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Characteristics of II–VI semiconductor thin films grown by MBE on InSb substrates

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Abstract. Single and multiple layers of CdTe and CdMnTe have been grown by MBE on InSb substrates. Considerable attention has been given to the prepartion of the substrate surface which was cleaned under vacuum using a series of argon ion etching and thermal annealing cycles, with progress being monitored by AES and RHEED. The subsequently deposited epilayers were grown, typically, at a rate of 0.5 μm per hour. All undoped films studied so far have been found to be n-type with carrier concentrations in the range 10^{14}–10^{15} cm^{-3}, while layers doped with indium have exhibited a saturation in carrier concentration as the In atom concentration was increased, due to the generation of compensating acceptor states.

1. Introduction

The controlled growth of semiconducting materials provided by the molecular beam epitaxy (MBE) technique has provided the stimulus for development of a variety of low-dimensional structures (LDS) and associated devices. Special interest in II–VI based systems has recently been generated by work on alloys containing magnetic ions, as these materials display an interesting variety of magneto-optical and magneto-transport properties with obvious device possibilities. Several members of this new and interesting class of materials are now under investigation, including the CdTe–$Cd_{1-x}Mn_xTe$ system which is the subject of this paper.

Our current LDS programme is the growth by MBE of single and multiple layers of CdTe and $Cd_{1-x}Mn_xTe$, including multiple quantum well (MQW) and superlattice structures. For growth by MBE the structural quality of the layers is of course highly dependent on the lattice structure, surface cleanliness and orientation of the substrate material. Accordingly considerable attention has been paid to the surface preparation of the InSb substrates and in this paper we discuss the conditions necessary to achieve high-quality epilayers and the effects of In doping.

2. Experimental details

2.1. The growth system

The structures were prepared in a VG Semicon V80H MBE system. The Cd and Te_2 components were provided by a single source of high-purity polycrystalline CdTe (MCP Ltd), while the Mn (Johnson Matthey Ltd, 4N; vacuum distilled) was provided by a

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separate Knudsen cell. A further cell contained In (MCP Ltd, 6N). The cell crucibles were pyrolytic boron nitride. The base pressure in the system was ~5×10^{-11} mb and growth rates of ~0.5 μm h^{-1} were employed with the substrate temperature in the region 200–250 °C.

2.2. Substrate preparation

The substrates were ~0.5 mm thick wafers of (001) InSb (MCP). InSb was chosen partly because it is available in the form of large-area single crystals with good structural quality and, most importantly, because it is well lattice matched to CdTe (to within 0.05%). The wafers were first polished and etched in lactic acid : nitric acid : hydrofluoric acid (25 : 4 : 1) and then attached to a molybdenum plate using Ga–In eutectic solder. The surface oxides we removed by argon ion etching using a 500 V ion beam followed by thermal annealing at the intended growth temperature for 30 min. The oxide removal process was monitored by AES and RHEED and typically required 5 etch/anneal cycles to produce a clear 2 × 4 RHEED pattern characteristic of a clean InSb surface [1].

2.3. Material characterisation

Information about the structural quality of the layers has been provided by photoluminescence and by double-crystal x-ray diffraction rocking curve analysis. While the linewidths obtained by such measurements are consistent with high-quality material [2], more detailed information concerning the layers close to the InSb interface require the use of depth profiling and cross-sectional transmission electron microscopy (TEM) techniques. TEM has been carried out at RSRE (Malvern) and at Bristol University and secondary ion mass spectroscopy (SIMS) profiles have been obtained from Loughborough Consultants, while profiles of the electrical characteristics have been provided by capacitance–voltage (C–V) and electrochemical techniques in this laboratory.

For the C–V studies ohmic contacts were made using evaporated indium, and Schottky batrriers were formed using either evaporated gold contacts or an electrolyte which allowed electrochemical etching between measurements.

3. Results and discussion

3.1. Undoped CdTe and CdMnTe layers and superlattices

All the CdTe and CdMnTe layers grown on InSb have been found to be n-type with carrier concentrations generally in the range 10^{14}–10^{15} cm^{-3}. For CdTe samples there is a trend toward higher carrier concentration as the growth temperature increases from 200 to 250 °C. For CdMnTe alloy layers grown on a CdTe buffer layer a similar dependence on substrate temperature has been found, but the carrier concentrations were generally smaller and there appears to be a trend to lower values as the Mn concentration increased, but more samples need to be evaluated to confirm this point.

In general, the structural quality of the CdMnTe layers grown on a CdTe buffer layer has been found to be good, as judged from photoluminescence spectra and cross-sectional TEM micrographs, although the latter indicate some undulations at the CdTe–CdMnTe interface. Similar interfacial undulations have been observed on micrographs of multilayer structures, although these structures appear otherwise well defined and

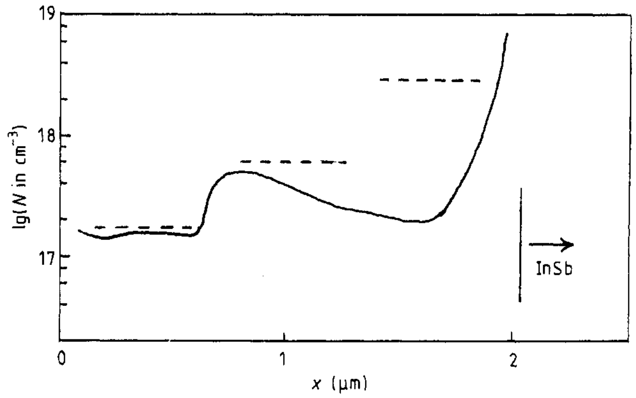

Figure 1. Carrier concentration as a function of depth (full curve) in a CdTe layer doped with In at three different concentrations indicated by SIMS measurements (dotted lines).

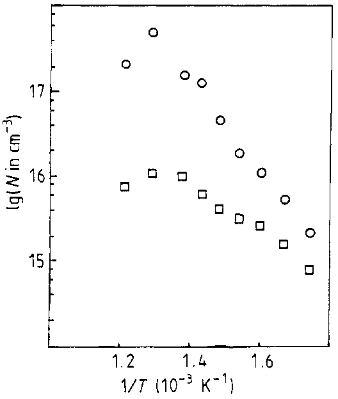

Figure 2. Carrier concentrations for In-doped CdTe (circles) and $Cd_{0.9}Mn_{0.1}Te$ (squares) layers as a function of the In source temperature.

defect free. However, it should be noted that some samples do show evidence of severe dislocations which appear to stem from the original InSb–CdTe interface which is relatively diffuse. It is possible that these growth defects arise from incomplete removal of the oxide layer from the substrate surface, or from some surface damage resulting from the substrate cleaning procedure. Indeed, if the annealing temperature is too low or the annealing period too short, the RHEED pattern shows only a weakly reconstructed surface after the fifth etch–anneal cycle together with a relatively intense diffuse background. The latter indicates the presence of additional scattering centres, possibly associated with the development of free In at the surface, the existence of which becomes very clear after excessive argon beam damage. Under these circumstances, body-centred tetragonal In crystallites have been observed. These crystallites in the form of square-based pyramids with base widths of ~30 μm can be observed by optical microscopy. Under normal surface cleaning conditions such crystallites are not observed, but it is possible that an In excess is present and this could lead to the formation of an In_2Te_3 interfacial layer prior to the establishment of the required CdTe layer, as has been suggested by Golding and co-workers [3]. This could account for the diffuse nature of the CdTe–InSb interface.

3.2. In-doped CdTe and CdMnTe layers

The presence of an In flux during the growth of CdTe layers has resulted in carrier concentrations of up to 5×10^{17} cm^{-3}. Attempts to raise this to higher values, by increasing the In cell temperature and thereby the In beam flux, have resulted in reduced carrier concentrations. The problem is clearly demonstrated in figure 1, which shows the carrier concentration–depth profile together with the corresponding In concentrations from SIMS analysis for a sample grown in three stages (0.7 μm each), to produce three different doping densities. The SIMS data show that In incorporation into the lattice was successfully achieved at three different densities ($\sim 10^{17}$ cm^{-3}, $\sim 6 \times 10^{17}$ cm^{-3} and $\sim 3 \times 10^{18}$ cm^{-3}). While an expected carrier concentration step at 0.7 μm from the surface is clearly evident, there is no corresponding step at 1.4 μm. In fact the carrier concentration diminishes close to the substrate interface, rather than rising to a higher level. Similar features have been observed in In-doped CdMnTe layers, but for these alloy layers (on CdTe buffer layers) the carrier concentrations are significantly lower than achieved for CdTe layers under identical growth conditions.

In view of the presence of defects in the vicinity of the interface, as discussed in § 3.1, it is possible that these might be responsible for the reduced carrier concentration in this region; dislocations could act as sinks for the incorporated In atoms, thereby making them electrically inactive. However, an alternative explanation is suggested by the data in figure 2, which displays the carrier concentration variations in a CdTe layer and a $Cd_{0.9}Mn_{0.1}Te$ layer as a function of the In cell temperature during growth. As the In doping increases steadily with In source temperature, the fall-off in carrier concentration at high temperature suggests that incorporation of high In concentrations is accommpanied by the formation of compensating acceptor states. Evidence for the existence of acceptor states in In-doped MBE grown CdTe has previously been reported [4], and this is supported by photoluminescence studies in this laboratory which show that the expected donor bound exciton emission peak is accompanied by an additional peak attributed to acceptor bound exciton emission.

The acceptor defects are assumed to involve Cd vacancies and it is expected that their concentration might be reduced by maintaining an excess flux of Cd atoms during growth in the same way that the electron concentration in bulk-grown material has been found to be enhanced by In diffusion doping in a Cd-rich atmosphere [5]. The use of an excess Cd flux has recently been shown to improve the quality of the CdTe layer and particularly the abruptness of the CdTe–InSb interface [3], so that its application with In-doped layers may prove to have dual benefits.

4. Summary

MBE has been used to form single and multilayer structures involving CdTe and CdMnTe on InSb substrates. The quality of the resultant layers has been shown to be critically dependent on the substrate cleaning process which can lead to excess In at the CdTe–InSb interface. In doping increased the carrier concentration from 10^{14}–10^{15} cm^{-3} in the undoped material to over 10^{17} cm^{-3}, but compensating acceptor levels have prevented further increases. The possibility of improving the structural quality of the layers and increasing the uncompensated donor density by use of an excess Cd flux is discussed.

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