p-type CdTe epilayers grown by hot-wall-beam epitaxy

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Highly conducting p-type CdTe films were grown by photoassisted hot-wall-beam epitaxy using Li₃N as a dopant source. Doping levels can be controlled from $p=4\times10^{16}$ to 2×10^{18} cm⁻³, as determined by Van der Pauw measurements. The hall mobility ranges from 30 to 100 cm²/V·s, depending on the hole concentration. Photoassisted growth enhances the incorporation of dopants by one order of magnitude and decreases the growth rate.

CdTe, a wide band gap semiconductor with a direct band gap of 1.5 eV at room temperature, is one of the basic II-IV materials. CdTe attracted large interest because of potential applications for optoelectronic devices such as solar cells and gamma ray detectors. Another important application of CdTe is its use as substrate for the tunable infrared detector material $Hg_{1-x}Cd_xTe$. The use of CdTe in device applications has been limited due to the tendency of this material to self-compensation. The use of dopants in growth techniques for bulk material or thin films has always shown low activation of the impurities resulting in highly resistive as-grown CdTe samples. Especially in the case of p-type bulk CdTe, the growth temperatures used create a high density of native defects which causes the p dopant to be incorporated on electrically inactive sites or to have amphoteric character.

The growth of high crystalline quality CdTe on GaAs wafers to be used as substrates for $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ is well-known, however, the CdTe layers grown on GaAs substrates were always highly resistive. Besides the self-compensation effect mentioned above, the Ga diffusion from the substrate into the CdTe layer as determined from secondary ion mass spectrometry was also thought to be responsible for the high resistance in the CdTe epilayers. In order to avoid Ga diffusion the use of buffer layers between the GaAs substrate and the CdTe layer, such as $\mathrm{Zn}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ or ZnTe —CdTe superlattices was proposed. In agreement with Wagner et al., our investigations of GaAs/ZnTe/CdTe heterostructures showed a reduction of the Ga diffusion into the CdTe layer up to one order of magnitude.

In order to enhance the substitutional doping in CdTe layers photoassisted epitaxial growth techniques were proposed. Using the group V elements Sb and As as dopant sources in photoassisted molecular beam epitaxy (MBE)^{5,6} and metalorganic vapor phase epitaxy⁷ p-type conductivity

of CdTe was achieved. However, most of these films were grown on CdTe substrates.

It is well-known that Li, an element of group I, is a shallow acceptor in II–VI compounds. Li itself is very difficult to handle due to its high reactivity. Therefore, dispensers were used for p-type doping of II–VI compounds with Li in MBE⁸ or a stable compound of Li is necessary as a dopant source. Lithium nitride (Li₃N) was successfully used as a dopant source in metalorganic vapor phase epitaxy of ZnSe.⁹ It has never been used with CdTe. In this communication, we report the first growth of p-type CdTe on GaAs using Li₃N as a dopant source.

The hot-wall-beam epitaxy (HWBE) system¹⁰ was installed in a vacuum chamber and consisted of a preheating stage, a ZnTe and a CdTe HWBE reactor with a Li₃N dopant source. Figure 1 shows the schematic setup of the HWBE system. Since Li₃N reacts with the conventional silica ampouls, the dopant material was evaporated from a tantalum tube. To enable the photoassisted growth the light of a Xe arc lamp (230–800 nm) was directed to the substrate by focusing lenses and a silica fiber bundle. To avoid any condensation of material at the entrance window a heated silica disk was mounted in front of the window in order to keep the light intensity constant during growth.

The source materials ZnTe and CdTe were synthesized with excess Te from elements with a purity of 6 N. After sublimation in vacuum and removing the excess Te, high purity polycrystalline source material was obtained. The substrates were semi-insulating undoped [001]-oriented GaAs with a misorientation of 2° toward the next [011] direction. Prior to growth, the substrates were degreased and etched in a solution of H₂SO₄:H₂O:H₂O₂=5:1:1. Before initiating the growth the GaAs substrate was thermally cleaned at 600 °C in order to remove the oxide. After transferring the substrate from the preheating oven to the ZnTe HWBE reactor, a 1 μ m thick ZnTe buffer layer was grown at a substrate temperature of 380 °C and at a source temperature of 580 °C. Then the sample was moved to the CdTe HWBE reactor to grow the p-type CdTe epitaxial layer. The transfer time between both reactors was ~ 1 s.

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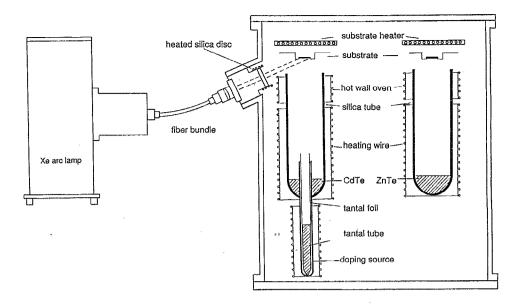


FIG. 1. Schematic drawing of the HWBE reactor with the illumination setup.

The CdTe layers were grown at a substrate temperature of 390 °C and a CdTe source temperature of 500 °C. The illumination power density for photoassisted doping was 30 mW/cm². In order to provide various hole concentration, the temperature of the Li₃N doping source was varied from 350 to 550 °C. At a substrate temperature of 390 °C, the growth rate of the CdTe epilayer decreased from 2 μ m/h without illumination to 1 μ m/h when the substrate was illuminated with a power density of 30 mW/cm². It decreased further to 0.4 μ m/h when the illumination power density was increased to 150 mW/cm².

The crystalline quality of the samples were investigated with high resolution x-ray diffraction, using a goniometer equipped with a four crystal Ge monochromator. The full width at half-maximum (FWHM) of the (004) Bragg reflection was taken as criterion for the crystalline quality of the layers. The FWHM decreases from 450 arcsec for 2 μ m thick CdTe layers to 100 arcsec for CdTe layers with a

thickness of $14 \mu m$. In comparison to the results obtained for CdTe layers grown without ZnTe buffer layer, ¹¹ the FWHM of the $14 \mu m$ thick CdTe layer was reduced by a factor of 3. In other words, the $14 \mu m$ thick CdTe epilayer with ZnTe buffer had a crystalline quality which was obtained for CdTe epilayers grown on GaAs with a thickness of more than $38 \mu m$. This improvement of the crystalline quality is most likely due to the fact that the ZnTe buffer layer reduces the large lattice mismatch of 14.6% between GaAs and CdTe into two steps of 8% from GaAs to ZnTe and 6.6% from ZnTe to CdTe.

The electrical properties of the CdTe films were investigated by Hall effect measurements in Van der Pauw geometry. Ohmic contacts were made by evaporating Au (600 Å). Before evaporation, the samples were etched in concentrated HCl to remove the oxide and rinsed in methanol. Contacts prepared in this way showed an ohmic behavior down to ~ 150 K. All samples investigated were

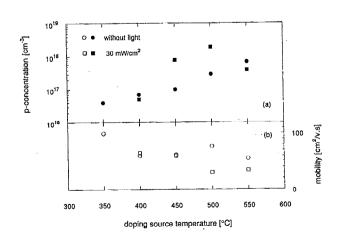


FIG. 2. Dopant source temperature dependence of carrier concentration and Hall mobility for p-type CdTe doped with Li₃N.

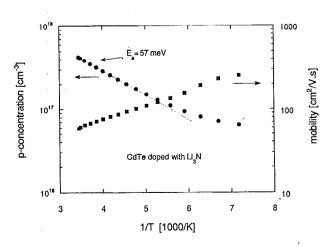


FIG. 3. Mobility and carrier concentration for a p-type CdTe epilayer doped with $\mathrm{Li}_3\mathrm{N}$.

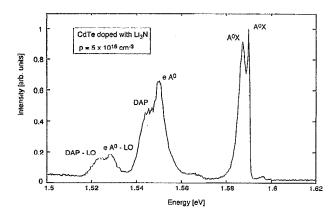


FIG. 4. PL spectrum of p-CdTe at 1.7 K.

p-type. Figure 2(a) shows the room-temperature hole concentration of CdTe films grown without illumination and with an illumination of 30 mW/cm² as a function of the Li₃N doping source temperature. The hole concentration increases from 4×10^{16} to 2×10^{18} cm⁻³ when the Li₃N temperature increases from 350 to 550 °C. These results demonstrate that the hole concentration can be controlled varying the doping source temperature and that the light illumination can significantly enhance the doping efficiency at doping source temperatures below 500 °C. The corresponding hall mobility at room temperature is shown in Fig. 2(b). It increases from 30 to 100 cm²/V s when the hole concentration varies between 2×10^{18} and 4×10^{16} cm⁻³. These mobility values are comparable to the highest Hall mobilities observed in p-type bulk CdTe at 300 K.¹² Figure 3 shows the temperature dependence of the carrier concentration and mobility of a sample grown with a doping source temperature of 450 °C under illumination (150 mW/cm²). An acceptor ionization energy of 57 meV was found from the slope of the curve.

Photoluminescence (PL) spectra obtained with our p-type CdTe films were used to determine their optical quality. The PL measurements were performed at 1.7 K using an argon-ion laser (488 nm) at a power density of $\sim 3 \text{ W/cm}^2$. Figure 4 shows a typical PL spectrum of a 2 μ m thick CdTe sample with a hole concentration of

 5×10^{16} cm⁻³. The spectrum is dominated by the excitonic emission. The peaks at 1.590 and 1.588 eV are associated with excitons bound to neutral acceptors $(A^{\circ}X)$.¹³ The luminescence line ~1.55 eV is due to the free-electron to neutral acceptor (eA°) and donor-acceptor (DAP) recombination. Besides the phonon replica of these transitions $(eA^{\circ}$ -LO and DAP-LO) no remarkable luminescence was detected at lower energies.

In conclusion, we have shown for the first time that p doping of CdTe is possible in an HWBE system using Li₃N as dopant source. CdTe layers with a carrier concentration between 4×10^{16} and 2×10^{18} cm⁻³ were grown. The doping level can be controlled by varying the doping source temperature. Photoassisted growth enhances significantly the doping efficiency at doping source temperatures below 500 °C and reduces the growth rate.

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