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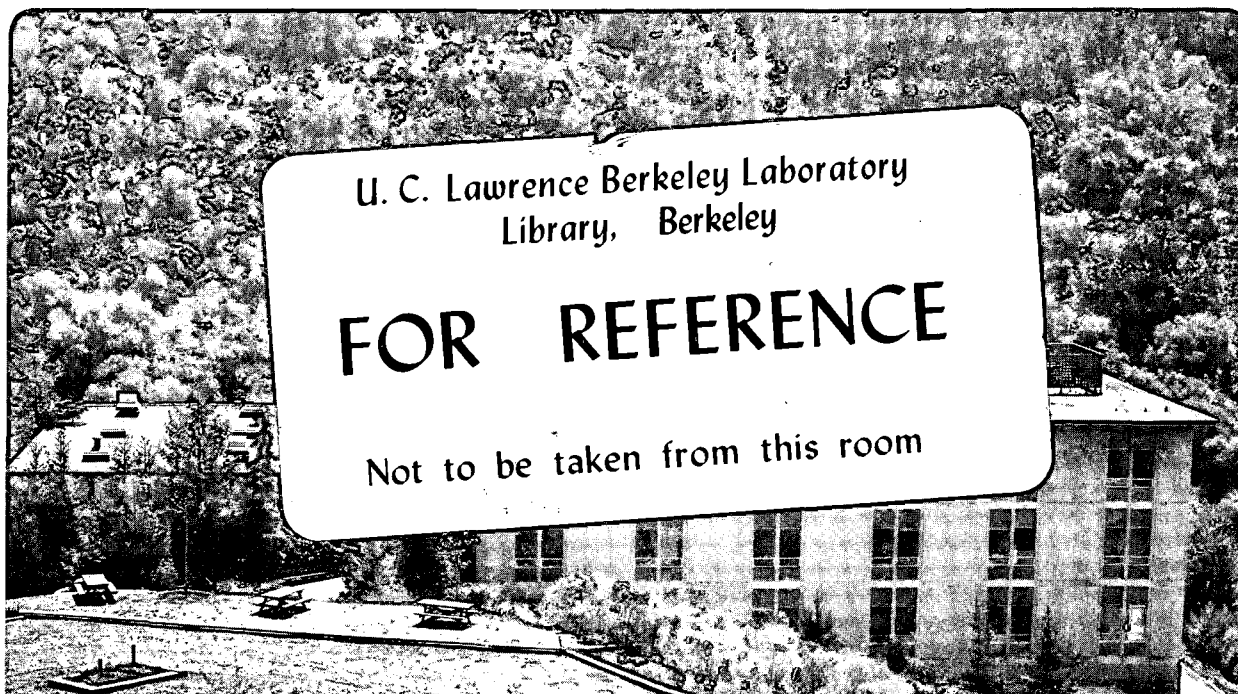
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**Photoluminescence Spectroscopy and Rutherford Backscattering
Channeling Evaluation of Various Capping Techniques for Rapid
Thermal Annealing of Ion-Implanted ZnSe**

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May 1994

PHOTOLUMINESCENCE SPECTROSCOPY AND RUTHERFORD BACKSCATTERING CHANNELING EVALUATION OF VARIOUS CAPPING TECHNIQUES FOR RAPID THERMAL ANNEALING OF ION-IMPLANTED ZnSe

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ABSTRACT

We report on the effectiveness of proximity caps and PECVD Si₃N₄ caps during annealing of implanted ZnSe films. OMVPE ZnSe films were grown using diisopropylselenide (DIPSe) and diethylzinc (DEZn) precursors, then ion-implanted with $1 \times 10^{14} \text{ cm}^{-2}$ N (33 keV) or Ne (45 keV) at room temperature and liquid nitrogen temperature, and rapid thermal annealed at temperatures between 200°C and 850°C. Rutherford backscattering spectrometry in the channeling orientation was used to investigate damage recovery, and photoluminescence spectroscopy was used to investigate crystal quality and the formation of point defects. Low temperature implants were found to have better luminescence properties than room temperature implants, and results show that annealing time and temperature may be more important than capping material in determining the optical properties. The effects of various caps, implant and annealing temperature are discussed in terms of their effect on the photoluminescence spectra.

INTRODUCTION

Successful fabrication of ZnSe-based, blue-green light emitting devices [1] has been achieved using a nitrogen free radical source [2] to obtain p-type ZnSe layers in MBE growth. Though OMVPE growth may have more potential as a commercial process, attempts at p-type doping have been only moderately successful. Ohki *et al.* [3] attained low hole concentrations using NH₃ doping of MOCVD films; Taskar *et al.* [4] improved the hole concentration to $3 \times 10^{16} \text{ cm}^{-3}$ by post-growth rapid thermal annealing of SiO₂-capped films.

The observation of nitrogen related donor acceptor pair lines and acceptor bound exciton lines has been reported after implantation and furnace annealing of LPE [5] and after rapid thermal annealing of MBE [6] films. Skromme *et al.* [7] investigated the effect of annealing caps on ion-implanted and unimplanted MBE films. Annealing with Si₃N₄ caps resulted in better optical properties as compared to SiO₂, while capless anneals and anneals with diamond-like carbon films increased the formation of zinc vacancies at the surface. The effectiveness of various encapsulants in activating implanted nitrogen during annealing, as well as the effect of implant temperature and annealing kinetics on damage recovery, have not been fully investigated.

EXPERIMENTAL

OMVPE ZnSe films were grown on semi-insulating GaAs substrates using diisopropylselenide (DIPSe) and diethylzinc (DEZn) precursors at 460°C and 300 Torr [8]. The 2 μm thick films were ion-implanted at room temperature and at liquid nitrogen temperature with either N (33 keV) or Ne (45 keV), at a dose of $1 \times 10^{14} \text{ cm}^{-2}$. The Ne implants were used to separate the damage-related PL features from the active N-related features. PECVD SiN_x caps were deposited at 300°C using NH₃ and SiH₄ at 1 kHz. The films were rapid thermal annealed for 10 seconds at 400°C to 850°C, or furnace annealed for 10 seconds to 30 minutes at 200 - 300°C in nitrogen, using either SiN_x caps or proximity caps. Rutherford backscattering spectrometry (RBS) in the channeling orientation was used to investigate damage recovery, and photoluminescence

spectroscopy was used to investigate crystal quality and the formation of point defects. The PL was performed at 10K using the 325 nm line from a 30 mW HeCd laser and a 0.85 m Spex double monochromator.

RESULTS AND DISCUSSION

Rutherford Backscattering Spectrometry

Figure 1 shows the $\langle 111 \rangle$ aligned spectra of the unannealed N and Ne implants in ZnSe. The room temperature (RT) implanted sample has the lowest channeling yield, indicating the least damage in the film. The damage level in the low temperature (LT) implant is higher than the RT implant, which is consistent with results in III-V materials [9]. The as-implanted Ne implant shows considerably more damage, as expected for the heavier ion.

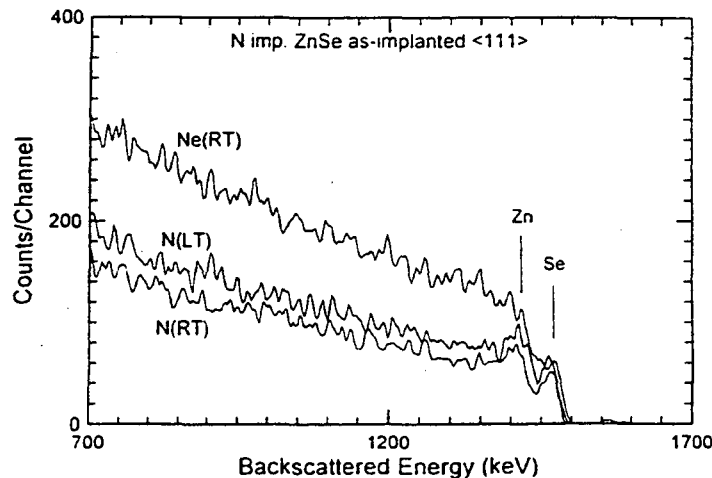


Figure 1. The $\langle 111 \rangle$ aligned spectra of the unannealed N and Ne implants in ZnSe.

Damage recovery in the N implanted films during rapid thermal annealing (RTA) is dependent on both the implant temperature and the capping material. Figure 2 shows the total damage observed on the samples after RTA, measured by channeling along the $\langle 110 \rangle$. The total damage is defined by the following expression [10]:

$$\text{total damage} \equiv \ln \left[\frac{1 - \chi_v(t)}{1 - \chi_D(t)} \right] \quad \text{Eqn (1)}$$

where $\chi_v(t)$ and $\chi_D(t)$ are the minimum RBS yields for the virgin epilayer and the implanted layer, respectively, at depth t . t is taken to be the thickness of the implanted region in this case.

The low temperature implant damage is recovered after annealing at 550°C only when a SiN_x cap is used; proximity cap annealing does not allow full damage recovery. On the other hand, the room temperature implant damage is fully recovered after a proximity-capped anneal at 550°C, but not as completely after a SiN_x -capped anneal. Further annealing at higher temperatures results in increased damage level in all samples which were measured.

The apparent increase in damage after annealing above 650°C may not be real structural damage, but may be due to the degradation of the ZnSe surface. Figure 3 shows a series of $\langle 110 \rangle$ aligned RBS spectra of the SiN_x -capped low temperature implanted samples annealed at 550 and 650°C. A large Se surface peak is observed from the samples annealed at 650 and 750°C. No such Se peak appears in the proximity cap anneals of the room temperature implants, which is consistent with their lower integrated damage values (Figure 2). However, this Se-rich layer does not appear to hinder the photoluminescence characteristics of the film.

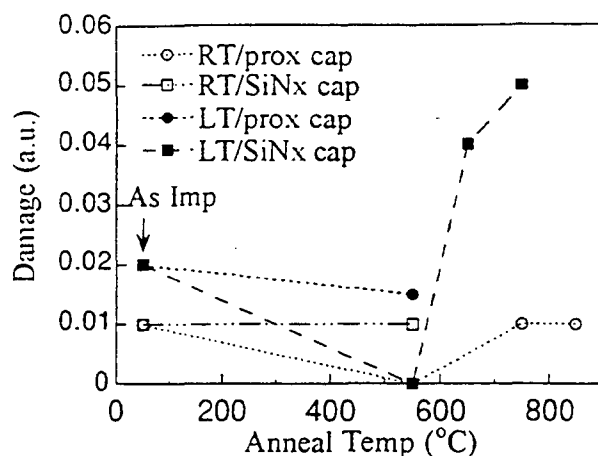


Figure 2. Integrated damage from $\langle 110 \rangle$ channeling spectra for LT and RT nitrogen implants before and after annealing.

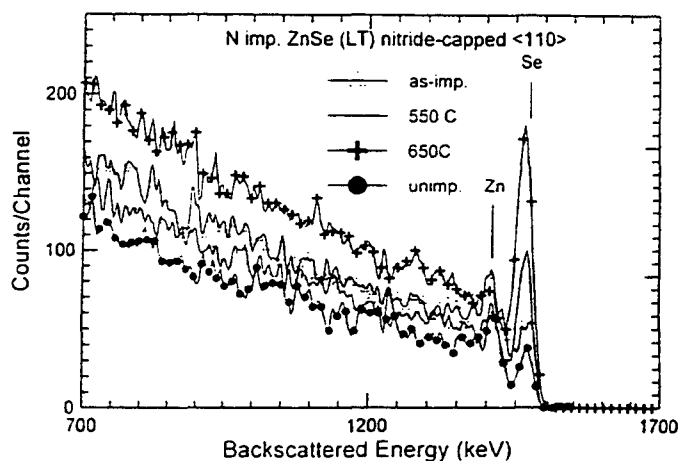


Figure 3. $\langle 110 \rangle$ channeling yield for SiN_x -capped ZnSe film N^+ implanted at low temperature and after annealing.

Photoluminescence Results

Unimplanted Films

Figure 4 shows the 10K PL spectra for the ZnSe epilayer, as-grown and annealed for 10 seconds at 550°C . The inset shows the near band-edge high resolution spectrum. The background electron concentration as measured by Hall effect was $4.8 \times 10^{14} \text{ cm}^{-3}$, assumed to be due to the incorporation of Ga from the substrate during growth. The as-grown spectrum is dominated by the near band-edge emissions, and deep level emission is low. The peak at 2.799 eV and the high energy shoulder at 2.802 eV are attributed to the free exciton (FE), while the peaks at energies of 2.794 (I_x) and 2.797 eV (I_2) are attributed to a neutral donor-bound exciton, probably related to the background Ga [11]. Both features are split into light and heavy hole components due to the internal strain of the heteroepitaxial layers. The broad peak at approximately 2.77 eV is probably due to the two-electron satellite lines of the donor-bound exciton as well as possible contributions from the LO phonon replicas of the free exciton. The Y peak at 2.601 eV has been attributed to dislocation-related recombination [12].

Unimplanted films were annealed with either proximity or silicon nitride caps. There were no significant changes to the deep level emissions after annealing. Figure 4 shows the PL spectrum for a sample after proximity cap anneal at 550°C . The FE, I_x and I_2 peaks are strong, indicating no degradation of crystal quality; however, a peak (I_1^d) has emerged at 2.780 eV.

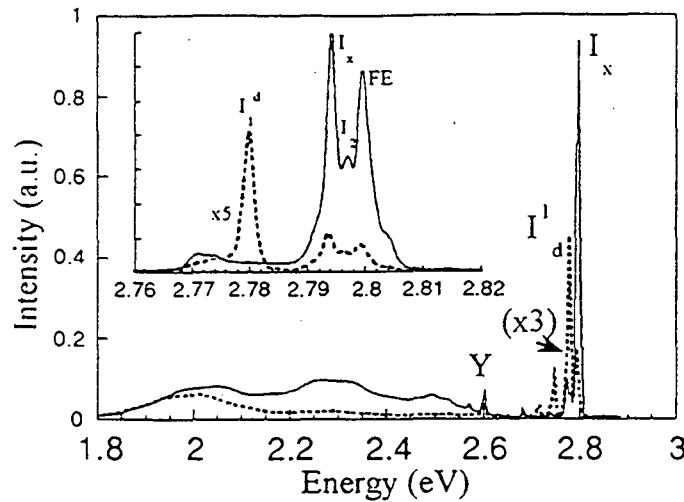


Figure 4. Photoluminescence spectra for a 2 μm thick OMVPE ZnSe epilayer on GaAs, as grown (solid line) and after 550°C RTA (dotted line).

This peak has been attributed to the zero phonon line of an exciton bound to a deep native acceptor which is probably a zinc vacancy [12]. LO phonon replicas were also observed (not shown). This peak appears in all of our ZnSe films after annealing, even for anneals at temperatures as low as 200°C, which is well below the growth temperature. The low energy shoulder on the I_1^d peak is due to the same defects responsible for the broad peak (at 2.77 eV) in the as-grown spectrum. With either proximity or SiN_x caps, annealing induces the formation of defects responsible for the I_1^d line and the reduction in FE and I_x intensity.

Figure 5 (lower curve) is a plot of the absolute intensity of the I_1^d peak as a function of anneal temperature for unimplanted films. Both types of caps result in a maximum in the I_1^d intensity after 650°C anneals; the intensity is reduced after higher temperature anneals and the SiN_x -capped films have lower emission from the I_1^d defect. The FE and I_x lines also decrease in intensity after high temperature anneals, indicating loss of crystal quality. In an effort to separate contributions of lifetime effects from changes in the concentration of the defect responsible for I_1^d , we have plotted the ratio I_1^d/FE (upper curve). The ratio for the SiN_x -capped films is nearly constant, indicating that the I_1^d intensity varies in the same way as the free exciton intensity. This suggests that the defect concentration does not increase with further annealing at high temperature. On the other hand, the proximity capped films have a maximum in the I_1^d/FE intensity, indicating that the defect concentration increases with anneal temperature at least up to 650°C. The SiN_x caps appear to be more effective at preventing Zn vacancy formation; however, the overall PL intensity is higher from the proximity capped films. This seems to indicate that the Zn vacancy concentration is not the lifetime-controlling defect in these layers. The differences observed using the two caps may be due only to the 300°C furnace anneal which is part of the PECVD process, rather than significant effects due to the capping material.

Implanted Films

In the following two sections we will compare the photoluminescence spectra for nitrogen implanted ZnSe layers. Except for Figure 6, all spectra have been measured under similar conditions and therefore the intensity scales may be used to compare the PL intensities of these samples. The spectra in Figure 6 were measured using a different grating with an efficiency that is about a factor of 4-10 lower in the spectral region of interest.

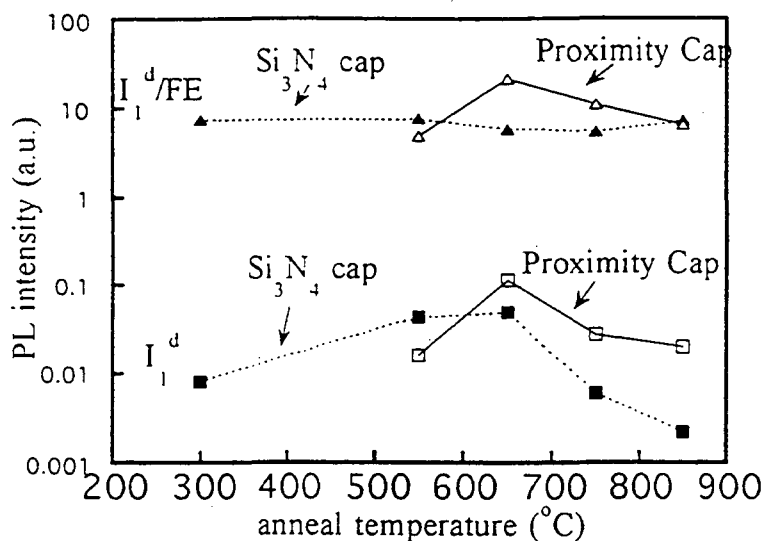


Figure 5. Absolute intensity of I_1^d peak and the ratio I_1^d/FE as a function of 10 s. anneal temperature for ZnSe epilayer.

Room Temperature Implants

Figure 6 shows the PL spectra from a room temperature implanted ZnSe film, as-implanted and after annealing at 550, 650 and 750°C with a PECVD SiN_x cap. After implantation, emission from the excitonic region is considerably reduced, and an emission from the nitrogen donor-acceptor pair band (N-DAP), with zero phonon line at 2.696 eV and LO phonon replicas separated by 31 meV, is observed. This energy is consistent with other observations from nitrogen-doped ZnSe films [2] and provides evidence that the implanted nitrogen behaves as an active acceptor. The N-DAP intensity increases with increasing annealing temperature, and although PL intensity cannot be assumed to directly correspond to the concentration of an impurity, this trend may indicate that more of the nitrogen is active after each successive anneal. Alternatively, the intensity increase could reflect a decrease in other available radiative or non-radiative channels. A peak at 2.788 eV is observed after 650 and 750°C anneals, which may be the I_1^N line attributed to an exciton bound to a shallow nitrogen acceptor. The excitonic emissions I_x and FE are only weakly present in the as-implanted sample and are further suppressed by annealing. The I_1^d intensity increases with annealing temperature, following a trend similar to that of the N-DAP emission.

Figure 7 shows the PL spectra from a room temperature implanted ZnSe film, as-implanted and after annealing at 550, 650 and 850°C with a proximity cap. In these samples, the N-DAP band at 2.697 eV is still observed; however, the spectra are dominated by a deeper DAP band centered around 2.63 eV. On annealing, emission from this second band increases relative to the N-DAP band. Yang *et al.* [13] observed a broadened DAP band at high nitrogen concentration and attributed it to a compensating donor introduced by the plasma doping method used. Hauksson *et al.* [14] observed a second DAP band which they believe is due to a $V_{Sc}-Zn-N_{Sc}$ complex forming at high N concentration. Possibly the nitrogen in this high concentration region is forced onto interstitial shallow donor sites [15] which complex with a deep acceptor, giving rise to this deeper emission band. The intensity of emission from the I_1^d line is higher for the proximity capped samples as compared to the SiN_x capped samples. The fact that this band is not formed during SiN_x-capped annealing suggests that during the 30 minute, 300°C furnace PECVD step, significant damage may have been removed, preventing further nitrogen complexing associated with the deeper DAP band, and/or keeping the nitrogen on acceptor sites. If this is the case, it

suggests that further work should focus on the low temperature activation and annealing of implant damage. The near bandedge emission remains strongly suppressed for all annealing temperatures, indicating low carrier lifetime in these layers. This is consistent with the increased damage detected by RBS, at least at higher annealing temperatures, and indicates that the ZnSe crystal quality is not improved by high temperature annealing. However, the nitrogen-DAP emission is very strong, indicating activation of the nitrogen. SiN_x capping is more effective than proximity capping for activation of room temperature nitrogen implants.

Neon implants produce good crystal quality after low temperature annealing, with formation of I₁^d, but at higher temperature an unidentified DAP band centered at 2.74 eV is observed.

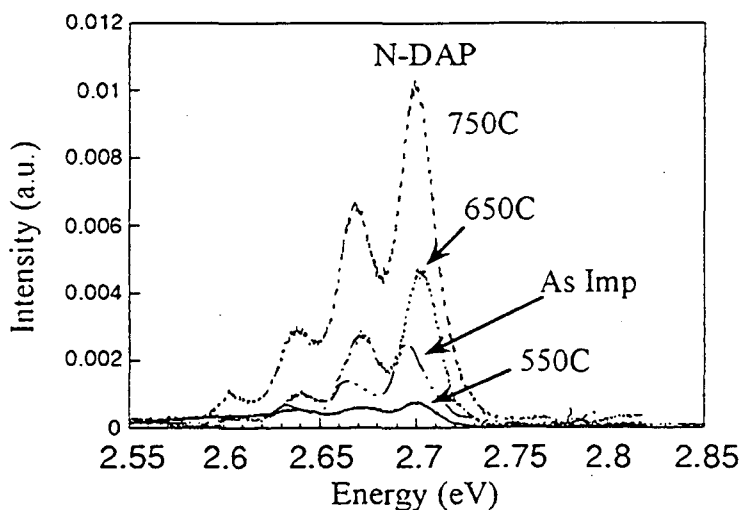


Figure 6. PL spectra for room temperature N-implanted films after SiN_x capped RTA.

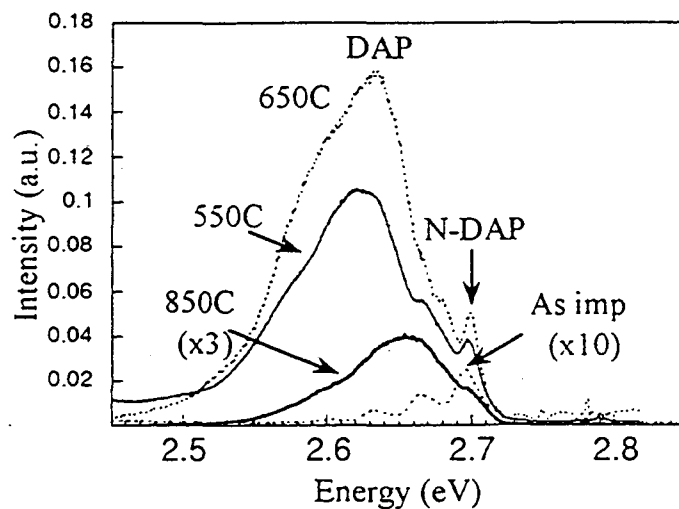


Figure 7. PL spectra for room temperature N-implanted films after proximity cap RTA.

Low Temperature Implants

Figures 8 and 9 show the near bandedge PL spectra for the ZnSe films implanted at liquid nitrogen temperature and annealed with SiN_x and proximity caps, respectively. The PL emission intensity is larger from the LT implants (both as implanted and annealed) than the RT implants by at least an order of magnitude in both the excitonic and the DAP transitions, as well as deep levels.

Figures 8 and 9 show the near bandedge PL spectra for the ZnSe films implanted at liquid nitrogen temperature and annealed with SiN_x and proximity caps, respectively. The PL emission intensity is larger from the LT implants (both as implanted and annealed) than the RT implants by at least an order of magnitude in both the excitonic and the DAP transitions, as well as deep levels.

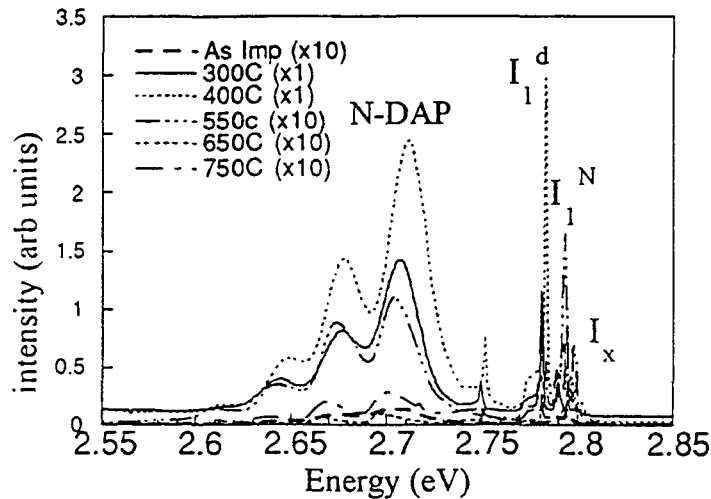


Figure 8. PL spectra from low temperature implant after SiN_x-capped RTA.

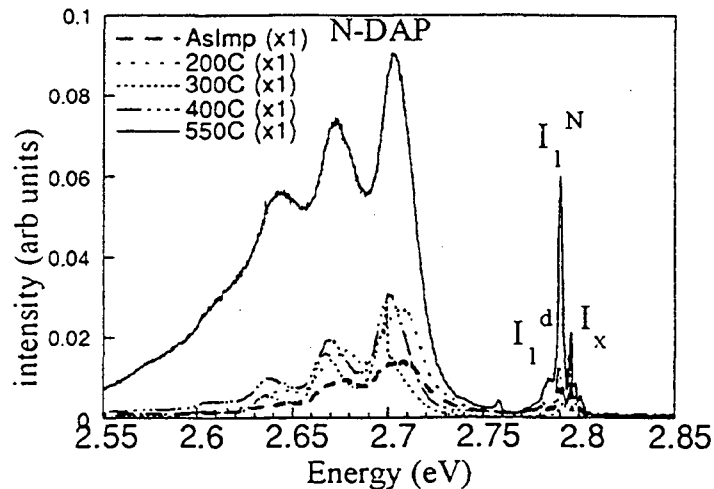


Figure 9. PL spectra from low temperature implant after proximity cap RTA.

This indicates that the recovery of implant damage and crystal quality is better after annealing the LT implants and may be due to a difference in the as-implanted defect structures. Also, the I₁^N emission intensity is much more pronounced in these samples. Unlike the RT implants, the PL spectra from the SiN_x-capped and proximity capped films are qualitatively similar, although the overall emission intensities are higher from the SiN_x capped films. The similarity indicates that the defect structure of the low temperature implant is less sensitive to the type of anneal treatment; regardless of whether the 300°C 30 minute anneal is performed, neither type of sample produces a second, deeper DAP band. The RBS results show higher integrated damage in the LT implants which may be due to the presence of more extended defects in these films. These extended defects appear to enhance nitrogen occupation of Se sites and reduce complexing or interstitial occupancy. This idea is consistent with the order of magnitude higher emission intensity from these films.

the N-DAP, I_1^N , I_x and FE lines continuously increase in intensity for anneals up to 400°C, and then decrease, indicating that the most damage recovery and nitrogen activation occurs during the 400°C anneal, with degradation of the sample occurring at higher temperatures. The proximity capped anneals show the highest intensity after the 550°C anneal (they did not undergo higher anneals). A deep level which is observed in the as-implanted film at about 2.28 eV, increases in intensity dramatically after 300 and 400°C anneals, and then is removed at higher temperature under both types of caps. These observations suggest that an extended defect or cluster which forms during the initial stages of damage recovery is removed at higher temperature. Both the DAP and I_1^d emissions degrade above 400°C.

CONCLUSIONS

We have observed nitrogen-related donor-acceptor pair emission as well as nitrogen acceptor-bound exciton emission from ion-implanted OMVPE ZnSe epilayers after rapid thermal annealing. We conclude that low temperature nitrogen implants result in better photoluminescence properties than room temperature implants. Room temperature implants are very sensitive to the annealing conditions, with a long low temperature (300°C) anneal before RTA providing better activation of the nitrogen than RTA alone. Low temperature implants are less sensitive to capping and annealing conditions. The highest N-DAP intensity was obtained after a 400°C RTA following a SiN_x PECVD deposition step which included a 30 minute furnace anneal. High temperature annealing (above 550°C) of either type of implant results in degradation of PL intensity and possible formation of a Se-rich surface phase. A peak which has been associated with Zn vacancies appears after annealing at temperatures as low as 200°C; however, the presence of this peak does not appear to reduce emission from the N-related levels.

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