CHAPTER I

INTRODUCTION AND OBJECTIVES

A brief historical discourse on gray tin, why gray tin is interesting, some recently experimental results, why the author proposed the liquid phase epitaxy (LPE) of gray tin on indium antimonide, and a brief summary of results are presented in this chapter.

Tin, the element that lies below germanium in the periodic table, is the end member of the series (carbon, silicon, germanium, tin) which has the crystal structure similar to diamond but only at temperatures below 13.2 °C called gray tin. The fact that metallic tin (white, β-Sn) may transform to the semiconducting modification (gray, α-Sn) after exposure for long periods at -20 to -70 °C is well known perhaps even in antiquity.(1) Apocryphal tales relating the woes suffered as a result of this transformation are legion. For example, it is said that Napoleon's retreat from Moscow was seriously impeded by the fact that trouser buttons made of tin were regular issue to his army. There were reports of the deterioration of ancient tin artifacts, when subjected to prolonged storage in unheated museums. Such phenomenon is known as tin-pest or museum disease, as one partially transformed item may "infect" an adjoining one.

In 1851 Erdmann reported(2) on the failure of tin organ pipes as a result of the $\beta \rightarrow \alpha$ transformation. This was the first scientific report of the existence of a low temperature modification of tin. The discovery in 1950(3) of the semiconducting properties of α-Sn stimulated many attempts at preparation of single crystal samples.

In 1950 Kendall(4) succeeded in preparation of gray tin a few millimeters in length by transformation a kilogram of spectroscopically pure tin. A few lumps of gray tin were found among the large quantity of fine powder.

In 1953 Ewald(3,5)succeeded in preparing gray tin filaments. The method of preparation involved drawing out glass capillaries filled with tin to a core diameter size of about 0.1 mm. The glass is then removed with hydrofluoric acid and the filaments are transformed by storing them in gray tin powder at a temperature of -30 °C. X-ray Laue patterns showed the well-defined spots which indicated that the filaments propably were single crystals.

In 1958 Ewald and Tufte(6) succeeded in preparing gray tin single crystals from a saturated mercury solution at -30 °C.

All gray tin preparation methods mentioned above provide gray tin which is stable up to 13.2 °C. Above this temperature it transforms to white tin which has a tetragonal crystal structure.

In 1954 Groen(7) described a method of preparing large pieces of grey tin by transforming an alloy of tin containing about 2% atomic of mercury. And Ewald(1) reported that the grey tin produced by transforming a Sn -0.75% weight of germanium alloy could exist even when exposed for prolonged periods at temperatures up to about 60 °C.

Grey or white-tin whiskers or filaments between 0.5 and 5 μm in diameter and 0.1 and 10 mm in length, can exist naturally or can be grown artifically on some forms of tin plate. In 1974, Morris and Bonfield(8) prepared grey tin whiskers at room temperature by the "squeeze grown" method and studied the crystallography of grey tin whiskers by electron microscope and for the first time showed that grey tin whiskers contained crystallites. Grey tin whiskers' temperature stability range was not studied at that time.

In 1980 Vnuk(9) produced the compact α -tin specimens (containing 0.1 atomic percent of germanium) of fairly large dimensions (1.5 x 10 x 100 mm) by the one-dimensional growth method. The specimens were stable up to about 60 °C.

In 1983 Gallerneaut, Vnuk, and Smith(1) succeeded in preparing grey-Sn -0.6% weight of silicon tape samples. It was seen to be stable up to approximately 90 °C.

Although bulk single crystals of α-Sn were prepared by Ewald and Tufte, all attempts at growing single crystal films(2) were reported as unsuccessful. Grey tin in common occurrence is a loose, dark grey powder. As evident in table 1(10), the densities of the

two modifications differ markedly. The conversion of white tin into grey tin is accompanied by an appreciable change in volume. This makes it difficult to obtain a sizeable grey tin single crystal from white tin.

Table 1 Properties of the α and β modification of tin

Property	α-Sn	β-Sn
Lattice spacing, Å	a=6.4892	a=5.8197, c=3.1749
Specific gravity, g/cm³	5.765	7.298
Coefficient of linear expansion, deg⁻¹	20.9x10⁻⁶	5.0x10⁻⁶ (-130 to 25° C)
Forbidden gap width, eV	0.08	-
Debye temperature, °K	2.30	-

As the closest electronic and crystallochemical analogue of grey tin, indium antimonide can be used as the seed for crystallization of grey tin especially in an epitaxial growth. The lattice constants of InSb and α-Sn differ by only 0.14% so that substrate stabilized formation of α-Sn should be possible InSb (a = 6.4798 Å), α-Sn (a = 6.4892 Å) at 25°C.

Farrow attempted to grow 11.5 μm α-Sn films on InSb in a 10^{-6} torr standard evaporator. This method yielded some reasonably epitaxial films, as judged by electron diffraction. These films showed the usual bulk α →β transformation at 13°C.

The first(12) α-Sn thin film of high crystalline perfection were grown by Farrow et al. by Molecular Beam Epitaxy (MBE) at the UK Royal Signals and Radar Establishment (RSRE) in 1981. They grew B-doped α-Sn films on InSb (001) wafers up to a thickness of 5000 Å. Such specimens allowed more accurate property characterization and had great potential in infrared applications. Due to the smallness of its band gap, ~ 0.12 eV, α-Sn fills the long-standing need in photovoltaic detection of long wavelength infrared (Farrow, R.F.C, Robertson, D.S., 1981 British Patent Application No. 81 09471).

The close lattice match between InSb substrate material and α-Sn allows the latter to grow in thin epitaxial film form and, very importantly, stays as a metastable phase significantly above its bulk transformation temperature. The latter can be exceeded by more than 60 °C before the transformation occurs in films 2000 Å thick.(13) The high temperature β-phase may be preferentially nucleated at preexisting irregularities, and the islands so formed spread rapidly across the deposited film and may cause eventual destruction of the α-phase film at room temperature. Nevertheless, because some measure can be taken to enhance the stability of α-Sn, such as with slight addition of Ge(12), the semiconducting α-Sn at room temperature is likely to be important for infrared detection applications.

In 1983, Mattern and Luth(14,15) grew Sn overlayer on cleaved InSb (110) surface by evaporation of Sn from a spiral tungsten filament surrounded by a liquid nitrogen cooled copper shroud in ultra high vacuum (UHV) chamber. During evaporation, the pressure stayed

below 10^{-9} torr. According to electron energy loss spectroscopy (ELS) study the bonding configuration appeared to be tetrahedral like in α-Sn for coverage below 50 monolayers, whereas thick layers of several hundred monolayers showed β-Sn character.

Following the method of Farrow et al., Hernandez- Calderon and Hochst succeeded(16) in producting α-Sn (111) films on top of InSb (111)A and (111)B substrates by MBE in 1985.

Noting that 1) the α-Sn single crystals can be grown from the saturated Hg-Sn solution by Ewald and Tufte and 2) Hernandez-Calderon and Hochst succeeded in producting α-Sn (111) films on InSb (111)A and (111)B by MBE, the author and Chatraphorn(17) tried and succeeded in producing α-Sn island cubic forms on InSb (111)B substrates by liquid phase epitaxy (LPE) from the saturated Hg-Sn solution at about 13 °C in 1987. The stability of island cubic form of α-Sn was also up to about 60 °C.

From Farrow's work it was known that the α-Sn have a photoconductive response corresponding to an energy gap of about 0.12 eV (10 μm in wavelength) which fits the 8-14 μm transmission "windows" of the atmosphere as shown in Fig. 1. It is a plot of the transmission through one mile of air as a function of wavelength. Clearly, the α-Sn detector can detect the infrared emission from room temperature objects such as people, trees and trucks without the aid of reflected light.

From the MBE's work of α-Sn on InSb, Goodman(19) suggest that its electronic band configuration could perhaps be exploited in a 4-terminal heterojunciton device, based on the injections of holes from p-InSb into n-α-Sn. It should be possible for holes to enter the α-Sn valence band ballistically, close to the Γ-point, with normal

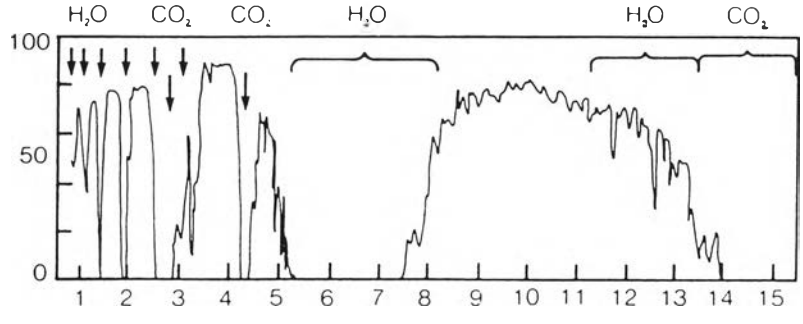

Fig. 1 Transmission versus wavelength for 1 mile of air. Water and carbon dioxide absorption bands are indicated.

effective mass. Such holes would, however, be rapidly scattered into the negative effective mass states. There they would gradually thermalise, eventually recovering normal hole behaviour, and eventually recombine or could be extracted by a normal bias field. The change from negative to possitive effective mass could be utilized to obtain a dynamic negative resistance state under conditions of very low power consumption, via a transverse field. Similar effects should be observed with (Hg, Cd) Te semimetals. It may therefore prove possible to obtain significantly high mobility, a matter of particular interest for HEMT (high electron mobility transistor) device.(20)

In this thesis, the author pursues the growth of α-Sn by the liquid phase epitaxy technique on indium antimonide (111)B substrate by dipping into mercury-tin saturated solution in ultra purified hydrogen atmosphere. There are four important reasons for doing this, namely 1) the α-Sn crystallites can be grown from Hg-Sn solution according to Ewald and Tufte's work, 2) the α-Sn epitaxial layer can be grown on InSb (111)B according to Calderon and Hochst's work, 3) the surface preparation of InSb (111)B to accept the epitaxial growth by chemical etching is possible according to Noreika and Francombe's work(21) and 4) the reducing atmosphere of ultra purified hydrogen should prevent the contamination from O_2 which is very critical in epitaxial growth.

The objectives of this thesis are 1) to design and construct a vertical liquid phase epitaxy system (VLPE), 2) to evaluate some chemical etchants for indium antimonide surface for liquid phase epitaxy growth, 3) to find suitable parameters of good epitaxial growth such as, temperature, rate of growth, growth time and impurity and 4) to characterize the epitaxial material.

Briefly the results of this thesis are presented below. Only islets form of α-Sn can be grown on InSb (111)B. There are four major problems which prevent the successful. 1) The growth temperatures are too low to avoid the O_2 contamination on the InSb surface before dipping. (The surface is heat cleaned at about 475 °C in LPE system, but it cannot stay clean while its temperature decrease to room temperature before dipping), 2) since the temperatures of Hg-Sn melt in crucible is lower than the environment H_2 temperature, the melt

adsorbs O_2 on its surface, 3) some experimental samples showed that the (111)B InSb surface were dissolved in Hg-Sn solution, (the oxide layer of indium or antimony can be detected in electron probe microanalysis) and 4) the concentration of O_2 in LPE system could not be measured so that the H_2 atmosphere in LPE system may not be sufficiently low in O_2 content.

The contents of this thesis include: chapter II liquid phase epitaxy experiments, describing the design and construction of LPE system, sample preparation, melt preparation, epitaxy procedure, growth morphologies, and summary; chapter III structural analysis which described SEM technique for studying morphologies, EPMA technique for quantitative and qualitative analysis of α-Sn, x-ray reflection technique for structural analysis of α-Sn and its temperature dependent transformation investigation; chaper IV contains results and discussion and the appendix serves as the operation manual for the LPE system.