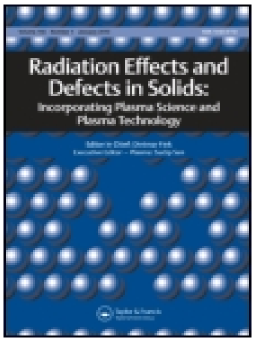

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Neutron irradiation-induced enhancement of electronic carrier transport in ZnO

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Irradiation of ZnO single crystals by thermal neutrons with a dose up to 7×10^{17} cm^{-2} and subsequent annealing at 400 °C for 1 h leads to a significant increase in majority carrier mobility and concentration in this material, with the corresponding decrease of its sheet resistance. Additionally, cathodoluminescence spectra taken before and after neutron irradiation are consistent with the growing carrier lifetime. The observed effects are attributed to irradiation-induced formation of electrically active species of interstitial Zn and improvement of lattice crystallinity due to annealing.

Keywords: zinc oxide; cathodoluminescence; neutron irradiation; carrier mobility

1. Introduction

Device applications, becoming possible with the maturing of ZnO technology, require better understanding of this material's fundamental properties. ZnO is much more resistant to radiation damage than other common semiconductor materials, such as Si, GaAs, CdS and GaN (*1*, *2*). Together with excellent optical and electrical properties, ZnO devices are, therefore, promising for space applications (*3*). Difficulties in p-doping have been the main obstacle to realizing ZnO photonic devices. The insight of donor and acceptor behavior is, therefore, needed for the development of efficient ZnO p–n junctions. Knowledge of material properties' dependence on irradiation and thermal treatment is similarly important.

The previous irradiation studies in ZnO were focused either on the effects of electron or proton bombardment (*4*, *5*) or ion implantation (*6*). In this paper, we report the impact of neutron irradiation on the transport properties of bulk ZnO.

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2. Experimental procedure

Samples: Bulk (500 μm thick) semi-insulating ZnO crystal grown by hydrothermal technique was supplied by MTI Corporation. The choice of semi-insulating material can be explained by the goal of this work, which is understanding the impact of neutron irradiation on ZnO electrical properties.

2.1. *Irradiation*

One part of the ZnO crystal was used as a control sample and three other parts were irradiated in the central vertical port of the University of Florida Training Reactor (5×10^{13} n/cm^2 s thermal neutron flux) for 1, 10, and 20 h. Neutron-irradiated ZnO samples were annealed at 400 °C for about 1 h in flowing argon. As the annealing time is the same for all three irradiated samples, the effect of annealing can be decoupled from that of irradiation.

2.2. *Hall measurements*

Hall measurements were used to determine the effect of dose and annealing on resistance, mobility, and carrier concentration. The experiments were conducted at room temperature and a magnetic field of 0.2 T using the Van der Pauw technique. Gold–platinum contacts were sputtered on each sample and an indium solder was used to attach copper wires from the contacts to the four terminals of the Hall set-up.

2.3. *Cathodoluminescence measurements*

Cathodoluminescence (CL) spectroscopy at 300 K employed a Gatan MonoCL3 system integrated with a Philips XL-30 scanning electron microscope. The CL was dispersed by a single grating (1200 lines/mm, blazed at 500 nm) and collected by a Hamamatsu photomultiplier tube. Excitation by the 20 keV electron beam corresponds to a 1.5 μm penetration depth into the material.

3. Results

The results of the Hall measurements for the control sample are summarized in Table 1. It has been confirmed that the sample is, indeed, highly resistive (doped with N-acceptor to compensate native donors) with weak n-type conductivity. Figure 1 shows the results of the Hall measurements for three irradiated and annealed samples. It is evident from Figure 1 and Table 1 that the irradiation by neutron flux results in a significant decrease in ZnO resistivity and an increase in carrier density and mobility. We can, therefore, claim that neutron irradiation resulted in pronounced enhancement of the material's n-type conductivity. Note that the bulk carrier density values, shown in the inset

Table 1. Comparison of Hall measurement results for control and irradiated samples.

Dose (cm^{-2})	Sheet resistance (Ω/□)	Sheet carrier density (cm^{-2})	Bulk carrier density (cm^{-3})	Mobility (cm^2/Vs)
0	3×10^6	2.1×10^{11}	4.2×10^{12}	10
3.6×10^{16}	3×10^4	9×10^{12}	1.8×10^{14}	23
3.6×10^{17}	93	1.8×10^{15}	3.6×10^{16}	37
7.2×10^{17}	47	3.2×10^{15}	6.4×10^{16}	43

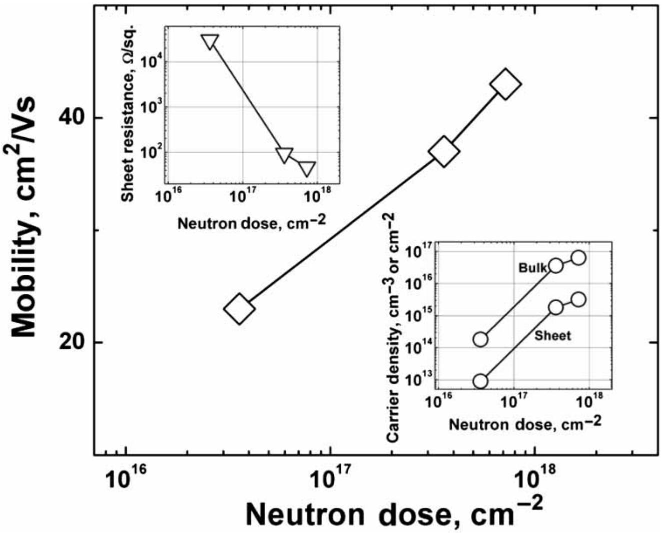

Figure 1. Dependence of electron mobility in ZnO on neutron irradiation dose. Upper inset: sheet resistance dependence on neutron irradiation dose. Lower inset: carrier density dependence on neutron irradiation dose.

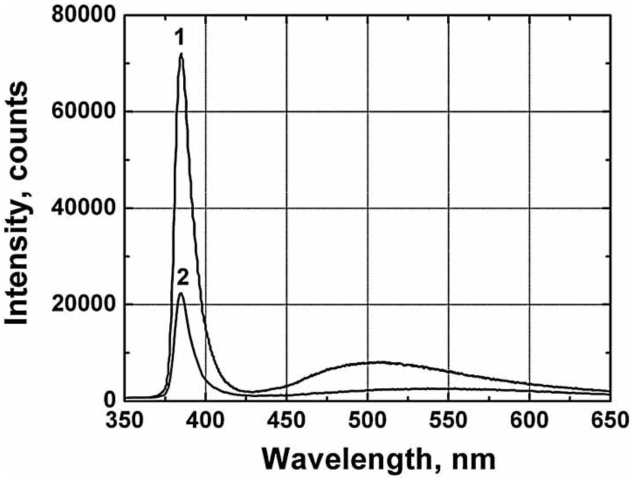

Figure 2. Room temperature CL spectra taken from the control sample (1) and the sample exposed to the maximum dose of 7×10^{17} cm^{-2} (2).

of Figure 1, were obtained by measuring the sheet carrier density and accounting for the crystal thickness.

CL spectra are compared for samples with zero and maximum doses in Figure 2. The spectra feature a near-band-edge (NBE) emission at ∼385 nm and a broad band centered in the visible region. NBE emission includes both conduction band-to-neutral acceptor transitions (e, A^0) and shallow donor–acceptor pair transitions (*5*). These transitions are consistent with the N-acceptor location in the ZnO forbidden gap (∼150 meV) (*7*). Neutron irradiation significantly decreases the intensity of the NBE emission (spectrum 2) when compared with that in the control sample (spectrum 1), and shifts the visible band center from ∼505 to 550 nm. Note that the irradiation does not change the ratio of NBE-to-broad band emission.

4. Discussion and remarks

We suggest the following model to explain the experimental results in Figures 1 and 2: neutron irradiation of ZnO displaces zinc atoms into interstitial sites, thus producing neutral point defects, Zn_i^0, which by themselves do not yet contribute to electrical conductivity (*8*). Hole traps in ZnO, such as impurities or positive-ion vacancies are available to stabilize Zn interstitial in the neutral state, as the crystal's temperature during neutron irradiation is low enough (not more than 100–150 °C). The annealing that is carried out after neutron irradiation leads to the thermal ionization of hole traps, with the holes returning to the interstitial Zn_i^0 atoms and forming $\mathrm{Zn}_\mathrm{i}^{1+}$ and $\mathrm{Zn}_\mathrm{i}^{2+}$ species, acting as shallow donors with the activation energy of $\sim$30 meV (*2*) and, thus, contributing to enhancement of the n-type electrical conductivity via an increase in the majority carrier (electrons) density. We note that in addition to thermal ionization of native point defects (interstitial Zn atoms), thermal annealing leads to the improvement of the material's crystallinity, and thus, to the reduction of carrier scattering. The latter effect is manifested in an increase in carrier mobility, as seen in Figure 1 and Table 1. It should be emphasized that the annealing temperature and duration are insufficient to induce a significant recombination of ionized interstitial Zn species with vacancies.

The improvement in the material's crystallinity is consistent with an increase in carrier (electron) lifetime (also due to a reduced scattering) in the conduction band, as is evident from a significant decrease in the NBE luminescence intensity after annealing: a longer lifetime determines the smaller number of radiative recombination events and, therefore, the lower intensity of CL, as observed in Figure 2 (spectrum 2). Based on the experimental results, one may conclude that the impact of carrier lifetime increase on CL intensity (leads to lower CL signal; compare spectra 1 and 2 in Figure 2) is stronger than that of donor density increase on the same parameter (increase in donor density (Figure 1) may lead to an additional radiative recombination and, therefore, enhanced NBE CL).

It should also be emphasized that we do not discard the impact of neutron transmutational doping (NTD) on the enhancement of carrier density in the irradiated ZnO samples (*1*). We note, however, that the amount of created (due to transmutations) potential donors (^{65}Cu, ^{69}Ga, ^{71}Ga, ^{19}F), which varies for different isotopes from 10^7 to 10^{12} cm^{-3}, is much lower than the observed majority carrier density in Figure 1. It is, therefore, concluded that the NTD impact on electrical conductivity is secondary in our case.

5. Conclusions

The irradiation of ZnO single crystals by thermal neutrons with a dose up to 7×10^{17} cm^{-2} and subsequent annealing at 400° C for 1 h leads to a pronounced increase in the majority carrier mobility ($\times 4$) and concentration (more than four orders of magnitude) in this material, with a corresponding decrease in its sheet resistance (five orders of magnitude). Additionally, CL spectra taken before and after neutron irradiation are consistent with the growing carrier lifetime. The observed effects are attributed to the irradiation-induced formation of electrically active species of interstitial Zn and improvement of lattice crystallinity due to annealing.

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