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Identification of the $V_{\text{Al}}$-$O_N$ defect complex in AlN single crystals

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In this Rapid Communication, we report positron annihilation results on in-grown and proton irradiation-induced vacancies and their decoration in aluminium nitride (AlN) single crystals. By combining positron lifetime and coincidence Doppler measurements with ab initio calculations, we identify in-grown $V_{\text{Al}}$-$O_N$ complexes in the concentration range $10^{18}$ cm$^{-3}$ as the dominant form of $V_{\text{Al}}$ in the AlN single crystals, while isolated $V_{\text{Al}}$ were introduced by irradiation. Further, we identify the UV absorption feature at around 360 nm that involves $V_{\text{Al}}$.

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Aluminium nitride (AlN) is a promising extremely wide band-gap ($E_g = 6.2$ eV) semiconductor for use in deep ultraviolet optoelectronics.¹ AlN can also be alloyed with other III nitrides in order to tailor the active wavelength from infrared to deep ultraviolet. To exploit the full potential of devices based on III nitrides, lattice-matched bulk substrates are needed in order to minimize the defects caused by lattice mismatch. This is driving the need to develop nitrogen growth methods capable of creating either true bulk crystals or several millimeter thick heteroepitaxial layers that can be separated from the substrate.²,³ Synthesis of large enough AlN single crystals has been difficult with problems ranging from threading dislocations to vacancy type point defects. Physical vapour deposition (PVT) has emerged as a method of choice for producing AlN single-crystal substrates.²⁻⁷ However, vacancy defects produced during the synthesis still play a major role in the general crystal quality. Vacancies in the AlN substrate can have a major impact on the device operation. For example, vacancy-impurity complexes have been reported to affect the thermal conductivity of the material,⁸⁻¹⁰ affecting the device operation. Also, it has been reported that point defects can cause UV absorption,¹⁰ which should be minimized in order to achieve effective light extraction through the substrate.

Positron annihilation spectroscopy is a powerful tool in studying cation vacancies in nitride semiconductors.¹¹⁻¹³ A few reports on positron annihilation results in both bulk¹⁴ and thin film¹⁵⁻¹⁶ AlN exist, but conclusive evidence on the identity and decoration of the observed vacancies is missing. In this Rapid Communication, we report positron annihilation spectroscopy results on the identification of in-grown and irradiation-induced defects in PVT-grown bulk AlN crystals. We show that in as-grown AlN crystals, Al vacancies are present at a concentration in the range of $10^{18}$ cm$^{-3}$. The in-grown Al vacancies are complexed with oxygen ($V_{\text{Al}}$-$O_N$), while isolated $V_{\text{Al}}$ can be produced by irradiation.

The measured bulk AlN crystals were grown by PVT at 2600 K in tungsten crucibles (for details, see Ref. 17). 300-μm-thick wafers were cut from the ingot for the measurement. Energy-dispersive x-ray spectroscopy (EDS) measurements show that the wafers contain less than 100 ppm impurities ($10^{19}$ cm$^{-3}$) with gas discharge mass spectrometry (GDMS) showing at most 10 ppm of oxygen impurities ($10^{18}$ cm$^{-3}$). Positron lifetime measurements were performed at temperatures between 20 and 750 K with conventional lifetime instrumentation.¹⁸ The increase of average positron lifetime $\tau_{ave}$ (the center of the mass of the spectrum) above the lifetime in the lattice of the material is an indication of vacancy defects being detected. The positron Doppler broadening experiments were performed using high-purity Ge detectors with energy resolution of 1.3 keV. When the positrons are trapped at vacancies, the probability of annihilation with high-momentum core electrons is reduced, narrowing the Doppler broadening spectrum. In order to identify the chemical surrounding of the vacancy, coincidence Doppler measurements were performed.¹⁸ The optical absorption and transmission spectra of the AlN films were measured with a xenon lamp, monochromator, and photomultiplier tube at room temperature.

We also calculated the positron-electron momentum density from first principles for vacancy defects and the AlN lattice. The valence electron densities were calculated self-consistently using the local-density approximation (LDA) employing the projector augmented wave (PAW) method¹⁹ and a plane-wave code VASP.²⁰ The Doppler spectra were calculated in the direction of the $c$ axis of the wurtzite AlN with the relaxation caused by a positron to the vacancy taken into account. For details on the computational methods, see Ref. 21. Two of the AlN wafers were irradiated with 9.5 MeV protons to a fluence of $10^{16}$ cm$^{-2}$ with a tandem accelerator.²² The energy of the protons is high enough to penetrate the 300-μm-thick wafer and generate a homogeneous defect profile, but low enough to create only monovacancies. From SRIM²³ calculations, we estimate that $4 \times 10^{18}$ cm$^{-3}$ Al vacancies and $3 \times 10^{18}$ cm$^{-3}$ N vacancies are generated for the irradiation fluence of $10^{16}$ cm$^{-2}$. 
present in the sample acting as shallow traps for positrons. The decomposition of the lifetimes was not possible above 600 K due to the use of a different spectrometer for the high T experiments.

The temperature dependence of the average lifetime can be modeled using the kinetic trapping model for positrons. The average lifetime can be written as $\tau_{\text{ave}} = (1 - \eta_1 \tau_B + \eta_1 \tau_V$, where $\tau_B$ and $\tau_V$ are the positron lifetimes in the AIN lattice and the Al vacancy, respectively, and $\eta_1$ is the annihilation fraction at Al vacancies given by $\eta_1 = \frac{\kappa_V}{(1 - \kappa_V)}$. The trapping rate $\kappa_V$ is related to the vacancy concentration $[V] = [V]_0 e^{-E_a / kT}$, where $[V]_0$ is the atomic density of AlN. Vacancy and negative ion concentrations, and also the binding energy of positrons to the negative ions, can be obtained from the behavior of the average lifetime by taking into account also the thermal escape from the Rydberg states of the negative ions.

The trapping model with negatively charged vacancies and negative ions fits well to the experimental data in Fig. 1. For the as-grown sample we obtained an Al vacancy concentration of $1 \times 10^{18}$ cm$^{-3}$ and a negative ion concentration of $1 \times 10^{19}$ cm$^{-3}$. Here we have used $\mu_V = 3 \times 10^{15} \times (300 K)^{3/2} s^{-1}$ for the negative defects. In the case of the irradiated samples, the fit gives concentrations of $4 \times 10^{18}$ cm$^{-3}$ and $3 \times 10^{19}$ cm$^{-3}$ for vacancies and negative ions, respectively, with the Al vacancy concentration being in good agreement with the SRIM estimate. The fit deviates from the experimental data slightly above 400 K. This is due to a slight recovery of the irradiation damage starting at above 400 K, and is observable as a decrease of $\tau_{\text{ave}}$ by 3 ps at RT after the measurement at 600 K. This behavior is, however, the only effect on the data: The $\tau_{\text{ave}}$ versus T after measuring the irradiated sample at 600 K is qualitatively similar (not shown) to that measured right after irradiation. The positron binding energy to the shallow traps (negative ions) is $E_B = 140 \pm 5$ meV in both cases. The high binding energy suggests that the negative ions are in the 2$\bar{\text{+}}$ charge state.

Coincidence Doppler measurements were performed in order to obtain direct evidence of the chemical surroundings of the Al vacancy. The measurements were performed at 600 K for the as-grown sample in order to minimize the effect of the negative ions, and at 400 K for the irradiated sample in order to avoid recovery of the defects. Based on the lifetime experiments, the annihilation fractions of positrons at Al vacancies are 43% for the as-grown sample at 600 K and 27% for the irradiated sample at 400 K. The annihilation fractions are used to extract the vacancy-specific Doppler spectrum $\rho_V$ through $\rho_{\text{meas}} = (1 - \eta_1 \rho_B + \eta_1 \rho_V$, where $\rho_{\text{meas}}$ is the measured spectrum and $\rho_B$ that specific of the AIN lattice.

Figure 2 shows the experimental coincidence Doppler spectra as a ratio to the spectrum of the AIN lattice (obtained in the AlN crystal with the lowest $\tau_{\text{ave}}$ = $\tau_B$). The figure also shows theoretical calculations for the isolated $V_{\text{Al}}$, $V_{\text{Al}}^\text{O}_N$, $V_{\text{Al}}-V_N$ and $V_{\text{Al}}-H$. Clearly the experimental curve of the as-grown sample is in the best agreement with $V_{\text{Al}}^\text{O}_N$. Especially the shoulder with intensity $\geq 1$ around 1.5 a.u.;
Hence it is evident that the transition involves concentration (10 cm$^{-1}$ V). Although it has been theoretically predicted to have an energy level above the valence-band edge (VBE),$^{28,29}$ whereas N vacancies have an energy level at around 5.9 eV above the VBE.$^{30}$ Hence it is evident that the transition involves V$_{Al}$ and some unidentified donor: V$_{N}$ is a good candidate as they are rather certainly introduced by the irradiation as well. The increase in the absorption observed above 4.0 eV may also be related to V$_{Al}$, but conclusive evidence cannot be obtained due to the high position-related variation at these wavelengths.

Defect complexes such as V$_{Al}$-O$_{N}$ and V$_{Al}$-2O$_{N}$ have been reported to cause absorption in the deep UV,$^{10}$ but our results suggest that isolated Al vacancies can also cause absorption at these wavelengths. Interestingly, the comparison of the GDMS-estimated O concentration ($\lesssim$10$^{18}$ cm$^{-3}$) and the V$_{Al}$-O$_{N}$ concentration (10$^{18}$ cm$^{-3}$) indicates that most, if not all, of the O atoms have a neighboring Al vacancy in as-grown single-crystal AlN. This is very different from, e.g., GaN, where typically $[V_{Ga}-O_N]$ $\approx$ 0.01 $\times$ [O] for O concentrations well above 10$^{17}$ cm$^{-3}$.

In summary, we have studied in-grown and irradiation-induced Al vacancies in AlN single crystals. By combining coincidence Doppler broadening spectroscopy with $ab$ initio calculations, the as-grown samples were found to contain V$_{Al}$-O$_{N}$ vacancy complexes (concentration $1 \times 10^{18}$ cm$^{-3}$) as the dominant form of V$_{Al}$, whereas irradiation introduces isolated V$_{Al}$. Our results indicate that UV absorption is caused by Al vacancies, and that most if not all of the O atoms have a neighboring Al vacancy. Hence reducing O concentration in AlN should lead to improved UV transparency.

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