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IMPULSE STIMULATED "EXPLOSIVE" CRYSTALLIZATION OF SPUTTER DEPOSITED AMORPHOUS (In,Ga)Sb FILMS

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Rapid irreversible exothermic amorphous-to-polycrystalline phase transformations have been observed in sputter deposited (In,Ga)Sb films. The transformation was triggered in approximately 10^{-7} sec in a local region of the film using a sufficiently large energy pulse induced by, for example, a pulsed laser or a mechanical impulse. When the sum of the heat of crystallization released from a given domain and the energy supplied by external heating was sufficient to trigger a neighboring domain then the transformation propagated throughout the sample with an average velocity on the order of 200 cm/sec. The critical temperature for propagation was dependent upon the film composition, growth conditions, and thermal history. A qualitative model to explain these results is discussed.

"Explosive" irreversible amorphous to crystalline phase transformations were first reported over a century ago in electrolytically deposited Sb films.[1,2] More recent work investigating "explosive" transformations occurring at room temperature in sputtered a-Ge films has shown that crystallization of the entire sample does not occur by a single explosion, but rather by a series of cascading "micro-explosions" each of which triggers a further micro-explosion.[3-5] The transformation is highly exothermic and the initial triggering has been accomplished using both mechanical and thermal impulses. The propagation velocity has been reported to be on the order of 100 cm/sec.[3-5] Cooling the sample in a liquid nitrogen bath suppressed the transformation.[6]

In this communication we report on the impulse stimulated crystallization (ISC) of sputter deposited "amorphous" (In,Ga)Sb films. The results show that the ability to trigger the transformation in a local region of the film does not imply that the crystallization front will propagate. The minimum temperature at which propagation of ISC will occur, T^*, depends upon the film composition as well as the thermal annealing history of the film. In all cases T^* was observed to be greater than room temperature and was found to increase with higher pre-annealing temperatures and longer pre-annealing times. ISC appears to be competing with normal nucleation and growth processes. The wavelength of the advancing crystallization front, as determined from striations remaining in the crystallized sample, was also found to be related to the thermal history of the film. ISC in these alloys was always associated with large changes in sample resistivity and reflectivity which were used to investigate the transformation. A simple kinetic model, incorporating some of the ideas proposed earlier by Kikuchi et al.[4] and Messier et al.[5] from their studies of a-Ge, is presented to qualitatively explain the results reported here.

(In,Ga)Sb films were grown by multi-target sputtering (MTS) on Corning 7059 glass substrates. In the MTS technique,[7,8] the substrate is continuously rotated through two or more electrically and physically isolated sputtering discharges. For this work, InSb and GaSb targets were used and (In,Ga)Sb pseudobinary films were formed by sequentially depositing partial monolayers of InSb and GaSb. With the deposition conditions used, ion bombardment enhanced diffusion[9,10] during film growth was sufficient to form homogeneous alloys with no evidence of compositional modulations. The MTS system is described in detail in references 7 and 8. In the present experiments the system base pressure was $\sim 10^{-7}$ Torr (10^{-5} Pa). Sputtering was carried out in high purity gettered Ar at a pressure of 15 mTorr (2 Pa). The target voltages were varied between 0 and -1500 V depending on the desired film composition and the target to substrate separation was 3.9 cm. The substrate rotation rate for all growth runs was 8 rev/min. While no substrate heating was applied, a steady state growth temperature of 100 $\pm$ 25°C was attained due to energetic particle bombardment from the discharges. The films ranged in thickness from 0.2 to 4 μm. Corning 7059 glass wafers were used as substrates because of their excellent thermal expansion match with (In,Ga)Sb.

Triggering of ISC was carried out using either a stainless steel stylus or a pulsed Ar laser. The stylus had a tip radius of 10 μm and a normal load of 130 g. The velocity of the stylus at impact with the film was 10 cm/sec. During these experiments, the samples were

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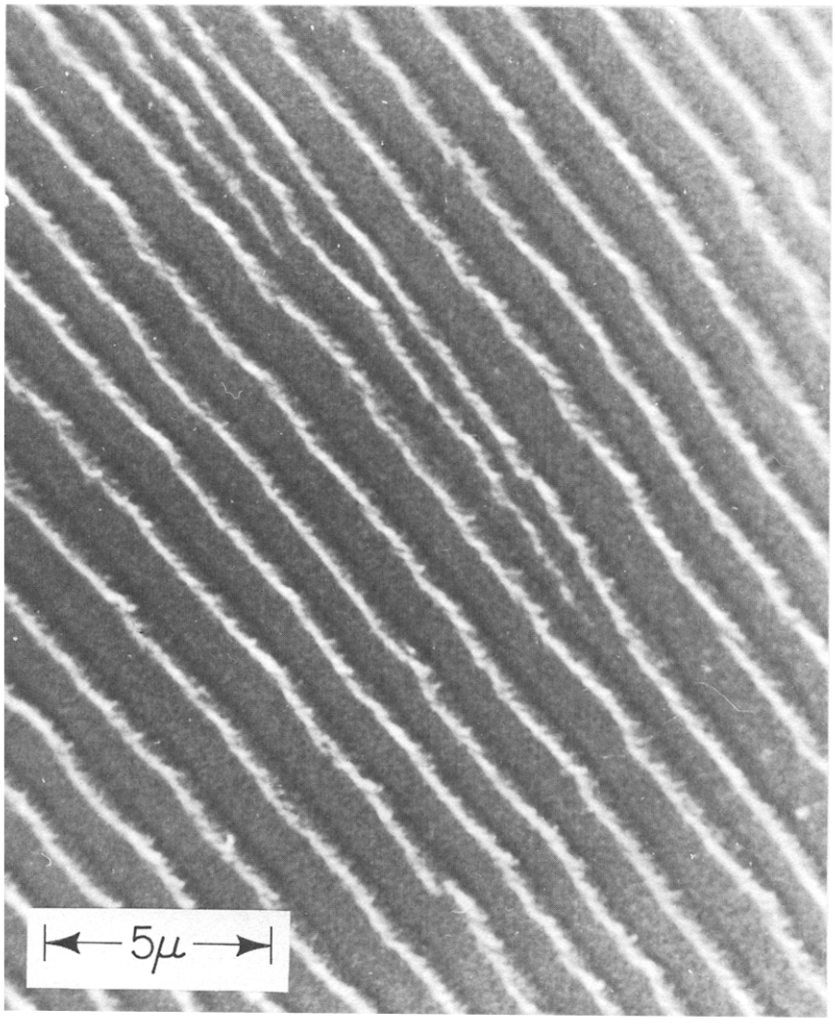

Fig. 1. Scanning electron micrograph of a GaSb film ISC transformed at $\simeq 90^{\circ}$C.

placed in thermal contact with a heater and the temperature was monitored continuously using a 10 mil alumel-chromel thermocouple attached to the film surface. Ohmic contacts to the films for resistivity measurements were made using conducting Ag ink. The thermocouple circuit was designed such that upon triggering, a voltage spike was superimposed on the thermocouple output indicating the temperature at which the transformation was initiated. In addition to resistivity, the films were characterized by x-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and scanning electron microscopy (SEM).

Figure 1 is a scanning electron micrograph of a film which has undergone an ISC transformation initiated at a temperature $\simeq T^*$. Surface undulations of varying amplitude and wavelength and a wide variety of complex topographical structures were observed depending on the film composition and thermal history. However, in all cases the surface roughness of a transformed sample was found to decrease as the triggering temperature was increased above T^*.

ISC transformations were investigated using film resistance vs sample temperature measurements as shown in Figure 2 for GaSb films with different thermal histories. These results were obtained using a 27°C/min heating rate while impulse loading the sample at a rate of approximately 10 min^{-1}. The as-deposited film used to obtain curve A exhibited a T^* of $\sim 90°C$. Curve B corresponds to a GaSb film which was subjected to a prior annealing cycle at 180°C for 90 min and yielded an increased T^* of 180°C. The hysteresis effect upon cooling displayed in curves A and B is due to the highly exothermic nature of the transformation. The sample corresponding to curve C was not triggered but allowed to partially crystallize by the normal nucleation and grain growth process after which ISC could not be initiated. In all cases the final value of film resistivity was approximately the same and XRD studies showed that the final state of all ISC transformed films was polycrystalline with no preferred orientation. SEM examination of sample C indicated a featureless surface up to magnifications of 10,000 X.

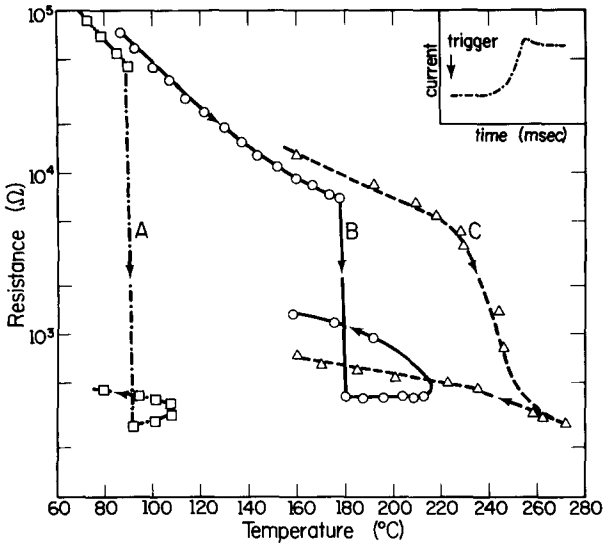

Fig. 2. Sample resistence vs temperature for GaSb films heated at a rate of 27°C/min. (A) ISC transformed as-deposited film. (B) ISC transformed film pre-annealed at 180°C for 90 min. (C) GaSb film crystallized by a normal nucleation and growth process. The inset shows an oscilloscope trace of sample current vs time during the transformation of sample A.

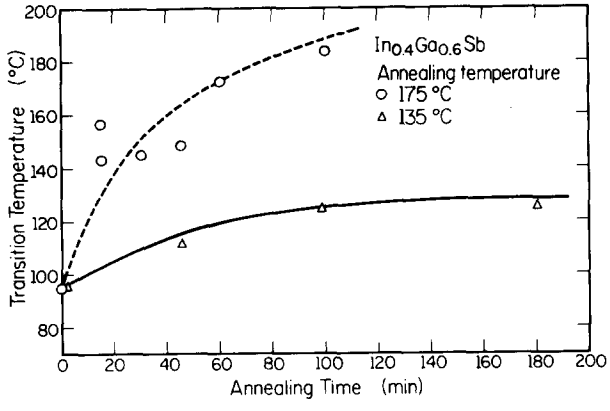

Fig. 3. Minimum ISC transition temperature for $In_{0.4}Ga_{0.6}Sb$ films as a function of pre-annealing time for annealing temperatures of 135°C and 175°C.

The insert in Figure 2 shows an oscilloscope trace of the current through sample A vs time during the ISC transformation. From curves such as this, the propagation velocity v was found to vary between 200 and 500 cm/sec.

The critical temperature for propagating ISC increased with pre-annealing at temperatures greater than the value of T^* for the as-deposited sample. Figure 3 shows the effect of annealing time on the value of T^* for $In_{0.4}Ga_{0.6}Sb$ films annealed at 135°C and 175°C. The ISC transformation was completely suppressed by anneals longer than 150 min at 175°C.

Results similar to those shown in Figure 3 were obtained using different annealing temperatures and film compositions.

T^* was also found to increase with decreasing mole % GaSb in the film as shown in Figure 4. Propagation of ISC was never observed in films with less than 40% GaSb. XRD studies of as-deposited films indicated that In-rich alloys were polycrystalline as grown with a {110} preferred orientation, films containing between approximately 40 and 52 mole % GaSb exhibited crystalline regions in an amorphous matrix, while films with greater than 52% GaSb appeared to be amorphous. XRD spectra for representative films are shown in Figure 5. The

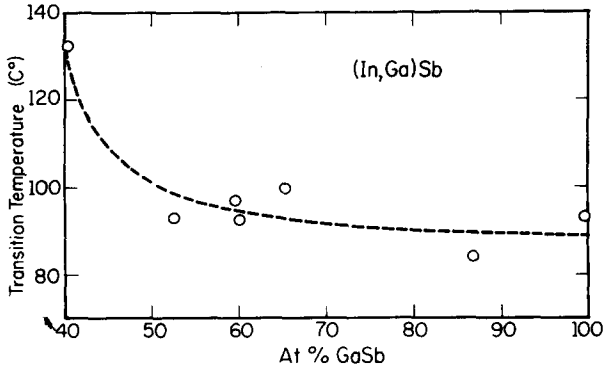

Fig. 4. Minimum ISC transformation temperature as a function of (In,Ga)Sb film composition.

$In_{0.48}Ga_{0.52}Sb$ alloy transformed by ISC at 90°C, the $In_{0.6}Ga_{0.4}Sb$ alloy at 132°C and the $In_{0.63}Ga_{0.37}Sb$ alloy did not exhibit ISC. The composition dependence of T^* shown in Figure 4 thus appears to be more directly related to film crystallinity than film composition. STEM examination of transformed films showed regions with an average grain size of approximately 500 Å periodically mixed with regions which appeared to be amorphous.

The above results can be explained by a simple qualitative model. The as-deposited "amorphous" films are in a metastable state and require an activation energy to transform into the crystalline state. The initial triggering impulse must provide sufficient energy for a local region of the film to transform but spontaneous propagation of the crystallization front is not assured. The latter requires that the heat of crystallization released from one domain be sufficient, allowing for thermal losses at the film interfaces, to trigger the next domain. All (In,Ga)Sb films investigated required additional external heating for propagation. Furthermore, if the film was partially crystallized (either as-deposited or by annealing) the total amount of heat liberated from a triggered domain was reduced and consequently increased external heating had to be added in order to propagate the crystallization front.

Films which were ISC transformed at temperatures in excess of T^* were observed to exhibit smoother surfaces. Such experiments were car-

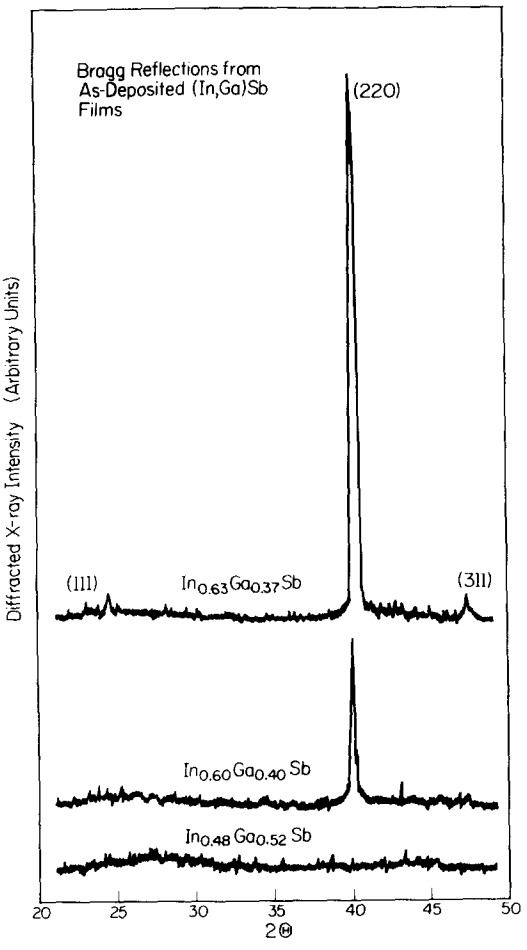

Fig. 5. X-ray diffraction spectra for as-deposited (In,Ga)Sb alloys.

ried out using rapid heating in order to avoid normal crystallization. Examination of high magnification scanning electron micrographs indicated that some transformed films exhibited hispidulous surface structures with topographical features which suggested local surface melting. We presently believe that the surface structure is due to two causes, either one of which may dominate depending on the transformation conditions. One such cause is periodic density variations due to incomplete crystallization within each domain (this has been observed in bright and dark field TEM pairs) and the other is local surface melting.

The time constant τ for raising the domain temperature above T^* is given approximately by λ^2/k where λ is the domain size and k is the thermal diffusivity of the untransformed film. Using the average wavelength of the surface undulations observed in transformed films for λ, τ is approximately 5×10^{-7} sec which is on the order of the experimentally determined transformation time given by λ/v. This agreement is consistent with the notion that the propagation of ISC is controlled by thermal diffusion. However the qualitative model described in the above paragraphs requires that τ be less than the total time for domain transformation including any incubation or nucleation time. It also predicts that for a given set of growth and thermal history conditions, propagation will not occur below a critical film thickness since the total energy released from a crystallized domain depends upon the domain volume as well as the fraction of the domain which is amorphous. However the maximum domain volume is itself limited by thermal diffusivity. To establish this point, a set of samples were deposited with gradients in film thickness. Propagation of ISC could be initiated in the thick regions but the crystallization front always halted abruptly at a critical thickness and ISC could not be propagated at all in regions thinner than the critical thickness.

The above model also predicts that ISC propagation will be halted if the thermal conduction losses become sufficiently large. This was demonstrated by preparing a set of samples which were partially covered by In_2O_3 films of various thicknesses. ISC could not be propagated into areas covered by a 4000 Å thick film, however propagation could be continued in films covered by 1000 Å thick In_2O_3 layers by raising the sample temperature.

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