**Crystal preparation and study**

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**Abstract**

The preparation procedure of a high purity InSb single crystal by using direct solidification method is reported. The dimensions of the crystal are 4cm length and 1.1cm diameter. The plane (022) is the preferred direction of crystal growth. Sequence thermal evaporation under vacuum is used to grow InSb films on Si (111) substrate. Antimony (Sb) film of thickness ~0.12μm is first evaporated on Si(111) wafer at substrate temperature (T_s) ~150 °C then InSb polycrystalline compound evaporated in sequence times on the same Si(111) wafer with gradient in substrate temperature (300 – 330) °C. Films with thickness 3μm were obtained. The structure of the grown InSb crystal and thin films are studied by X-ray diffraction (XRD) technique. The optical absorption spectra of deposited InSb films have been carried out at room temperature in the wavelength range (2.5-10)μm. The onset of absorption fits a direct electronic transition formula in these films and the direct optical band gap (E_g) is 0.17eV. The value of the width of the tails of localized states in the forbidden gap, the Urbach energy, is 0.0073eV.

**Key words:** Crystal growth, vacuum deposition, InSb films, optical gap, Urbach energy.

**Introduction**

InSb is the higher electron mobility (76000cm²/Vs) [7] with the smallest energy gap 0.17 eV at room temperature (R.T) [23], compared to other III-V compound semiconductors which make it more suitable for high-speed devices, magnetic sensors and infra-red detectors. The band structure of this material[20] is shown in Fig. 1. The structure shows that InSb is a direct band gap material.

![Band structure of InSb](image)

**Fig.1:** Band structure of InSb

Crystal preparation and study       S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim, and M. A. Mahdi

The preparation of InSb films by thermal evaporation is usually indium rich because of the loss in antimony amount that possess a higher vapor pressure due to non stoichiometry in InSb films. So, impurity concentration will increase [17].

This problem can be avoided by using different preparation techniques, for example the co-evaporation of (In) and (Sb) from individual sources, and can control their ratios of them [11], or using the same technique but evaporate InSb from one source and (Sb) from another source, in this case (Sb) loss amount in films will be compensated [17].

Molecular beam epitaxy (MBE) [21], liquid phase epitaxy (LPE) [5], D.C. sputtering [18] and other techniques [2] are used to prepare InSb films.

Epitaxy is the growth of a thin film on a substrate in which the crystal properties of the film are inherited from those of the substrate. Since an epitaxial film can (at least in principle) grow as a single crystal without grain boundaries or other defects, this method produces crystals of the highest quality. In heteroepitaxy, the lattice mismatch between the substrate and the film plays a key role on growth mode.

Large lattice mismatch (>19%), different thermal expansion coefficient (\(\alpha_{\text{InSb}} = 2\alpha_{\text{Si}}\) at 300K), and antiphase domain formation (polar on non-polar growth) between InSb and Si, made the growth of InSb films (layer) on Si very difficult [19]. Buffer layer such as BaF\(_2\), CaF\(_2\), GaAs, In can ease the growth of InSb on Si crystal [5,8,19]. Figure (2) explains the lattice mismatch between Si and some III-V semiconductor compounds [7].

In this paper, we present the preparation technique of InSb crystal showing the direct heteroepitaxial growth of InSb films on Si(111) substrate, using antimony (Sb) as a buffer layer to compensate the loss of antimony. The conditions of epitaxial, structural, and optical properties of these films are also reported.
Figure (2) Lattice mismatch between Si and some semiconductors compound [7]
Crystal preparation and study .......... S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

II. Experimental
II. A-Crystal preparation:

Part of this study is to prepare (15gm) InSb single crystal, thus equivalent quantities of high purity (99.9999%) indium (In) and antimony (Sb) Fluka AG company are taken. Clean quartz tube of 20 cm length, 1.1 cm diameter and 1.2 mm thickness is being used. One of the tube ends tapered to be as the seed of the crystal growth. It is washed again with acetone, ethanol and distilled water. The tube is then connected to Edwards high vacuum system (England) until it reaches a vacuum of $10^{-3}$ torr, and is cleaned again with oxyacetylene flame to ensure cleanliness from any impurities.

The In ($T_m=157 \, ^\circ C$) and Sb ($T_m=630 \, ^\circ C$) are put inside the tube in sequence according to their melting point ($T_m$). The tube is connected to the vacuum system until it reaches a vacuum of $\sim 10^{-6}$ torr, then is closed by oxyacetylene flame and become ready to be inserted in a furnace of regular temperature gradient type (Linberg 304 Hart ST. Watertown Wis,53094) is connected to a computer to control the temperature increasing.

The tube is fixed inside the furnace by Ni-Cr cable so the tapered end is located in low temperature regime, then the gradual increase of temperature is being started with a rate of 25 $^\circ C$/h until reaching a temperature $\approx 750 \, ^\circ C$, depending on the phase diagrams of InSb compound[3].

The furnace temperature is fixed at this temperature for 18 hours with a rocking process carried out from time to time to ensure the mixing of the two materials. After that, the furnace is sloped towards the narrow end with an angle $\sim 30^\circ$. The slow cooling process was then started with 2 $^\circ C$/h rate until it reaches a temperature $\sim 50 \, ^\circ C$ and the furnace is then switched off. Finally, the crystal is taken out from the quartz tube becoming grey color and highly reflective (Fig. 3). The dimensions of the crystal are 4 cm length and 1.1 cm diameter.

![InSb single crystal](image)

Figure 3: InSb single crystal
Crystal preparation and study, S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

II.B- Films preparation

A mixture of undoped InSb polycrystalline is used to prepare InSb films by successive thermal evaporation method and from a single boat.

The InSb compound is alloyed and carried out in Varian (3117) unit and is used to prepare the films where the preparation pressure is below 1 x 10⁻³ torr.

The n-type Si(111) single crystal wafer is used as a substrate. The wafer at first, immersed in HF acid for 5 minutes to remove SiO₂ layer from the surface and is cleaned by using acetone and hot water, then immersed in ultrasonic agitation for few minutes.

At first, antimony (Sb) thin film of thickness (0.12) μm on Si(111) at substrate temperature (Tₛ) = 150 °C is deposited. InSb thin film is then deposited on the same substrate at Tₛ = 300 °C of thickness 0.5 μm.

The second deposition of the InSb thin film of a thickness of 0.9 μm is deposited at Tₛ = 310 °C.

The work is continued by evaporating the InSb compound on the same substrate. The 3rd film thickness is of 1.4 μm and is prepared at Tₛ = 320 °C.

Then, InSb film of a thickness of 2.1 μm is deposited at Tₛ = 330 °C.

Finally and at the same Tₛ = 330 °C, InSb film of a thickness of 3 μm is produced. Figure (4) displays the InSb film preparation process.

In all preparation process, the rate of deposition was about 2 nm/s.

![Figure 4: InSb film preparation process](image)

II.C- Measurements and calculations

From the X-ray examination, the sample as a disc shape is cut perpendicular to the crystal axis and polished by using Buchler equipment with Al₂O₃ powder to reach light mirror surface.

X-ray diffraction (XRD) analysis, Philips X-ray diffractometer PW1253 employing CuKα radiation source, were used to obtain information about the crystal and films structures.

The optical absorption measurements at room temperature (RT) is conducted by using infrared spectrophotometer (Hitachi 270-30) in the wavelength range (2.5-10) μm.

The absorption coefficient α(ω) at angular frequency of radiation(ω) is calculated by using the relation[6]:

\[ \alpha(\omega) = \frac{2.303 (\Lambda - \Lambda')}{t} \]  

Where t is the film thickness

Crystal preparation and study .......... S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

\[ \Lambda \text{ is the absorbance} \]
\[ \Lambda' \text{ is the corrected absorbance to get rid off the reflectance following the procedure in} \]
\[ \text{references [6].} \]

III. Results and Discussions

The X-ray diffraction pattern of the InSb crystal (a polished disc) presented in Figure (5) shows an intense reflection peak from the plane (220) which indicates the preferred direction of crystal growth. The pattern showed a single peak which mean the ingot was a single crystal in cubic(zine blend) structure and the sharp peak indicated that a high crystalline of InSb crystal.

From the other work (unpublished), we noticed that the seed and the slope angle of furnace effect on crystal growth direction. Inter-planer spacing \( d_{400} \) for (220) plane and lattice constant \( a \) for single crystal were measured by using Bragg's relation [4] and the values were 0.227nm, 0.64nm respectively which agree with standard values.

The reflection peaks in the XRD analysis of the first prepared InSb film \[ Si(111) + 0.12 \mu m(Sb) + 0.5 \mu m(InSb) \] is increased with antimony amount, its peak is clear as shown in figure 6.

The second evaporation is the system \[ Si(111) + 0.12 \mu m(Sb) + 0.5 \mu m(InSb) + 0.4 (InSb) \] which also shows an increase in the (Sb) amount but this ratio is less than the first one.

The XRD of the system \[ Si(111) + 0.12 \mu m(Sb) + 0.5 \mu m(InSb) + 0.4 (InSb) + 0.5(InSb) \] shows a decrease in the (Sb) ratio of the films, and the film is a polycrystalline structure.

The fourth run shows a decrease in the (Sb) ratio of the films, and the film increases its crystallization.

By continuing deposition of InSb film on the same substrate, the antimony amount decreases and the film structure becomes more crystalline.

Finally, a single crystal film on Si(111) substrate at \( T\text{=330} \text{C}^\circ \) is obtained with a thickness of \( (3 \mu m) \). It is noted, from Figure (6), that the antimony ratio was disappeared and the preferred orientation to a single crystal film is the (111) direction. Evaporation InSb from single source led to get thin films rich in indium. So with existence heat substrate, antimony atoms will bind with indium atoms to form InSb. Some authors get InSb polycrystalline thin film on Si(111) wafer without thin buffer layer [15]. Using Ge as a buffer layer lets Mori et al. [12] to synthesize InSb single crystal film on Si(001) which means that using buffer layer sometimes leads to deposited single crystal films due to the decreasing in lattice mismatch between InSb and Si [12].

Nair et al. [16] have prepared InSb films by deposition Sb\(_2\)S\(_3\) thin films on glass substrate and thin indium (In) layer was then deposited on Sb\(_2\)S\(_3\). By annealing those films, the InSb thin films were formed. Mori et al. [13] deposited InSb thin films on Si(001) single crystal by MBE technique and also they used AlSb as a buffer layer to decrease lattice mismatch between Si and InSb from 19.3% to about 5.6%.

![Fig. 5. X-ray diffraction pattern of InSb crystal single crystal](image)

Crystal preparation and study .......... S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

![Graph](Figure 6)

(a) X-ray diffraction for InSb films on Si(111), Ts=300°C first deposition
(b) X-ray diffraction for InSb films on Si(111), Ts=310°C second deposition
(c) X-ray diffraction for InSb films on Si(111), Ts=320°C third deposition
(d) X-ray diffraction for InSb films on Si(111), Ts=330°C forth deposition
(e) X-ray diffraction for InSb films on Si(111), Ts=330°C fifth deposition

The optical band gap $E_g$ of these films is calculated by using the relation [14]:

$$\alpha(\omega)h\omega = B(\omega - E_g)^r$$

(2)

where $h\omega$ (or $hv$) is the photon energy, \(\alpha\) is the angular frequency of radiation, $B$ constant and $r = 1/2$ for direct band gap material or $r = 2$ for indirect band gap material. The relation between $\alpha(\omega)$ vs. $h\omega$ is presented in Figure (7). It is noticed that $\alpha$ is highly increased when the energy of the
Crystal preparation and study .......... S. K. J. Al-Ani, Y. N. Ohaid, S. J. Kasim and M. A. Mahdi

incident photon becomes equal to that of the band gap. However, the high values of α indicate a
direct electronic transitions and that InSb thin films possess a direct gap. Therefore, using equation
(2) with \( r = \frac{1}{2} \), the function \((αhν)^2\) is drawn vs. \( hν \) in Figure (8). The extrapolation of the
straight line to the energy axis, i.e at \((αhν)^2 = 0\) is obtained to calculate and the optical band gap of
the film was \( E_g = 0.17\) eV. Before proceeding further, it is useful to refer to some optical results of
other worker’s as follows. Reported values of band gap for InSb epitaxial films grown on a GaAs
substrate and using liquid phase epitaxy [5], are 0.17, 0.22, and 0.23 eV at RT and at 80 and 10 K
respectively, whereas for films prepared by thermal evaporation on indium tin oxide (ITO), coated
conducting glass substrates are in the range (0.169 - 0.153) eV[10]. Mahdi [9] has deposited InSb
thin films, using flash evaporation technique on Si(111) wafer and NaCl(111) single crystal
obtaining values of energy band gap equal to 0.165 eV and 0.16 eV, respectively. Obviously, in
addition to the preparation method of the epitaxy InSb films, the type of substrates have also an
important effect on the band gap value.

From the figures above, it is seen that the value of \( E_g \) of InSb films, deposited onto crystal Si
wafer, is equal to the standard value of InSb compound. Dixit et al [5] have obtained \( E_g = 0.198 \) eV
when they deposited InSb on GaAs crystal substrates using LPE technique. From their results, it is
noticed that the value of \( E_g \) is larger than ours although the lattice mismatch between the
compound and the crystal GaAs substrate is 14% less than the mismatch between the compound,
and the Si substrate 19%. Thus, our results are better, due to the use of different preparation
method.

Following the work of Al-Ani [1], the coefficient B in (2) may be obtained from the (slope) of the
linear region of the plot \((αhν)^2\) vs. \( hν \) and its units can be calculated according to \( \text{cm}^2 \text{eV}^{-1} \). Thus
the value of B in Figure (8) is calculated to be \( 1.35 \times 10^5 \) \( \text{cm}^2 \text{eV}^{-1} \) of the same order of \( 2.39 \times 10^5 \)
\( \text{cm}^2 \text{eV}^{-1} \) for flash deposited thin films [10]. It may be noted that the constant B in a quadratic
relation i.e. eqn (2) with \( r = 2 \) is equal to \( \frac{(4\pi^2 \varepsilon_0 c^2 \Delta E_i^2 \sigma_{\text{max}})}{2} \), where \( \varepsilon_0 \) is the refractive index, c
is the velocity of light, \( \Delta E_i \) the width of the tails of localized states in the forbidden gap, and \( \sigma_{\text{max}} \) is
the minimum metallic conductivity. For amorphous semiconductors, such as GeTe and As5Se3,
where \( r = 2 \), the value of B is of the order of \( 10^7 \) \( \text{cm}^2 \text{eV}^{-1} \). Other semiconductors (Si and Ge) which have
\( r = 3 \), their B’s value becomes of the order of \( 10^6 \) \( \text{cm}^2 \text{eV}^{-2} \) [1].

For many amorphous and crystalline semiconductors, an exponential dependence of \( \alpha(\omega) \sim 10^\omega \)
\( \text{cm}^2 \) may take the Urbach relation [22]:

\[
\alpha(\omega) = \alpha_0 \exp(\omega / \Delta E_i) \quad \text{................. (3)}
\]

where \( \alpha_0 \) is a constant and \( \Delta E_i \) is an energy characterizing the degree of disorder introduced from
defects and grain boundaries and, hence, it is interpreted as the width of the tails of localized states
in the forbidden gap. Figure (9) represents In α vs hν in accordance with equation (3) for InSb film.
The value of \( \Delta E_i \) is calculated from the slope of the linear part of the curve which is equal 0.0073
eV and of the order of \( \Delta E_i = 0.0025 \) eV of flash deposited InSb film [9]. Both values of \( \Delta E_i \) are in a
qualitative accordance with the variation of the values of \( E_g \) for both films. The value of \( \Delta E_i \) obtained
here is, however, one order of magnitude lower than the range of values (0.045-0.066 eV) reported
by Mott and Davis [14] for other amorphous semiconductors.

Crystal preparation and study  S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

Figure 7  The variation of $\alpha(\omega)$ vs. $\hbar\omega$ for 3$\mu$m single crystal film deposited on Si(111) substrate

Figure 8  The energy gap of a 3$\mu$m single crystal film deposited on Si (111) substrate

$E_g = 0.17eV$
Crystal preparation and study ...... S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

IV. Conclusion

InSb single crystal is prepared by using direct solidification method. The present method is easier than other published methods to prepared InSb single crystal. From X-ray pattern the plane (220) is the grow direction of the single crystal.

The difference in vapor pressures between In and Sb makes it impossible to obtain a stochiometric InSb thin films by thermal evaporation method (usually loss in Sb ratio).

Sequence deposition of InSb thin films on a thin layer of Sb led us to get stochiometric InSb films because of the compensation of Sb ratio loss.

The Sb thin layer ease growing the InSb films on Si(111) wafer getting a single crystal layer InSb in spite of lattice mismatch with Si indicating that Sb works as a buffer layer. Substrate plane direction affects the film growing direction, so it takes the (111) direction. Our InSb films are further characterized by their value of the energy gap (0.17 eV) extracted from a direct electronic transitions formula as well as the value of the width of the tails of localized states in the forbidden gap (Urbach energy) which is 0.0073 eV.
Crystal preparation and study .......... S. K. J. Al-Ani, Y. N. Obaid, S. J. Kasim and M. A. Mahdi

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تحضير بلورات ودراسة الخصائص الكيميائية لأغشية الأنيديوم انتيمونتايد الفحمية محورياً على رفائق السيليكون (111)

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المتخص

تركز العمل على تحضير بلورات المركب الأنيديوم انتيمونتايد عالية التقاوة باستخدام طريقة التصلب المباشر. أبعاد البلورة كانت 4 سم طولاً، 1.1 سم قطر، 0.2 سم سمك. كان الإنتاج المضاعف للمادة البلورية. التبخير الحراري المتتابع تحت ضغط واطي استخدم لإنتاج أغشية المركب على رفائق السيليكون (111) كقاعدة.

رسوم إشعاعات التصوير باستخدام مكرويغامتر على مادة السيليكون البلورية عند درجة حرارة قاعدة 150 درجة مئوية ومن ثم تبخير المركب الأنيديوم انتيمونتايد المضاعف البلور بدرجات متعددة عند درجات حرارة ضمن المدى (300-330) درجة مئوية.

لقد كان حجم الغشاء المحضر بعدد 3 مكرويغامتر. تم دراسة التركيب البلوري للمادة المحضر وأغشية المركب باستخدام تقنية حيود الأشعة السينية. وتم قياس طيف الإحساس البصري للأغشية المحضر عند درجة حرارة الغرفة عند أطوال موجية ضمن المدى (2.5-10) مكرويغامتر. كانت حافة الإحساس عند فجوة طاقة مباشرة قيمتها 0.17 الكلترون- فولت. تم حساب عرض الذيل المتمركز في فجوة الطاقة المحترفة من علاقة أورباخ وكانت قيمتها 0.0037 الطاقة الوربية.

الكلمات المفتاحية: تحضير بلورات، الإنتاج النظيف للمركب، أغشية الأنيديوم انتيمونتايد (InSb)، فجوة الطاقة، عرض الذيل الموضعي (طاقة أورباخ).