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Stimulated crystallization of polycrystalline GaSb films

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Ultra-thin (about 15 Å) initial deposits of Bi, Cu, Ag, Sn, Pb, Au and In–Bi solder have been used for subsequent deposition of the GaSb films by a flash evaporation technique. TEM studies reveal that the deposits stimulate grain growth in the films to different extents, with Au giving the best results. Also, the increase in the Au stimulator deposit thickness substantially increased the grain size. The electrical measurements made on the GaSb films grown with or without Au stimulators (below 30 Å) reveal that considerable improvement in the film properties can be obtained by using the stimulator.

1. Introduction

Polycrystalline semiconductor films are of considerable technological importance and play a highly significant role in electronic devices. High mobility and low carrier concentration are the desirable features of the films; such features cannot be achieved in films comprised of very small crystallites. The crystallite size in the evaporated films can be increased by employing higher deposition temperatures and by post deposition thermal treatments. The usefulness of the thermally-treated films is reduced by cracking and pin-holing effects [1], whereas the high-temperature deposited films tend to develop intercrystalline barriers [2] which limit the Hall mobility, increase the film resistivity [3] and introduce electronic noise [4]. If the deposition temperature for obtaining good crystalline films could be lowered without sacrificing the high mobility and low carrier concentration attainable, better use could be made of the films. The achievement of low temperature epitaxy of Si and of impurity crystallization of Si [5] and the large size grains in Te films produced by the stimulated crystallization technique [1] demonstrate the applicability of such methods for elemental semiconductors. The aim of this paper is to report the results of an investigation of the latter technique for the III–V semiconductor compound GaSb. The improvement in the electrical characteristics of the films due to stimulated crystallization in the films is demonstrated by the Hall effect and by field effect measurements.

2. Experimental details

The GaSb compound was prepared by fusing (at 800° C) high-purity antimony and gallium (99.999% pure) in stoichiometric proportions in vacuum-sealed quartz ampoules. A metal belt feeder arrangement [6] was used to feed the charge material to the evaporation source. Sputtering of the charge particles due to release of the enormous amount of gases absorbed during the powder charge evaporations create the main difficulty in controlling flash evaporation rates [7]. Also, the trapping of the released gases affects the quality of the films. To reduce these effects, only grains in the size range from 200 to 300 μm, degassed by heating to above 150° C in vacuum prior to evaporation, were used as evaporation charge. Vacuum of the order of 10^{-6} torr was maintained during evaporation. Deposition of the initial deposits was carried out at the ambient temperature of about 25° C. The GaSb films were deposited at 350° C (using a cylindrical furnace) with a deposition rate of about 40 Å sec^{-1}.

Carbon films (500 Å thick), backed by NaCl crystals, were used as the substrates for stimulated crystallization studies. The initial deposits of Bi, Cu, Ag, Sn, Pb, Au and In–Bi solder of thickness about 15 Å (calculated thickness) on carbon films

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were obtained by vacuum evaporations. GaSb films, of thickness about 1000 Å, were deposited simultaneously by flash evaporation over the initial deposits. The films were examined by transmission electron microscopy (using Phillips EM 400). To study the effect of initial deposit thickness on the subsequently grown GaSb films, Au initial deposits of different thicknesses were used. GaSb film samples with or without Au stimulators (below 30 Å thickness) were obtained on good quality mica substrates for the resistivity and the Hall effect measurements. The thickness of the grown films was kept to about 2000 Å. Evaporated silver electrodes (over the GaSb films), with silver pasted leads which provide ohmic contacts, were used for the electrical measurements. The GaSb films exhibited secondary photoconductivity. To eliminate the effect of stray light on the electrical properties, all the measurements were conducted under a thick black paper covering, i.e. under perfect darkness. All the measurements were carried out at room temperature ($\approx 30^\circ$ C). Resistivity of the GaSb films was measured by using Van der Pauws [8] four-probe method. To eliminate the electrode size errors, the resistivity measurements were made on four-leaf clover-shaped specimens obtained by use of suitable mica sheet masks. Hall effect studies were made by using samples in the form of Hall bridge geometries. Large-area electromagnets with maximum magnetic field strengths of about 1 T were used for the Hall measurements. To obtain the Hall voltage, the sample was rotated in the magnetic field and the maximum and minimum meter readings were recorded. This was done to eliminate the standing voltage across the Hall electrodes. A high impedance EC EA 814 electrometer (10^{16} Ω) and a Phillips d.c. microvoltmeter were used for recording Hall voltages. Stabilized d.c. power supply for the electromagnets and stabilized a.c. mains input to the measuring instruments were fed to attain good stability in the meter readings.

For the field effect measurements, thin (10 to 20 μm) mica sheets were used as substrates and also as insulators in the thin film transistor structure. GaSb films, grown on the thin mica sheets either without stimulator or with 5 Å and 10 Å Au stimulator deposits, were used for these measurements. Evaporated silver electrodes were used as the source and drain contacts. An aluminium gate electrode was deposited onto the other side of the mica substrate to obtain the "GaSb/Au (stimulator)/Mica/Al-gate" structure. The field effect arrangement was used to measure the source–drain conductance modulation with the perpendicular electric field applied by means of the Al-gate electrode.

3. Results

Fig. 1a to d shows the electron micrographs and the transmission electron diffraction patterns of the GaSb films obtained using no stimulator and using Ag, Sn, and Au stimulators (15 Å), respectively. The micrographs and the diffraction patterns reveal that Ag, Sn and Au stimulate crystallization in the GaSb films in increasing order. The micrographs of the GaSb films with Pb stimulator (not included here) revealed grain growth of size intermediate to that observed for Au and Sn stimulated films. In–Bi solder, Bi and Cu stimulated films revealed grain growth in increasing order and intermediate to plain (no stimulator) and Ag stimulated films. Of all the films tried, Au was found to be the best stimulator for the crystallization of GaSb films.

Fig. 2a to d shows electron micrographs of GaSb films obtained using Au stimulators of thicknesses 0, 2 Å, 5 Å and 10 Å (calculated), respectively. The micrographs show that an increase in the thickness of the stimulator deposit increased the grain growth remarkably.

The results of the electrical studies on the stimulated crystallized films are represented in Figs 3 and 4. The resistivity increases with increased stimulation whereas the carrier concentration decreases. The Hall mobility increases and the carrier concentration decreases with increasing stimulator thickness (Fig. 4).

The results of the field effect measurements are represented in Fig. 5. A plot of the conductance modulation, $\Delta I/I$, against the modulating voltage, V, (Fig. 5) reveals that the modulation response of the unstimulated film is weak; the 5 Å Au stimulated film shows a considerably improved response and the modulation response of the 10 Å Au stimulated film even greater.

4. Discussion

The carbon film substrates used for the depositions provide an amorphous substrate surface that avoids the preferred nucleation and orientation effects; because the crystallization without stimulator is kept to minimum by the amorphous substrate, the carbon film substrates assist to achieve

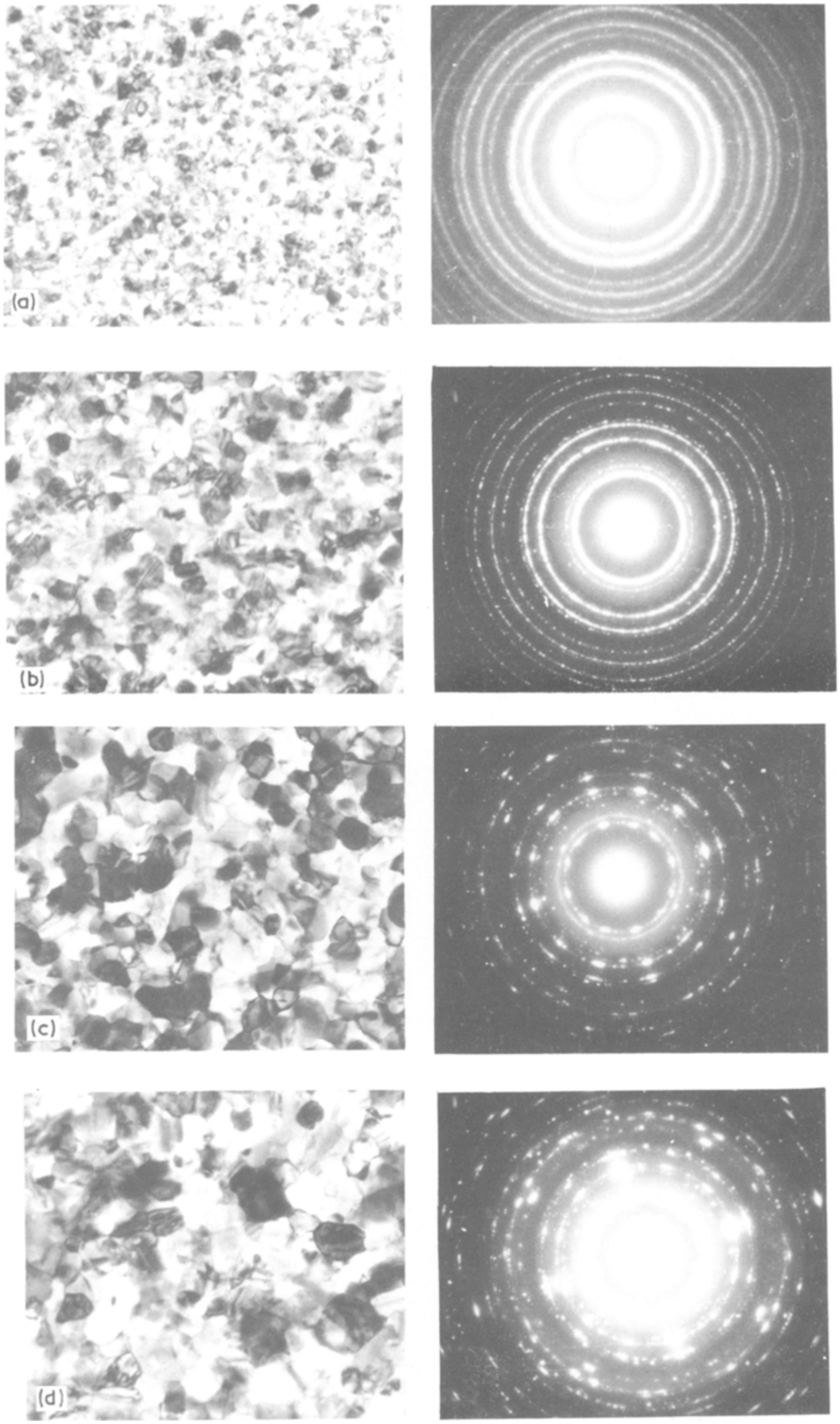

Figure 1 Electron micrographs of GaSb films deposited on carbon film substrates, (a) without stimulator; (b) with 15 Å In–Bi solder film; (c) 15 Å Ag film and; (d) 15 Å Au film stimulators (× 65 000).

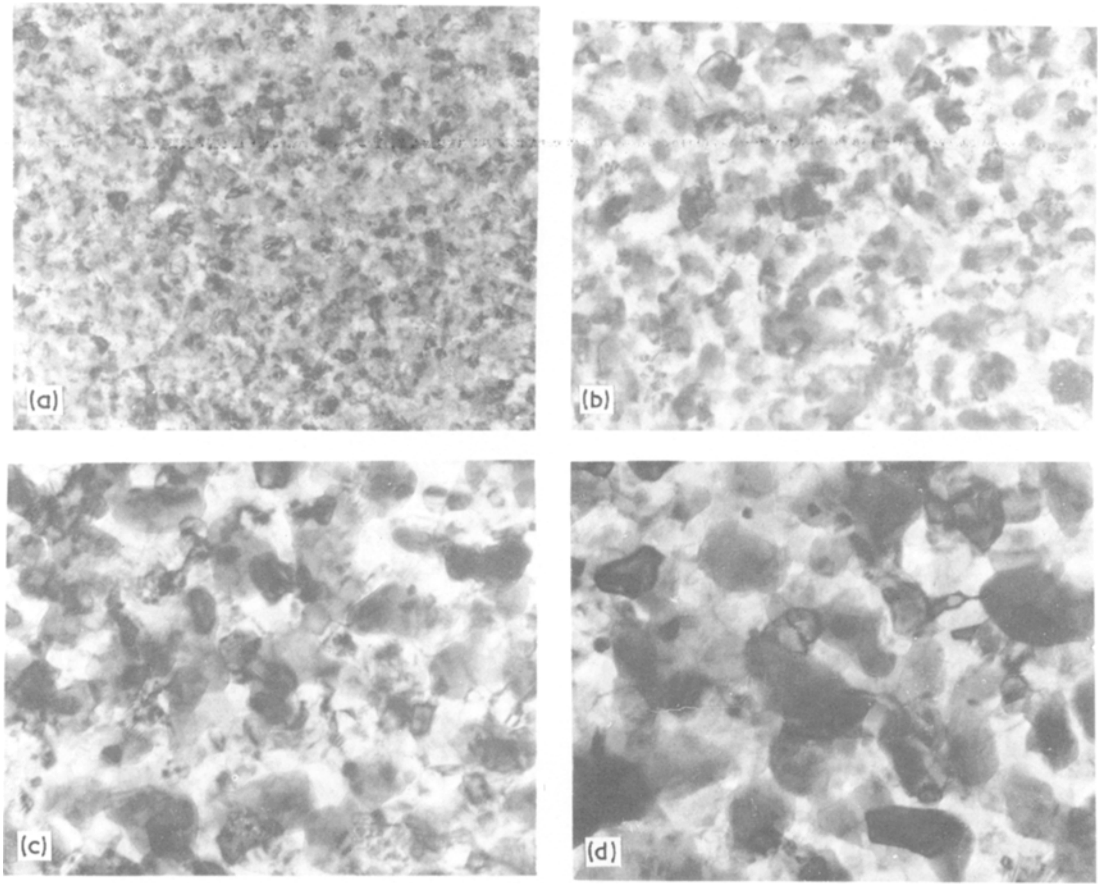

Figure 2 Electron micrograph of GaSb films deposited on carbon film substrates with gold stimulator. The stimulator thicknesses are (a) 0 Å, (b) 2 Å, (c) 5 Å, (d) 10 Å. (× 90,000).

better distinction, with regard to the enhancing character of different stimulators. Also, the reproducibility and uniformity of the carbon film substrates helps to obtain uniformity in the deposited films and therefore in the results. As is evident from Figs 3 and 4, the effect of the stimulator in improving the electrical characteristics is noticable up to a stimulator thickness of about 30 Å. Therefore, the maximum stimulator thickness was maintained at about 30 Å.

The increase in the resistivity may be attributed to the decrease in the carrier concentration (Fig. 3). The decrease in the carrier concentration and the increase in Hall mobility (Fig. 4) may be accounted for by the increased grain-size and perfection of the deposited film resulting from an in-

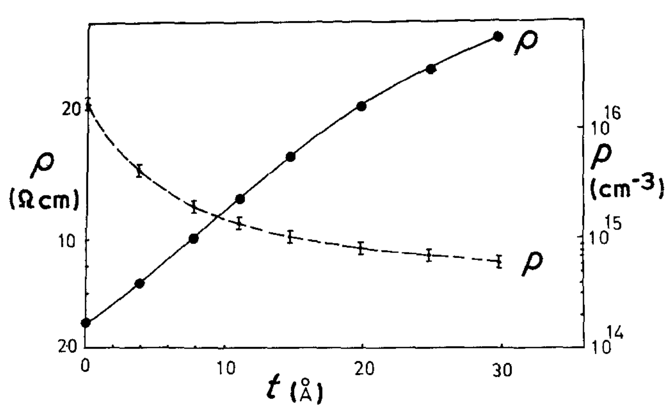

Figure 3 Variation of resistivity (ρ) and carrier concentration (P) with gold stimulator thickness (t).

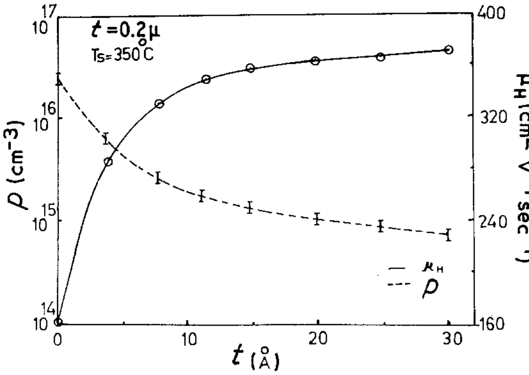

Figure 4 Variation of Hall mobility (μ_H) and carrier concentration (P) with gold stimulator thickness (t).

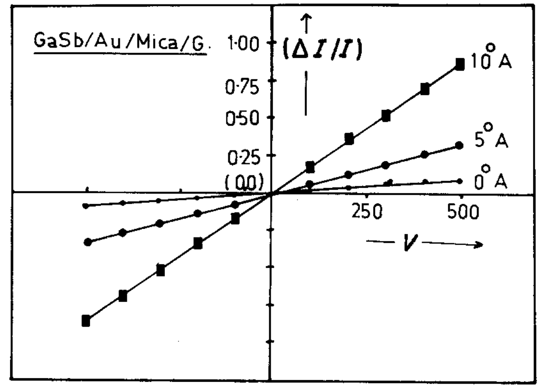

Figure 5 Conduction modulation response ($\Delta I/I$) of unstimulated and 5 and 10 Å gold stimulated GaSb films with modulating voltage (V).

crease in the stimulator thickness; the increased grain-size and perfection increases the mean free path of the carrier, which increases the Hall mobility. The conductance modulation response of the Au stimulated films is considerably larger than that of the unstimulated films. This may be attributed to the increased perfection and decreased carrier concentration resulting from the use of a stimulator.

In the impurity crystallization or vapour–liquid–solid process [5, 9] the role of the impurity layer (of thickness several μm) is to form a liquid alloy with the material to be grown from the vapour. The depositing material diffuses through the liquid alloy layer to the substrate, therefore, making incorporation of the impurity in the grown layers unavoidable. In the case of the ultra-thin stimulator deposits the diffusion process appears unimportant, but the energetics of nucleation and growth process may change. Dutton [10] has proposed ultra-thin Au initial deposits in the form of non-overlapping islands acting as "nucleation sites" stimulating large crystallites in Te films.

No adverse effects caused by the incorporation of the stimulator material in the crystallites were observed from the electrical measurements. In fact, the carrier concentration in the crystallites decreased with increased stimulations. Similarly, the stimulated films showed an improved conductance modulation response instead of showing the ill effect of the stimulator material on the surface properties (Fig. 5). This suggests that the stimulator material may be segregating in the intercrystalline regions (after stimulating large crystallites in the GaSb films) and its inclusion into the crytallites may be negligible.

5. Conclusions

The results of this investigation indicate that, by using Au ultra-thin initial deposits as a stimulator for crystallization, a number of properties of the polycrystalline GaSb films such as grain size, Hall mobility, and carrier concentration can be improved.

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