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Electric-dipole spin resonance in wurtzite ZnO

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The electron spin resonance (ESR) measurements of the electric-dipole spin resonance (EDSR) of donor-bound electrons in ZnO wurtzite crystals are reported. This phenomenon was measured in longitudinal Voigt geometry ($\mathbf{E_1} \,||\, \mathbf{B_0} \perp \hat{c}$) at low magnetic field and at low microwave frequency. The ESR transitions observed consist of two comparable signals: magnetic dipole spin resonance (MDSR) and electric dipole spin resonance (EDSR).

Keywords: semiconductors, spin-orbit coupling, Zeeman and Stark splitting, Jahn–Teller effect, electron paramagnetic resonance and relaxation.

1. Introduction

We report on our observation of the electric-dipole-induced spin resonance (EDSR) of donor-bound electrons in ZnO crystals based on the dominant magnetic-dipole spin resonance (MDSR). Taking advantage of low microwave frequencies both phenomena are measured.

The origin of EDSR was theoretically discussed by RASHBA [1] and RASHBA and SHEKA [2]. They predicted that the EDSR transition probability is proportional to the B_0^2. The first EDSR measurements were done by DOBROWOLSKA *et al*. [3–6]. Using far-infrared (FIR) radiation the authors induced electric-dipole transitions in $Cd_{1-x}Mn_xSe$ wurtzite crystals and observed EDSR resonance at magnetic field of the order of 1 T. The electric-dipole resonance has been observed in samples characterized by low resistivity with donor concentration of 10^{16} cm^{-3}. Measurements were done in both Voigt and Faraday configurations. To determine selection rules governing EDSR, they used linear and circular polarization of incident light. The experimental results obtained by DOBROWOLSKA *et al*. [3–6] were in agreement with theoretical predictions by RASHBA and SHEKA [2].

2. EDSR origin

In the presence of external magnetic field $\mathbf{B_0}$, the 1*s* state of effective mass donor splits into two magnetic levels with "spin up" and "spin down". Using microwave radiation transition with $\Delta l = 0$, $\Delta m = \pm 1$ between $1s\uparrow$ and $1s\downarrow$ states is possible. This effect is

called magnetic dipole spin-flip and provides a basis for standard ESR measurements. In many physical systems, the spin-orbit (SO) interaction mixes states with different symmetry allowing electric-dipole as well as magnetic-dipole transitions to be observed in ESR.

In ESR measurements, one uses a microwave cavity which is constructed in a way that electric component of standing wave diminishes in the center of cavity (mode TE_{102}). In practice, it is not possible to put a sample exactly in a central position so that there is always a non-zero electric field component that acts on the sample. The presence of electric component of microwave radiation causes the formation of electric dipoles. Direct transition between two spin states in level 1*s* is normally forbidden by electric-dipole selection rules. However, these rules are relaxed in crystals in which spin-orbit interaction arises. Furthermore, if the system exhibits the lack of inversion symmetry, the spin splitting proceeds. In this case, the spin-orbit perturbation mixes states with different orbital angular momentum. In consequence, the perturbed donor states contain a mixture of up and down spins of 2*p* and 1*s* levels. This effect enables electric-dipole spin-flip transitions within the ground state doublet.

3. Experiment

The ZnO bulk crystals were grown in closed quartz ampoule using the chemical vapor transport (CVT). Pure ZnO powder was synthesized at 650°C, by reaction between high purity Zn (6N) and spectrally pure oxygen. The crystal growth took place in a graphite covered quartz ampoule. The mixtures: $H_2 + C + H_2O$, or $N_2 + C + H_2O$ were used as transporting chemical agents. Polycrystals obtained by this method have the volume of about 3 cm^3 and consist of monocrystal grains of 0.2–0.5 cm^3 volum. The crystals were red coloured for both chemical agents used in this work. From ESR measurements we estimate the donor concentration to be about 10^{17} cm^{-3}. The origin of the native donors has not been identified. Since the crystals were not intentionally doped, the donors may originate from native defects associated with either oxygen vacancies or zinc interstitials.

The EDSR measurement was carried out at 9.5 GHz (*X*-band). The spectra were recorded by means of Bruker ESP-300 spectrometer (standard commercial setup). The experiments were performed in longitudinal Voigt geometry. In this configuration, the propagation of the microwave is perpendicular to the homogeneous external magnetic field $\mathbf{B_0}$ while microwave electric field $\mathbf{E_1}$ is parallel to the $\mathbf{B_0}$. We used standard TE_{102} cavity for which standing electromagnetic wave has the maximum magnetic field component $\mathbf{H_1}$ in the center of the cavity ($\mathbf{E_1}$ is zero at the central point). Therefore, in the middle of the cavity the sample interacts only with magnetic field component which oscillates with frequency of about 9.5 GHz. The electric field component that oscillates with microwave frequency may appear either due to displacement of the sample from central position or perturbation of standing wave by the sample. In ESR measurements, the *c* axis of the crystal was oriented at angles α, varying from 0 to 360 deg, with respect to $\mathbf{E_1}$ and $\mathbf{B_0}$. For all measurements the MDSR

amplitude is isotropic because $\mathbf{H_1} \perp \hat{c}$ and $\mathbf{H_1} \perp \mathbf{B_0}$. Since EDSR can be observed only when $\mathbf{B_0} \times (\mathbf{E_1} \times \hat{c}) \neq 0$ [3–6], therefore EDSR amplitude is α dependent as opposed to MDSR.

All measurements were done using as grown, red monocrystals. The measurements were performed in a magnetic field up to 1 T, and the temperature was kept constant at 2.3 K.

4. Results and discussion

In 1961, SCHNEIDER *et al*. [7] made the first ESR observation of shallow donors in ZnO, followed in 1962 by KASAI [8]. At the temperature of 77 K they observed a single line with linewidth of about 2 G without any hyperfine structure. Kasai concluded that there were two types of donors. The first connected with the presence of oxygen vacancy with $g_{||} = 1.957$, $g_{\perp} = 1.956$. The second interpreted as halogen donors set on by a heat treatment of pure ZnO together with alkali halides. The first identification of shallow donor with hyperfine structure in ZnO was reported by GONZALES *et al*. [9], and BLOCK *et al*. [10]. They detected a ten line spectrum to originate from $I = 9/2$ of ^{115}In. The hyperfine constant was $A = 36.6$ G and the linewidth was 21 G. In the same work, the first experimental evidence was given also for the Ga donor ($A = 4.2$ G) [9]. Similar interpretation was used quite recently ($A = 6.7$ G) [11]. Also hydrogen could be identified as a shallow donor [12, 13], with a hyperfine constant $A = 0.5$ G (1.4 MHz).

In our experiment, the ESR spectrum consists of a very narrow single line with linewidth in the range from 0.5 to 0.9 G. Typical ESR spectra observed at 2.3K in the longitudinal Voigt geometry are shown in Fig. 1. We present spectra recorded at different angles α between the c axis and $\mathbf{B_0}$. The $\alpha = 0$ indicates that c axis is parallel to $\mathbf{B_0}$.

The ESR measurements provide g-values to be $g_{||} = 1.9568$ and $g_{\perp} = 1.9552$, respectively. These are in agreement with published data on shallow donors in ZnO [7, 8, 13]. Since the hyperfine structure was not detectable in our experiment, we suggest that observed donor is not coupled to any nucleus spin with energies higher than 5×10^{-5} cm^{-1}. The ESR measurements identify the observed object as a shallow effective mass donor. These findings confirm presumptions that shallow donors arise from intrinsic defects like zinc interstitial or oxygen vacancy [14–16].

The concentration of donors obtained from ESR measurements is about 10^{17} cm^{-3} for as-grown samples and is much smaller than expected concentration of color centers estimated from the intensity of red color of the sample. After annealing in oxygen atmosphere at 900–1000ºC, the crystals become colorless while the electron concentration decreases by only one order of magnitude. Therefore, we conclude that color centers are not electrically active and the ESR signal cannot be related to color centers.

The anisotropy of the ESR line position shown in Fig. 1 corresponds to anisotropy of g-factor ($\sim 10^{-3}$). Assuming that the whole anisotropy of g-factor arises from

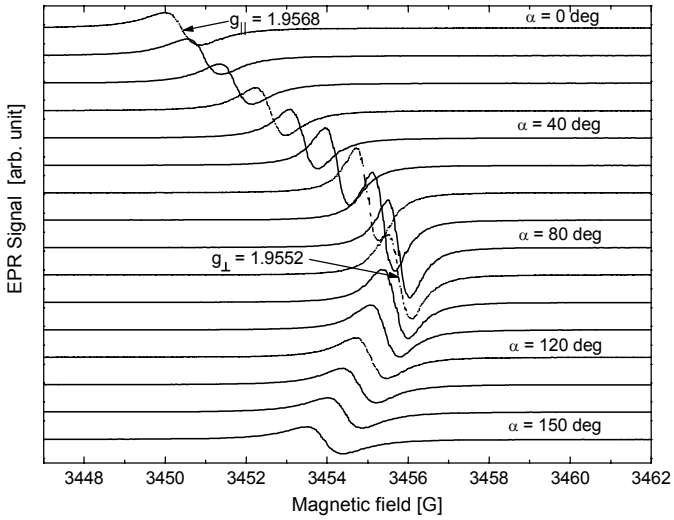

Fig. 1. Angular dependence of electron spin resonance spectra in ZnO wurtzite crystal at 2.3 K in longitudinal Voigt geometry. Anisotropy of linewidth, *g*-factor, and ESR intensity is observed.

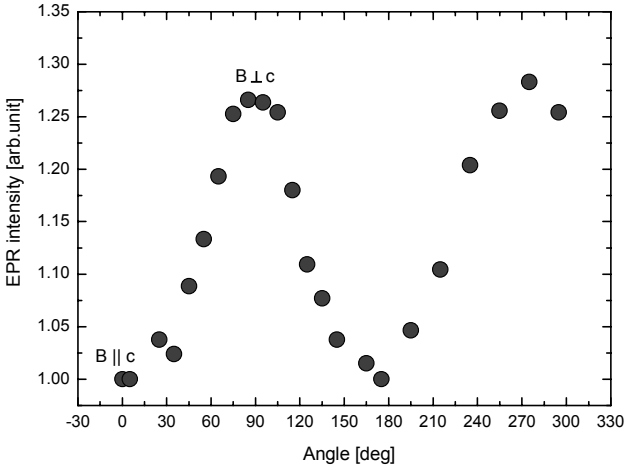

Fig. 2. Electron spins resonance intensity in ZnO at 2.3 K as a function of angle between crystal *c* axis and electric field. The ESR measurements were done in longitudinal Voigt geometry. The ESR signal consists of two types of transitions: isotropic magnetic dipole spin resonance and anisotropic electric dipole spin resonance.

the spin-orbit interaction it is possible to estimate SO field to be about 200 G. Since the *g*-factor variations may have different origins the calculated value of SO field is just an upper limit approximation.

The second important feature of ESR signal is the angular dependence of linewidth (see Fig. 1). It changes in the range 0.5–0.9 G for an angle varying form 0 to 90 deg.

This effect can be related to fluctuations of local electric field $\mathbf{E_c}$, which affects SO field.

The most striking feature of the data is variation of resonance intensity. In Fig. 2, the integrated amplitude of ESR line is plotted as a function of sample orientation. The ESR amplitude, in the case where $\mathbf{B_0} \perp \hat{c}$, is higher by a factor of 1.25 in comparison to the case where $\mathbf{B_0} \| \hat{c}$ (see Fig. 2). We suggest that this effect is related to the electric-dipole spin resonance phenomenon. Microwave cavity used in our experiment is characterized by $\mathbf{E_1} \| \mathbf{B_0}$, so we expected to the measure maximum of EDSR signal when the *c* axis of crystal is perpendicular to the field $\mathbf{B_0}$ (α = 90 deg, α = 270 deg). In the case of longitudinal Voigt geometry and magnetic field being parallel to *c* axis (α = 0 deg and α = 180 deg) no electric-dipole transition can exist. This configuration corresponds to minima in Fig. 2. We identify maxima as an EDSR transition of native donor (see Fig. 2). Therefore, we conclude that α dependence of ESR intensity is a *fingerprint* of EDSR transition.

By extracting EDSR signal from the data shown in Fig. 2 we obtained strong background which does not show any angular dependence. We identify this as a standard magnetic-dipole spin resonance. Therefore, we conclude that the ESR spectra which we observe result from two types of transitions: MDSR and EDSR. Magnetic-dipole transition produces about 75% of the total ESR intensity and the rest corresponds to electric-dipole transition. The EDSR signal observed in our experiment is much weaker than that obtained by DOBROWOLSKA *et al*. [3–6] as expected due to B_0^2 dependence of EDSR transition probability [1, 2].

5. Summary

The ESR measurements in undoped ZnO bulk crystals identify the existence of native shallow donors. The concentration of occupied donors obtained from ESR is of the order of 10^{17} cm^{-3} for as-grown crystals. In the samples under investigation we observed electric-dipole spin resonance transition. The EDSR signal is about 25% of MDSR intensity. The amplitude of EDSR for the *c* axis perpendicular to the external magnetic field changes by a factor of 1.25 as compared to the case where the *c* axis is parallel to $\mathbf{B_0}$. The ESR linewidth anisotropy observed corresponds to local fluctuations of spin-orbit field, which are two orders of magnitude smaller than a mean SO field.

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