sb migration from the crystallized region, which has the tendency of being stoichiometric. For this reason we assume that the main defects responsible for the disorder are the C_3 centers and the related bond angle distortion. Our measurements of the partially crystallized material reveal both the high degree of disorder (absorption edge) and the existence of the long range order in the crystallites (X-Ray and reflectance patterns).

As we are considering that the disorder in the unbalanced material and in the crystallized one are essentially due to the same cause, we could expect that the amplitude of variation of the disorder parameter E_0 (Urbach energy) would be similar. Fig.5 shows E_0 as a function of composition

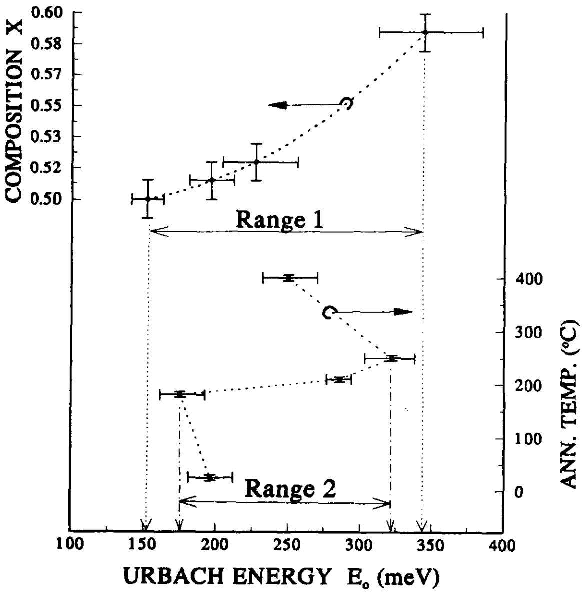

Fig.5 Urbach energy as a function of composition and of thermal annealings . The *Range* 1 corresponds to the composition variations, while the *Range* 2 corresponds to the annealing induced variations in a nearly stoichiometric (X = 0.51) sample.

for unbalanced samples and as a function of temperature for the annealed one. As expected the ranges of variation of E_o are similar.

CONCLUSIONS

From this work we could conclude that the thermal annealings at temperatures lower than that necessary to crystallize the a-GaSb, produced changes that are compatible with the local ordering or the elimination of point defects in the material. Higher temperature partially crystallize the material creating regions with a high density of defects and higher Sb concentration in the vicinity of the c-GaSb grains.

The absorption edges of both unbalanced and partially crystallized GaSb films, are less steep than stoichiometric a-GaSb. In both cases the effect can be interpreted by the formation of C_3 centers favored by the Sb excess.

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