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Rapid Research Note

The Oxygen Vacancy as the Origin of a Green Emission in Undoped ZnO

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The recently reported ability to dope ZnO p-type opens novel possibilities for opto-electronic emitters in the blue spectral range [1]. However, in ZnO emission in the green spectral range is commonly reported, but the responsible defects are not identified; extrinsic (copper) as well as intrinsic defects (O- or Zn-vacancies) are discussed [2, 3].

We have investigated undoped ZnO single crystals, which are commercially available from Eagle-Picher, by photoluminescence (PL) and optically detected magnetic resonance (ODMR) spectroscopy. The electrical properties of this material are very similar to the samples investigated in Ref. [4]. The total residual shallow donor concentration is about 1×10^{17} cm^{-3}. The low temperature emission is dominated by the donor bound exciton (D^0X) at 3.366 eV. At 2.45 eV the broad, unstructured "green" emission is located, its full width at half maximum is 320 meV (Fig. 1). The temperature dependence of the PL reveals that this green band maintains its peak energy up to 450 K, which is a feature typical of a recombination within a localised defect, while the D^0X emission follows the shrinkage of the bandgap with increasing temperature.

Performing the ODMR experiment on the green band, i.e. applying an external magnetic field (B_0) and exposing the sample to microwaves (24 GHz, 200 mW, TE_{011}-cavity) we find two types of ODMR signals (Fig. 2). Two resonance signals enhance the luminescence intensity in the order of 0.5%, and one signal decreases the emission intensity. Using amplitude modulation of the microwave power which serves as reference for the lock-in detection, we find that the two intense signals are detected in phase (spectrum I in Fig. 2a). The low intensity signal (spectrum II in Fig. 2a) is detected with a "90° phase". These observations indicate that the two types of signals are of different origin. This is also evident from the orientation dependence of the resonances with respect to B_0 (Fig. 2b). The small signal is isotropic and the corresponding g-value is $g = 1.956$, i.e. the g-value of shallow donors in ZnO [5]. Its small anisotropy, originating from the wurtzite crystal structure ($g_\parallel = 1.957$ and $g_\perp = 1.956$, $\parallel$ and $\perp$ to the crystallographic c-axis) is not resolvable in our experiment. The two intense resonances show the characteristic angular dependence of a spin-triplet system ($S = 1$). The spectra are explained by solutions of the spin Hamiltonian:

$$H = \mu_B \mathbf{B}_0 g \mathbf{S} + D[S_z^2 - \tfrac{1}{3} S(S+1)] \tag{1}$$

with $g_\parallel = 1.984$ and $g_\perp = 2.025$, and a fine-structure splitting D of $D = 260 \times 10^{-4}$ cm^{-1}. It was proven that the triplet resonances are detectable only in the energy range of the green emission band. The shallow donor resonance is also detectable in the excitonic range, but as an emission enhancing signal. This strongly indicates that the shallow donor signal is transferred to green emission by a shunt process or a spin-dependent energy transfer mechanism.

Discussing the origin of the triplet emission we find striking similarities to the anion vacancies (F-centres) in CaO and MgO [6]. The ground state of the centre is a singlet state with two electrons, the neutral oxygen vacancy, it is diamagnetic. Excitation leads to an excited singlet state, from which the electrons can relax into the triplet state ($S = 1$) in which the ODMR is detected, the optical cycle is closed by radiative recombination back to the $S = 0$ ground state. This kind of cycle explains also our results on the green band in ZnO (see inset in Fig. 1). Taking into account that the bandgap energy of ZnO is considerably smaller than that of CaO, or MgO, the oxygen vacancy and the excitonic recombinations are simultaneously excited by above bandgap light.

It should be noted that the presence of Cu in ZnO can also cause an emission band in the green spectral range [2]. However, the Cu-related emission shows a distinct phonon structure which is

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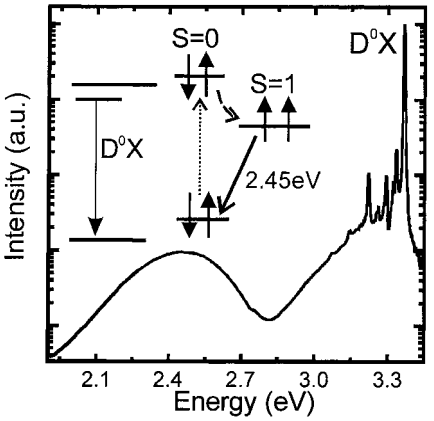

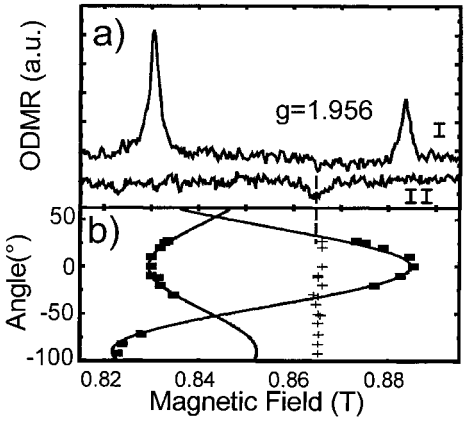

Fig. 1. Emission spectrum of undoped ZnO excited with the 325 nm line of an HeCd laser (5 K). The inset shows a recombination model for the "green" emission located at 2.45 eV

Fig. 2. a) ODMR spectra detected on the 2.45 eV emisssion: (I) "in phase" with the microwave pulses, (II) "90° phase"; for details see text. b) Angular dependence of the ODMR signals (0°: $\mathbf{B}_0 \| \mathbf{c}$, 90°: $\mathbf{B}_0 \perp \mathbf{c}$)

not observed in our samples and, further, the ground- and excited-state *g*-values obtained by Zeeman spectroscopy are incompatible to our results.

In conclusion, our results show that the oxygen vacancy causes a green emission band in ZnO.

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