short note

reprinted from

physica
status
solidi (a)

phys. stat. sol. (a) 58, K141 (1980)
Subject classification: 16; 13.4; 22.6

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Photoconductivity Lifetimes in ZnO Single Crystals

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In earlier studies of ZnO it was suggested /1/ that excess Zn atoms act as donors in ZnO, and the ionized donors (Zn^+) act as deep hole traps. The first role of excess Zn was later proved /2/ and is well accepted. Pure "as-grown" crystals always contain excess Zn, and are therefore always n-type. The other role was deviced to explain the dependence of photoconductivity lifetimes upon samples' dark conductivities. Hole trapping was assumed to be the mechanism that quenched the electron-hole recombination process. As yet, no independent confirmation exists that the ionized zinc donors indeed act as hole traps.

We have studied the temperature effect on photoconductivity lifetimes in ZnO crystals of different dark conductivities. Our results support the above model, and characterize the Zn^+ hole traps by their energy depth, and trapping and recombination cross-sections. The samples used were either commercial (Airtron), grown hydrothermally /3/, or laboratory vapour grown[1], K and Cu being used as donor compensators, respectively. A constant current was driven through the sample. Light flashes from a Xe flash lamp, 5 μs long, filtered by another optically polished ZnO crystal, 2 mm thick, were focused onto the crystal surface area between two voltage probes. The filter ensured uniform bulk excitation of photo-carriers by weakly absorbed light. The transient voltage-change between the probes, that followed the excitation, was displayed on an oscilloscope screen. The sample was placed in a cryogenic system, and the temperature could be varied between 100 and 350 K. The photoconductivity signals were always directly proportional to the light intensity. The concern of this work is in the initial dominating fast component of the decay curves. Long decay tails also existed, but were relatively small. In Fig. 1 the initial decay rates $\beta(=1/\tau$, where τ are the decay times) are plotted versus $10^3/T$, where T is the absolute temperature, on a semi-log scale. In all samples, the high-temperature decay rates vary exponentially

1) We are grateful to Prof. G. Heiland of 2. Physikalisches Institut, Technische Hochschule, Aachen, BRD, for making some of his self-grown samples available to our laboratory.

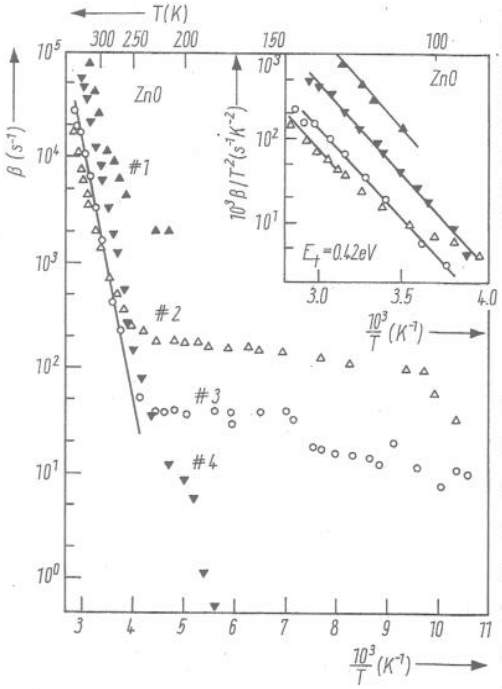
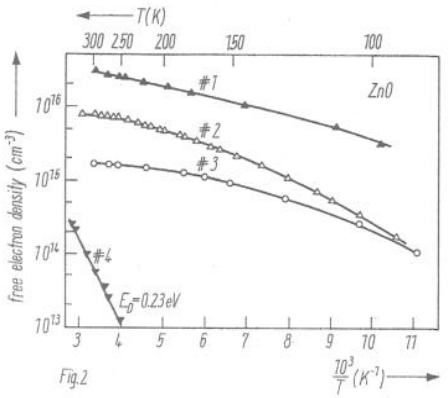


Fig. 1. Semi-log plot of initial photocurrent decay rate $\beta(=1/\tau)$ versus $10^3/T$. Open and full symbols indicate results taken with hydrothermally or vapour-grown samples, respectively. Insert is a semi-log plot of β/T^2 versus $10^3/T$ of the same results

with $10^3/T$, becoming larger upon temperature increase. The activation energy is common to all samples: ≈ 0.4 eV. Upon cooling the rates decrease, and at a certain temperature the curves flatten, changing only slightly with temperature. We interpret the low-temperature decays as direct recombination of free electrons with the photo-generated holes, trapped by the Zn^+ ions. The involvement of free electrons is proved by consideration of the free electron densities, n_o, in the various samples, as shown in Fig. 2. The variation of n_o with $10^3/T$ is plotted in a semi-log scale for the samples



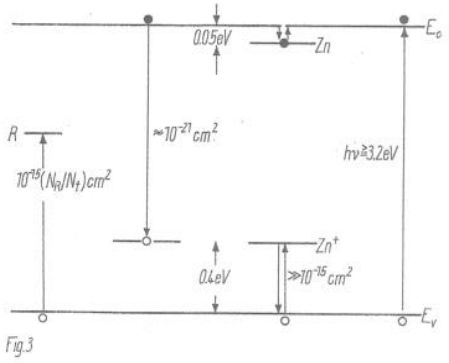


Fig. 2. Semi-log plot of free electron density versus $10^3/T$ for the samples of Fig. 1. Results of Hall effect measurements

Fig. 3. Energy levels and cross-sections involved in the processes responsible for the photoconductivity decays

of Fig. 1. Reported donor ionization energies, E_D, in ZnO, range from 0.016 eV /4/ to 0.26 eV /5/, depending on the dopant. For samples #1, #2, and #3 the n_o versus $10^3/T$ curve is typical of undoped crystals, where the donors are the excess Zn atoms ($E_D \approx 0.05$ eV). Crystal doping with copper is normally used for donor compensation, but sometimes it introduces donor levels /5/, as deep as 0.26 eV, and a similar case is observed for sample #4. The low temperature recombination rates (Fig. 1) are approximately proportional to n_o in the various samples. Then, β may be expressed as

$$\beta = \sigma \langle v_n^{th} \rangle n_o , \qquad (1)$$

where σ is the recombination cross-section and $\langle v_n^{th} \rangle$ is the average electron thermal velocity. At, say, 200 K, $\langle v_n^{th} \rangle \approx 2 \times 10^7$ cm/s, then we get that $\sigma \approx$ $\approx 10^{-20}$ to 10^{-21} cm^2. The estimate of $\langle v_n^{th} \rangle$ is based on an electron effective mass ratio /6/ of 0.29.

When the temperature increases, thermal release of the trapped holes becomes important. Released holes recombine with free electrons, causing fast increase of the recombination rate (Fig. 1). No consistent dependence of β on n_o is seen (Fig. 1 and 2). Then it must be that electron-hole recombinations take place via centers in the forbidden-gap rather than directly across the gap. We assume that a hole capture in a recombination center is followed by an immediate capture of a conduction electron (very reasonable assumption for an n-type semiconductor). Under the above conditions β would be given by

$$\beta = \sigma_R \langle v_p^{th} \rangle (N_R/N_t) N_v \exp(-E_t/kT) , \qquad (2)$$

where σ_R is the cross-section for a free hole capture in a recombination center, N_R is the center density, N_t the density of the hole traps (excess Zn^+), E_t their energy above the valence-band, $\langle v_p^{th} \rangle$ the average free hole thermal velocity, N_v the valence-band effective density of states, and k the Boltzmann constant. The product $\langle v_p^{th} \rangle N_v$ is proportional to T^2. To obtain an accurate estimate of E_t we plotted the ratios β/T^2 versus $10^3/T$ on a semi-log scale, and inserted it in Fig. 1, with an expanded $10^3/T$ scale. We get $E_t = 0.42$ eV. We attribute the differences in the absolute values of β between different samples (Fig. 1) to differences in the ratios (N_R/N_t) (see (2)). The values of N_v

and $\langle v_p^{th} \rangle$ may be estimated theoretically from calculated ZnO band structure /7/ using the large polaron transport model /8/ as follows: $N_v = 1.6 \times 10^{20}$ cm^{-3} and $\langle v_p^{th} \rangle = 8 \times 10^6$ cm s^{-1}. With these values we get: $\sigma_R \approx 5 \times 10^{-16} \times (N_t/N_R)$ cm^2. The condition of very fast initial hole trapping requires that $\sigma_R N_R \ll \sigma_t N_t$, where σ_t is the trapping cross-section. Then we get $\sigma_t \gg 10^{-15}$ cm^2. At present, nothing can be said about the origin of the recombination centers, their density or energy position. The relevant energy levels and cross-sections are visualized by the energy level diagram in Fig. 3.

Additional support to our present results is seen in recent thermally stimulated current measurements in ZnO photo-electrets /9/. A dominant 0.4 eV deep trapping level was located, which the authors suggested as an electron trapping level. In view of our present results, the origin of this set should be reinterpreted as the ionized excess Zn donors that act as a hole trapping level.

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(Received December 27, 1979)