Effect of process conditions on microstructure and performance of thermally evaporated InSb thin films

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Technologically important Indium Antimonide (InSb) thin films have been grown on different substrates (NaCl, KCl, KBr, quartz and glass) maintained at varied temperatures (300, 373, 473, 623 and 703 K) using a thermal evaporation technique under vacuum (~10^{-3} Pa). These films have been prepared by utilizing a single phase stoichiometric InSb compound produced by vertical directional solidification (VDS) technique. Scanning and transmission electron microscopy (SEM & TEM), X-ray diffraction (XRD), fourier transform infrared spectrometry (FTIR) and electrical resistivity measurements are the important characterization methods used for analyzing these films deposited under different process conditions. The conditions have been determined to deposit good quality epitaxial films of InSb. The effect of the type of substrate and its temperature on the quality of thin films in terms of their structure and microstructure and different properties has been evaluated.

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InSb is an important semiconductor for the preparation of various devices. It is a low band gap semiconductor with high electron mobility and excellent galvanometric properties. It is particularly useful in high speed electronic and galvanometric devices. It is a promising material for the production of magnetic and infrared detectors in 3-5 µm wavelength range, and is also useful for large area detector arrays and optoelectronic devices. The material is also utilized in phase change optical storage. Bulk InSb crystals have been grown using different methods such as Czochralski, Bridgman, zone refining, vertical gradient and centrifuge. In the present investigations we have undertaken the growth of undoped bulk InSb crystals by vertical directional solidification (VDS) method. Thin films of InSb are applicable as Hall Effect devices, magnetoresistance and tuning in infrared lasers and detectors. These films have been finding significant applications in device fabrication, used as position detectors, direct drive motors or components of electronic equipments. Extensive work has been devoted to improve the quality of InSb films, using various methods. These films have been grown by various methods such as liquid phase epitaxy, metalorganic vapour phase epitaxy, molecular beam epitaxy, hot wall epitaxy and sputtering. It is generally observed that the behaviour, properties and microstructure of the InSb films depend on the deposition conditions such as the substrate temperature, time of evaporation and evaporation source, material temperature and pressure in the system during synthesis. An optimum vacuum and substrate temperature for the production of high quality films are always required.

In the past several aspects of InSb thin films have been studied. The structural and optical properties of narrow band gap semiconductors such of InSb, InP, InAs and AlSb have been investigated. X-ray diffraction and auger spectroscopy photoemission were used to study the interface and subsequent growth of InSb on Si(100). In_{1-x}Sbx films prepared by flash evaporation technique were characterized to correlate the microstructure with optical properties. Subsequently, exposure to laser beam of these films showed phase transformation and the material was found applicable in multiple recording.

Relatively little work has been carried out on the structural investigations of thin films of InSb. The present work has been devoted to the preparation of InSb thin films deposited on KCl, NaCl, quartz and glass substrates maintained at different temperatures in order to obtain good quality epitaxial films. The InSb compound used for evaporation, in this case has

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been grown by VDS method. These films have been characterized in respect of microstructure, composition, resistivity and transmittance by using SEM and TEM, energy dispersive spectrometer (EDS), four probe method and FTIR respectively. Detailed set of experiments has been discussed to elucidate the effect of deposition conditions on the microstructural features and performance of these films.

**Experimental Procedure**

**Growth and characterization of InSb compound**

InSb compound was prepared using VDS system. In this method, the compound was grown in a conical quartz ampoule without using seed. The loss of Sb related problem was reduced by employing a closed quartz ampoule, evacuated under high vacuum. High purity indium (99.999%) and antimony (99.999%) were taken in stoichiometric proportions and loaded in the quartz ampoule of 12-15 mm diameter and 150 mm in length with conical shape at one end. Ampoule of cone angle below 20° was preferred in the growth experiment. The temperature of the furnace was raised up to 1073 K and maintained for four hours for synthesis and homogenous mixing of the source material. For the growth of good quality crystals, the ampoule was lowered to the gradient zone of the furnace at the rate of 5 mm/h where the temperature range was 848-923 K.

XRD measurements of as grown InSb powder were carried out by X-ray diffractometer (model Philips PW 3020) using CuKα line. The morphology of InSb compound was examined using scanning electron microscope (SEM, model LEO 440) having an attachment of energy dispersive spectrometer (EDS, model Link ISIS-300, Oxford). The infrared transmittance of the as grown InSb bulk compound and its thin films deposited onto KCl substrate at different deposition temperatures was recorded using FTIR, model Perkin and Elmer, System 2000 in the wave number range 400-4000 cm⁻¹.

**Preparation and characterization of InSb thin films**

Bulk InSb compound grown by VDS technique was used to deposit thin films by thermal evaporation technique under vacuum. In these experiments bulk material was taken in the tungsten boat and evaporated in a vacuum (~10⁻³ Pa) system equipped with liquid nitrogen trap. The films were deposited onto freshly cleaved KCl, NaCl, quartz and glass substrates at different temperatures (300, 373, 473, 623 and 703 K).

Detailed process parameters and post annealing conditions of thin films are illustrated in Table 1. The films deposited onto KCl, NaCl and quartz substrates were used for microstructural investigations while the films deposited onto glass substrate was used for studying the electrical resistivity. The distance between the source and the substrate was kept 135 mm. The thickness of these films varied from 50 to 100 nm and was measured by ellipsometric method as well as gravimetric method. The temperature of deposition was measured using a Chromel-Alumel thermocouple of 32 gauge wire fixed with the substrate holder. Thin films thus prepared were examined for elemental analysis and stoichiometry by EDS system attached to SEM. The films grown at 300, 373, 473 K were further annealed at 473K for two hours under high vacuum to study the structural stability and grain growth.

The microstructure of these films has been investigated by TEM (JEOL model JEM-200 CX)

![Table 1—Experimental details](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Film deposition temperature(K)</th>
<th>Annealing temperature(K), annealing time: 2 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>300</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>473</td>
</tr>
<tr>
<td>NaCl</td>
<td>300</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>703</td>
<td>473</td>
</tr>
<tr>
<td>KBr</td>
<td>373</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>473</td>
</tr>
<tr>
<td>Glass slide</td>
<td>300</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>473</td>
</tr>
<tr>
<td>Quartz slide</td>
<td>703</td>
<td>473</td>
</tr>
</tbody>
</table>

Fig. 1—A photograph of bulk InSb compound as grown by vertical Directional Solidification technique
operated at 200 kV. The specimen for TEM examination were prepared by removing the films from KCl, NaCl and quartz substrates and subsequently, these films were picked up on 200 mesh copper grids of 3.05 mm in diameter.

Results and Discussion

Morphology and structure of InSb compound

The ingots of InSb grown by VDS were found to be void free and having good shining. Figure 1 shows the photograph of a typical as grown InSb ingot which is 12 mm in diameter and 30 mm in length. The X-ray diffraction pattern of the powder from the as grown ingot shows very sharp and well resolved peaks of InSb compound (Fig. 2). The powder data are in excellent agreement with the international center for diffraction data (ICDD) file of InSb (No. 6-208) which indicated the formation of a single phase InSb compound with cubic structure \( (a = 0.647 \text{ nm}) \). Some of the reflections due to CuK\( \alpha_2 \) are also indicated (Fig. 2). The production of single phase InSb compound by VDS is a noteworthy feature. SEM micrographs of small pieces of the compound indicate the growth of the InSb compound, synthesized by VDS technique as depicted in Fig. 3 (a and b). The fractured surfaces depict a set of cleavage planes in the microstructure. Some of these planes are indicated by a set of arrows in the micrograph (Figs 3a and 3b). Figure 4 shows the energy dispersive spectra (EDS) of bulk crystalline InSb compound indicating In and Sb peaks at different energy levels. The percentage of In and Sb in this compound was found to be 49.3 and 50.7 respectively showing that the stoichiometry of In and Sb in the compound is maintained after the growth.

Microstructural features evolved in InSb films deposited on KCl

InSb films deposited on KCl maintained at room temperature (300 K) were examined under TEM. A typical bright field micrograph of the film is depicted

Fig. 2—X-ray powder diffraction pattern of as grown InSb compound

Fig. 3—SEM micrographs indicating the growth of InSb compound. A set of cleavage planes are indicated in the microstructure.

Fig. 4—Energy Dispersive Spectroscopy data of as grown InSb bulk.
in Fig. 5. A corresponding electron diffraction ring pattern is shown as an inset of Fig. 5. From the micrograph and electron diffraction pattern it is observed that the film has polycrystalline growth. The detailed study of the film showed that the entire film was homogeneous in microstructure with the size of the crystallites between 20 to 60 nm. Polycrystalline growth was further reflected in the electron diffraction pattern recorded from different regions of the film. Table 2 shows the detailed analysis of the $d$-spacings and corresponding planes calculated from the diffraction pattern. These values are also in agreement with standard data of face centered cubic InSb structure (Table 2). As deposited InSb films were also studied for elemental composition by EDS system attached with SEM. The EDS spectra of the InSb thin film is as shown in Fig. 6. It has been observed that the stoichiometry of In and Sb in thin film is maintained throughout the specimen. The presence of K and Cl peaks indicated in the EDS pattern corresponds to the KCl substrate used for the deposition during the synthesis of the films. Grain growth in thin film deposited at 300 K was studied after annealing at high temperature. The film annealed at 473 K for two hours showed that the microstructure still consisted of polycrystallites and the electron diffraction investigation of the films revealed ring pattern. However, the grain growth was noticed in the film and after annealing the size of the crystallites was found to vary from 30 to 100 nm.

The films of InSb deposited at a substrate temperature of 373 K also showed polycrystalline nature of thin film. It was somewhat surprising to note that a large area of fraction under TEM, revealed moiré fringes in the microstructure. These moiré

Table 2—Intensity and $d$-spacing of observed and standard InSb

<table>
<thead>
<tr>
<th>Ring number</th>
<th>Intensity</th>
<th>Observed spacing ($d$ Å) and (hkl) values corresponding to InSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Strong</td>
<td>3.742 3.74 0(111)</td>
</tr>
<tr>
<td>2.</td>
<td>Mod.</td>
<td>2.299 2.290 (220)</td>
</tr>
<tr>
<td>3.</td>
<td>Mod.</td>
<td>1.960 1.953 (311)</td>
</tr>
<tr>
<td>4.</td>
<td>V.W.</td>
<td>1.618 1.620 (400)</td>
</tr>
<tr>
<td>5.</td>
<td>V.W.</td>
<td>1.486 1.486 (331)</td>
</tr>
<tr>
<td>6.</td>
<td>V.W.</td>
<td>1.327 1.323 (422)</td>
</tr>
<tr>
<td>7.</td>
<td>V.W.</td>
<td>1.247 1.247 (511)</td>
</tr>
<tr>
<td>8.</td>
<td>V.W.</td>
<td>1.097 1.095 (531)</td>
</tr>
</tbody>
</table>

S- Strong, Mod.-Moderate, W-Weak, V.W.- Very Weak

Fig. 5—TEM bright field micrograph of InSb thin film deposited on KCl substrate at 300K. Inset shows the electron diffraction pattern of thin film indicating polycrystalline nature of the film.

Fig. 6—Energy dispersive Spectroscopy data of InSb thin film deposited on KCl substrate at 300K.

Fig. 7—Microstructural features of film deposited on KCl substrate at 473 K. Inset reveals the polycrystalline nature.
fringes are stable even after annealing at 473 K for two hours. A detailed study of on the structure and microstructure of moiré patterns has been presented elsewhere\textsuperscript{24,27}.

Figure 7 shows the microstructural features of thin film deposited at 473 K. It is seen that the size of crystallites is further increased, as compared to the film synthesized at 300 and 373 K. An average size of these crystallites was 60 nm. However, the polycrystalline nature of these films was still maintained. As an illustrative example, the ring pattern recorded from the microstructure has been shown as inset in Fig.7. The films annealed further at 473 K for two hours was studied to investigate the grain growth in fine crystallites. It was found that the grain coarsening in the crystallites occurred. The average grain size noticed after the annealing was 100 nm and the polycrystalline nature of the film was still maintained.

The phenomenon of epitaxial growth was observed in the case of thin film deposition onto KCl crystal having (001) orientation at 623 K. Microstructural feature evolved at this temperature are elucidated in Fig. 8a. Epitaxial nature of the film was revealed from the long crystallites of the lathe shaped. This type of microstructure was originated due to the preferred growth direction, at the substrate-film interface. These long crystallites of 300 nm, were arranged parallel in most of the cases. These crystallites also appeared to be abutting each other in the microstructure. On indexing the electron diffraction pattern recorded from different regions showed the zone axes of the type \{001\} of cubic structure (Fig. 8b). Accordingly the planes reflected in orientation are &lt;200&gt; and &lt;220&gt;. Since the films were deposited on KCl substrate having (001) orientation, the electron diffraction pattern along \{001\} zone axes was expected in epitaxial condition. The diffraction pattern also exhibited some weak reflection, maintaining the periodicity. These weak reflections were predicted due to the underlined surrounding crystallites abutting perpendicular to each other. This evidence is very much reflected in micrographs.

![Fig. 8](image1.png)
![Fig. 9](image2.png)
Microstructure evolved in InSb films deposited on NaCl

InSb films were also deposited on NaCl substrate at various temperatures. It was interesting to note that the films grown at temperatures 300, 373 and 473 K, showed almost same polycrystalline nature, as seen in case of films deposited onto KCl substrate maintained at same temperatures. Only a little variation in grain size was noticed. However, the films deposited at 703 K revealed a microstructure as depicted in Fig. 9a. The micrograph shows some variation in microstructure and the crystallite size was found approximately between 40 to 160 nm. The micrograph also showed a growth tendency in the films towards epitaxial in nature. Nevertheless, the fine crystallites are still present and therefore a complete epitaxial film could not be obtained. Electron diffraction pattern corresponding to these film has been shown in Fig. 9b. The pattern clearly shows spots superimposed on the rings indicating polycrystalline nature of the film. On indexing the electron diffraction pattern it is observed that all the reflections (rings) in the pattern correspond to InSb phase only having cubic structure with preferred (111) orientation revealing a tendency towards epitaxial growth of the InSb film in case the temperature of NaCl substrate is further increased.

Thin films of InSb were also deposited on quartz substrate at 703 K to study the phenomenon of epitaxial growth. It was noticed that the material consisted of a polycrystalline grain growth during synthesis. The size of the crystallites were found to vary from 40 to 200 nm. These micrographs also showed the tendency in the film towards epitaxial in nature. Nevertheless, the fine crystallites were still present and therefore a complete epitaxial film could not be obtained.

Parameters affecting the microstructural features during deposition

A detailed analysis has been carried out to investigate the various parameters and their effect on grain size obtained in thin films grown on to KCl and NaCl substrate at various temperatures. From the above mentioned microscopic details, further analysis was carried out quantitatively to investigate the effect of lattice mismatch and thermal conductivity of the substrate on the grain size. Figure 10 shows an elucidatory result of grain size variation with different substrate temperatures. A significant variation in grain size was noticed at 623 K in case of KCl substrate. This phenomenon can be explained on the basis of relatively small mismatch (~ 2.9 %) in InSb (a = 0.647 nm) and KCl (a = 0.629 nm) parameters along a common 001 orientation and the temperature 623 K was sufficient for the epitaxial growth. In contrast to KCl, the lattice mismatch between InSb and NaCl (a = 0.564 nm) is relatively high (~13 %) and therefore the epitaxial growth was not possible even at high temperatures, such as 703 K (Fig. 9a). However, the microstructural evolution in InSb films grown on NaCl at 703 K indicates that a further increase in temperature of the substrate could lead to a clear epitaxial growth of InSb on NaCl also.

Another important parameter which may influence the microstructural features evolved during deposition of the films is the substrates thermal conductivity. The thermal conductivity of NaCl is higher at different temperatures as compared to KCl. For example, the thermal conductivity of KCl at 460 K is 0.0385 W cm\(^{-1}\) K\(^{-1}\), whereas it is 0.0418 W cm\(^{-1}\) K\(^{-1}\) in NaCl. Due to this difference, it is possible that the film grown on KCl substrate would not have enough cooling time due to substrate during deposition and therefore would have sufficient time to settle up the atom by atom matching at lattice scale between InSb and KCl. This is also a reason for the epitaxial growth of thin film on KCl at lower temperature, compared to NaCl. This effect was clearly reflected in films grown at 623 K, using KCl substrate.

Electrical resistivity measurement

The variation of electrical resistivity with temperature of the stoichiometric InSb thin films (thickness: 60 nm) deposited at the temperature of 300 K and annealed at 473 K for two hours is shown in Figs 11a and 11b, respectively. From these plots it
is observed that in both the cases the electrical resistivity decreases with increase in temperature. This clearly shows that the films are semiconducting in nature. The other important point to be noticed is that the resistivity of the films decreases after annealing. This may be ascribed to the comparatively growth in grain size and more ordered structure thereby reducing the number of grain boundaries in the film and hence smaller number of defects/scattering centres in the film after annealing at 473 K for two hours.

Figure 12 depicts the variation of electrical resistivity with temperature plot of the InSb thin films deposited at substrate temperature of 473 K. From this plot, it is observed that the electrical resistivity of the films has further decreased as the deposition temperature is increased. It is also observed that the film still shows semiconducting behaviour. When this film is annealed at 473 K for two hours it has been noticed that the electrical resistivity has further decreased as revealed in Fig. 12b. This may be due to the bigger crystallites size in the film at higher substrate temperature as compared to the film deposited at lower substrate temperature. The increase in crystallite size at the higher deposition temperature has resulted in the reduction of grain boundaries ultimately leading to the decrease in electrical resistivity of the InSb thin films. It has been observed that the resistivity of the InSb thin films deposited at 473 K is decreased by a factor $10^2$ as compared with the InSb films deposited at room temperature.

The variation of electrical resistivity with temperature of the InSb thin films deposited at 623 K has been shown in Fig. 13. The plot of electrical resistivity versus temperature clearly shows that the resistivity of InSb thin films deposited at 623 K has decreased and approached towards the resistivity of the InSb bulk compound ($5\times10^3$ ohm of intrinsic InSb) indicating the formation of more ordered structure at higher substrate temperatures. It has also
been observed during the microstructural investigations of the InSb thin films that the films deposited at 623 K has shown the epitaxial growth. The resistivity data of the InSb thin films also suggest and support the formation of epitaxial films at the substrate temperature of 623 K indicating the resistivity of the order of bulk crystal. At higher substrate temperatures, the films show lower values of electrical resistivity indicating the formation of more ordered films and ultimately reducing the grain boundary effect which play an important role in the resistivity.

The electrical resistivity measurements were also conducted on the thin films deposited at the substrate temperature of 373 K. It has been seen that though the overall trend of the films deposited at 373 K was semiconducting in nature, as in the in the case of the films deposited at 300 and 473 K, there were local fluctuations in the resistivity data. The results were surprising and the phenomenon was unusual at this deposition temperature. Since the microstructure seen at this deposition temperature in these films was not uniform and contained defects and moiré fringes as described presumably explain the local fluctuations in the resistivity data.

**IR transmittance measurement**

The infrared transmittance measurement of the bulk InSb compound as well as thin films was recorded using Fourier transform infrared spectrometry (FTIR) in the wave number range of 400-4000 cm\(^{-1}\) (25-2.5 µm wavelength range). From the transmittance spectra of bulk InSb compound, it is observed that the material becomes transparent for the wavelength longer than 7.5 µm (Fig. 14a). The energy band gap calculated from the IR transmission data of 7.5 µm wavelength was found to be 0.17 eV at 300 K.

The result of InSb thin films deposited at 300, 473 and 623 K revealed that the transmittance increases with the increase in the temperature of thin film deposition (Fig. 14b). The as deposited (room temperature, 300 K) film has nano-crystalline structure and has large number of grain boundaries. The grain boundary reflections results in more scattering of infrared radiation in the film. The scattered light has more chance to be absorbed by the films. Therefore a reduction in transmittance is observed for the as deposited films. As the temperature of deposition is increased (473 K), only thermodynamically stable phases are present, in addition to this the grains also coarsen resulting in the reduction of grain boundaries. This decrease in grain boundary areas will reduce the scattering of the infrared radiation in the film and result in the increase in the transmittance.

The films grown at 623 K which is epitaxial in nature as depicted from the microstructural analysis revealed that the grain size have further increased but the transmittance has decreased as compared to the films deposited at room temperature (300 K) and 473 K. It is because of the fact that the impurities which were trapped in the grain boundaries at lower deposition temperatures may diffuse into the grain at higher deposition temperatures (623 K) resulting in impurity scattering and consequently reduction in the IR transmittance. Energy band gap of the InSb thin films deposited at different temperatures has been calculated from recorded transmittance spectra and found to be 0.08 eV. It has been shown that IR transmittance in InSb thin films depends on grain boundary and intra grain impurity scattering.

**Conclusions**

Stoichiometric InSb compound (length 30 mm, diameter 12 mm) with cubic crystal was grown using
vertical directional solidification. The as grown InSb was used to deposit thin films on KCl, NaCl, quartz and glass substrates maintained at different temperatures (300, 373, 473, 623 and 703 K). All the films deposited have shown the cubic structure with nearly maintained stoichiometry of In and Sb. A systematic grain growth was noticed with increase in substrate temperature from 300 to 473 K. However, a sharp increase in size of the grains with epitaxial in nature on KCl substrate was observed in InSb thin films deposited at 623 K. Electrical measurements and IR transmittance have been evaluated on these films to examine the utility of the material for different device applications.

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References