Self-Compensation of Shallow Donors in AlN: High-Frequency EPR and ENDOR Studies

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Experimental and theoretical studies on the electronic properties of semiconductors have demonstrated that a donor can give rise to two types of electronic states. Either a shallow level with a delocalized effective-mass-like wave function associated with the normal substitutional (interstitional) site configuration, or a deep level with a localized wave function. The latter deep state is usually called a *DX* center and it arises from a lattice distortion at or near the donor site exhibiting a negative correlation energy *U* for electrons trapped at this site. A transition of a shallow donor to a *DX*-like center is an important property that affects the *n*-type conductivity of semiconductors.

The formation of *DX* centers leads to a self-compensation of a shallow donor (SD) according to the reaction, $2d^0 = d^+ + DX^- + U$. Here *d* denotes a substitutional SD impurity and *DX* the displaced deep impurity. In this model a SD can lower its energy by the capture of a second electron followed by a lattice relaxation of the donor impurity away from the substitutional site. The energy gain associated with electron pairing in the dangling bonds of a defect, coupled to a large lattice relaxation, was suggested by Anderson to overcome the Coulombic repulsion of the two electrons.

The III-V nitrides could potentially be fabricated into optical devices that are active at wavelengths ranging from the infrared into the ultraviolet. Unfortunately the properties of donors in the nitrides remain contradictory. There were data that the *DX* state is the stable configuration for Si in AlN, and in contrary it was argued that Si is a shallow effective-mass donor in AlN in contrast to oxygen that forms a *DX* center. To our knowledge there is no data about the spatial distribution of the electronic wave function of SD's in the III-V nitrides and even more generally in the III-V semiconductors. Moreover the spin state of *DX* centers in semiconductors has not been demonstrated experimentally.

We report the results of high-frequency electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) experiments on as-grown single crystals of AlN that prove the presence of effective-mass-like shallow donors in these crystals with a strongly delocalized electronic wave function. Secondly we demonstrate how the conversion of a shallow donor to an ionized shallow donor and a deep *DX*-like center and the reversed process take place.

The EPR and ENDOR experiments were performed at 1.5-5 K on a home-built spectrometer operating at 94.9 GHz. The spectra were recorded by monitoring the electron-spin echo (ESE) signal. The crystal growth was accomplished by sublimation of the AlN charge placed in the hot zone of a tungsten crucible and subsequent condensation of the vapor species in a cooler region. Two wurtzite polytype small samples labelled I and II were cut from larger boules of AlN grown with similar conditions.

Figure 1 shows the EPR spectra measured at 94.9 GHz in the two samples marked I (curve 1) and II (2,3) at 1.8 K after cooling from room temperature (RT) in the dark (1,2) and after 10 min light illumination (3). The EPR signals were detected with the magnetic field perpendicular to the crystal *c* axis ($B \perp c$). The observed EPR signal at 3.408 T is characterized by a slightly anisotropic g factor of $g_{//}=1.9900$ and $g_{\perp}=1.9894$. This g factor is somewhat smaller than the free electronic g factor as expected for SD's or conduction electrons in a wide-band-gap semiconductor such as AlN [1]. The anisotropy is consistent with the hexagonal symmetry of the AlN crystal. These factors support the assignment of the indicated resonances in Fig. 1 to the shallow donors.

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After cooling in the dark only a weak EPR signal of SD's is observed in sample II. After illumination with light with a wavelength shorter then 700 nm, a strong EPR signal of SD's appears. This EPR signal, once excited at low temperature, persists at low temperature after switching off the light, however disappears after heating above 200 K. The EPR signal of the SD's in sample I did not increase upon optical illumination.

The EPR line of the SD's does not exhibit a resolved hyperfine (HF) structure and for this reason ENDOR measurements were performed. Figure 1(b,c) shows the ENDOR signal of ^{27}Al nuclei (I = 5/2, abundance 100 %) observed in the EPR line (1) in sample I and the EPR lines (2,3) in sample II at 1.8 K. The ENDOR signals were measured in two orientations. The nuclear Zeeman frequency of ^{27}Al is indicated by an arrow. For S=1/2 the HF interaction constant for each ^{27}Al nucleus gives rise to two ENDOR transitions symmetrically placed around its nuclear Zeeman frequency when the quadrupole interaction (QI) is neglected. This symmetrical behavior is indeed observed for the "dark" SD signal although the HF lines are not resolved. In contrast, a considerable difference in intensity is observed for the ENDOR signals of light-induced SD's that are positioned in Fig. 1(b,c) above the nuclear Zeeman frequency of ^{27}Al and below this frequency. This difference in the intensities strongly depends on the temperature and increases when the temperature reduces. The ENDOR spectra consist of a multitude of lines which are indicated by arrows. These lines correspond to HF interaction of 9.044, 7.994, 6.564, and 4.194 MHz with different Zn shells.

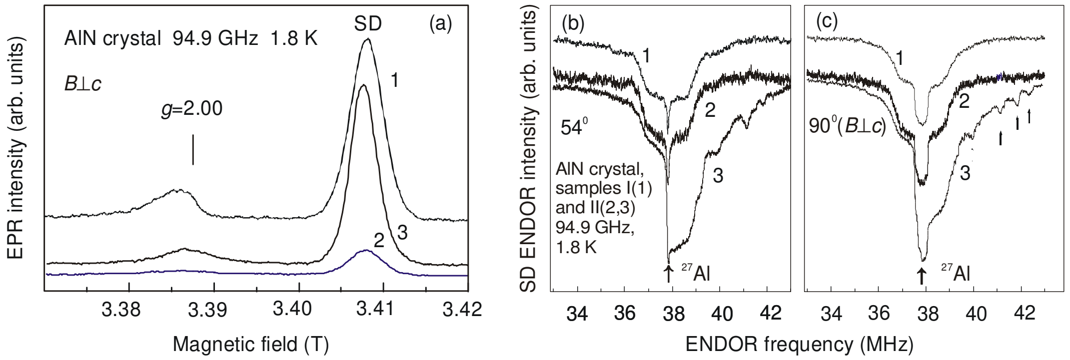

Fig. 1. (a) The EPR spectra of SD's for sample I (curve 1) and the sample II (2,3) at 1.8 K after cooling from room temperature in the dark (1,2) and after 10 min light illumination (3). The signal near g=2 is thought to originate in a deep-level defects. (b)(c) The ENDOR signal of ^{27}Al nuclei for samples I (1) and II (2,3) measured at two orientations after cooling from RT in the dark (1,2) and after 10 min illumination (3).

The ENDOR spectrum of the light-induced SD's shown in Fig. 1(b,c) can be understood by assuming that we are dealing with the triplet ground state of two exchange-coupled SD spins. The more intense signals above the nuclear Zeeman frequency of ^{27}Al are related to ENDOR transitions in the lower M_S=-1 sublevel, whereas the less intense signals below the nuclear Zeeman frequency correspond to the transition in the M_S=1 sublevel. The intensities of the related ENDOR transitions differ strongly as a result of the extreme difference in the populations of the triplet sublevels at this low temperature and large Zeeman splitting. The ENDOR transition in the M_S=-1 sublevel will lie at a frequency $h^{-1}(1/2a_i)$ above or below the nuclear Zeeman frequency, depending on the sign of the HF constant a_i of i shell. The spin-lattice relaxation measurements show that the light-induced SD's correspond to coupled pairs with an exchange interaction of about 24 cm^{-1} and with a lowest triplet state. These pairs are believed to show a negative correlation energy *U.* Their Coulombic center is most probably located at the N position. For this reason we propose that oxygen forms the core of this donor in agreement with van der Walle prediction [2].

[1] M. W. Bayerl et al., Phys. Rev. B 63,165204 (2001).
[2] C. G. Van de Walle, Phys. Rev. B 57, R2033 (1998).