Hydrogenation of undoped and nitrogen-doped CdTe grown by molecular beam epitaxy

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The effect of atomic hydrogen during the growth of undoped and nitrogen-doped CdTe by photon-assisted molecular beam epitaxy was investigated. Hydrogen incorporation is enhanced by the presence of nitrogen. Infrared absorption measurements strongly suggest the formation of N–H complexes. Hall measurements indicate that the complexes are donorlike in nature. Hydrogenation radically changes the low temperature photoluminescence in both undoped and nitrogen-doped layers. Exciton-related luminescence is quenched at low temperature. Nitrogen-related donor-acceptor pair luminescence is also absent from N-doped hydrogenated layers, consistent with complex formation. Copper donor–acceptor pair luminescence appears to be enhanced by hydrogen. © *1996 American Institute of Physics.* [S0003-6951(96)04604-X]

The ubiquitous nature of hydrogen during the growth and processing of semiconductors requires an understanding of its effects on dopant compensation and point defect formation.[1] For example, residual hydrogen in a molecular beam epitaxy (MBE) system can cause significant dopant compensation for materials such as Mg in GaN.[2] Effects due to hydrogen are significantly larger for metalorganic chemical vapor deposition (MOCVD) and metalorganic MBE growth (MOMBE).[3–5]

Reports on hydrogenation of II–VI semiconductors remain scarce. Studies of bulk CdZnTe exposed to a hydrogen plasma indicated quenching of donor–acceptor pair (DAP) and electron–acceptor (e, *A*) photoluminescence assigned to Cd vacancies.[6,7] Similar quenching was observed for ZnSe[8] for an unspecified donor and acceptor. Annealing of nitrogen-implanted CdTe in hydrogen reduced DAP luminescence attributed to nitrogen.[9] Absorption studies using a Fourier transform infrared spectrometer (FTIR) indicate the formation of complexes between H and As in CdTe and ZnTe, between H and P in ZnTe grown by MOCVD,[10] and between H and N in ZnSe grown by MOCVD and MOMBE.[3–5] In this letter, we report on the use of a thermal atomic hydrogen source to investigate hydrogenation of undoped and nitrogen-doped CdTe grown by MBE.

The CdTe layers were grown at West Virginia University using photon-assisted MBE in a system similar to that described elsewhere.[11] CdTe films were grown on (100) and (211)B substrates using a single source of CdTe, all provided by II–VI, Inc. (Saxonburg, PA). The 2 μm thick layers were grown at 230 °C at a rate of 0.3 μm/h under an illumination intensity of 75 mW/cm^2 (514.5 nm line, argon ion laser). Doped layers were grown with an undoped 0.3 μm buffer layer. A cryogenically cooled rf plasma source (Oxford Applied Research CARS-25) was used for nitrogen doping. Atomic hydrogen was produced using a thermal cracker (EPI).

X-ray diffraction rocking curve measurements indicated no measurable difference in crystal quality between epilayers grown with or without hydrogen and the original substrates. Undoped layers were *p*-type with carrier concentrations of about 5×10^{16} cm^{-3} as determined by Hall measurements. Secondary ion mass spectrometry (SIMS) performed at Charles Evans and Associates (Redwood City, CA) indicated Cu at this level, apparently diffusing from the substrate. No other impurities were detectable by SIMS above instrumental background in these layers.

Low-temperature PL measurements were performed using the 514.5 nm argon ion laser line at a power density of 3.1 W/cm^2. All spectra shown are corrected for system response. A 4.8 K PL spectrum typical of the undoped layers is shown in Fig. 1(a). The dominant emission line at 1.5894 eV is due to the copper-acceptor (Cu$_{Cd}$) bound-exciton recombination[12] with an LO-phonon replica at 1.568 eV. The absence of significant emission at lower energies, particularly DAP emission, indicates an absence of donor impurities in the undoped layers.

Nitrogen doping was accomplished using a 3×10^{-6} Torr beam equivalent pressure (BEP) from the rf plasma source operating at 275 W. By varying growth conditions, N concentrations were obtained that ranged from 5×10^{16} to 2×10^{17} cm^{-3} with an instrumental background of about 3×10^{16} cm^{-3}. Hall measurements indicated *p*-type layers with a high degree of dopant activation. However, interpretation was complicated by a large nitrogen accumulation at the doped layer/buffer layer interface in many of the layers.[13]

A PL spectrum typical of the CdTe:N layers is shown in Fig. 1(b). The dominant recombination at 1.5898 eV is attributed to nitrogen-acceptor (N$_{Te}$) bound-exciton recombination.[14] The LO-phonon replica of the bound-exciton line appears at 1.568 eV. The (e,A^0) and the DAP emission related to N$_{Te}$ occur at 1.550 and 1.543 eV, respectively, with several orders of phonon replicas.[9,14–16] Note that the DAP band indicates the presence of a shallow-ionization-energy donor in the layers. Two-electron-transition spectroscopy indicates the donor is a halogen impurity, most likely fluorine, and not a defect complex as
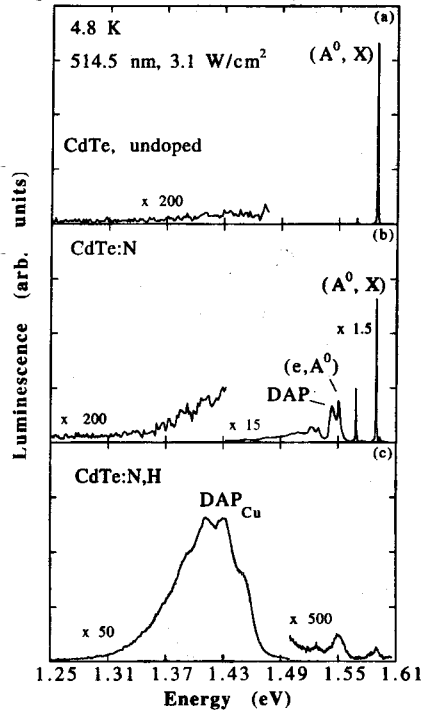

FIG. 1. Photoluminescence spectra of (a) undoped CdTe, (b) CdTe doped with nitrogen, and (c) CdTe doped with nitrogen grown under a hydrogen flux.
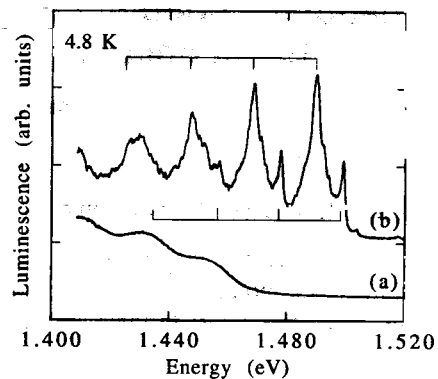

FIG. 2. Selective excitation photoluminescence of CdTe:N,H with (a) above band-gap excitation and (b) excitation tuned below the shallow donor energy level. The curves are displaced for comparison.

some studies have suggested.[14,16] Consistent with this finding, the only n-type impurity measured by SIMS was F at concentrations of about 1×10^{15} cm^{-3} in the CdTe:N samples, evidently related to either the nitrogen doping or the nitrogen source itself.

Hydrogenation was accomplished using 1×10^{-6} Torr BEP from the thermal source operating at 9.5 A. Hall measurements made on undoped CdTe layers grown under a H flux were indistinguishable from undoped layers. SIMS background levels in the high 10^{17} cm^{-3} for hydrogen were too large to allow quantitative determination of H in these samples.

A 4.8 K PL spectrum typical of both CdTe:N layers grown under a H flux (CdTe:N,H) and CdTe:H layers is shown in Fig. 1(c). The bound-exciton, (e,A^0) and DAP emissions related to the shallow nitrogen acceptor are greatly reduced in intensity, similar to an earlier report.[9] In contrast, there is a significant enhancement of the DAP emission related to Cu$_{Cd}$ and a shallow donor. The zero-phonon band occurs at about 1.45 eV and is accompanied by phonon replicas with energy spacing of about 20 to 21 meV. SIMS analysis did not indicate copper segregation in the epilayers, as is sometimes observed.[17] The enhanced Cu-related DAP either indicates that hydrogenation results in an increase in the background concentration of shallow donors, or that competing recombination pathways are removed by hydrogenation.

Selective excitation PL studies were performed on the CdTe:H and CdTe:N,H layers using a Ti:sapphire laser. Figure 2(a) shows a portion of the total copper-related DAP observed when using above-band-gap excitation. When the energy of the exciting light was lower than the 4.2 K band

gap of 1.606 eV, we observed a distinct set of PL lines occurring only in films grown in the presence of hydrogen. The curve shown in Fig. 2(b) was obtained using excitation at 1.5867 eV (7811.9 Å) which is below the shallow donor level in CdTe. The DAP band is gone as expected. However, two series of sharp lines with zero-phonon peaks at 1.4991 and 1.4899 eV appear, along with several orders of phonon replicas occurring at 21 meV intervals (indicated by the lines). The two series of lines show distinctly different temperature behavior. The 1.4899 eV lines decrease with increasing temperature, while the 1.4991 emission increases up to a temperature of 45 K, whereby it then decreases. In addition, the 1.4991 eV emission is extremely sensitive to excitation energy and is best seen when the Ti:sapphire laser was tuned to about 1.587 eV. In contrast, the recombination mechanisms resulting in the 1.4899 eV transition have a very broad absorption band ranging from 1.50 to 1.59 eV.

The origins of the new PL lines shown in Fig. 2(b) are not yet completely understood although the emission appears to be related to the presence of hydrogen during growth. In the previous report of hydrogen interactions with nitrogen acceptors in CdTe,[9] no new PL features were observed. The excitation energy and temperature behavior of the 1.4899 eV transition is similar to that attributed to isoelectronic oxygen centers in ZnTe.[18] However, the emission energies do not correspond to that associated with isoelectronic oxygen in CdTe.[19] We are currently performing a more detailed study of this interesting transition.

A SIMS depth profile for hydrogen and nitrogen was obtained from a CdTe:N,H sample consisting of 1 μm CdTe grown under both a nitrogen and hydrogen flux on top of 1 μm of CdTe grown only under a hydrogen flux. A distinct step was observed in the hydrogen signal that correlated with the increase in nitrogen concentration from background to about 1×10^{17} cm^{-3} in the top layer. Within the accuracy of the measurement, the increase in hydrogen concentration matched or exceeded that of nitrogen indicating nitrogen-enhanced hydrogen incorporation similar to that reported for ZnSe:N,H.[5] Hall measurements indicated that the CdTe:N,H samples were heavily n type, with carrier concentrations of about 1×10^{17} cm^{-3}.

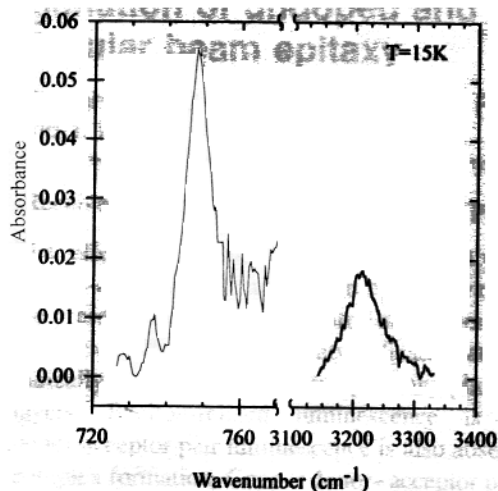Absorption spectra were taken using a Nicolet model

FIG. 3. Fourier transform infrared spectroscopy measurement showing absorption features related to nitrogen–hydrogen complex formation in CdTe:N,H.

550 FTIR spectrometer at 15 K. Two new absorption features, shown in Fig. 3, were observed at about 3210 and 749 cm^{-1} for the CdTe:N,H samples. These features, absent for undoped layers, nitrogen-doped layers grown without a hydrogen flux, undoped layers grown under a hydrogen flux, and bare substrates, are taken as an indication of N–H bonding. The 3210 cm^{-1} peak can be associated with the N–H stretching mode, similar to the N–H stretching mode absorption at 3193–3194 cm^{-1} in ZnSe,[3,4] the 3336 cm^{-1} stretching mode in ammonia molecules,[20] and the 3340 cm^{-1} absorption band observed for a-SiN:H.[21]

Wolk et al.[3] observed an FTIR peak in ZnSe:N,H at 783 cm^{-1}. Using polarized Raman spectroscopy measurements, they verified that this feature was only observed for the scattering geometries consistent with a N–H wagging mode. Following their reasoning, we assign the feature at 749 cm^{-1} to the N–H wagging mode in CdTe. The presence of both features only in the sample with significant nitrogen and hydrogen strongly implies that H forms a complex with N acceptors in CdTe. Thus, it is easy to understand the quenching of PL associated with nitrogen due to complex formation. The presence of the N–H bond removes the N from acting as an acceptor. Indeed, the N–H complex appears donorlike based on the Hall results.

These data, coupled with previous reports of N–H bonding in ZnSe,[3–5] As–H bonding in CdTe and ZnTe,[10] and P–H bonding in ZnTe,[10] indicate a trend that H will form a strong bond to group V dopant atoms. Thus, care must be taken to minimize hydrogen compensation not only in the growth but also in subsequent processing steps. The presence of Cu-related DAP PL implies that H either does not form complexes with Cu, or the complexes are unstable at the growth

temperature. A speculation is that p-type dopants on the metal sublattice may not form compensating bonds with hydrogen.

In summary, hydrogenation during the growth of undoped and nitrogen-doped CdTe has been investigated. Quenching of exciton-related PL was observed, while Cu-related DAP luminescence was enhanced. New PL features were measured that appear to be related to hydrogenation. Results of PL, SIMS, and FTIR measurements made on CdTe:N,H samples are consistent with N–H complex formation.

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