Optically detected magnetic resonance and optically detected ENDOR of shallow indium donors in ZnO

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Resolved hyperfine structure was observed in time-resolved optically detected electron-paramagnetic-resonance (ODMR) spectra obtained via a donor-acceptor emission band of ZnO. Optically detected electron-nuclear double-resonance (ENDOR) experiments showed that the structure results from hyperfine interaction with ^{115}In. The values measured for the g and hyperfine tensors ($g_{\parallel}=1.957$, $g_{\perp}=1.956$, $A_{\parallel}/h=100.3$ MHz, $A_{\perp}/h=100.1$ MHz) lead to attribution of the ODMR spectrum to shallow indium donors.

In spite of the strong influence of donors on the electrical properties of zinc oxide, which is an n-type semiconductor, no sure identification has ever been given for the chemical nature of a shallow donor in this compound. Doping ZnO with elements expected to act as donors, such as Ga, In, gives high conductivity. However, this is not absolute proof that these elements are shallow donors, for doping experiments can have unexpected indirect effects in low-purity, compound semiconductors like ZnO. For instance, attempting to dope with an impurity element may generate intrinsic (that is, oxygen-deficiency) donor defects or increase the solubility of a donor impurity already present as an inclusion in the sample.

Donors also intervene in the optical properties of ZnO. For example, the classic "yellow" luminescence of uv-excited ZnO is at least partly due to donor-acceptor (D-A) recombinations involving deep lithium acceptors and shallow donors. We have shown this using an optically detected electron-paramagnetic-resonance (ODMR) technique.[1,2] Unfortunately, our ODMR spectra showed no features that could allow identification of these donors. This also applies to the conventional electron-paramagnetic-resonance (EPR) spectra attributed in the literature to shallow donors in ZnO.[3–7]

This Communication concerns a new series of studies of Li-doped ZnO in which we have observed a resolved hyperfine structure in the ODMR spectra. This led us to do optically detected electron-nuclear double-resonance (ODENDOR) experiments which provided positive identification of a shallow donor in our samples. This donor participating in the luminescence process turns out to be the group-III impurity indium.

In our earlier work,[1,2] we measured the effect of microwaves on the luminescence intensity under continuous laser excitation (see also similar work by other authors, e.g., Refs. 8 and 9). In the study described now, using new apparatus, we measured instead the effect of microwaves on the *phosphorescence* intensity, that is on the intensity of the luminescence observed at an adjustable time delay after cutting off the excitation. For brevity, we call this time-resolved technique ODMRP (P for phosphorescence) in this paper. It was designed for measurements of the lifetime dependence of the ODMR spectra and for studies of the recombination dynamics. Its usefulness in the study described here is that it gives much improved signal/noise ratios; also, if we use a sufficiently long time delay, we obtain ODMR lines for which the influence of donor-acceptor exchange interaction (see Refs. 1 and 2) is very small.

Our ODENDOR experiments are also done on the phosphorescence, consisting of measurements of the effect of an additional, radio-frequency (rf) field on the ODMRP signals.

We present here ODMRP and ODENDOR results obtained with time delays 10^{-2}–10^{-1} s for a crystal of ZnO provided by R. Helbig. The crystal was doped with lithium during growth but there was no intentional doping with a donor impurity.[10]

The sample is irradiated with uv light from an argon cw laser; the laser beam is chopped with an acousto-optic modulator. The light emitted by the sample is directed to an EMI 9816G gated photomultiplier (PM); we obtain a signal at the PM output only when a positive voltage is applied to the gating electrode. An optical filter and the PM's S 20 response restrict the detection sensitivity to the 400–800-nm range.

The sample is immersed in liquid helium at 2 K in a microwave cavity placed in a dc magnetic field, $\vec{B}$. The incident microwave power ($f\simeq 9$ GHz) is chopped by a p-i-n modulator. A lock-in amplifier referenced to this chopping frequency detects the effect of the microwaves on the phosphorescence intensity. The ODMRP signal, that is the lock-in output, is recorded as a function of B to give an ODMRP spectrum.

The acousto-optic modulator and the PM gating pulses have the same frequency, which is twice that

of the p-i-n modulator pulses [see Fig. 1(a)].

In an ODENDOR experiment, the field B is set to give an ODMRP signal at the lock-in output, then an rf field is applied by a 5-mm diameter, single-turn loop surrounding the sample. The variation of the ODMRP signal amplitude, recorded as a function of the rf frequency, constitutes the ODENDOR spectrum.

The phosphorescence emission spectrum of this sample in the 400–800-nm range, obtained at 50-ms time delay, consists of a single band 150 nm wide with its peak near 600 nm.

The ODMRP spectra obtained with the pulse conditions of Fig. 1(a) contain, as well as the neutral Li acceptor lines described previously,[1,2] an entirely new set of lines. It is this new set that we will attribute to spin transitions of neutral indium donors. (An additional, weak line at $g \simeq 1.96$, which we will not discuss further, is attributed to unidentified shallow donors.)

Figure 1(b) shows a spectrum with $\vec{B}$ perpendicular to the crystal c axis. For low microwave powers (10^{-5} W), the new line group consists essentially of 10 almost equidistant lines. The 10 lines shift only very slightly when the orientation of $\vec{B}$ is changed; no departure from axial symmetry around the c axis is found. When we increase the microwave power, extra lines grow in intensity relative to the 10 lines. All these lines correspond to transitions of an electronic effective spin $S=\frac{1}{2}$ interacting with a nuclear spin $I=\frac{9}{2}$. We use as spin Hamiltonian

$$H=\beta\vec{B}\cdot\tilde{g}\cdot\vec{S}+\vec{I}\cdot\tilde{A}\cdot\vec{S}+P_{\parallel}I_z^2-g_n\beta\vec{B}\cdot\vec{I} \ , \quad (1)$$

where z is parallel to c and the tensors $\tilde{g}$ and $\tilde{A}$ have axial symmetry around c.

The 10 lines correspond to the $2I+1$ "allowed" transitions $\Delta m_I=0$ of the electronic effective spin, where m_I is the nuclear quantum number. The extra lines observed at high microwave power are "forbidden" transitions ($\Delta m_S=\pm1$; $\Delta m_I\neq0$).

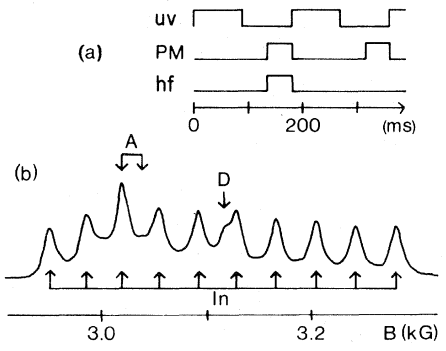

FIG. 1. (a) Typical pulse timing for ODMRP experiments. uv, hf, PM mean laser beam, microwave power, photomultiplier (high=on, low=off). (b) ODMRP spectrum (microwave-induced change in phosphorescence intensity) for $\vec{B}\perp c$, $f=8.53$ GHz. Lines A, D, and In correspond to Li acceptor, unidentified shallow donors, and In donor, respectively.

Three high-abundance isotopes have spin $I=\frac{9}{2}$: ^{93}Nb (100% abundance), ^{209}Bi (100%), and ^{115}In (95.8%). Because the ODMRP lines were too wide for identification of the nucleus, we undertook ODENDOR experiments.

In the ODENDOR experiments, the pulse conditions remained those of Fig. 1(a). By setting B to the peaks of various $\Delta m_I=0$ ODMRP lines, all possible $\Delta m_I=\pm1$ ($\Delta m_S=0$) transitions of the $I=\frac{9}{2}$ nucleus were observed for both $\vec{B}\parallel c$ and $\vec{B}\perp c$. The widths of these ODENDOR lines were $\sim$100 kHz at low powers (10^{-3} W microwaves, 10^{-1} W rf).

From the combination of the ODMRP and the ODENDOR results, we obtained the parameters of spin Hamiltonian (1) using perturbation calculations and taking $g_n\beta/h=0.9329$ kHz/G, the value given in NMR tables for ^{115}In. It is *impossible* to reproduce the ODENDOR results with the ^{93}Nb or ^{209}Bi nuclear Zeeman interactions. We obtain

$$g_{\parallel}=1.9574\pm0.001, \quad g_{\perp}=1.9562\pm0.001 \ ,$$
$$A_{\parallel}/h=100.28\pm0.07, \quad A_{\perp}/h=100.14\pm0.1 \text{ MHz} \ ,$$
$$P_{\parallel}/h=1.27\pm0.03 \text{ MHz} \ .$$

The fit requires parameters $A_{\parallel}$, $A_{\perp}$, and $P_{\parallel}$ to have the same sign, shown later to be positive.

Since indium atoms (group III) have one more valence electron than zinc atoms, indium substitutional on zinc sites is expected to be a single donor with effective electronic spin $S=\frac{1}{2}$ when in the neutral state. Also, zinc sites have C_3 symmetry around the c axis. We conclude therefore that the $S=\frac{1}{2}$, $I=\frac{9}{2}$ system is a neutral, indium single donor on a zinc site.

The $\tilde{g}$ tensor values appearing in the spin Hamiltonian are in the range obtained in EPR studies of shallow donors in ZnO [$g_{\parallel}=1.956$–1.958, $g_{\perp}=1.955$–1.956 (Refs. 3–6)]. Now, in a given semiconductor, the g shift $\Delta g=g-2.0023$ depends on donor depth (cf. in ZnS, $g=1.88$ for shallow donors, 1.99 for the deep indium donor[11,12]). Therefore, we conclude that the indium donor in ZnO is a shallow donor.

If we neglect core polarization, the hyperfine interaction is essentially due to the unpaired electron of the neutral donor. Since the hyperfine tensor $\tilde{A}$ in (1) is almost isotropic, the Fermi contact interaction predominates

$$A_{\parallel}\simeq A_{\perp}\simeq(8\pi/3)g_Sg_n\beta^2|\Psi(0)|^2 \ , \quad (2)$$

where $g_S=2.0023$ and $|\Psi(0)|^2$ is the probability of presence of the unpaired electron on the ^{115}In nucleus. Since $g_n\beta$ is positive, we conclude that $A_{\parallel}$ and

$A_\perp$ are both positive (and therefore $P_\parallel$ is also positive).

We deduce from (2): $|\Psi(0)|^2 = 6.90 \times 10^{23}$ cm^{-3}. This value is two orders of magnitude smaller than the value $|\Psi(0)|^2 = 6.5 \times 10^{25}$ cm^{-3} deduced from hyperfine interaction measurements for the substitutional indium donor in zinc sulfide.[11,12] In ZnS, indium is a deep donor with highly localized unpaired electron [its value of $|\Psi(0)|^2$ is almost as high as that for In^{2+} ions in KCl: 1.01×10^{26} cm^{-3} (Ref. 13)]. Clearly the unpaired electron is much more delocalized in ZnO, confirming that indium is a shallow donor in this crystal. The difference between the properties of indium in the two closely related compounds ZnO and ZnS (they have similar bandgap, electron effective mass, dielectric constant) is quite striking; we suggest this is evidence that local-distortion energies may be critically important in determining whether a donor in a semiconductor forms a shallow or a deep state.

We believe that at least a major part of our In donor and Li acceptor ODMRP signals results from the effect of microwaves on In-donor–Li-acceptor radiative recombinations. To illustrate the types of process to which we attribute the ODMRP and ODENDOR mechanisms, we will consider the response of pairs of centers consisting of a neutral In donor and the nearest neutral Li acceptor (more complex but related multicenter phenomena may occur in the real system). Part of the energy splitting scheme of such a pair is given in Fig. 2. We suppose that the laser pulse feeds all levels equally.

D-A radiative recombination is allowed only when the donor and acceptor have antiparallel (electronic) spins. During the delay time following the laser pulse, phosphorescence emission reduces the concentration of radiative states $|m_A = +\frac{1}{2}, m_S = -\frac{1}{2}, m_I\rangle$ relative to that of nonradiative states $|+\frac{1}{2}, +\frac{1}{2}, m_I\rangle$. A subsequent microwave pulse inducing spin transitions of the donor transfers population from nonradiative to radiative levels. This increases the phosphorescence intensity, giving an ODMRP signal.

Suppose now that B is set so that the microwaves are resonant with donors having $m_I = +\frac{3}{2}$, see Fig. 2. Then the microwave pulse, by reducing the population of $|+\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}\rangle$ and increasing that of $|+\frac{1}{2}, -\frac{1}{2}, +\frac{3}{2}\rangle$, has induced population differences between these levels and the other hyperfine levels. An rf source of appropriate frequency can then transfer population from more populated to less populated hyperfine levels (see the four different $\Delta m_I = \pm 1$ rf transitions in Fig. 2). These transfers allow an increase of the microwave-induced population transfer of Fig. 2. Thus, the nuclear transitions increase the ODMRP signal; this consititutes optical detection of ENDOR.

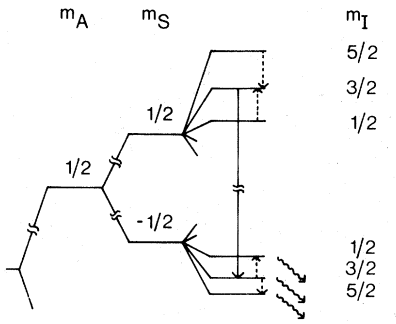

FIG. 2. Energy-level splitting for a Li acceptor-In donor pair in a magnetic field; m_A, m_S, m_I, are quantum numbers for acceptor spin, donor electronic spin, donor nuclear spin, respectively. Full arrow is a microwave transition, dotted arrows are rf transitions, curly arrows are luminescence transitions.

From the many published EPR studies of various II-VI compounds, it appears very difficult to observe hyperfine interactions for shallow donors in these compounds. This has been attributed to the low purity typical of II-VI materials: It appears difficult to achieve neutral donor concentrations high enough for detection by EPR but low enough to avoid donor-donor exchange, which averages the hyperfine interaction to zero; also, hopping of the donor electrons can have similar averaging effects (see Ref. 14). We suggest two reasons for the success of our ODMRP experiments. Firstly, in the *D-A* luminescence process, donor-donor exchange or hopping renders inoperative the spin selection rules that allow optical detection of magnetic resonance. Thus ODMR is sensitive only to well-isolated donors and only a nonaveraged spectrum can be seen. Secondly, ODMR techniques, being much more sensitive than EPR, can detect very low neutral donor concentrations.

In conclusion, the experiments described in this paper have allowed us to identify a shallow donor in ZnO and provide insight into its electronic structure. They confirm that a group-III impurity can act as a shallow donor in this material. More generally, the spectra show that a shallow donor can have a resolved hyperfine structure in a II-VI compound.

Our work appears to represent the first direct identification of a shallow donor in any II-VI compound without help from chemical analyses or doping experiments. The time-resolved ODMR and ODENDOR techniques used successfully here should be generally useful for studying donors in II-VI and other semiconductor materials.

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