# HYDROGENATION OF UNDOPED AND NITROGEN DOPED CdTe AND ZnSe GROWN BY MOLECULAR BEAM EPITAXY

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## ABSTRACT

Hydrogen incorporation in both undoped and nitrogen-doped CdTe and ZnSe is investigated. Evidence for a strong nitrogen-hydrogen interaction is presented. Preliminary data indicate that the growth of CdTe and ZnSe under an atomic hydrogen flux results in a significant concentration of paramagnetic defects possibly accompanied by enhanced auto-doping from residual impurities.

## INTRODUCTION

Hydrogen is pervasive in semiconductors. It is a component of most chemicals used in the fabrication of electronic and photonic devices, is easily incorporated into semiconductors and it is a model impurity for studying defect reactions in solids. Hydrogen passivation of deep level impurities and defects has been broadly investigated in Si and III-V compound semiconductors. Recently, compensation by hydrogen has become of interest for research on II-VI compound semiconductors, particularly p-type doped ZnSe.[1,2,3] While sources of hydrogen are obvious in growth techniques involving hydrogen-containing compounds such as metal-organic chemical vapor deposition (MOCVD), what is often not considered is that even a background pressure of around $10^{-10}$ Torr can result in potential hydrogen incorporation at levels of about $10^{18}$ $cm^{-3}$ for high incorporation efficiencies. Hydrogen partial pressures during growth by the UHV technique of molecular beam epitaxy (MBE) can easily reach this or higher levels during growth. Therefore, it is necessary and useful to examine conditions for hydrogen incorporation using a single, controllable hydrogen source. In this paper we report on the incorporation of hydrogen in ZnSe and CdTe during MBE growth under various conditions. It is clear that atomic hydrogen interacts strongly with nitrogen when used as a p-type dopant. We also present preliminary evidence that growth of undoped layers under an atomic hydrogen flux may introduce a significant concentration of paramagnetic point defects.

## EXPERIMENT

Details of the ZnSe and CdTe growth are presented elsewhere. [4,5] In brief, both CdTe and ZnSe were grown using standard effusion sources (CdTe, Zn and Se) in a custom MBE chamber equipped with a 1000 l/s cryopump. A commercial atomic hydrogen source (EPI-AHS-L) was used to generate atomic hydrogen. The hydrogen flow used resulted in a beam flux monitor reading of about $2\times10^{-6}$ Torr. After considering the ion gauge sensitivity for $H_2$ and the reported cracking efficiency, this results in an atomic hydrogen flux of ~$9.6\times10^{14}$ $sec^{-1}$ $cm^{-2}$. Nitrogen doping was achieved using one of two rf plasma atomic/radical nitrogen sources (Oxford CARS25 or EPI Unibulb). The nitrogen sources were typically operated with a plasma power between 150 to 300 W and a nitrogen flow resulting in a 1 to $6\times10^{-6}$ Torr system pressure. For doping with molecular nitrogen, the plasma power of the nitrogen source was turned off

while nitrogen gas was flowing through the plasma source. Deuterium was used to replace hydrogen in some growths. The reasons for using deuterium are that deuterium is easier to detect than hydrogen in a SIMS measurement since deuterium is less abundant than hydrogen in the air, yielding at least two orders of magnitude improvement in the SIMS detection limit, and deuterium allows a clean investigation of N-H bonding in ZnSe through isotope related effects. Since the isotopic shift in vibrational frequency of hydrogen bond is unique for a particular H-X bond (X is the other atom attached to H), the observation of an isotope shift is a signature of the corresponding H-X bond. This approach is widely used for confirming bond formation with hydrogen in other material systems. The sample thickness was nominally about 2 μm in most cases.

## RESULTS

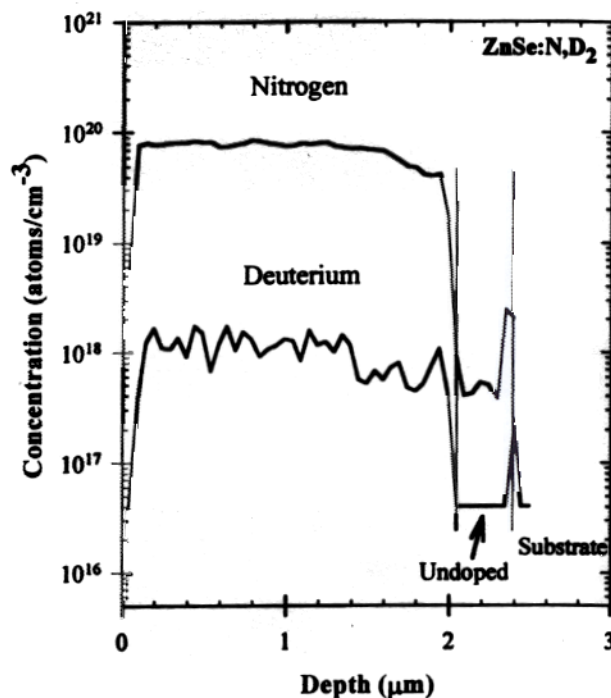Table I contains a summary of hydrogen, deuterium and nitrogen concentrations



Fig. 1 Secondary ion mass spectrometry depth profile of nitrogen and deuterium in a ZnSe layer grown under both a molecular deuterium and nitrogen flux.

for various growth conditions determined from SIMS. Hydrogen incorporation in ZnSe and CdTe was most significant only when both atomic hydrogen and atomic nitrogen were present during the growth (ZnSe:N,H, CdTe:N,H). Hydrogen incorporation in ZnSe also depends on the growth conditions. The highest nitrogen and hydrogen concentrations are obtained for Zn-rich conditions and at the lower growth temperatures. The highest hydrogen level is $5 \times 10^{20}$ cm$^{-3}$, more than one order higher than the nitrogen level in the same layer. Note that this level implies almost 1 atomic percent! As expected, Zn-rich conditions are more favorable to nitrogen incorporation in ZnSe since nitrogen occupies a Se site for p-type doping in ZnSe. Two other cases deserve special notice. First, in nitrogen-doped ZnSe exposed to molecular deuterium during growth (ZnSe:N,D$_2$), a deuterium level at $10^{18}$ cm$^{-3}$ and nitrogen level at $8 \times 10^{19}$ cm$^{-3}$ were observed as shown in Fig. 1. This indicates that a mechanism exists for incorporating a significant amount of hydrogen from molecular species during doped-layer growth, and so hydrogen must be seriously considered as a potential candidate for compensation in MBE growth. Second, growth of either ZnSe or CdTe under an atomic deuterium flux results in deuterium concentrations in the mid-$10^{17}$ cm$^{-3}$ range. Hydrogen is being pursued as a surfactant for growth of heteroepitaxial systems, such as CdTe on Si. The latter case clearly indicates that significant amounts of hydrogen will be incorporated during such growths.

Fourier transform infrared spectroscopy was performed at room-temperature and 15K on the ZnSe samples using a Nicolet model 550 FTIR spectrometer. Absorption bands are observed at 783 cm$^{-1}$ and 3193 cm$^{-1}$ in nitrogen-doped ZnSe samples grown under atomic hydrogen flux.

## Table I. Hydrogen, Deuterium and Nitrogen Concentrations In ZnSe and CdTe for Various Growth Conditions

### ZnSe

| Sample | $T_{growth}$ (°C) | Zn/Se ratio | N flux ($\times 10^{-6}$ torr BEP) | [N] ($\times 10^{19}$ cm$^{-3}$) | [H] or [D] ($\times 10^{19}$ cm$^{-3}$) |
|---|---|---|---|---|---|
| ZnSe:N,H | 250 | 1.8 | 3.0* | 3.0 | 50 |
| ZnSe:N,D | 250 | 2.0 | 4.7* | 8.0 | 30 |
| ZnSe:N,D | 250 | 0.6 | 4.7* | 1.5 | 1.8 |
| ZnSe:N | 300 | 0.5 | 3.2* | 1.5 | background |
| ZnSe:D | 300 | 0.5 | 0 | background | 0.03 |
| ZnSe:N,$D_2$ | 300 | 1.2 | 5.1* | 8.0 | 0.1 |

### CdTe (Single Source)

| Sample | $T_{growth}$ (°C) | N flux ($\times 10^{-6}$ torr BEP) | [N] ($\times 10^{17}$ cm$^{-3}$) | [H] or [D] ($\times 10^{17}$ cm$^{-3}$) |
|---|---|---|---|---|
| CdTe:N | 300 | 2.0* | 0.6 | Background |
| CdTe:N,H | 300 | 2.0* | 2.0 | 2.0 |
| CdTe:N | 300 | 5.4** | 50 | Background |
| CdTe:N,H | 300 | 5.6** | 20 | 20 |
| CdTe:D | 300 | 0 | background | 4.0 |

* Oxford source, **EPI source, rf power was 200 W and the hydrogen/deuterium system pressures were maintained at $1 \times 10^{-6}$ Torr whenever present.

These peaks are absent from ZnSe samples grown only with atomic nitrogen or atomic hydrogen flux, as well as from undoped ZnSe samples. Similar features were observed at 783 cm$^{-1}$ and 3194 cm$^{-1}$ in nitrogen-doped ZnSe grown by MOVPE [3] and at 3194 cm$^{-1}$ in nitrogen-doped ZnSe grown by MOCVD. [1] The 3194 cm$^{-1}$ band has been tentatively assigned to the stretching mode, and 783 cm$^{-1}$ band to the wagging mode of the N-H bond in ZnSe [3] based on absorption bands observed in ammonia [6] and N-H bonding in GaAs and GaP. [7]

The effect of isotopic substitution on the observed vibrational frequency is very useful for the identification of the species that comprise a defect complex. For example, the large frequency shift that results upon the substitution of deuterium for hydrogen can lead to an unambiguous assignment of hydrogen bonding. In the harmonic oscillator approximation, the vibrational frequency of an X-H oscillator is assumed to be inversely proportional to the square-root of the reduced mass of the oscillator. Thus, the ratio of the measured frequencies obtained for hydrogen and deuterium-containing samples should be inversely proportional to the ratio of respective reduced masses. The calculated ratio of frequencies is 1.369 for an ideal N-H bond which can be compared to the experimental value of 1.342 for the N-H bond stretching mode in ammonia. The decrease is due in part to the fact that nitrogen is also bonded to other atoms. In the nitrogen-doped ZnSe sample grown under a deuterium flux by MBE, an absorption band is observed at 2368 cm$^{-1}$ indicating a ratio of 1.348. The excellent agreement between this value, that of ammonia, and with the predicted value leads us to conclude that the 2368 cm$^{-1}$ absorption band

belongs to the N-D stretching mode in ZnSe. This result unambiguously identifies that N-H bonding is occurring in the ZnSe:N,H samples.

Similar features were observed at about 3210 and 749 cm$^{-1}$ for CdTe:N,H samples, which we also assign to N-H bonding. We were unable to observe an absorption band for the isotope shift in CdTe. The maximum H (D) concentrations in CdTe were more than an order of magnitude less than that for ZnSe, yielding a smaller absorption signal. The strength of the N-D signal in ZnSe was about 20% of that of the N-H signal for similar concentrations. If the same proportion holds in CdTe, the N-D signal would have been hidden by our instrumental noise.

Another interesting aspect of this study is the large concentration of hydrogen observed for ZnSe samples grown under Zn-rich conditions. Theoretical studies, such as the recent one by Neugebauer and Van de Walle [8] concerning GaN, indicate that hydrogen is more stable (and thus highly incorporated) in p-type than in undoped or n-type material, in agreement with the present study. Neugebauer's calculation implies a one-to-one incorporation of hydrogen-to-acceptor, which is what we observed for Se-rich ZnSe:N,H growth and for hydrogen incorporation in nitrogen-doped CdTe. Indeed, for levels up to about $10^{18}$ cm$^{-3}$, we see an enhanced incorporation of nitrogen that appears one-to-one with hydrogen when growing under an atomic hydrogen flux. Above $10^{18}$ cm$^{-3}$ of nitrogen, the presence of atomic hydrogen no longer enhances nitrogen incorporation. However, we can then begin to incorporate quite a significant concentration of hydrogen, up to 16 times more than the nitrogen concentration, as shown in Table I. It is not clear how the "excess" hydrogen is being incorporated in the samples grown for this study based on the measurements made to date. One possibility is that hydrogen is incorporating on vacancy sites (either Zn or Se) similar to observations for Si and Ge.

A Bruker ESP-300 electron paramagnetic resonance (EPR) spectrometer, operating at a microwave frequency of 9.45 GHz, a static modulation of 100 kHz, and a microwave power of 5 mW, was used to study nitrogen-doped and undoped samples. In general the undoped samples did not exhibit an EPR signal. Both nitrogen-doped ZnSe and ZnSe grown under Zn-rich conditions exhibited an EPR line approximately 5 to 6 Gauss in width and centered at g = 2.0027±0.0004. This previously reported [9] signal has been tentatively assigned as originating from a singly-ionized Se vacancy ($V_{Se}^{+}$). A $V_{Se}^{+}$ is a charged defect, and requires an additional defect of the opposite charge to obtain overall charge neutrality. In the case of p-type material, the necessary charge compensation can be provided by singly-ionized acceptors. A similar signal is observed in nitrogen-doped CdTe, as shown in Fig. 2(a). The analogous defect in this case would be a Te vacancy, $V_{Te}^{+}$. Again, the signal was not observed for undoped layers.

However, a strong EPR line essentially identical to that observed for nitrogen-doped layers was observed for both CdTe and ZnSe layers grown under an atomic hydrogen/deuterium flux. Indeed, as shown in Fig. 2(b), the magnitude of this signal could be larger than for the nitrogen-doped case. The width of the EPR line at 5 to 6 Gauss is too narrow to be attributed to H directly because of the expected hyperfine structure. Thus, one possibility is that the presence of atomic hydrogen is causing the formation of chalcogen vacancies. It is known that atomic hydrogen can remove both Se and Te by forming volatile hydrides. This could then form vacancies directly, or possibly shift the growth kinetics to the metal-rich side, which is more favorable for forming chalcogen vacancies. All that is lacking is a mechanism for introducing an oppositely-charged defect to provide charge neutrality.

A possible compensation mechanism if the defect causing the EPR signal is indeed a vacancy is suggested by low-temperature photoluminescence measurements. As shown in Fig. 3(a), PL spectra of undoped ZnSe samples were dominated by strong excitonic features with free exciton (X) and donor-bound exciton ($D^0$,X) transitions at 2.802 and 2.798 eV, respectively.
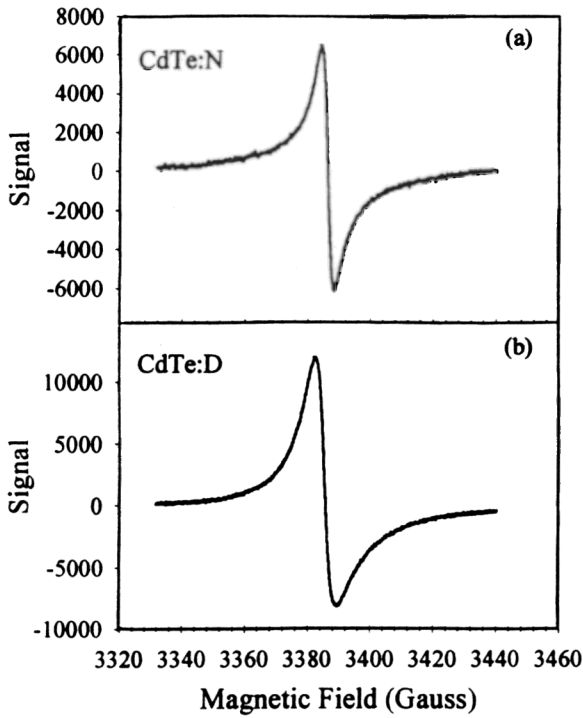
Figure 2. EPR spectra in the g = 2.00 region showing an EPR signal in (a) nitrogen-doped CdTe and (b) CdTe grown under a deuterium flux
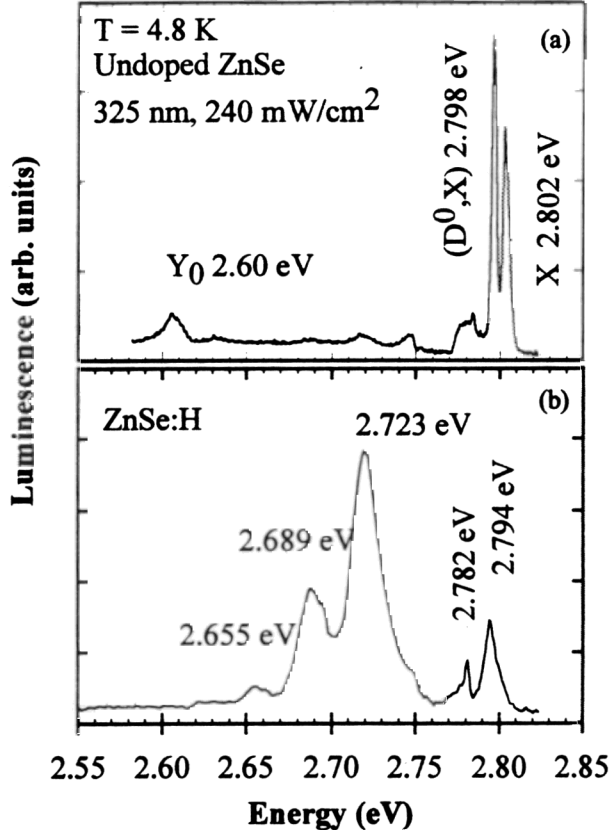


Figure 3. Comparison of photoluminescence observed in the near-edge region for (a) undoped ZnSe and (b) ZnSe grown under an atomic hydrogen flux.

For undoped ZnSe grown under an atomic hydrogen flux, however, the PL spectrum is quite different as shown in Fig. 3. The 2.794 eV line can be attributed to an acceptor-bound exciton . The peak at 2.782 eV is significantly stronger than that observed for undoped ZnSe , while the $(D^0,X)$ and $(F^0,X)$ peaks are much weaker than for typical undoped layers. This 2.782 eV peak is normally observed in low-doped p-type ZnSe and attributed to a deep acceptor-bound exciton. [10,11] The origin of the peak at 2.782 is not clear at the moment. However, previous reports in low level nitrogen-doped ZnSe [10] also speculate that this PL could be from residual species such as As, O, and S, whose incorporation is possibly enhanced by the presence of atomic hydrogen. A strong and broad emission around 2.72 eV, which has been reported in both As and N-doped ZnSe [12,13] and whose origin is unidentified, also appears. This peak is accompanied by phonon replicas, indicative of donor-acceptor pair recombination (DAP). Assuming a normal shallow donor energy of 30 meV, the acceptor energy is estimated to be about 90 meV assuming a 20 meV pair term. This energy is very close to that for a P acceptor in ZnSe. [14] However, this transition has also been reported in As-doped ZnSe.[12] The structural-defect-related transitions $I_v$ and $Y_0$ lines are further suppressed in those undoped ZnSe grown with atomic hydrogen samples, which may imply that these defects are further reduced in these layers. All of the above suggest enhanced p-type impurity incorporation/auto-doping for growth under atomic hydrogen. If an atomic hydrogen flux causes vacancies to form as singly ionized species, an impurity or defect of opposite charge state is required to obtain charge neutrality and possibly

defect stability. This could result in an enhanced diffusion of impurities from the substrate or enhanced incorporation of residual gas species during growth.

## CONCLUSION

In conclusion, hydrogen and deuterium were incorporated into undoped and nitrogen-doped ZnSe and CdTe grown by MBE. Surprisingly high levels of hydrogen and deuterium were observed, with hydrogen concentrations as high as $5x10^{20}$ cm$^{-3}$ in a ZnSe:N layer with a nitrogen concentration at $3x10^{19}$ cm$^{-3}$. It was found that hydrogen incorporation closely tracks the nitrogen incorporation.. Local vibration modes were observed at 3193 cm$^{-1}$ and 783 cm$^{-1}$ for ZnSe:N,H samples and at 2368 cm$^{-1}$ for ZnSe:N,D samples. The isotopic peak shift strongly supports the formation of N-H bonds in ZnSe. Similar features were observed at about 3210 and 749 cm$^{-1}$ for CdTe:N,H samples and also assigned to N-H bonding. Preliminary data indicate that the growth of CdTe and ZnSe under an atomic hydrogen flux results in a significant concentration of paramagnetic defects possibly accompanied by enhanced auto-doping from residual impurities.

## ACKNOWLEDGMENTS

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