Physica B 404 (2009) 4873–4876

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Defects in AlN: High-frequency EPR and ENDOR studies

Sergei B. Orlinskii [a], Pavel G. Baranov [b], Anna P. Bundakova [b], Matthias Bickermann [c], Jan Schmidt [d,*]

[a] Federal Center of Shared Facilities of Kazan State University, 42008 Kazan, Russia
[b] Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia
[c] Department of Materials Science 6, University of Erlangen, 91058 Erlangen, Germany
[d] Huygens Laboratory, Leiden University, Leiden, The Netherlands

ARTICLE INFO

Keywords:
Defect
EPR
ESE
ENDOR
AlN
Donor
Negative *U*

ABSTRACT

Compensation by deep-level defects and self-compensation of shallow donors in AlN are discussed in the light of results of a high-frequency pulse electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) study. It was suggested on the basis of the large mostly isotropic hyperfine interaction with $A(^{27}\mathrm{Al}) = 406\,\mathrm{MHz}$ that one of the deep-level defect is isolated interstitial Al^{2+} atom. Two types of effective-mass-like shallow donors with a delocalised wave function were shown to exist in unintentionally doped AlN. The experiments demonstrate how the transformation from a shallow donor to a deep (DX) centre takes place and how the deep DX centre can be reconverted into a shallow donor forming a spin triplet and singlet states with an exchange interaction of about $24\,\mathrm{cm}^{-1}$ and with a lowest triplet state.

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1. Introduction

The III–V nitrides could potentially be fabricated into optical devices that are active at wavelengths ranging from the infrared into the ultraviolet [1]. In general, as-grown, nominally undoped AlN crystals exhibit a *n*-type conductivity and are highly resistive, indicating that native defects present are sufficiently deep. Electron paramagnetic resonance (EPR) and EPR-related methods are known to be the most effective methods for identifying point defects in semiconductors and these methods have recently been used to study deep-level defects in AlN [2,3].

Another important factor which may affect the *n*-type conductivity of semiconductors is a transition of shallow donors (SDs) to a deep state. 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 delocalised effective-mass-like wave function, or a deep level with a localised wave function. The latter deep state is usually called a DX centre 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 [4–6].

The formation of DX centres leads to a self-compensation of a SD according to the reaction $2d^0 = d^{+} + \mathrm{DX}^{-} + U$. Here *d* denotes a 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 normal 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 [7] to overcome the Coulombic repulsion of the two electrons.

The properties of donors in the nitrides remain contradictory. There were data that the DX state is the stable configuration for Si in AlN [8,9], and in contrary it was argued that Si is a shallow effective-mass donor in AlN in contrast to oxygen that forms a DX centre [10]. Based on spectroscopically resolved photoconductivity and EPR measurements, Si donors in heavily Si-doped MBE-grown AlN samples have been shown to exhibit a DX-like relaxation [11].

High-frequency EPR and electron-nuclear double resonance (ENDOR) experiments were demonstrated [12–14] to be methods of choice for identification and study of effective-mass-like SDs in semiconductors.

In this report, we will concentrate on compensation of as-grown AlN single crystals by deep-level defects.

2. Experimental

AlN crystal growth of wurtzite polytype was accomplished by sublimation of an AlN charge placed in the hot zone of a tungsten crucible and subsequent condensation of the vapor species in a cooler region [14]. To facilitate self-nucleation of separate single AlN crystals, the condensation section of the crucible was separated from the evaporation zone by a diaphragm and kept under nearly isothermal conditions. Three small samples with size

* Corresponding author. Tel./fax: +31 71 527 5910.
E-mail address: mat@molphys.leidenuniv.nl (J. Schmidt).

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doi:10.1016/j.physb.2009.08.239