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Growth and electrical characterization of Zn-doped InAs and $InAs_{1-x}Sb_x$

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ABSTRACT

The electrical properties of Zn doped InAs and InAsSb layers grown on semi-insulating GaAs by metal organic vapour phase epitaxy, using dimethyl zinc as the *p*-type dopant source, have been studied. The influence of dopant flow rate, V/III ratio and substrate orientation on the electrical properties of these InAs and $InAs_{1-x}Sb_x$ layers have been studied at a few appropriate growth temperatures. A promising group V source, tertiary butyl arsenic was used as an alternative to arsenic hydride in the case of InAs growth. The electrical properties of the InAs and $InAs_{1-x}Sb_x$ epitaxial layers were mainly studied by the Hall effect. However, surface accumulation in these materials results in deceptive Hall results being extracted. A two layer model (assuming the layer to consist of two parallel conducting paths viz. surface and bulk) has therefore been used to extract sensible transport properties. In addition, conventional Hall measurements ignores the high electron to hole mobility ratio in InAs and InAsSb leading to erroneous transport properties.

1. Introduction

The realisation of semiconductor light emitting diodes and lasers operating in the mid-infrared spectral region offers a wide range of potential applications. A number of important gas molecules, for example, are known to strongly absorb in the mid infrared region, examples being methane (3.3 μm), CO_2 (4.6 μm), NO_x (6.5 μm) and SO_x (7.3 μm) rendering these devices ideal for applications such as optical gas sensing, environmental pollution monitoring and chemical process control. In addition, various drugs and drug intermediates, pharmaceuticals, narcotics and bio-chemicals have unique absorption fingerprints in the mid infrared region allowing for highly selective and accurate identification [1]. Furthermore, there is an atmospheric transmission window in the 3–5 μm region, permitting optical communication as well as imaging from objects radiating in this spectral range.

$InAs_{1-x}Sb_x$ has emerged as an excellent alternative to $HgCd_{1-x}Te_x$ (MCT) for mid- to long-wavelength infrared detection covering both the 3–5 μm and 8–12 μm atmospheric windows. This is due to the fact that MCT suffers from a number of fundamental material deficiencies. Firstly, the Hg–Te bond is predominantly ionic, consequently resulting in the material's observed inferior thermal stability. Secondly, a very sensitive band gap dependence on composition as well as technical challenges related to high temperature device processing also restrict the exploitation of the potential that MCT offers [2]. Conversely, bonding in $InAs_{1-x}Sb_x$, is predominantly covalent, resulting in stronger material, able to withstand harsher processing steps and operating environments [3]. The band gap also varies slowly with Sb mole fraction, allowing for controlled band gap engineering for predetermined applications while simultaneously contributing towards homogeneous layer growth [4]. Furthermore, the small direct bandgap, high electron mobility, and high saturation drift velocity of InAs, a binary endpoint of InAsSb, render it an extremely attractive material for high frequency (THz), low power electronic device applications [5].

This paper primarily reports on the electrical properties of Zn-doped InAs and $InAs_{1-x}Sb_x$ layers grown by metal organic vapour phase epitaxy (MOVPE), using dimethyl zinc (DMZn) as the *p*-type dopant source. The influence of dopant flow rate, V/III ratio and substrate orientation on the electrical properties of InAs and $InAs_{1-x}Sb_x$ layers grown on semi-insulating GaAs have been studied at a few appropriate growth temperatures. A promising group V source, tertiary butyl arsenic (TBAs) is used as an alternative to arsenic hydride (AsH_3) in the case of InAs growth. TBAs pyrolyses at a much lower temperature than AsH_3 and pyrolysis is 50% complete at 425 °C [6]. The growth temperature could however not be reduced accordingly since complete dissociation of TMIn was only achieved at 550 °C and that of TMSb at 600 °C [7]. The electrical properties of the InAs and $InAs_{1-x}Sb_x$ epitaxial layers were mainly studied by the Hall effect. Both InAs and $InAs_{1-x}Sb_x$ surfaces are typically characterized by an electron rich surface layer (probably caused by intrinsic donor-like surface states) which masks the properties of the bulk of the epilayers [8]. This has been concluded from the thickness [9,10] and magnetic field dependence of the Hall coefficient and the absence of carrier freeze out in temperature dependent Hall measurements [11]. These results are generally attributed to parallel conduction resulting from three distinct regions, the surface, characterized by donor like surface states [9,12], the bulk of the layer and an interface layer [13]. The latter is attributed to defects,

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primarily dislocations, arising from the large lattice mismatch between the InAs epilayer and the substrate, causing scattering of carriers, consequently influencing the carrier mobility in this region. Hence, in order to extract meaningful mobilities and carrier concentrations for the surface and the bulk of the InAs and InAsSb layers grown in this study, the Hall measurements were interpreted in terms of a two-layer model initially proposed by Nedoluha and Koch [14] and adjusted for this study by Botha et al. [15]. It is instructive to note that although various parallel conduction models have been considered by others, this study omits the effect of the interface on the electric properties [16–19].

2. Experimental procedure

Epitaxial InAs layers were grown by atmospheric pressure MOVPE in a horizontal quartz reactor. The growth procedure is described in detail elsewhere [20]. In this work, the influence of substrate orientation and V/III ratio on the Zn incorporation was studied. For this purpose semi-insulating GaAs substrates, both (100) and 2° off the (100) towards the nearest <110>, were used. These substrates were loaded simultaneously, side by side, onto a molybdenum susceptor. No cleaning was required except simply blowing the substrates with N_2 after cleaving and prior to being loaded into the reactor. In a preliminary study (not discussed here) it was found that the surface morphology and electrical properties of InAs epitaxial layers grown using TBAs were superior to those grown using AsH_3. Similar observations were made by Haywood et al. [21]. Consequently, we discuss hereafter, InAs epitaxial layers grown with TBAs as the group V source. Trimethyl indium (TMIn) was used as the group III source whilst *p*-type doping was achieved by diluting 200 ppm dimethyl zinc (DMZn) in H_2. The TMIn and TBAs bubblers were held in temperature controlled baths at 25.6 °C and 5.5 °C respectively. Palladium diffused hydrogen with a flow rate of 2.2 standard litres per minute was used as the carrier gas. For InAs, the growth temperature and Zn mole fraction were maintained at 600 °C and 4.3×10^{-6} respectively, whilst the V/III ratio was varied between 5 and 40. The TBAs mole fraction varied between 1.8×10^{-4} and 1.4×10^{-3}, whereas the TMIn mole fraction was kept constant at 3.5×10^{-5}. InAs layers were grown at temperatures ranging from 550 °C to 650 °C. For InAsSb layers, trimethyl antimony (TMSb), kept at −5 °C was used as a source of Sb. The $InAs_{1-x}Sb_x$ ($x\sim0.09$) layers too were grown on SI GaAs substrates misoriented by 2° from the (100), at growth temperatures of 575 °C and 625 °C, whilst the V/III ratio ranged from 2.5 to 10. AsH_3 (note: not TBAs) was used as arsenic source for these layers. The AsH_3 mole fractions used were 1.1×10^{-4} and 2.8×10^{-4} whilst the TMIn mole fraction was 6.5×10^{-5}.

The thickness and surface morphologies of the epitaxial layers were examined using a Nomarski interference contrast microscope after etching a cleaved sample in an acid solution consisting of 10 g potassium ferricyanide, 10 g sodium hydroxide, 100 ml de-ionized water for 10 s. Layer thicknesses typically ranged from 3 µm to 6 µm. The electrical characteristics of the material were investigated by Hall measurements at 77 K and 300 K respectively. Sample dimensions were typically 5 mm × 5 mm while electrical contact to the samples was achieved through four In (soldered on) ohmic contacts using the Van der Pauw geometry.

For the purpose of simulating the true and apparent carrier concentration and mobility of the InAs layer, the technique introduced by Krug et al. was used to extract the room temperature bulk mobility (μ_n), surface mobility (μ_s) and surface free carrier concentration (n_s) [20]. These parameters were then fixed in the execution of the simulations, while n was varied. The hole concentration was subsequently determined from $p=\frac{n_i^2}{n}$, where $n_i=8.75\times10^{14}$ cm^{-3} is the room temperature intrinsic carrier concentration of InAs [12]. The effective thickness of the surface accumulation layer is given by the screening length of the surface charge and was estimated by the Debye length (L_D) (see Appendix A).

3. Results and discussion

3.1. Zn doped InAs

Fig. 1 depicts the variation in the carrier concentration with V/III ratio for Zn doped InAs measured at 300 K. The measured electrical parameters presented here are an average of the bulk and surface, obtained directly from conventional Hall measurements without applying the two-layer model. A comparison of the measured carrier concentration values for Zn doped layers grown on GaAs (100) substrates and misoriented substrate is also shown. From the results depicted it is reasonable to assume that Zn incorporation is independent of substrate orientation.

From Fig. 1 it is clear that the lowest Zn incorporation occurs at a V/III ratio of 5 and that layers grown at this V/III ratio exhibit *n*-type conductivity. The highest Zn incorporation appears to occur at a V/III ratio of 10. However, the carrier concentrations measured at 300 K, at this particular V/III ratio, were approximately an order of magnitude higher than at 77 K (not shown here) whilst at other V/III ratio values the 77 K and 300 K carrier concentration measurements were almost indistinguishable. Most importantly, the layers grown at V/III ratios between 10 and 40 exhibited *p*-type conductivity at 77 K. The measurements at 300 K also revealed *p*-type conductivity except for the layer grown on a (100) oriented substrate at a V/III ratio of 10, which exhibited *n*-type conductivity at 300 K, but *p*-type conductivity at 77 K. This result may be confusing at first but can be explained well using a two-layer model.

Fig. 2 depicts the variation in carrier mobility with V/III ratio measured at 300 K for the same layers. The highest mobility is obtained for layers grown at a V/III ratio of 5, correlating well with the lowest free carrier concentration (as expected) obtained for this layer. There is a significant decrease in mobility for Zn doped layers grown at V/III ratios in the range 10–40 due to the much higher hole effective mass.

Zinc is expected to substitute on the In site. Consequently an increase in the acceptor concentration with increasing V/III ratio and hence an increase in the hole concentration is expected. It is therefore suggested that the presence of a surface accumulation layer of electrons on *p*-type InAs surfaces, shields the increasing hole concentration (especially for growth at a V/III ratio of 10, where for one of the samples high *n*-type conductivity was measured). Furthermore, the large mobility of electrons compared to that of holes, will result in a dominant contribution of electrons to the Hall voltage, even in cases where electrons are minority carriers ($n<p$) in

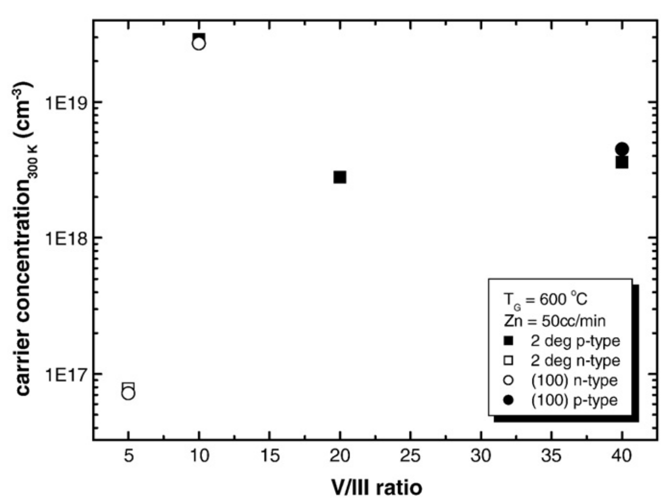

Fig. 1. Variation in free carrier concentration measured at 300 K as function of V/III ratio for Zn doped InAs layers grown at $T_G=600$ °C and a DMZn flow rate of 50 cc/min. All open symbols denote *n*-type layers, as obtained from conventional Hall effect measurements.