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Compensating defects in Si-doped AlN bulk crystals

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Abstract

The rather low n-type conductivity observed in Si-doped sublimation-grown AlN bulk crystals is explained by the formation of high concentrations of compensating defects. The model is based on the experimental verification of a shallow impurity band formed by Si donors and the presence of acceptor-like electron traps within 1 eV below the conduction band edge. Further it is suggested that the majority of the Si donors is compensated by deep acceptors in the lower half of the band gap. This compensation model is an alternative to the controversially discussed assumption of Si DX center formation.

Keywords: AlN bulk crystals; Si doping; Compensation

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1. Introduction

Effective n- and p-type doping of the extremely wide-band-gap (~6 eV) semiconductor AlN is a prerequisite for its utilization in III-nitride-based optoelectronic devices for the ultraviolet wavelength region [1]. Theoretical investigations predict that doping of AlN is strongly limited by compensating defects such as vacancies and hardly avoidable impurities [2,3]. In particular, n-type doping is expected to be accompanied by an enhanced formation of negatively charged Al vacancies. The impurity O is believed to form DX centers counteracting the electrical activity of other donors. There is still a controversial discussion of theoretical as well as experimental data whether the donor dopant Si forms a DX center in AlN or acts as an effective-mass donor [2–7]. The broad scatter of the Si donor activation energy between 80 and 320 meV is also awaiting a convincing explanation.

Si-doped AlN bulk crystals grown at our institute showed weak n-type conductivity at room temperature [8]. We report here on the compensation mechanism in these crystals.

2. Experimental details

AlN crystals were grown by physical vapor-phase transport in a TaC crucible at temperatures between 2000 and 2200 °C under a 600 mbar nitrogen atmosphere of high purity. Si doping was realized by adding SiC to the AlN source material. The AlN boules showed a columnar structure with strong $\langle 0001 \rangle$ texture and single-crystalline grains of up to 6 mm diameter.

Chemical analysis with respect to the most important impurities was performed by secondary ion mass spectrometry (SIMS). The Si concentrations of $1–3 \times 10^{20}\,\mathrm{cm}^{-3}$ exceeded those of C and O by at least an order of magnitude.

The electrically active defects were studied by capacitance–voltage (*C*–*V*), admittance, thermoluminescence (TL), temperature-dependent photoconductivity, and electron paramagnetic resonance (EPR) measurements. For the *C*–*V* and admittance measurements Ni Schottky contacts were deposited in vacuum either on the as grown surface or on polished, KOH etched surfaces. Large-area ohmic back side contacts were prepared by silver glue. The temperature-dependent investigation of the Schottky diodes was accomplished by means of a frequency-variable LCR meter and a temperature-stabilized sample chamber (100–700 K). TL curves were recorded in a scanning electron microscope equipped with a cathodoluminescence system enabling a spatial resolution on the μm scale and

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temperature sweeps from 10 to 450 K. Single-shot electron-beam excitation was applied at 10 K using typical beam parameters of 20 kV and 200 nA. During linear heating to 450 K with a rate of 0.15 K/s the polychromatic luminescence signal was detected by a photomultiplier tube. The TL analysis took retrapping of charge carriers into account, i.e. second-order kinetics [9]. The EPR data were taken by an X-band spectrometer equipped with a helium-gas-flow cryostat.

3. Results and discussion

The *C–V* characteristics undoubtedly proved the n-type conductivity of the Si-doped AlN crystals. A typical example of a *C–V* measurement is shown in Fig. 1. The net donor concentrations determined by using the well-known formulas for the depletion layer capacitance [10] amounted to mid $10^{17}\,\mathrm{cm}^{-3}$. The SIMS data yielded Si concentrations of few $10^{20}\,\mathrm{cm}^{-3}$ exceeding the C and O concentrations by one order of magnitude. If one assumes a high degree of electrical activation of the incorporated Si, the Si donors must be mainly compensated by a high density of unknown acceptors.

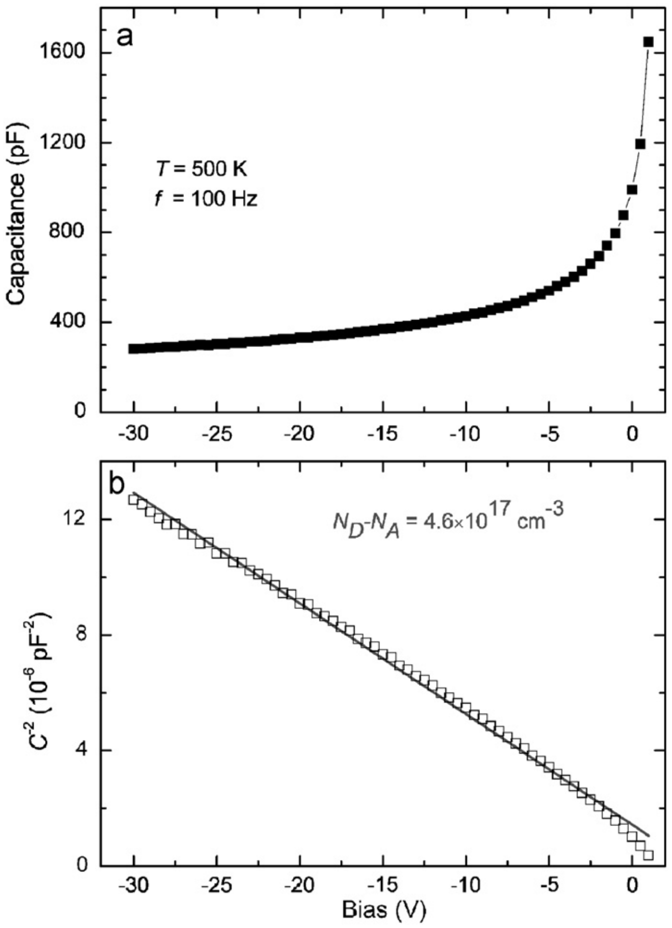

Fig. 1. (a) *C–V* curve of a Ni Schottky contact on the as grown surface of an Si-doped AlN crystal measured at 500 K and 100 Hz. (b) C^{-2} vs. bias plot yielding a net donor concentration of $4.6 \times 10^{17}\,\mathrm{cm}^{-3}$.

Meaningful *C–V* measurement necessitated the application of a high temperature (500 K) and a low frequency (100 Hz) indicating a high thermal activation energy of the conduction electrons. To determine the activation energy we performed frequency and temperature dependent admittance measurements of the Schottky diodes in the freeze-out region of conduction electrons [11]. This is exemplified in Fig. 2 for a sample in which at least two trap levels can be identified to be responsible for the thermal electron activation. In average, activation energies in the range from 0.5 to 1 eV were determined for all investigated samples. This is much higher than one would expect for the ionization energy of the Si donor.

Further information on the presence of trap levels in our samples we obtained by thermoluminescence measurements. A comparison of the TL spectra of Si-doped (Fig. 3) and -undoped (not presented here) AlN crystals shows that trap levels with lower activation energies than about 1 eV are pronounced only in Si containing samples. In particular, the shallow defect level at around 120 meV, that is not detectable in admittance measurements, is

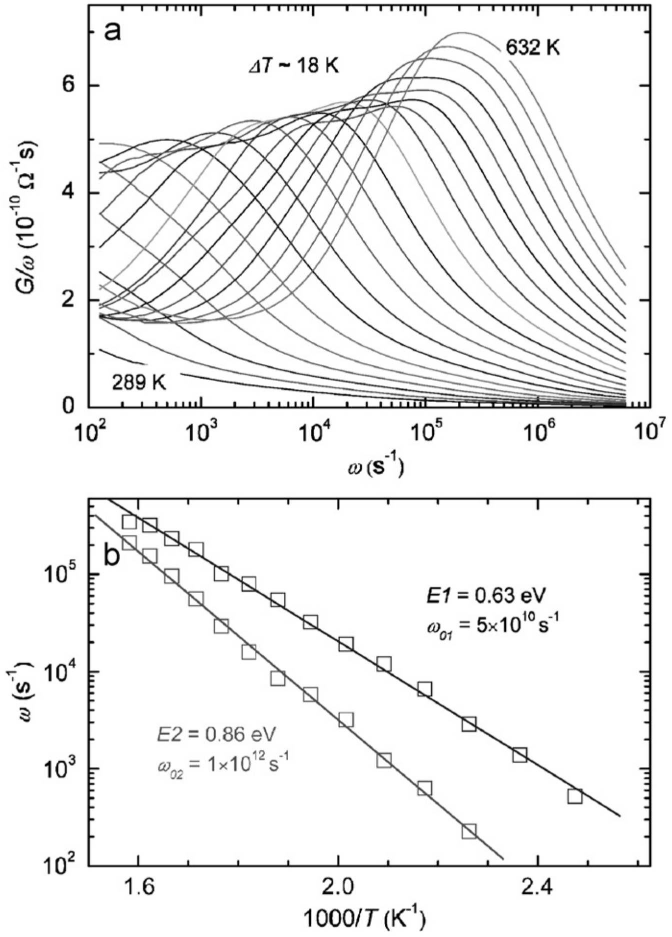

Fig. 2. (a) Frequency and temperature dependence of the conductance divided by the angular frequency (Schottky contact on the as grown surface). (b) Arrhenius plot of the G/ω peak maxima yielding activation energies of 0.63 and 0.86 eV.

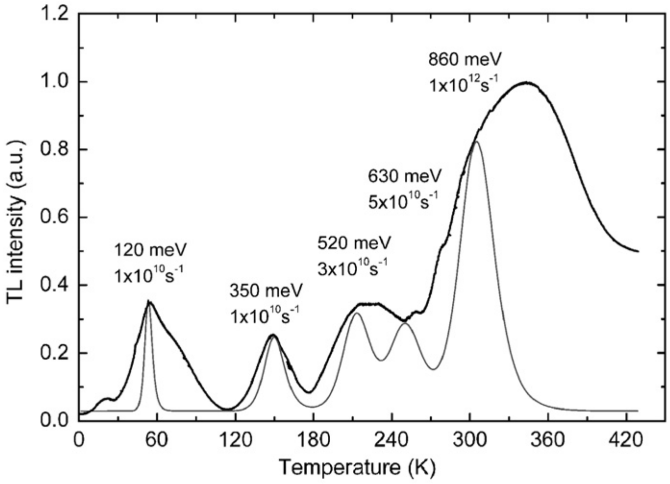

Fig. 3. Thermoluminescence spectrum of an Si-doped AlN crystal. The smooth curve is calculated with the given trap parameters, partly including results of admittance spectroscopy (520, 630, and 860 meV).

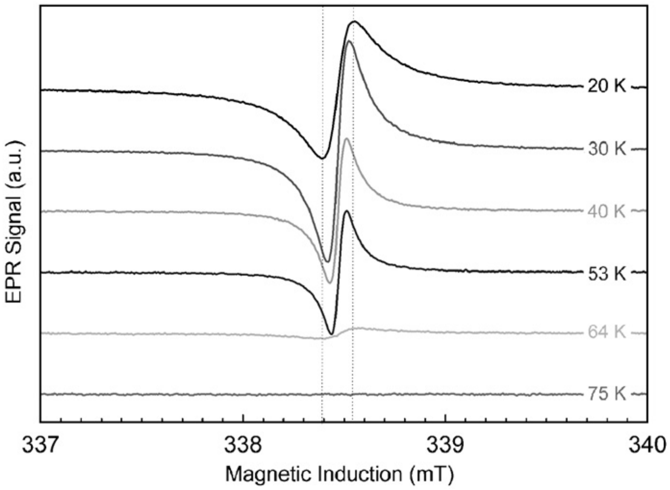

Fig. 4. Isotropic EPR signal ($g = 1.990$) arising after prolonged illumination ($\lambda \sim 500$ nm) of an Si-doped AlN crystal at low temperature.

related to Si. The TL peak is unusually broadened indicating a defect level distribution or an impurity band.

EPR spectroscopy reveals an isotropic signal with a g-factor of 1.990 in AlN:Si samples after prolonged illumination ($\lambda \sim 500$ nm) at low temperature as shown in Fig. 4. The resonance line is persistent up to 60 K. The abrupt disappearance of the EPR signal above 60 K, coinciding with the 120-meV-TL, is best explained by thermal electron emission from Si donors. The observed line narrowing with increasing temperature can be interpreted by an averaging of hyperfine interactions due to exchange interaction in an impurity band. (The effect is much more pronounced than recognizable from Fig. 4 when signals recorded below 20 K are included.) All features of this EPR signal are identical to those reported by Zeisel et al. [6] who observed the line in Si-doped AlN films grown by plasma-induced molecular beam epitaxy. They interpreted it as arising from a Si donor band.

Finally, we observed persistent photoconductivity in AlN:Si samples after illumination with photons of $h\nu > 1$ eV at low temperature. An example is given in Fig. 5. The photoconductivity persists up to 60 K. Then it decreases slowly and passes on to the dark conductance curve at above 190 K. A similar persistent photoconductivity curve was already reported in Ref. [6], where it was used as a strong argument in favor of a Si DX center formation in AlN.

However, an alternative explanation may be as follows. From our experimental results we deduce the simple energy level scheme presented in Fig. 6. The incorporated Si atoms form a shallow donor band centered at about 0.1 eV below the conduction band edge. The majority of the donors is suggested to be compensated by acceptors in the lower half of the band gap. Possible candidates are triply negatively charged Al vacancies [2,3] and, to a lower extent, C on N

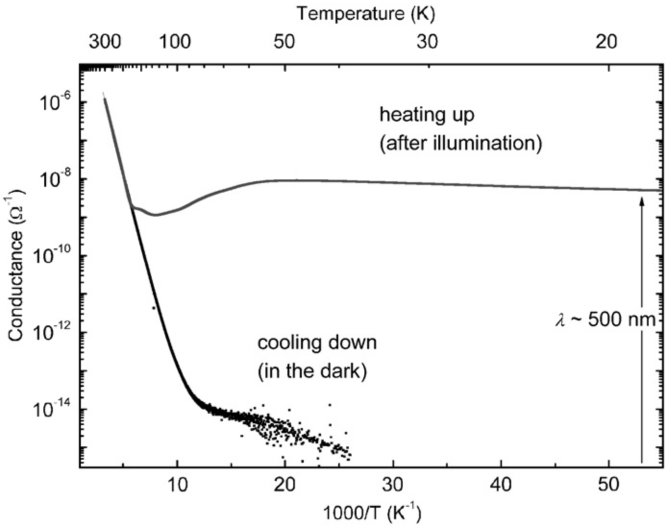

Fig. 5. Temperature-dependent conductance of AlN:Si in the dark and after illumination at low temperature.

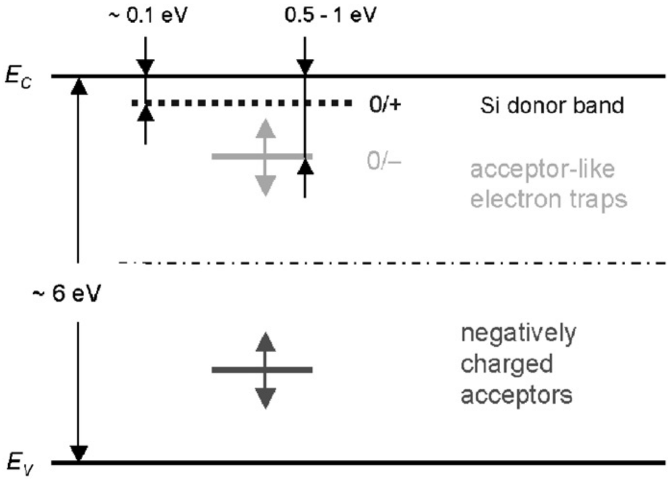

Fig. 6. Energy level scheme of the basic features of the compensation model.

sites [12]. This compensation results in the net donor concentration measured by *C–V*. The electron concentration at room temperature, however, is strongly reduced by the presence of acceptor-like electron traps in the range from 0.5 to 1 eV below the conduction band edge. The thermal activation of electrons from these traps is responsible for the temperature variation of the conductance observed in the admittance measurements. The persistent photoconductivity is excited at low temperature by photoionization of the acceptor-like traps filling the Si donor band with electrons. Hopping conduction of these electrons explains the persistent conductivity in the absence of light. At above 60 K the electrons are reemitted to the conduction band but not immediately recaptured by the traps. The slow recapture process can be explained by a capture barrier of the acceptor-like traps which is not unusual for defects with strong lattice coupling (well known as multiphonon capture and emission processes). This model consistently explains all our experimental observations for AlN:Si without the assumption of Si DX center formation. A clear conclusion whether a Si DX center is real or not, however, can only be drawn by an investigation of Si-doped AlN crystals containing strongly reduced defect and impurity concentrations which, in our opinion, are not available at present.

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