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Recharging behavior of nitrogen-centers in ZnO

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Electron Paramagnetic Resonance was used to study N_2 -centers in ZnO, which show a 5-line spectrum described by the hyperfine interaction of two nitrogen nuclei (nuclear spin $I = 1$, 99.6% abundance). The recharging of this center exhibits two steps, a weak onset at about 1.4 eV and a strongly increasing signal for photon energies above 1.9 eV. The latter energy coincides with the recharging energy of N_O centers (substitutional nitrogen atoms on oxygen sites). The results indicate that the N_2 -centers are deep level defects and therefore not suitable to cause significant hole-conductivity at room temperature. © 2014 AIP Publishing LLC.

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INTRODUCTION

Nitrogen doping has been suggested to be a way to obtain p-type conductive ZnO. In a simple model, one assumes that nitrogen substitutes an oxygen atom in the crystal lattice and thus causes an acceptor. First evidence for nitrogen incorporation in ZnO was found by Carlos *et al.* in 2001 using Electron Paramagnetic Resonance technique (EPR).¹ The hope was that the recharging level of the nitrogen acceptors is shallow enough to accept electrons from the valence band and to promote hole conductivity. This hope was nourished from the circumstance that the samples treated with nitrogen showed in many cases a shallow donor to shallow acceptor pair (DAP) type of photoluminescence. Shallow (residual) donors are omnipresent in ZnO and therefore it seemed plausible that nitrogen is related to the shallow acceptor. An acceptor level position of $E_{vb} + 170$ meV was estimated from the experiments.² Arguments opposing this assignment came from problems to reproduce the results, which hindered a clear quantification, as well as from optical measurements.³ EPR and photo-EPR investigations eventually revealed that substitutional nitrogen centers (N_O) are deep defects with a recharging level 1.3 eV above the valence band.⁴

In the following, it was considered that nitrogen-pair centers or complexes consisting of nitrogen and vacancies or hydrogen atoms might act as the shallow acceptors causing the shallow DAP-PL. However, performing model calculations for such species the results for their recharging properties (being donor or acceptor) and the energy position of the recharging levels were strongly depending on the theoretical method used.⁵ Nickel *et al.* calculated that N_2 causes localized states in the band gap either by forming an N_2O molecule or by breaking a Zn-O bond.⁶ The latter was calculated to have a level about 170 meV above the valence band. Liu *et al.*⁷ calculated that $N_O - V_{Zn}$ shallow acceptors complexes

can evolve from the double donor state of $N_{Zn} - V_O$. Recently, Lambrecht and Boonchun⁵ brought N_2^+ located on the Zn site into play. Other Zn site configurations such as $(N_O)_{Zn}$, $(N_2)_{Zn}$, $(NH_4)_{Zn}$ were also considered and calculated to be acceptors in ZnO.⁸

Compared to these promising calculations for nitrogen related shallow acceptors the experimental evidence for the existence of such centers is quite limited. By EPR, it was also possible to identify N_2 -pair centers which were considered to be acceptors with probably deep level character.⁹

This situation motivated us to investigate the recharging behavior of the N_2 centers in more detail by photo-EPR. We find N_O and N_2 centers being present in our samples and upon photon irradiation with energies larger than 1.9 eV both signals were greatly enhanced. However, for the N_2 centers a first photo response was noticed at energies greater than 1.4 eV.

EXPERIMENTAL

ZnO bulk crystals were grown via a seeded chemical vapor transport method in an ammonia ambient, which provided nitrogen as well as hydrogen dopants.¹⁰ The crystals are c-oriented and have a cloudy brownish appearance, which can be taken as evidence for an inhomogeneous impurity distribution.

EPR experiments were carried out on a commercial Bruker EPR 300E spectrometer with a modulation amplitude of 0.5 G and a microwave frequency of 9.5 GHz. All measurements were performed in liquid Helium at 4.2 K and results will be shown with the external magnetic field perpendicular to the crystallographic c-axis ($B \perp c$).

RESULTS AND DISCUSSION

In the absence of photon irradiation, two EPR signals could be observed in the spectrum (see Fig. 1(a)). The single signal on the high-field side at $g \approx 1.958$ is the well known shallow donor in ZnO.¹¹

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FIG. 1. EPR spectrum of ZnO:N (a) taken without irradiation and (b) during UV illumination. The five-line signal and the single line on the high-field side in both spectra are attributed to N_2 molecules and shallow donors, respectively. The three-line signal seen in the lower spectrum stems from substitutional N_O defects.

The second group of signals centered at $g \approx 1.996$ is split into five lines with intensity ratio 1:2:3:2:1. This structure is caused by a hyperfine coupling of an EPR active electron to two nitrogen atoms ($I = 1$, natural abundance 99.6%). In agreement to the results of Garces *et al.* we determine the spin Hamiltonian parameters of the N_2 center to $g_{\parallel} = 2.0036$, and $g_{\perp} = 1.9935$ for the Zeeman splitting and $A_{\parallel} = 9.8$ MHz, and $A_{\perp} = 20.1$ MHz for the hyperfine parameters, assuming a spin of $S = 1/2$ for the system.⁹ Comparing these parameters to those of the N_O centers ($g_{\parallel} = 1.995$, $g_{\perp} = 1.963$ and $A_{\parallel} = 81.1$ MHz, $A_{\perp} = 8.5$ MHz) one finds that the anisotropy for the N_2 g -values is smaller and the hyperfine interaction constants indicate a higher localization of the spin density in the basal plane. Thus, it was suggested that one nitrogen of the N_2 molecule is substituting for one oxygen ion and the other is an adjacent interstitial oriented along the c -axis. In the paramagnetic form of the molecule, the unpaired spin occupies a σ -like bonding orbital and has nearly equal interactions with the two nitrogen nuclei.⁹

Upon irradiation with UV light (Fig. 1(b)), a new group of signals appears centered at $g \approx 1.966$. It consists of three strong lines with almost equal intensities and is caused by hyperfine coupling of an electron to a single nitrogen atom. This nitrogen atom is substituting an oxygen anion and hence is forming the N_O center. Most recently, Golden *et al.* studied the numerous small lines, which can be seen on the left and right side of the N_O signal in Fig. 1(b).¹² They attributed these signals to hyperfine interaction of the N_O center with axial and nonaxial Zn atoms (nuclear spin $I = 5/2$, natural abundance 4.1%). The lines in between the major N_O signals result from forbidden transitions, which were discussed in prior studies.⁴

After illumination both the N_2 and the N_O signals are found to be very stable at 4 K and persist for a long time (up to hours). Heating the sample up to room temperature restores the initial state in which only the N_2 resonances are observable.

Most interestingly, illumination increases the intensity of the N_2 signal by a factor of about ten compared to its intensity in darkness. This behavior is somewhat surprising as Garces *et al.* have reported a nearly complete quenching of the N_2 signal upon irradiation.⁹

Estimating the concentrations of the N_2 and the N_O centers from the EPR signal-area we find that the concentration of paramagnetic N_O centers is roughly four times higher than that of the N_2 centers, with the latter being in the upper 10^{17} cm^{-3} range.

To further investigate the recharging phenomenon, we performed systematic photo-EPR measurements. For this purpose, the sample was illuminated with light of varying photon energy using a halogen bulb lamp and multiple absorption filters. Initial conditions were restored after each recharging experiment. In Fig. 2, the EPR intensity of the molecular nitrogen defect (full symbols) as well as the intensity of the single nitrogen defect (open symbols) are plotted versus the energy of the incident photons. For the N_O center signals, we find a strong increase in intensity for photon energies above 1.9 eV. For the N_2 centers, the signals start rising already above 1.4 eV, but they also exhibit a strong increase at 1.9 eV as the N_O centers do.

The drawn line gives the calculation of the optical cross-section as described by Stehr *et al.*⁴ We obtain a very similar result for the recharging of the N_O defect in the samples used here compared to their earlier work, where the optical ionization energy E_{opt} was calculated to be 2.1 eV.

The weak increase of the N_2 signal for photon irradiation at 1.4 eV is likely to be caused by an electron capture from the valence band. The fact that there is no significant enhancement observable at lower photon energies proves that molecular nitrogen indeed forms a deep center in the ZnO band gap.

From Fig. 2, it is easy to see that the strong optical absorption starting at about 1.9 eV is almost identical for both defect species. This leads to the assumption that both

FIG. 2. Photo-EPR intensities of the N_O defect (open symbols) and the N_2 defect (closed symbols). Both nitrogen centers show a steep increase in intensity for photon energies of about 1.9 eV. The N_2 center also exhibits a weak onset at 1.4 eV. The calculation of the optical cross-section for the N_O center (solid line) is in good agreement with the recharging behavior found by Stehr *et al.*⁴

FIG. 3. Schematic overview for the energetic levels for the nitrogen centers in the band gap. In (a) the situation is shown for areas with Fermi level close to the conduction band, while (b) shows the energy positions in areas with high concentration of nitrogen centers and thus lower Fermi level.

recharging effects are linked to each other. As the recharging behavior of the N_O centers observed here is very similar to the behavior reported by Stehr *et al.*, it is very likely that the recharging of the N_2 centers above 1.9 eV is dominated by the $N_O^- \rightarrow N_O + e_{cb}$ process.

A plausible explanation for the recharging of the N_2 centers is given by the following mechanism:

- 1) Starting at an energy of about 1.9 eV electrons in N_O states get excited to the conduction band, hence converting the defect into its paramagnetic state (N_O signal rises).
- 2) Excited electrons in the conduction band relax into free states in the N_2 defects, converting them into a paramagnetic state (N_2 signal rises).
- 3) Charge carriers are trapped in N_O and N_2 defects and cannot leave this states (EPR signals persist for very long time).
- 4) Heating up the sample releases the trapped carriers from the defects restoring the initial conditions (N_O signal vanishes, N_2 signal decreases).

The crucial step in this mechanism is (2). This requirement can be met, if the recombination rate for conduction band electrons to the N_2 defects is much higher than for the competing excitation process. As we found the concentration of N_O centers to be much higher than for the N_2 centers the absorption by N_O centers could provide conduction band electrons at a sufficiently high rate to outweigh the optical excitation process of the N_2 defects.

We observed that the five-line signal from the N_2 center is already present in darkness and yet rises with illumination. This means that there have to be N_2 molecules in both charge states present at equilibrium, i.e., the Fermi level is located at or near the N_2 level in the band gap. However, if the Fermi level was pinned to the N_2 defect level in the whole sample, there should be no shallow donor signal observable in EPR measurements without illumination. Thus, we have to consider areas with different Fermi level positions in the samples. On the one hand, there are areas with low Fermi energy, most likely pinned to the N_2 centers. On the other hand, there are also areas in which the ZnO samples maintain their typical n-type behavior with a Fermi level close to the conduction band. As we did not observe any hints of transition metal ions in EPR measurements, we assume a high concentration of N_O centers in areas of lower Fermi level, which act as acceptors in ZnO. This coincides with the inhomogeneous optical appearance of the ZnO crystals.

Figure 3(a) shows a sketch of the energetic levels in the band gap as well as the considered optical transitions for a domain of Fermi energy close to the conduction band. Here the concentration of shallow donors dominates and the material remains in its n-type character. Irradiation ($h\nu$, solid arrows) excites electrons from the N_O defect level as well as from the deep N_2 level into the conduction band.

In Fig. 3(b), the energetic levels are sketched for domains with high concentration of nitrogen defects and hence low Fermi energy. As the concentration of N_O was

FIG. 4. Transient photo-EPR intensities of the N_O defect (open triangles), the N_2 defect (open diamonds) and the shallow donor (open circles). The solid lines are the best fits for the nitrogen centers. For the substitutional nitrogen N_O the best fit is a mono-exponential slope, which indicates a direct recharging process. The molecular nitrogen center N_2 is fitted best using a bi-exponential slope indicating a non-direct recharging mechanism.

found to be much higher than the concentration of N_2 the optical excitation and the following-up recombination process outweigh the optical absorption of the N_2 defects (dashed arrow in Fig. 3(b)). In this model, the N_2 center is acting like a deep donor in ZnO. The paramagnetic state in this case would be the N_2^0 state, while N_2^+ would be the non-paramagnetic charge state. However, an unambiguous assignment of charge states is not possible from the current stage of experimental data.

In order to prove our proposed model, we performed transient photo-EPR experiments. These experiments open up the possibility to determine whether the recharging behavior of the observed photo transition is direct or indirect. To perform the transient photo-EPR experiments, the magnetic field position is kept at a constant value and the EPR signal intensity is monitored as a function of the time. While a mono-exponential slope of this signal indicates a direct recharging behavior, a non mono-exponential slope indicates a non-direct recharging behavior. Figure 4 depicts the transient photo-EPR signals for both substitutional nitrogen (N_O) and nitrogen molecules (N_2) as well as for the shallow donor. The N_O signal can be fitted best with a mono-exponential behavior indicating a direct recharging process, which is in agreement with the results of Stehr *et al.*⁴ The N_2 signal, however, cannot be fitted by a mono-exponential model; instead it exhibits a bi-exponential behavior indicating a non-direct recharging process. These results are consistent with our proposed model and prove that N_O is involved in the N_2 recharging process.

Moreover, in the frame of this interpretation, it is not only possible to explain our experimental results but also to bring them in line with the results found in the work by Garces *et al.* Assuming that their samples exhibit a more balanced distribution of nitrogen defects it seems natural that the recharging process of the molecular N_2 defect is not governed by the N_O center. In this case only Fig. 3(a) applies

and the N_2 signals quench by optical excitation of charge carriers to the conduction band.

CONCLUSION

In this article, we have shown the results of EPR and photo-EPR experiments on nitrogen doped ZnO volume crystals. The results found confirm that substitutional nitrogen (N_O) forms a deep acceptor level in ZnO. For the molecular nitrogen center (N_2), we found a weak onset in photo-EPR measurements for photon energies of 1.4 eV as well as a strong increase in intensity at about 1.9 eV. These results show that N_2 centers form deep levels in the band gap of ZnO as well and therefore cannot be responsible in the previously observed DAP-PL recombination.

A model involving inhomogeneous distribution of nitrogen centers in the samples was proposed to explain the results found here as well as by other groups.

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