O implantation in ZnSe: lattice distortion by Raman measurement

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We probe the "bulk" and near-surface regions of O-implanted heteroepitaxial ZnSe films, using the full-width at half-maximum (FWHM) of the Raman line. The results are compared to those after N implantation. A tensile stress attributed to a deformation in the lattice around O is found. Under rapid thermal annealing, the optimum temperature for the recovery of the implantation damage without suffering from thermally generated point defects is $T_a = 500^\circ C$. It corresponds here to the maximum FWHM from the uncompensated tensile stress, while identical FWHM's are found for the top and the "bulk" part of the film just after implantation, and after implantation and $T_a = 600^\circ C$.

1. Introduction

Because of its band gap width (2.7 eV), ZnSe is a promising material for blue emitting devices. However, problems still remain in achieving a sufficient level of p-type doping [1]. p-Doping is mainly obtained from Group I and V atoms in substitution for Zn and Se, respectively [1,2]. However, formation of isoelectronic acceptors by substitution of O for Se have been recently reported [3]. In this unusual doping process, O atoms trap electrons because of their high electronegativity, and thereby create holes. Oxygen doping has been achieved by molecular beam epitaxy (MBE) [3], but also by O implantation [3]. We check here the lattice distortion and its evolution after implantation plus rapid thermal annealing (RTA) under a Zn overpressure. The damage is followed by measurement of the full-width at half-maximum (FWHM) of the LO phonon Raman line.

The comparison of the results obtained after O and N implantation should give information about stress from specific lattice distortion around O atoms. As the escape depth of the light depends on its energy, the excitation energy for the Raman scattering, $E$, has been chosen to probe mainly the "bulk" or the near-surface part of the film [4].

2. Experimental set-up

2 μm thick ZnSe films were grown by MBE on undoped (100) GaAs substrates at 275°C and with a Zn-to-Se flux ratio of 1:2. The O atoms were implanted with an energy of 120 keV and a fluence of $7 \times 10^{12}$ cm$^{-2}$ at room temperature. The O concentration is gaussian with a maximum at $R_p = 2000$ Å, and $\Delta R_p = 900$ Å. With these light implanted atoms, the main (nuclear) damage is expected to have about the same profile as that of the O species. Rapid thermal annealing was performed at the annealing temperature, $T_a$ of 400, 500, and 600°C, under Zn vapor pressure at $T_a$.

The Raman spectrum was excited by the 5145 (400 mW) and 4578 (20 mW) Å lines of an argon laser, which probe respectively the "bulk" and the...
top 3000 Å of the film [4]. At the shorter wavelength, there is a photoluminescence signal which fortunately decreases with time. The spectra were recorded after 20 to 60 min of illumination, with a resolution of about 2 cm\(^{-1}\).

3. Results and discussion

3.1. Excitation by the 5145 Å line ("bulk film")

A typical raw Raman spectrum (after RTA at \(T_a = 500^\circ\text{C}\)) and its fit by a Lorentzian [4,5] curve, after subtracting the background, are shown in fig. 1. The variations of the FWHM versus the preparation conditions are given in fig. 2. From the virgin sample (FWHM = 5.5 cm\(^{-1}\)), there is first a slight minimum (4.8 cm\(^{-1}\)) below \(T_a = 400^\circ\text{C}\), then a monotonic increase until it equals 5.9 cm\(^{-1}\) at 600°C. These results are quite similar to those obtained from N implantation [4] and may be interpreted in the same way.

In comparison with the "natural" FWHM of 5 cm\(^{-1}\) reported for 2 μm thick virgin fully relaxed films [5] some strain remains in our "bulk" virgin films (e.g. from a deposition temperature of 275°C instead of 320°C [5]). This residual strain is relaxed by long-range dislocations induced by the implantation process at depth larger than \(R_p\), which is detected by the bulk signal.

![Fig. 1. Raman spectrum (after removing the background) of heteroepitaxial ZnSe thin films after implantation of \(7 \times 10^{12}\) O ions at 120 keV (-----) and its fit by a Lorentzian curve (- - - - -). (Excitation by 5145 Å.)](#)

![PREPARATION CONDITIONS](#)

Preparation Conditions

Fig. 2. FWHM of the Raman line of heteroepitaxial ZnSe under various preparation conditions (V virgin, I implanted, 400°C after implantation and RTA at 400°C,...). FWHM under excitation by the 5145 Å line (O—O, O implantation), and FWHM of the narrow line (X---X, O implantation, +---+, N implantation) under excitation by the 4578 Å line.
Annealing at $T_a \geq 400\,^\circ C$ results in an increasing stress, ascribed to the thermal generation of Zn vacancies, which has been identified otherwise [6] for films prepared under low-pressure conditions.

3.2. Excitation by the 4578 Å line (near-surface region of the film)

The photoluminescence background is removed by fitting the higher and lower wavenumber part of the spectrum by a polynomial function. The remaining part can be fitted by one (RTA at 400 or 500°C) or two (just after implantation, and RTA at $T_a = 600\,^\circ C$) Lorentzian curves. In this last case, the two Lorentzian curves are centered around the same wavenumber 252 cm$^{-1}$, but with different FWHM of 4.8 (I) or 5.9 (RTA 600°C) and 19 cm$^{-1}$, respectively. A typical raw spectrum (RTA at $T_a = 500\,^\circ C$) is given in fig. 3. These results are similar to those obtained after N implantation [4]. We propose similar interpretations and ascribe the narrower component to stress induced in the surface part of the film, while the wider peak results from the “coherent length” [7] in the unperturbed microscopic crystalline regions around $R_p$ (just after implantation) or in the very near-surface region of the film (implantation and $T_a = 600\,^\circ C$).

The variation of the FWHM of the narrower (stress widened) component is shown in fig. 2. The smaller values of the FWHM (just after implantation, and RTA at $T_a = 600\,^\circ C$), are close to those of the “bulk” with the same preparation conditions, but a striking maximum (8.7 cm$^{-1}$) is found after $T_a = 500\,^\circ C$. These variations are just opposite to those found after N implantation and annealing, fig. 2. From their neighbouring masses, after O and N implantation the stress contributions from implantation damage, and their recovery (i.e. “implantation” stress), should be identical for O and N after identical treatment. Thermal annealing at 600°C and above, induces stress (“thermal” stress) from generation of Zn vacancies, but this should also be identical after N and O implantation. Since there is small or no deformation around N in the ZnSe lattice during MBE growth, “implantation” or “thermal” stressed are the only stress contributors in the case of N implantation.

Thus, by comparing O and N data, the results are fully explained if there is a tensile stress contribution (“O” stress) more or less compensated by the compressive “implantation” stress. Just after implantation, there is a high “implantation” compressive stress contribution which fully compensates the “O” tensile stress (FWHM identical to that of “bulk” film). As annealing takes place, there is progressive recovery of the “implantation” stress. The maximum recovery ($T_a = 500\,^\circ C$) corresponds to the minimum of the FWHM after N implantation, and to the maximum FWHM here from the uncompensated “O” tensile stress contribution. A very similar temperature, $T_a = 470\,^\circ C$, has independently been reported to lead to optimized O implantation [3]. Annealing at higher $T_a$ (e.g. $T_a = 600\,^\circ C$), induces a compressive “thermal” stress contribution, which again fully (FWHM identical to that of “bulk”) compensates the “O” tensile stress. From fig. 2, the N “implantation” contribution (I) to the FWHM is 2.65 cm$^{-1}$ and is very close to the “O” contribution (500°C, 3.1 cm$^{-1}$), which supports our postulate of a constant “O” contribution in this processing range. Additional feature(s) decreasing the “O” contribution have to be deduced to explain the exact compensation at 600°C of the smaller (1.8 cm$^{-1}$) “thermal” strain.

As after N implantation, annealing up to 500°C has been found to be very effective to remove the
crystallographic damages. However, degradation instead of further improvement occurs with higher $T_a$, because the quality of the film is now limited by the thermal generation of Zn vacancies [4,6]. The Zn overpressure used in anneals corresponds to the Zn vapor pressure at the annealing temperature and this appears to be insufficient to avoid this problem. This might be solved by using high Zn overpressure during the annealing stages.

4. Conclusions

Variation of the FWHM of the ZnSe Raman lines from the “bulk” and the near-surface of the ZnSe after O implantation and annealing at $T_a$, and their comparison with those obtained after N implantation shows several interesting points:

- The FWHM of the narrow Raman component from the implanted region near the surface is equal to the bulk value, after (I)mplantation, and RTA at $T_a = 600^\circ$C, while there is a maximum for $T_a = 500^\circ$C.
- These results and their comparison with those from N implantation show the occurrence of a tensile stress from a deformation induced around O in the ZnSe lattice.
- As for N implantation, $500^\circ$C appears to be the optimum annealing temperature, resulting for O in a lower level of compensation of the tensile stress induced by this “isoelectronic” doping.
- Although most of the implantation damage is annealed at low $T_a$, creation of Zn vacancies in the same temperature range, even under a Zn overpressure, appears as a limiting feature. This might be solved by using high Zn overpressure during the annealing stages.

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References