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Defect properties of ion-implanted nitrogen in ZnSe

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Lattice sites and annealing behavior of implanted ^{12}N in semi-insulating ZnSe are investigated by use of β radiation detected nuclear magnetic resonance (β-NMR). For room-temperature implantation only a small part of the N impurities is found at sites with full T_d symmetry; this fraction is attributed to substitutional N_{Se}. Above 500 K the population of this site increases and saturates at a 10 times higher value for $T \geqslant 950$ K. This increase is assigned to the change of initially interstitial N (N_i), isolated or part of a complex, to unperturbed N_{Se}. An activation barrier $E_a = 0.47(5)$ eV is determined for this process representing an upper limit for the N_i migration energy. We do not observe configurations where N_{Se} is bound to a diamagnetic partner, like the $(V_{Se}\text{-Zn-}N_{Se})^+$ complex.

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Successful *p*-type doping of ZnSe became possible with the advent of suitable sources of atomic N in molecular-beam epitaxy (MBE).[1,2] The maximum hole concentration, however, is still limited by compensation processes to $\sim 10^{18}\,\mathrm{cm}^{-3}$ even though N incorporation up to levels of $10^{20}\,\mathrm{cm}^{-3}$ is possible.[3,4] Different mechanisms, such as the incorporation of N_2 molecules, compensation by donors, passivation due to formation of complexes or interstitial configurations, and a limited solubility of N at Se sites have been discussed to explain this limitation (see Ref. 5 for a review). In order to distinguish between different compensation models it is crucial to have microscopic information on the lattice sites and the local environments of the N impurities.

We applied β-radiation detected nuclear magnetic resonance (β-NMR) as a sensitive technique to explore local surroundings and annealing behavior of isolated N impurities after implantation in ZnSe. Our experiments were performed at the Ionenstrahllabor ISL of the Hahn-Meitner-Institut, Berlin. Radioactive ^{12}N nuclei (lifetime $\tau_\beta = 15.9$ ms, nuclear spin $I = 1$, daughter nucleus ^{12}C) were produced in a $^{10}\mathrm{B}(^3\mathrm{He},n)^{12}\mathrm{N}$ nuclear reaction using a primary beam of 3.0-MeV ^{3}He. The recoil emitted ^{12}N nuclei were spin polarized parallel to an external magnetic field $\mathbf{B_0}$ by selection of recoil angles of $17 \pm 6°$ relative to the incident beam and then implanted in the ZnSe sample. The broad spread of recoil energies from 0 to 1.7 MeV gave a rather homogeneous implantation profile up to a maximum depth of 2.0 μm. Different probe nuclei and even their respective implantation-damage cascades were well separated from each other: there were only some 100 active probe nuclei simultaneously in the ZnSe crystal ($[^{12}\mathrm{N}] < 10^6\,\mathrm{cm}^{-3}$). The probes could be selectively depolarized by resonant radio-frequency (RF) irradiation. Afterwards, the lifetime-averaged left/right asymmetry a of the emitted β radiation was detected which directly measures the remaining ^{12}N polarization. Due to the short ^{12}N lifetime the temperatures of implantation, ''annealing'' (within τ_β), and detection are always identical in this type of experiment. For a more detailed description of β-NMR and its application to point defects in semiconductors the reader is referred to previous publications.[6,7]

The sample was MBE grown on a *p*-GaAs:Zn substrate with an area of $10 \times 10\,\mathrm{mm}^2$. The 2.9-$\mu$m-thick ZnSe layer was deposited with a Zn/Se beam equivalent pressure ratio of 0.34 resulting in an undoped, semi-insulating film. To prevent surface decomposition at elevated temperatures the crystal was capped with a 25 nm Si_3N_4 layer.

First results of this investigation were described in Ref. 8. In that work we were mainly concerned with static properties, in particular the characterization of the implantation site. Now we are extending this study towards dynamic aspects like annealing behavior and site changes.

A β-NMR resonance of ^{12}N in ZnSe measured at 794 K is shown in Fig. 1; a similar spectrum was already presented in Ref. 8. The line is centered at the Larmor frequency ν_L implying that the corresponding probe fraction is diamagnetic and senses no electric-field gradient. It has the shape of a pure Lorentzian; we do not observe any inhomogeneous broadening. In the previous paper we also showed that such a resonance can only originate from either negatively charged substitutional N at Se sites (N_{Se}^-), or triply ionized

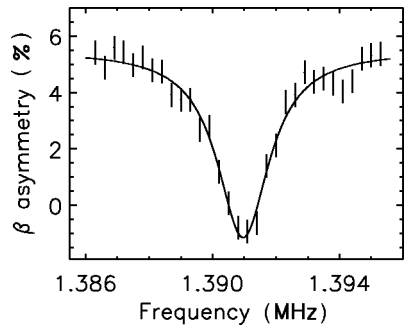

FIG. 1. β-NMR spectrum of ^{12}N implanted in ZnSe at $T=794\,\mathrm{K}$, $B_0=0.4\,\mathrm{T}$, $\mathbf{B_0}\|\langle 100\rangle$. The resonance is centered at the Larmor frequency. The solid line is a Lorentzian fit.

N at tetrahedral interstitial sites surrounded by four Zn atoms: $N_i^{3-}(T_{Zn})$. This conclusion was derived on grounds of charge state and symmetry considerations.

The ''cubic asymmetry'' a_{cub}, defined as the asymmetry signal corresponding only to ^{12}N nuclei in cubic environments, and the total asymmetry a_0 (from all implanted probe nuclei) are plotted vs temperature in Fig. 2. a_0 was recorded without any RF; a_{cub} was detected as the asymmetry change due to RF depolarization of all Larmor resonant ^{12}N nuclei. For that purpose RF was irradiated in a band of ± 3 kHz around ν_L and was on/off modulated at a rate of 0.5 Hz to suppress effects of instrumental drifts.

In several time-resolved measurements at temperatures from $T=340-890\,\mathrm{K}$ we always found $a_{cub}(t)=\mathrm{const.}$, i.e., no detectable spin-lattice relaxation (SLR). The reduced values of a_{cub} at lower temperatures are not a result of the lifetime averaging, therefore. The depolarization must rather take place *before* the cubic state is occupied. This allows the interpretation of a_{cub} as a true measure of the fraction f_{cub} of implanted N ions at lattice sites with T_d symmetry (right-hand scale of Fig. 2).

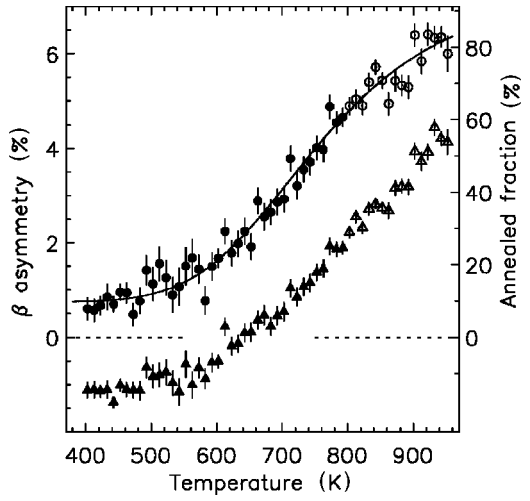

FIG. 2. Temperature dependence of the total asymmetry a_0 (bottom) and the cubic asymmetry a_{cub} (top) at $B_0=0.4\,\mathrm{T}$, $\mathbf{B_0}\|\langle 100\rangle$. The absolute position of the a_0 trace is affected by an unknown instrumental offset and has no significance. The a_{cub} signal intensity, in contrast, directly reflects the fraction of unperturbed $^{12}N_{Se}^{-}$ (right-hand scale). The solid line is a fit modeling a thermally activated conversion from N_x to N_{Se} (see text). The right-hand scale (a_{cub} only) is normalized to the predicted saturation value of this model. All data points above 800 K (open symbols) were measured in a separate run with a slightly lower initial polarization. They were shifted by $\Delta a=1.1\%$ to remove this artificial offset between both runs.

The solid line in Fig. 2 represents a fit of a simple annealing model assuming a so far unknown precursor state N_x and thermally activated conversion to the cubic defect state N_{cub}. The conversion rate μ is taken as

$$\mu(T)=\mu_0\exp(-E_a/k_BT), \tag{1}$$

with an activation barrier E_a. The model is explained in detail in Ref. 7 where the identical analysis was applied to the case of implanted ^{12}B in ZnSe, a system with very similar annealing properties.

As numerical results we obtain

$$\mu_0/r=10^{3.1(4)}, \quad E_a=0.47(5)\ \mathrm{eV}, \tag{2}$$

with E_a and μ_0 as defined by Eq. (1). r is a so far unknown depolarization rate in the N_x state with the lower bound $r\geqslant 1/\tau_\beta\approx 60\,\mathrm{s}^{-1}$. The cubic asymmetry varies from $a_{cub}(0)=0.8(1)\%$ to $a_{cub}(\infty)=7.7(5)\%$ in this annealing stage, in other words f_{cub} increases by a factor of 10.

At this point the question of the absolute values of f_{cub} with respect to the total amount of implanted ^{12}N arises. Previously,[8] we had stated $f_{cub}=40(10)\%$ at $T=800\,\mathrm{K}$. This was based on the comparison of the integrated areas of ^{12}N Larmor resonances in ZnSe and Cu as a well-known reference system.[9] The ^{12}N resonance in Cu exhibits strong dipolar broadening, however, and integrating such an inhomogeneous spectrum is only meaningful in the absence of diffusion and/or spin-lattice relaxation of the Cu host nuclei. Unfortunately we had not checked these necessary preconditions properly and in the given case they are not even likely to be fulfilled. This way we probably overestimated the total asymmetry belonging to a known ^{12}N fraction *in the reference system*, hence underestimated the fraction belonging to a known asymmetry in ZnSe. The correct statement for ^{12}N in ZnSe has to be $f_{cub}(800\,\mathrm{K})\gtrsim 40\%$, therefore.

Meanwhile we know the annealing process is not completed at $T=800\,\mathrm{K}$. From Fig. 2 we read $f_{cub}(800\,\mathrm{K})=0.62\times f_{cub}(\infty)$. Combining this with the given lower limit at 800 K we finally obtain $f_{cub}(\infty)\gtrsim 65\%$. Even 100% cannot be ruled out, however, due to the aforementioned uncertainties.

N_{Se}^{-} and $N_i^{3-}(T_{Zn})$ as possible candidates for N_{cub} could not be distinguished by their spectroscopic signature. From our annealing data, on the other hand, we get three independent arguments to identify N_{cub} as N_{Se}. First, we note it is a common situation that implanted light ions are located at interstitial sites, initially, and arrive at unperturbed substitutional sites only after thermal activation.[7,10–12] Such a site change typically involves a short-range migration of about 10^3-10^4 jumps until a correlated vacancy from the own implantation-damage cascade is encountered. We have never

observed the opposite case that an implanted impurity would need thermal activation to reach an *interstitial* location.

Second, we take into account that a postulated $N_x \rightarrow N_i$ conversion requires only one single step (say, the breakup of a pair with an intrinsic defect) since interstitial sites are everywhere available. This implies the pre-exponential factor for this process to be of the order of a lattice-vibration frequency, i.e., $\mu_0 \approx 10^{13}\ s^{-1}$. Using Eq. (2) to estimate the depolarization rate r in the N_x state we obtain $r \approx 10^{13}/s^{-1}/10^3 = 10^{10}\ s^{-1}$, i.e., a spin-lattice relaxation time of $T_{1,x} \equiv 1/r \approx 100$ ps. However, not even the hyperfine coupling to an itself strongly fluctuating electron spin of a paramagnetic N_x could explain such extreme SLR rates for a nuclear spin. Note that this argument does not hold for the assumption of a $N_x \rightarrow N_{Se}$ conversion. Here, the aforementioned short-range migration would reduce the estimated value of r by 3–4 orders of magnitude.

The third argument in favor of the assignment $N_{cub} = N_{Se}$ is its thermal stability. Interstitial N, if mobile, could easily recombine with a surrounding Se vacancy according to $N_i^{3-} + V_{Se}^{2+} \rightarrow N_{Se}^{-}$. A local supply of vacancies comes from the implantation event and the strong Coulomb attraction should lead to a highly directed migration of N_i towards its annealing partner. Estimating a number of 100 jumps needed for an encounter, we can express the recombination time as $\tau_{rec} = 100 \times 10^{-13}\ s \times \exp(E_m/k_B T)$, where E_m is the activation barrier for N_i migration. From the condition $\tau_{rec} > \tau_\beta$ up to at least $T = 950$ K, we would obtain $E_m > 2.1$ eV. The assumption of such a high migration energy for a nonbonding impurity (N_i^{3-} is electronically equivalent to a Ne atom) at a tetrahedral interstitial position is absolutely unreasonable, to our opinion. Interstitial Zn, Li, and B in ZnSe, for comparison, migrate with activation energies of $E_m = 0.6$–0.7 eV,[13,14] 0.48(5) eV,[15] and 0.61(3) eV (tentative assignment in Ref. 7), respectively, and a comparable value had to be expected for the assumed case of $N_i^{3-}(T_{Zn})$.

For the three given reasons we discard the $N_{cub} = N_i(T_{Zn})$ hypothesis and identify the cubic fraction with N_{Se}^{-} the unperturbed, ionized N acceptor.

Through the remainder of this paper we will be concerned with the nature of the precursor defect N_x. At first, we note from Fig. 2 that the total β asymmetry a_0 and the cubic asymmetry a_{cub} have the same temperature dependence: the conversion process $N_x \rightarrow N_{Se}$ is accompanied by an increase of the *total* polarization. The detected polarization after τ_β can never exceed the initial value directly after implantation, on the other hand. Higher values of a_0 at elevated temperatures necessarily imply, therefore, a rapid depolarization (in a time $T_{1,x} \ll \tau_\beta$) of the probe spins in the N_x configuration at lower temperatures, a process which is only stopped when the Se site is reached [this conclusion can independently be derived from the very low pre-exponential factor μ_0/r in Eq. (2)]. In a II-VI semiconductor only hyperfine interactions with unpaired electron spins can depolarize ^{12}N that quickly. In other words: N_x is a *paramagnetic* defect in our samples.

Additional properties of N_x can be deduced from the specific situation of our in-beam experiment. Because of the extremely low ^{12}N concentration we know, N_x contains one and only one N atom. Furthermore, N_x is formed with a high efficiency within a time much shorter than τ_β even at room temperature. Thus we can exclude all scenarios for the formation of N_x which involve long-range migration and interaction with distant native defects. A complex of one ^{12}N with one intrinsic defect D_{int}, vacancy or interstitial of either sublattice, created nearby in the implantation-damage cascade of the very same ^{12}N ion, is already the most complicated configuration we have to consider.

So far, our experimental information on N_x can be summarized as follows. (i) N_x is either an isolated N atom or a $N \cdot D_{int}$ complex (including the possibility of a somewhat separated pair). (ii) It is paramagnetic in semi-insulating ZnSe. (iii) N_x can convert into isolated N_{Se}^{-} with an activation energy of 0.47(5) eV. The participation of another intrinsic defect, especially a Se vacancy (V_{Se}) from the damage cascade, in the latter process is possible.

We will now discuss the various possible configurations of N_x and check whether their properties can match these three conditions. We want to start with the assumption of substitutional N. In this case, N_x would be a complex $N_{Se} \cdot D_{int}$ and we had the following restrictions for D_{int}: (i) it would have to be the paramagnetic partner since N_{Se} is known to be diamagnetic in our sample, (ii) after the dissociation of the postulated complex, D_{int} would have to migrate to leave the isolated N_{Se} behind. This implies a migration energy $E_m(D_{int}) \leqslant 0.47$ eV. From both conditions we can immediately exclude V_{Zn} and Zn_i as possible candidates for D_{int}: it is known from magnetic resonance data that both are diamagnetic in semi-insulating ZnSe and have higher migration energies.[13,16,17] There is little experimental information available on V_{Se} but first-principles theory[18] makes a clear statement that it should be diamagnetic, too, and therefore violate condition (i). We can also exclude Se_i, the last remaining possibility for D_{int} in this scenario. Se_i is an acceptor , its paramagnetic charge state is Se_i^{-}. This is not only a very large ion (ionic radius 2.32 Å) with an unfilled p shell for which a higher migration energy than 0.47 eV had to be expected, $N_{Se}^{-} \cdot Se_i^{-}$ pairs would also be Coulomb repulsive and are therefore unlikely to be formed, in the first place. The fact that, to our knowledge, no experimental or theoretical work ever postulated such a pair may be seen as indirect confirmation of this argument.

All this means that no configuration involving a substitutional N fits the properties of N_x. The precursor state of N_{Se} has to be *interstitial* N, therefore, either isolated or paired off with a single intrinsic defect, and in a paramagnetic charge state. The annealing process involves up to three steps: (i) the breakup of the $N_i \cdot D_{int}$ complex (dissociation energy E_d), (ii) migration of the isolated N_i to find a V_{Se}, and (iii) an annihilation reaction $N_i + V_{Se} \rightarrow N_{Se}$. Step (i) is not needed, of course, if N_x is just an isolated N_i. In this case E_a would just represent the N_i migration energy $E_m(N_i)$. Otherwise, $E_a = E_d + E_m(N_i)$, which still gives an upper limit for $E_m(N_i)$.

In summary, we implanted radioactive ^{12}N ions in nominally undoped ZnSe at stationary concentrations below $10^6\ cm^{-3}$ and studied its microscopic defect properties with

β-NMR. A resonance signal from ^{12}N in an unperturbed cubic environment is attributed to isolated N_{Se}; search scans for additional resonances were not successful. Despite the higher V_{Se} concentration around our implanted probe ions we have no indication of $N_{Se} \cdot V_{Se}$ complexes as proposed in the literature.[19] We observe the thermally activated population of the Se site from a precursor state N_x. It is shown that N_x is related to interstitial N in a paramagnetic charge state; probably isolated N_i but so far a complex of N_i with an intrinsic defect cannot be excluded. An upper limit of $E_m(N_i) \leqslant 0.47(5)$ eV is determined for the activation energy of N_i diffusion.

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