Thin Solid Films, *115* (1984) 97–107
ELECTRONICS AND OPTICS

PROPERTIES OF CdTe FILMS GROWN ON InSb BY MOLECULAR BEAM EPITAXY

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(Received October 17, 1983; accepted March 26, 1984)

The optical and electrical properties of molecular beam epitaxial layers of CdTe grown on InSb(001) substrates at 200–225 °C and either doped with copper, arsenic, antimony or indium or undoped were investigated. Non-intentionally doped layers are found to be n type and to contain indium and antimony atoms out diffused from the substrates. For copper- and arsenic-doped layers, acceptor-bound exciton annihilation lines become dominant in the exciton region of the photoluminescence spectra at 6 K, whereas for antimony-doped layers the acceptor-bound exciton line remains weaker than the donor exciton line even at antimony concentrations of up to 1.2×10^{18} cm^{-3}. P-type conduction was observed only in heavily copper-doped samples.

1. INTRODUCTION

Recently molecular beam epitaxy (MBE) has been used for the preparation of the lattice-matched CdTe/InSb heterostructures[1-4], which have potential applications for electronic and optoelectronic devices. By using the MBE technique, epilayers of high purity or with desired dopant concentrations are expected to be grown at relatively low temperatures.

In a previous note we have shown that indium is effective as a donor dopant in MBE CdTe such that n-type epilayers with electron concentrations between 10^{16} and 10^{18} cm^{-3} can be controllably deposited[2]. For the fabrication of devices, p-type doping techniques are also required to be established. It is known that CdTe can be prepared in low resistivity p-type form by conventional bulk crystal growth methods, and group I and group V elements are considered to act as acceptors, presumably substituting for cadmium and tellurium respectively[5].

In this work we examined the possibility of p-type conduction in MBE layers by using various amounts of the group I or group V elements copper, arsenic and antimony as dopants. For characterization of the doped layers, measurements of the photoluminescence (PL) at low temperatures and of the current–voltage (*I–V*) and capacitance–voltage (*C–V*) relations of Schottky diodes were carried out. The PL properties of undoped and indium-doped samples were also measured for comparison with the behaviour of other dopants, and secondary ion mass spectrometry (SIMS) was used for estimation of the out-diffusion effect from substrates.

0040-6090/84/$3.00

2. EXPERIMENTAL PROCEDURES

The MBE growth of CdTe was carried out in a conventional MBE system with a base pressure of 5×10^{-10} Torr. The source materials for the CdTe layers were polycrystalline CdTe and elemental cadmium and tellurium of purities 99.9999%; they were vaporized from quartz effusion cells. The polycrystalline CdTe source was mainly used, and the cell temperature was 530–550 °C. The elemental sources were employed with the intention of reducing contamination as a result of the lower cell temperatures, which were 250–310 °C and 370–430 °C for cadmium and tellurium respectively. The elemental sources were also used for variation in the stoichiometry of the beam fluxes, and the ratios J_{Cd}/J_{Te} of fluxes arriving at the substrate were determined with a quadrupole mass spectrometer by assuming the ratio from the compound CdTe source to be unity. Elemental indium, antimony, copper and arsenic were evaporated from pyrolytic BN cells; the purities of the indium, antimony and copper were nominally 99.9999% and that of arsenic was 99.99999%. The fluxes of the elements arriving at the substrate were estimated from the geometry of the set-up and the cell temperatures by the use of published vapour pressure data[6]. The temperatures were measured with a calibrated IR pyrometer which received radiation from the insides of the cells. The concentrations of dopants, with the exception of arsenic, in the CdTe layers were estimated on the assumption of a sticking coefficient of unity.

The substrates were (001)-oriented n-type InSb wafers with electron concentrations of 10^{15}–10^{16} cm^{-3} and a thickness of 0.5 mm. They were mechanochemically polished and etched with a 10%bromine–methanol solution and were then mounted with indium solder onto a molybdenum heating block and loaded into the MBE system through a vacuum interlock. The substrate surfaces were cleaned with 2 cycles of 600 V Ar^+ sputtering and subsequent annealing at 390 °C in a beam of antimony molecules for 30 min.

The CdTe MBE was performed at a substrate temperature T_s of 200 or 225 °C, T_s being measured with the IR pyrometer. The deposition rates and layer thicknesses were 0.25 μm h^{-1} and 0.5 μm for $T_s = 200$ °C and 0.4 μm h^{-1} and 1 μm for $T_s = 225$ °C. The CdTe layers had a mirror-smooth appearance and exhibited a (2×1) surface pattern when examined *in situ* by reflection high energy electron diffraction[2]. Prior to the CdTe epitaxy, InSb buffer layers were deposited at 365 °C under antimony-stabilized conditions[7], and the thicknesses were 0.04 μm and 0.15 μm corresponding to subsequent CdTe deposition temperatures of 200 °C and 225 °C respectively.

For characterization of the CdTe epilayers, PL measurements at 6 K were mainly used. The samples were attached to a cooling fin of a liquid helium cryostat and were excited with a 30 mW He–Cd laser emitting at 441.6 nm. The measurements were performed in the wavelength region from 770 nm to 1 μm using a cooled photomultiplier of the S-1 type and a monochromator with a resolution of 0.15 nm. The spectra to be presented were not corrected for the wavelength-dependent response of the measuring system.

For the determination of the conduction type and the carrier concentration in the CdTe epilayers, Schottky diodes were prepared by the vacuum deposition of gold dots 0.5 mm in diameter onto the surface, and indium layers used for the substrate mounting during the MBE growth served as ohmic contacts to the back surface. The I–V and C–V characteristics were measured at room temperature. SIMS and double-crystal X-ray diffraction using Cu $K\alpha_1$ radiation were also employed for evaluation of the epilayer qualities.

3. RESULTS AND DISCUSSION

3.1. *Undoped epilayers*

To determine the effect of the diffusion of indium and antimony atoms into a CdTe epilayer from the InSb buffer layer or substrate, their concentrations were estimated using the SIMS technique. The depth profile of the SIMS signal for antimony in a non-intentionally doped epilayer is shown in Fig. 1, and those of an antimony-doped epilayer and a CdTe bulk crystal are also included. The value for the bulk crystal is adopted as the background level of the antimony signals. The intensity of the antimony signal for the undoped layer is higher than the background level, which indicates that out-diffusion from the substrate takes place during epitaxy. The antimony SIMS signal intensities for epilayers are plotted in Fig. 2(a) as a function of the doped antimony concentration, which is determined from the arrival flux of molecules. Data for the undoped epilayers are also plotted on the ordinate of the figure. Similar data for indium atoms are shown in Fig. 2(b). From an extrapolation of the data for antimony- and indium-doped epilayers, both the antimony and indium concentrations in undoped layers are estimated to be $(0.3–1) \times 10^{16}$ cm^{-3}. The SIMS technique was also used for the investigation of other impurities in the undoped epilayers. Sodium and potassium were detected in the epilayers but no quantitative evaluation was performed. The signals for copper ions could not be identified because of overlapping with Te^{2+} signals. Ion intensities from other impurities such as carbon and lithium were below the detection limits of the SIMS analysis.

The Schottky diodes always showed the normal I–V dependence of n-type CdTe. The C–V measurements showed that some of the epilayers are depleted under zero bias and therefore have electron concentrations below 1×10^{15} cm^{-3}, but other samples have electron concentrations between 10^{15} and 10^{16} cm^{-3}.

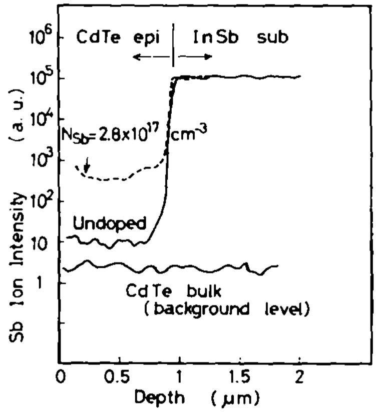


Fig. 1. SIMS profiles of antimony for undoped and antimony-doped epilayers (T_s = 225 °C) and a CdTe bulk crystal.

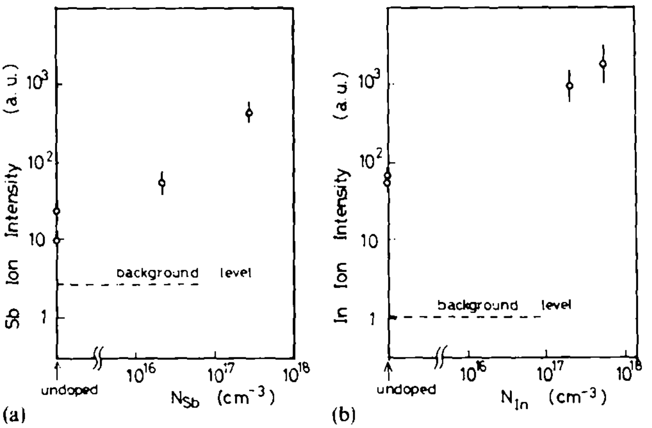


Fig. 2. SIMS signal intensities for (a) antimony and (b) indium atoms *vs.* the doping concentrations (T_s = 225 °C). Data for undoped layers are plotted on the ordinates.

An example of the PL spectra at 6 K is shown in Fig. 3. PL spectra of CdTe epilayers are generally divided into three regions as in the case of bulk crystals[5]: the exciton emission (775–790 nm), the so-called edge emission (790–830 nm) and the "1.45 eV emission" (830–950 nm) regions. There are several peaks in the exciton region, and the main peak A_2 in Fig. 3 is located at 1.593 eV and is considered to be due to bound excitons on neutral donors, which might be related to in-diffused indium atoms. On the shoulders of line A_2 lines A_1 (at about 1.596 eV) and A_3 (at about 1.590 eV) occur, which are considered to be due to free and neutral acceptor-bound excitons respectively. The origin of the acceptors in the undoped layer might be impurities, such as alkali metals, diffused from the substrate, or be related to native defects, but no definite identification can be made at present. On the lower energy side of lines A_1–A_3 another exciton line A_4 is observed at 1.585 eV, and it seems to have the same origin as a line at 1.584 eV observed in some bulk crystals[5].

In the edge emission region one to three lines, such as B_1–B_3 in Fig. 3, with their longitudinal optical (LO) phonon replicas, are observed. The number of lines changes from sample to sample, but the B_2 line is generally dominant in the region for undoped layers. In the 1.45 eV region, a peak C followed by a series of LO phonon replicas is observed. The properties of peaks B and C will be discussed in Section 3.2. The characteristics of MBE layers deposited from the compound CdTe

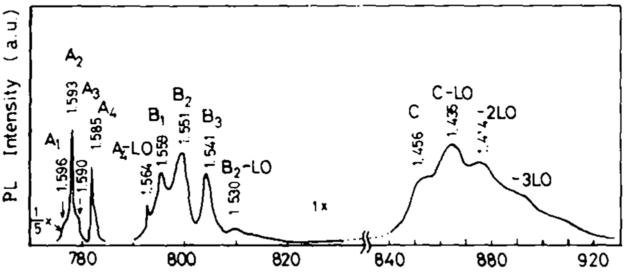


Fig. 3. PL spectrum at 6 K on an undoped CdTe epilayer (T_s = 225 °C).

source and from the elemental cadmium and tellurium sources were compared, but we could not find any marked differences in the behaviour of the layers.

3.2. Indium-doped epilayers

As reported in a previous note[2], indium can be doped controllably in epilayers with net donor concentrations of 10^{16}–10^{18} cm^{-3}. Typical examples of the PL spectra of indium-doped epilayers are shown in Fig. 4. The layers were deposited from the cell containing polycrystalline CdTe. The features of the PL spectra are similar to those of the spectra for the undoped layers. At low indium concentrations the A_2 line has the highest peak, but with increasing indium concentration the 1.45 eV line C and its replicas become dominant as in the case of PL at 77 K. In the edge emission region only line B_2 and its phonon replicas are observed, but their halfwidths are rather large. Lines B_2 and C shift to higher energies with increasing indium concentration N_{In}, and the peak energies are plotted in Fig. 5 as functions of $(\pi N_{\text{In}})^{1/3}$. Lines B_2 and C are therefore considered to be due to distant donor–acceptor pair recombinations, where indium is the donor and majority impurity. The emission energy from a donor–acceptor pair is represented by

$$h\nu = E_g - E_d - E_a + \frac{e^2}{\varepsilon R}$$

where E_g, E_d and E_a are the band gap, the donor ionization and the acceptor ionization energies respectively, R is the distance between the donor and the acceptor and ε is the dielectric constant (10.34 at 6 K [8]). When weak excitation is assumed, the peak energy of the zero-phonon line corresponds to a mean pair distance $R_m = (\pi N_{\text{In}})^{-1/3}$ (ref. 9). Therefore, if straight lines of slope e^2/ε are drawn through the measured points in Fig. 5, the points of intersection of these lines with the ordinate give estimates of $E_g - E_d - E_a$ as 1.543 eV and 1.445 eV for lines B_2 and C respectively. When values of $E_g = 1.606$ eV and $E_d = 14.5$ meV for the indium

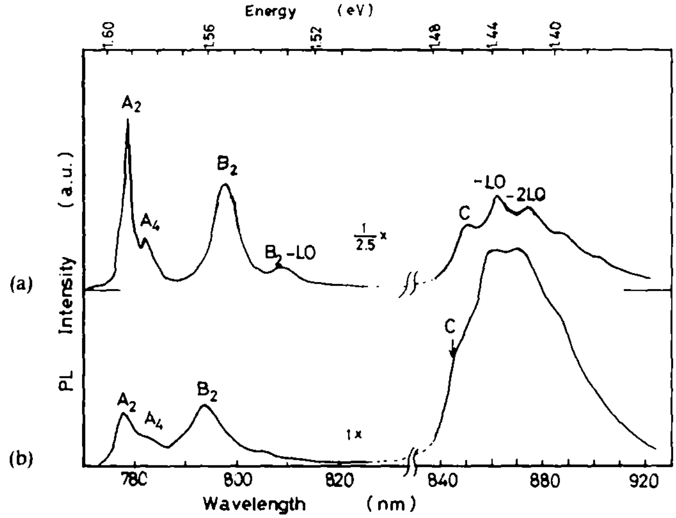
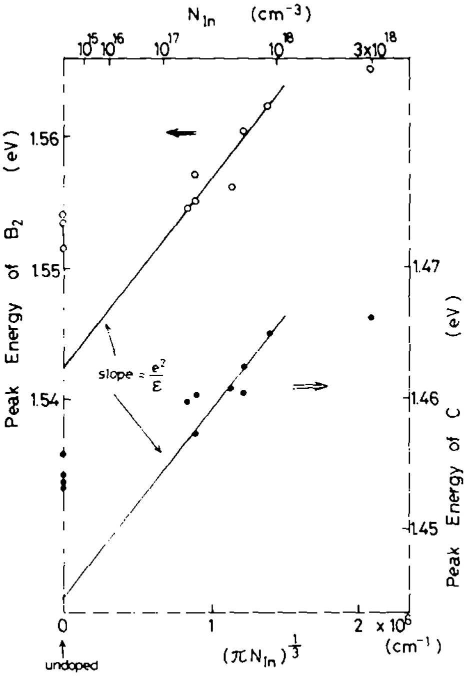


Fig. 4. PL spectra at 6 K of indium-doped CdTe epilayers (T_s = 200 °C): (a) $N_{\text{In}} = 1.9 \times 10^{17}$ cm^{-3}; (b) $N_{\text{In}} = 9 \times 10^{17}$ cm^{-3}.



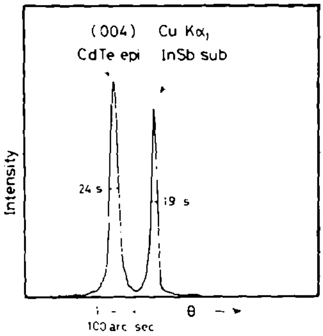


Fig. 5. Peak energies of the B_2 and C lines in the PL spectra of indium-doped CdTe epilayers at 6 K *vs.* $(\pi N_{In})^{1/3}$ (T_s = 200 °C). Straight lines with a slope of e^2/ε are drawn through the data points.

Fig. 6. Double-crystal X-ray rocking curve of a heavily copper-doped CdTe epilayer (T_s = 225 °C; $N_{Cu} = 2 \times 10^{19}$ cm^{-3}).

donor are used[5,10], values of 49 and 147 meV are obtained for the acceptor binding energy E_a. Because of the assumption of weak excitation, these values of E_a are considered to be underestimates.

For the deeper acceptor two models have been proposed. According to one model the acceptor is copper occupying a cadmium site[11], and the other model predicts that it is a complex of a cadmium vacancy and a donor (an indium atom occupying a cadmium site in this case)[5]. The copper acceptor is known to have an ionization energy E_a of 146 meV in bulk CdTe crystals[11] and this energy nearly coincides with the value obtained in our experiment for the indium-doped layers. Copper-doped CdTe shows a strong acceptor-bound exciton line (corresponding to line A_3) both in bulk crystals[11] and in MBE layers as shown in Section 3.3. However, in the undoped and indium-doped MBE layers line A_3 is very weak. Moreover, the intensity of the 1.45 eV line C increases with increasing indium concentration, whereas those of the exciton and the edge emission lines decrease. Hence, the complex centre model seems to be more plausible than the copper model.

The edge emission line B_1 observed in the undoped layers might be due to a conduction band–acceptor transition, where the acceptor is the same as that responsible for line B_2. On the basis of this model, the ionization energy of the acceptor is estimated to be 47 meV, which is somewhat lower than the value obtained from line B_2. Another edge emission line B_3 in Fig. 3 seems to be due to a donor–acceptor pair recombination. From the value of 49 meV obtained for the acceptor level related to line B_2, the acceptor responsible for line B_3 is considered to have an ionization energy of 59 meV, under the assumption that excitation is weak and that donors are common to the recombination processes in the edge emission region. The value is also an underestimate. The ionization energy of the shallow acceptor level in the effective mass approximation is known to be 55.5 meV [12] and those of alkali metals such as lithium and sodium are about 60 meV [10]. Hence these metals out diffused from the substrate are candidates for the acceptors related to the edge emissions. Other candidates are native defects, complex centres associated with the defects, and antimony out diffused from the substrate. There is no report indicating antimony to be a shallow acceptor and our doping experiment (Section 3.5) rules out the possibility that antimony is responsible for the edge emissions.

3.3. Copper-doped epilayers

MBE layers containing copper with concentrations from 1.5×10^{16} to 2×10^{19} cm^{-3} were prepared using the polycrystalline CdTe source, and their crystallinities were examined by double-crystal X-ray diffraction. The halfwidths of the rocking curves are small even for the heaviest doping as shown in Fig. 6, which indicates the high quality of the epilayers.

The *I–V* characteristics of Schottky diodes fabricated on the epilayers were measured at room temperature. For copper concentrations lower than 5×10^{18} cm^{-3}, the easy current flow direction corresponds to the application of a positive bias voltage on the gold electrode (Figs. 7(a) and 7(b)), and so the epilayer is considered to be n type. However, as shown in Fig. 7, current saturation occurs for voltages higher than 0.6 V. This behaviour can be understood as follows. For the undoped and indium-doped epilayers, electron flow through the InSb/CdTe heterojunction (Fig. 7(d)) takes place by tunnelling. However, for copper doping, the net donor concentrations are thought to be greatly reduced because of nearly

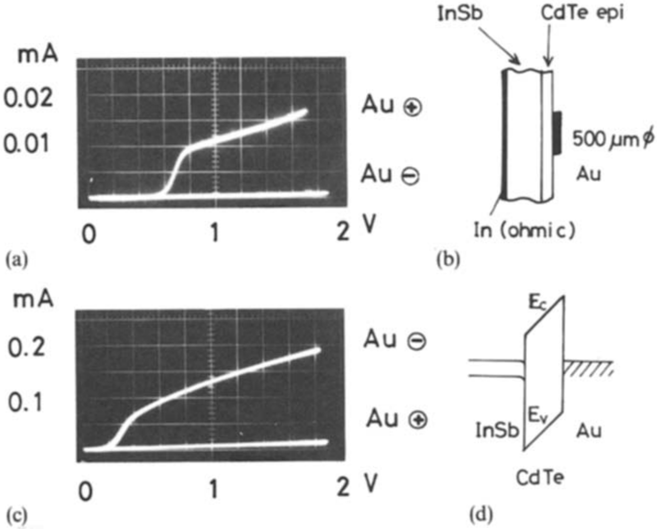


Fig. 7. Characteristics of Au/CdTe/InSb Schottky diodes: (a), (c) *I–V* curves for epilayers with copper concentrations of 1.5×10^{16} cm^{-3} and 2×10^{19} cm^{-3} respectively; (b), (d) schematic diagrams of (b) the diode and (d) its band structure.

complete compensation, and so electron flow occurs mainly by thermionic emission over the potential barrier of the InSb/CdTe heterostructure, which induces current saturation for positive bias of the CdTe relative to the InSb. The $C-V$ measurements also show complete depletion of the epilayers.

For copper concentrations higher than 5×10^{18} cm^{-3}, the forward and reverse current flow directions are inverted as shown in Fig. 7(c), which indicates that the epilayers are p type. In this case the current saturation is considered to be induced by the rectifying property of hole emission over the heterobarrier. For the p-type epilayers, the net acceptor concentrations are obtained as $(3-10) \times 10^{16}$ cm^{-3} from the $C-V$ measurements. The above results mean that only a small portion of doped copper atoms are electrically active.

PL spectra at 6 K for some of the copper-doped samples are shown in Fig. 8. In the exciton region the acceptor-bound exciton line A_3 at 1.590 eV is dominant, which agrees with the result for bulk crystals obtained by Chamonal *et al.*[11] This result suggests that the acceptor in the copper-doped MBE layer is due to copper incorporated on a cadmium site. According to the report by Chamonal *et al.*, the copper acceptor is also responsible for the 1.45 eV emission. In our experiment the 1.45 eV lines, *i.e.* line C and its replicas, are not so clearly separated for low copper concentrations as for intermediate concentrations. This might result from the overlapping of two emission spectra which originate from coexistent recombination mechanisms which have slightly different emission energies. Both the mechanisms are due to donor–acceptor pairs, and the relevant acceptors are the copper acceptor and the (cadmium vacancy)–(indium donor) complex respectively. For the intermediate doping region, the copper-related recombination is thought to become predominant, resulting in the well-resolved emission structure.

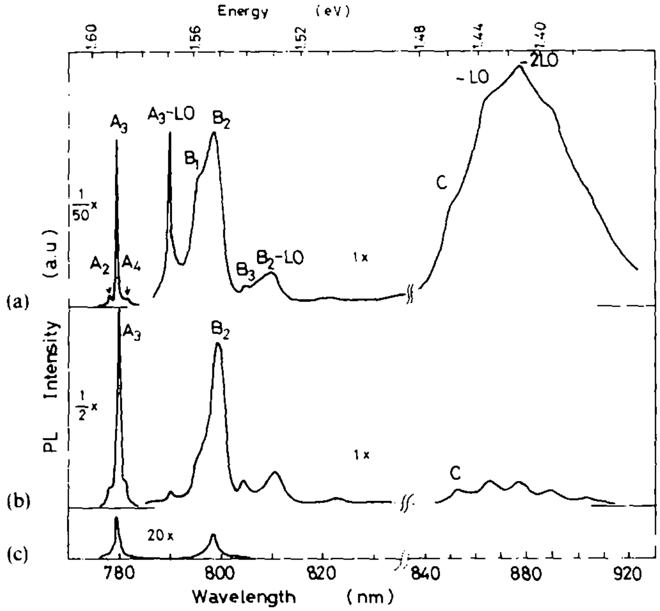


Fig. 8. PL spectra at 6 K for copper-doped CdTe epilayers (T_s = 225 °C): (a) $N_{Cu} = 1.5 \times 10^{16}$ cm^{-3}; (b) $N_{Cu} = 2 \times 10^{18}$ cm^{-3}; (c) $N_{Cu} = 2 \times 10^{19}$ cm^{-3}

3.4. *Arsenic-doped epilayers*

In the preparation of arsenic-doped epilayers, the arsenic arrival flux J_{As} at the substrate surface and the flux ratio J_{Cd}/J_{Te} were varied from 3×10^{11} to 1.5×10^{13} cm^{-2} s^{-1} and from 1 to 3 respectively. The arsenic molecules are very volatile at the MBE temperature, and hence their sticking coefficients are considered to be low. As the values are unknown, estimation of the incorporated arsenic concentration could not be performed.

The characterization of Schottky diodes fabricated from the epilayers shows that their conductivity is n type and that the net donor concentrations are below 1×10^{15} cm^{-3}. However, for the highly arsenic-doped sample ($J_{As} = 1.5 \times 10^{13}$ cm^{-2} s^{-1}; $J_{Cd}/J_{Te} = 2$), the forward current in the I–V relation shows saturation as for copper doping (Fig. 7(a)). This indicates that the remaining donors are almost completely compensated by acceptors introduced by the arsenic doping.

In Figs. 9(a)–9(c) PL spectra are shown for the epilayers prepared with $J_{Cd}/J_{Te} = 2$ and $J_{As} = (1–15) \times 10^{12}$ cm^{-2} s^{-1}. As shown in the figures, line A_3 at

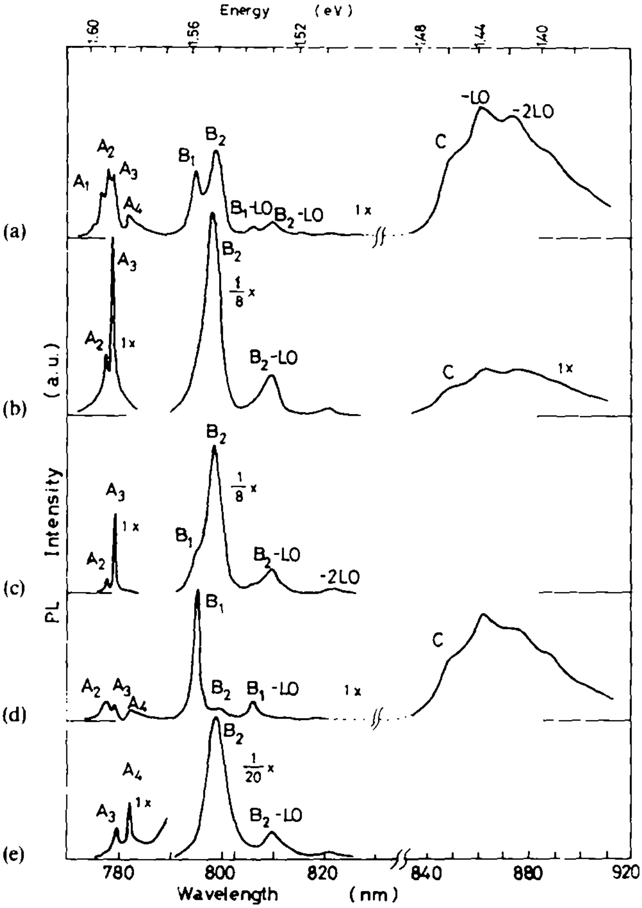


Fig. 9. PL spectra at 6 K for arsenic-doped CdTe epilayers ($T_s = 225$ °C): (a) $J_{Cd}/J_{Te} = 2$, $J_{As} = 1 \times 10^{12}$ cm^{-2} s^{-1}; (b) $J_{Cd}/J_{Te} = 2$, $J_{As} = 5 \times 10^{12}$ cm^{-2} s^{-1}; (c) $J_{Cd}/J_{Te} = 2$, $J_{As} = 1.5 \times 10^{13}$ cm^{-2} s^{-1}; (d) $J_{Cd}/J_{Te} = 1$, $J_{As} = 5 \times 10^{12}$ cm^{-2} s^{-1}; (e) $J_{Cd}/J_{Te} = 3$, $J_{As} = 5 \times 10^{12}$ cm^{-2} s^{-1}.

1.590–1.591 eV becomes dominant in the exciton region with increasing arsenic concentration. This result suggests that line A_3 for the arsenic-doped layers is due to excitons bound on acceptors, which are related to the arsenic atoms probably incorporated on tellurium sites. Moreover, it should be noted that the edge emission line B_2 increases in intensity with increasing arsenic concentration, while the 1.45 eV line C decreases and nearly disappears at higher doping levels. Therefore, the arsenic acceptor or its associate with another impurity or a lattice defect might be one of the origins of the acceptors responsible for line B_2 in the arsenic-doped samples. As line C can be considered to be related to a (cadmium vacancy)–donor complex, the decrease in the peak intensity of line C with increasing arsenic concentration will be explained in terms of a reduction in the vacancy concentration, which is caused by the occupation of the vacancy by the dopant (arsenic atom) as in the case of phosphorus doping[13].

The effects of the variation in J_{Cd}/J_{Te} on the PL spectra for epilayers grown with a constant J_{As} value of 5×10^{12} cm^{-2} s^{-1} are exhibited in Figs. 9(b), 9(d) and 9(e). A marked increase in the emission of line B_2 accompanied by a decrease in that of line C with increasing J_{Cd}/J_{Te} is also observed. The increase in the intensity of line B_2 can be interpreted to be induced by the increase in the concentration of arsenic, incorporated on a tellurium site, because of the abundance of cadmium and the deficiency of tellurium in the impinging molecular beams. The same fact also accounts for the decrease in the cadmium vacancy concentration and the resulting reduction in the intensity of line C.

The above-mentioned results indicate that arsenic atoms can be incorporated on tellurium sites and that they play the part of acceptor centres, independently of or in combination with other defects. P-type conductivity was not attained in our experiment by the use of arsenic as a dopant, which seems to be due to strong compensation by interstitial cadmium or substitutional arsenic at a cadmium site. The compensation mechanism has been suggested by Chu *et al.*[14] in a study of arsenic implantation into CdTe.

3.5. *Antimony-doped epilayers*

For doping with antimony to concentrations of between 2.4×10^{16} and 1.2×10^{18} cm^{-3} all the samples show n-type conduction and the donor exciton line A_2 dominates the exciton region of the spectra as shown in Fig. 10. The peaks of the

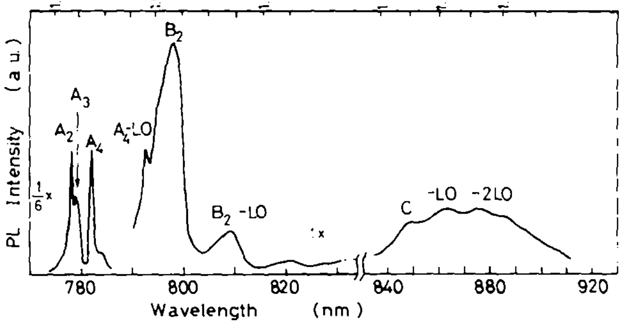


Fig. 10. PL spectrum at 6 K for antimony-doped CdTe epilayers (T_s = 225 °C; $N_{Sb} = 4.3 \times 10^{17}$ cm^{-3}).

edge emission do not increase so markedly as for the arsenic-doped samples. From the result it can be deduced that the possibility of antimony as an effective acceptor dopant in MBE is very slight.

4. CONCLUSIONS

From the study of doping effects on CdTe MBE layers the following conclusions can be drawn.

(1) Undoped CdTe layers contain indium and antimony atoms with concentrations of $(0.3-1) \times 10^{16}$ cm^{-3}, owing to out-diffusion from the InSb substrates.

(2) From the dependences of the peak energies of the low temperature PL spectra on the doped indium concentration, the ionization energies of the acceptors responsible for the edge and 1.45 eV emissions are estimated to be 49 meV and 147 meV respectively.

(3) In the copper-doped layers, the acceptor-bound exciton line dominates the PL spectra, as it does for copper-diffused bulk crystals, and p-type conduction occurs at high copper concentrations.

(4) With arsenic doping, the acceptor-bound exciton (1.590–1.591 eV) and edge emission (about 1.551 eV) lines increase in intensity, and this can be accounted for by the incorporation of arsenic on a tellurium site. However, conversion to p-type conductivity is not attained.

(5) Even with antimony doping at as high a concentration as 1.2×10^{18} cm^{-3}, the MBE layers are n type and no marked change in the PL spectra is observed.

ACKNOWLEDGMENTS

The author wishes to thank S. Kurosawa for SIMS measurements and Y. Furukawa, K. Oe and K. Tsubaki for helpful discussions.

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