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AMORPHIZATION OF ZnSe BY ION IMPLANTATION AT LOW TEMPERATURES

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Abstract

Radioactive Cd and Se ions were implanted into high-resistivity ZnSe single crystals around 60 K and 300 K. Their lattice sites were determined by measuring the channelling and blocking effects of the emitted conversion electrons or positrons directly after implantation and after annealing at different temperatures up to 600 K. Implantation doses were in the range of 3×10^{12}–$3 \times 10^{13}/\mathrm{cm}^2$. The experimental results of this emission channelling technique yield a high substitutional fraction of the implanted ions directly after implantation at room temperature. At 60 K the substitutional fraction of implanted ions is highly sensitive to the ion dose. Above a critical dose of around 1.4×10^{13} Cd/cm^2 or 2.1×10^{13} Se/cm^2 the substitutional fraction completely disappears indicating an amorphous surrounding of the probe atom. Damage recovery was observed below room temperature and at an annealing temperature around 500 K. A quantitative analysis of measured channelling yields will be given by comparison with calculated electron channelling profiles based on the dynamical theory of electron diffraction.

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1. INTRODUCTION

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Ion implantation as a means of doping II–VI semiconductors is beset with several problems different from those of ion-implanted elemental and III–V semiconductors: implantation damage reduces optical and electrical efficiency of the dopants [1]. On the other hand, even with high doses, no amorphization is observed with implantation at room temperature [2], [3]. Instead extended defects appear with a depth distribution corresponding to the implantation profile and point defects occur up to some µm deeper, thereby changing the electrical characteristics of the semiconductor [4]–[7]. This behaviour is attributed to the high ionicity of II–VI compounds which gives rise to high mobility of point defects and dynamic annealing during the implantation process. Naguib and Kelly [8] analysed several studies on ion implantation in various non-metallic compounds and derived several criteria for amorphization and recrystallization in such compounds, including the observation that compounds with an ionicity > 59% (e.g. ZnSe with 67%) are stable against amorphization.

All the measurements on II–VI semiconductors reviewed in Ref. [8], except for those in CdS [6], deal either with room temperature implantation or room temperature measurements. However, several authors [1], [3] have suggested that better electrical activity would result if the implanted layer were amorphized, thus suppressing defect mobility and preventing stoichiometry change during implantation. First evidence of enhanced electrical activity resulting from cold temperature implantation followed by rapid thermal annealing was reported in Ref. [1] for B ions implanted in HgCdTe. In addition, in ZnSe Frenkel pairs created via electron radiation were found to be stable at temperatures below 100 K [9]. These results suggest that the amorphous zones necessary for increased electrical activity may be achieved by defect accumulation during heavy-ion implantation at low temperatures.

In the present work we investigate the radiation damage generated in ZnSe by the implantation of Cd and Se ions at temperatures below 65 K. The structural damage of the crystals was determined as a function of ion dose directly after implantation using the emission channelling (EC) technique [10]. Annealing studies of the radiation damage were also done. For comparison emission channelling measurements were also carried out on samples into which the probe ions were implanted at room temperature. The implanted ions (Cd, Se) are isoelectronic and since their lattice positions reflect the sites of displaced host atoms in the implantation damage cascade, they allow the study of the microscopic structure of an ion track independent of the implanted species.

2. METHOD AND EXPERIMENT

In an emission channelling experiment (EC) single crystals are implanted with radioactive probe atoms which act as emitters of conversion electrons, β^-, β^+ or alpha particles. Depending on the emitter position, the emitted charged decay particles (in the case of ^{111m}Cd: conversion electrons with 127 keV and 147 keV, and in the case of ^{73}Se: positrons with an endpoint energy of 1320 keV) experience channelling or blocking effects along crystal axes and planes. The lattice sites of emitting atoms may be determined by detecting the angular dependent emission yield of particles outside the crystal with respect to major crystal directions. A detailed description of EC is given in Ref. [10].

As an example a positron emission yield around the <110> axis is shown in Fig. 1. This measurement was performed after implantation of 1.4×10^{13} ^{73}Se/cm^2 into ZnSe single crystal at 30 K and subsequent annealing up to 500 K for 5 min. The lower count rate along the axis and planes indicates that the positrons are blocked. Thus the Se ion, which is a positron emitter, has to be situated preferentially on substitutional lattice sites.

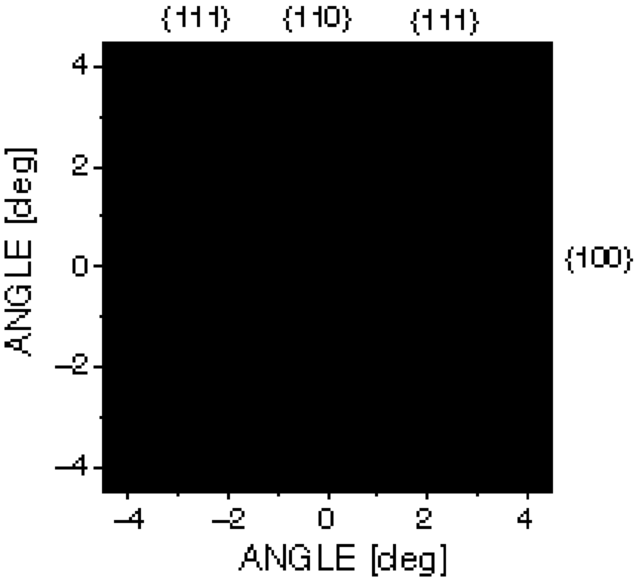

Fig. 1: Count-rate pattern of positrons emitted from ^{73}Se ions implanted into ZnSe around the <110> axis: darkest grey < 190 counts, white > 280 counts. The implantation was performed at 60 K and the crystal was annealed at 500 K for 5 min. The positron blocking in the axis and along the planes indicates a substitutional fraction of about 60%.

Theoretical electron channelling effects may be obtained by calculations using the so-called many-beam formulation of electron motion (described in detail in Ref. [11]). The comparison of measurement and calculation provides a precise determination of lattice site occupation [12]. In the calculation we used a Debye temperature for the Zn sublattice, T_D = 270 K, and for Cd on a Zn site, T_D = 213 K [13], and the implantation profile described below. The calculations are fitted to the experimental data assuming the occupation of only substitutional lattice sites or 'random' sites. The random sites are irregular sites in heavily disordered regions and result in an isotropic emission yield.

In the case of positron blocking effects a full Monte Carlo simulation formalism is not yet available. However, since for a positron-emitting ion implanted at a substitutional site the normalized axial emission yield must be zero, the measured normalized emission yield gives a direct estimate of the substitutional fraction of implanted ions.

For our investigations we used as grown ZnSe single crystals (10^8 Ωcm, presumed n-type, Bridgman grown and characterized at the Humboldt University, Berlin). Before implantation the mechanically polished crystal surface was etched in chromic acid (CrO_3:H_2O:HCl, as 1:1:1) to remove any preparation damage. These crystals were implanted with either radioactive ^{111m}Cd ions (half-life $t_{1/2}$ = 48.6 min) or ^{73}Se ions (half-life time = 7.18 h), produced at the on-line isotope separator ISOLDE at CERN [14] by nuclear reactions of a 1 GeV proton beam with a liquid Sn target, or a Nb foil target, respectively. The isotopes are available as isotopically pure 60 keV ion beams. At this energy the mean penetration depths in ZnSe are 235 Å (straggling 110 Å) and 285 Å (straggling 145 Å) for Cd ions and Se ions, respectively. TRIM simulation [15] show that in the slowing down of the 60 keV implanted ions each Cd ion displaces about 4000 crystal atoms and each Se ion about 3900 crystal atoms. The samples were mounted on a goniometer equipped with cooling and heating devices to perform measurements directly after implantation. The emission yields were recorded as a function of tilt angle relative to the crystal principal axial directions, with a Si surface barrier detector and angular resolution of 0.2°.

3. RESULTS AND DISCUSSION

First, low-dose implantation (0.3×10^{13} ^{111m}Cd/cm^2, 0.5×10^{13} ^{73}Se/cm^2) at room temperature (RT) was performed to record the substitutional fraction in order to compare this with results after low-temperature implantation. In the case of Cd, electron channelling effects around the <100> and <110> axes were measured at 60 K (see Fig. 2a). The comparison with the calculated emission pattern (solid line) indicates an occupation of substitutional lattice sites of 87 ± 8%. This high substitutional fraction directly after RT implantation shows the ability of ZnSe to heal most of the radiation damage during implantation in agreement with the observations of Ref. [3]. In the case of Se implantation the positron-blocking effects were recorded in all three principal axial directions and indicate a substitutional fraction of at least 75%.

In Fig. 3 the substitutional fractions of implanted isotopes are plotted as a function of implantation temperature and ion dose. At an implantation temperature below 65 K the substitutional fraction depends strongly on ion dose. At 0.8×10^{13} Cd/cm^2 the smaller channelling effect indicates a substitutional fraction of only 40 ± 7%.

Similar behaviour was found in the case of Se implantation at 50 and 30 K with ion doses of 0.8, 1.1, and 1.4×10^{13} Se/cm^2. The estimated error of 25% in the ion dose measurement may be responsible for the inconsistent dependence between ion dose and substitutional fraction. However, the results show roughly the same behaviour as in the case of Cd implantation.

The channelling effect disappeared completely at 1.4×10^{13} Cd/cm^2 (Fig. 2b) indicating that the Cd ions were situated on irregular lattice sites in heavily disordered surrounding. The same holds for Se ions at an accumulated dose of 2.1×10^{13} Se/cm^2 (see Fig. 3b). Considering the uniform kinetic behaviour of the implanted isoelectronic ions at the end of the implantation process and of all the displaced host atoms, the absence of any channelling and blocking effect indicates an amorphous structure inside the cascade core. Assuming a damage cascade size of roughly 100 Å in diameter (deduced from TRIM simulations), the ion dose for total disappearance of any anisotropic emission yield corresponds to a fourfold overlap of damage cascades. It seems that the damage has to accumulate. Thus we expect an amorphous implantation layer. This conclusion, however, can not be obtained from this investigation method since it is only sensitive to the microscopic surrounding of the ions.

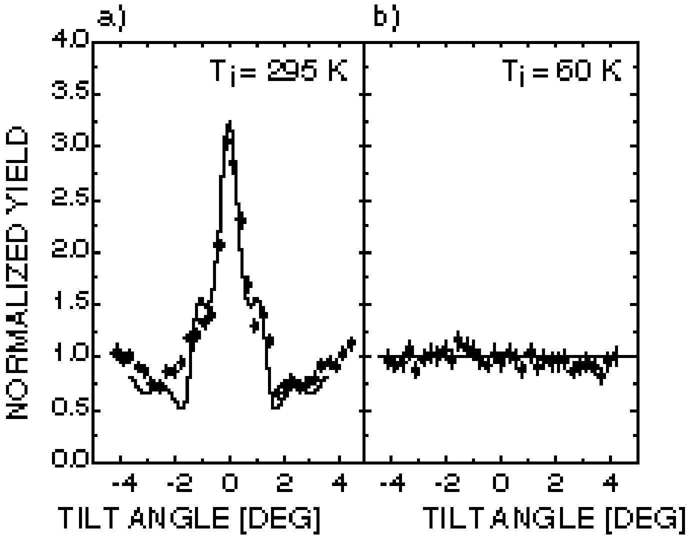

Fig. 2: One-dimensional count-rate pattern of conversion electrons emitted from ^{111m}Cd ions implanted into ZnSe single crystals around the <100> axis: a) implantation temperature T_i = 300 K, ion dose $D_i = 0.3 \times 10^{13}/cm^2$ and measurement temperature T_m = 60 K; b) T_i = 60 K, $D_i = 1.8 \times 10^{13}/cm^2$, T_m = 60 K. The solid line in a) is the calculated channelling effect corrected to the experimental resolution and fitted to the measurement. Thus substitutional fractions of a) 87 ± 8% and b) 0% are deduced.

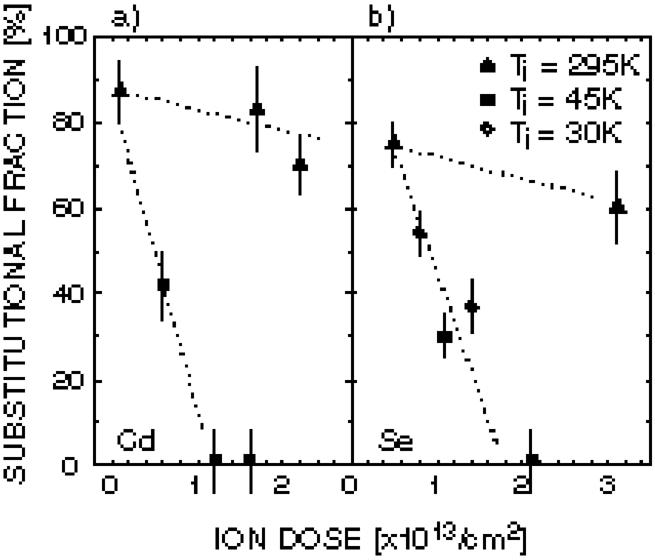

Fig. 3: Substitutional fractions of Cd and Se ions implanted at different temperatures as a function of ion dose.

The different ion dose for Cd and Se to obtain totally amorphous structure corresponds to the identical deposited energy density via displacements of $4.4 \pm 0.2 \times 10^{20}$ keV/cm^3. This energy density may be obtained roughly by multiplying the ion dose, the part of implantation energy lost via displacements divided by the half-width of the implantation profile.

After low-temperature implantation, isochronal annealing sequences were performed keeping the samples at the annealing temperature for 1 min in the case of Cd and 5 min in the case of Se (see Fig. 4). A slight increase of the substitutional fraction without any evident step was seen even below room temperature. This damage recovery is absent in the case of the high-Cd implantation doses, but an evident recovery step is found between 475 and 500 K resulting in a 70% substitutional fraction. This recovery is also evident in the Se-implanted samples, but is less pronounced. To investigate whether the reduced recovery in the Se-implanted crystals is due to remanent lattice damage or to some other effects, we repeated room temperature implantation after the annealing process. The observed emission-blocking effects corresponded to a substitutional fraction of approximately 60% which was twice that obtained after the annealing sequence. Our results suggest that during the annealing treatment the Se atoms diffuse to the surface and/or into the bulk thus resulting in a reduced positron-blocking effect.

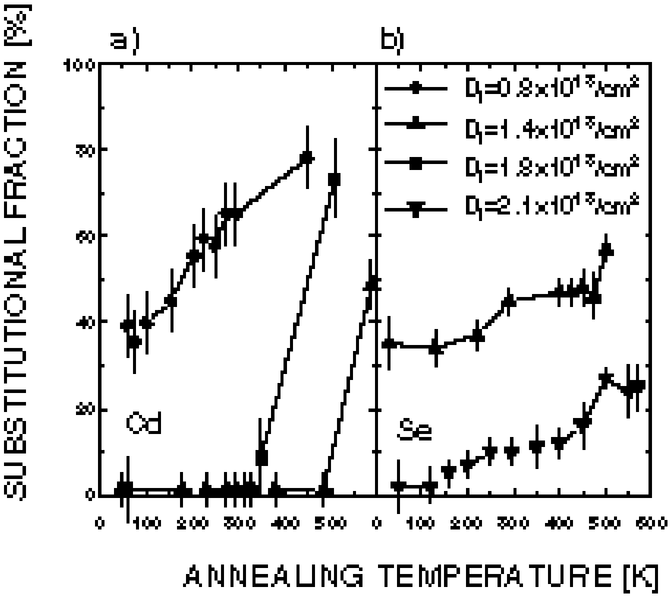

Fig. 4: Substitutional fractions of Cd and Se ions implanted at low temperatures as a function of annealing temperature.

4. CONCLUSION

We have shown that in ZnSe at implantation temperatures below 65 K lattice damage depends sensitively on the ion dose, in contrast with room temperature implantation. At an accumulated ion dose corresponding to a fourfold overlap of defect cascades, no implanted ions appear to occupy any site of high symmetry. Considering the uniform kinetic behaviour of the implanted isoelectronic Cd and Se ions at the end of the implantation process and of all the displaced host atoms, the absence of any channelling or blocking effect indicates an amorphous structure inside the core of the damage cascade. This type of damage appears to recrystallize at an annealing temperature just below 500 K. Furthermore, we suggest that damage recovery occurs below room temperature if the damage density is smaller than the upper overlap value. To obtain unambiguous information on the microscopic structure after cold-ion implantation, the present measurements must be supplemented with measurements using other techniques such as perturbed angular correlations.

Acknowledgements

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