Defect Dynamics Observed by NMR of Quadrupolar Nuclei in Gallium Nitride

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Defects in semiconductors can have a crucial influence on their electronic and optical properties. The influence of static defects has been extensively studied by NMR spectroscopy, but studies of defect dynamics, i.e. motion involving either atoms or electrons, are rare. In principle, quadrupolar nuclei with half-integral spin offer unique prospects for studying dynamical processes that produce changes in the electric field gradient (efg) at the nucleus, and hence the nuclear quadrupole coupling constant (NQCC). Such nuclei have the advantage that the central transition ($^1/_2 \rightarrow -^1/_2$) is unaffected by the NQCC to first order, whereas the satellite transitions (i.e. $\pm^1/_2 \rightarrow \pm^3/_2$) are so affected. We report here novel manifestations of such dynamics in high-field NMR results for ^{69}Ga and ^{71}Ga (both $I = ^3/_2$) in gallium nitride, which has two polytypes that we have characterized by ^{69,71}Ga and ^{14}N MAS NMR: the hexagonal wurtzite form (h-GaN) and the cubic zincblende form (c-GaN). Gallium nitride, because of its high bandgap (3.4 eV), is one of the most promising III–V semiconductors both for optical devices in the blue and UV regions as well as for high-power, high-temperature electronics applications.[1,2] Chemical synthesis of bulk GaN is important for several reasons. First, there is considerable interest in GaN nanodots, nanowires, and nanotubes, where defect concentrations are likely to be high. Second, growth of large single-crystals of GaN to serve as homoepitaxial substrates is desirable but not yet feasible. The novel spectroscopic signature of defects in some of the bulk GaN samples we have investigated comprises two features: much weaker (and broader) ^{71}Ga MAS NMR satellite transitions than expected, and a marked decrease in the apparent T_2 value measured by static ^{69,71}Ga spin-echo experiments on the satellite transitions with increasing temperature. Such behavior is wholly unexpected for a rigid solid with directional semi-covalent bonds that decomposes before it melts at very high temperatures. We show that a previously unidentified thermally activated process is responsible for the reduction in both spin–echo and rotational echo[3] amplitudes, and discuss as a possible mechanism a dynamic equilibrium involving partially ionized donor defects and electrons in the conduction band.

The sample of h-GaN was prepared in a Na/K flux as previously reported,[4] and the c-GaN sample was prepared by ammonothermal transport from a h-GaN feedstock using a $NH_4Cl/LiCl$ mineralizer according to the procedure described for experiment 62 in the same reference. The mixed sample (cubic + hexagonal) was prepared from an ammonothermal reaction between Ga and NH_4Br in a Pt-lined autoclave and consists of segmented needles of h-GaN covered with a dendritic "fuzz" that is mostly c-GaN. X-ray powder diffraction confirmed that the h-GaN, c-GaN, and mixed samples were 98% h-GaN/2% c-GaN, 97% c-GaN/3% h-GaN, and 55% h-GaN/45% c-GaN respectively.

The ^{71}Ga MAS NMR spectra of h-GaN and c-GaN are shown in Figure 1. The NQCC in h-GaN is ca. 1.76 MHz, and the efg tensor is axially symmetric (for ^{69}Ga the NQCC is ca. 2.8 MHz), as previously measured in single crystals.[5] Although the NQCC in the ideal cubic form should be zero due to the perfect tetrahedral bonding symmetry, the nearly-Gaussian envelope of the satellite
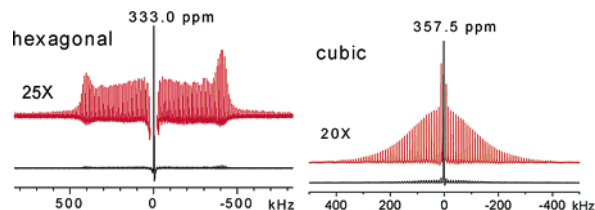
Figure 1. ^{71}Ga MAS-NMR spectra at 11.7 T (152 MHz) and 9.000 kHz spinning speed (sample at ca. 304 K) for two nearly-pure polytypes of GaN. Satellite transitions reflecting the NQCC's and spaced at intervals of the spinning speed are shown in the vertical expansions. Chemical shifts (1 M gallium nitrate reference) given above the central transitions include a +3 ppm correction for the second-order quadrupolar effect in h-GaN, whose shift has been reported previously.[6]
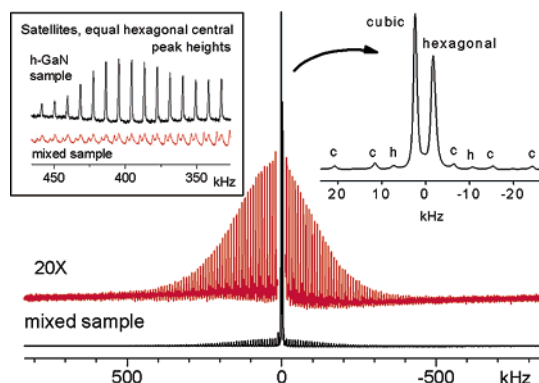

Figure 2. ^{71}Ga MAS-NMR spectrum at 11.7 T and 9.000 kHz spinning speed (sample at ca. 304 K) of the mixed sample. Satellite transitions reflecting the NQCC's in the cubic, but not hexagonal, form are evident in the vertical expansion (FID was left-shifted to second rotational echo to minimize artifacts). Using the same trapezoidal apodization as for h-GaN in Figure 1 shows (upper left inset) that the satellite transitions from the hexagonal form are much weaker and broader than in the h-GaN sample.

transitions has a half-height width of 297 kHz. This is over an order of magnitude larger than observed in other cubic III–V semiconductors for ^{71}Ga and other nuclei,[6] suggesting higher concentrations of defects and/or a greater effect from each individual defect.

The cubic and hexagonal forms can also be distinguished on the basis of their ^{14}N MAS NMR spectra (not shown). The chemical shift of h-GaN is −301.8 ppm, and that of c-GaN is −297.0 ppm relative to 1 M $Ga(NO_3)_3$ solution. The spinning sideband pattern of c-GaN has a Lorentzian envelope with a half-height width of 17.5 kHz, arising from defects in the sample.

Figure 2 shows the ^{71}Ga MAS NMR spectrum of the mixed sample, which contains comparable amounts of cubic and hexagonal polytypes based on the two central transition peaks seen at the corresponding chemical shift positions (as well as on the ^{14}N MAS NMR spectrum). The Gaussian envelope of satellite transition intensities for the cubic form has a half-height line width of ca. 300 kHz, the same as that seen for the c-GaN sample in Figure 1, suggesting that defects in the two different sample preparations are identical in type and level. However, the satellite transitions for the hexagonal phase in the mixed sample are much weaker (and
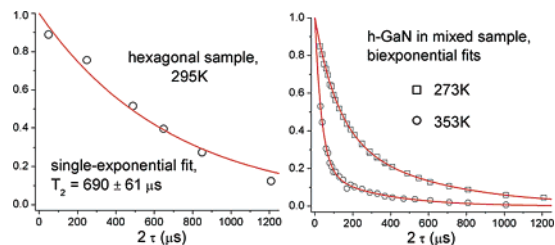
Figure 3. ^{71}Ga static Hahn spin−echo decay curves at the perpendicular edge position for hexagonal GaN in two different samples. The curves are normalized to unity at zero time for the theoretical fit. The left side shows a relatively long apparent decay time T_2 in the h-GaN sample. In contrast, the hexagonal form in the mixed sample exhibits significantly more rapid, and biexponential, decay at both higher and lower temperatures. The best-fit decay time and (percentage) amplitude values are: at 273 K, 116 μs (57%) and 509 μs (43%); at 353 K, 36 μs (81%) and 308 μs (19%).

broader) than those in the h-GaN sample. This behavior suggests that some dynamical process is interfering with the formation of rotational echoes.[3]

To verify the existence of such a process and to study it, we carried out static ^{71}Ga variable-temperature experiments at the predicted position of the perpendicular edge of the satellite pattern, 440 kHz to higher frequency than the center, where there is only a minor contribution from the satellite transitions of the cubic form. We used a 90-τ−180-τ Hahn spin-echo sequence with the *selective* pulse lengths appropriate for a $\pm^1/_2 \rightarrow \pm^3/_2$ satellite transition.

The results, shown in Figure 3, clearly demonstrate that the proximate cause of the strong attenuation of the ^{71}Ga satellite transitions of the hexagonal form seen in Figure 2 is a markedly shorter T_2 for the hexagonal form in this sample (the biexponential character may be due to a minor contribution from the cubic form). This decrease is more pronounced at higher temperatures, indicative of a thermally activated process. In principle, modulations of a number of terms in the NMR spin Hamiltonian could be responsible for frequency changes at a ^{71}Ga nuclear site, causing the spin-echo to decay more rapidly. We can rule out fluctuating chemical shift or Knight shift terms, since the ^{71}Ga T_2 biexponential decay parameters of the perpendicular edge at 313 K were measured to be identical at two field strengths, 11.7 and 7.05 T. Other possible interactions with the gallium nucleus' magnetic moment (e.g., electron hyperfine, dipolar, exchange) can be eliminated by the observation that the second-order broadened ^{69}Ga central transition at 7.05 and 313 K (which extends beyond the sharper cubic central transition) has a T_2 of ca. 518 μs, much longer than the perpendicular edge satellite transition short T_2 at the same temperature (49 μs, measured at 11.7 T for sensitivity), and decreases only slightly at 353 K. We conclude that a dynamical process involving modulation of the NQCC about some value reflecting the static structure is involved in the observed destruction of ^{71}Ga MAS NMR satellite transitions for h-GaN in the mixed sample.

We can view this process as a type of chemical exchange,[7] where the gallium sites remain fixed in space but movement of other atoms (or vacancies) or of electrons (or holes) produces a frequency shift via a changed electric field gradient, corresponding to a new site. (A process involving thermal ionization of donors to produce electrons in the conduction band would exhibit unusual effects of increasing temperature, since the modulatory effects are initially augmented by the increasing number of ionized donors with increasing temperature, but ultimately in a higher-temperature regime are diminished by the decreasing number of un-ionized donors with increasing temperature.) We note that a quadrupolar process in the weak-collision limit corresponding to fast chemical exchange[7]

follows the square of the nuclear electric quadrupole moment and would yield a ^{71}Ga-to-^{69}Ga spin-echo T_2 decay time ratio of 2.53 due to the larger nuclear quadrupole moment of ^{69}Ga. The ratio of the experimental ^{71}Ga and ^{69}Ga spin-echo T_2 decay times (short component) of the corresponding perpendicular edge satellite transitions measured at the intermediate temperature of 313 K yields a direct ratio of 1.51, and a ratio of 1.56 when the experimentally determined T_2 rates for ^{69,71}Ga in the h-GaN sample are subtracted from the corresponding much faster rates in the mixed sample (the long T_2 components, approximately 25% of the signal, were equal within experimental error). Thus, it appears that the dynamical process does not exclusively involve the fast-exchange regime.

In the slow-exchange regime, unlike the fast-exchange regime, spin-echo amplitudes for spin-$^1/_2$ nuclei have been calculated to decrease as the exchange rate increases,[8] but we would expect no simple relationship of the decay time either to the nuclear quadrupole moment or to the time constant of the process. Thus, a simple Arrhenius plot of $[T_2^{-1}(\text{observed}) - T_2^{-1}(\text{no dynamics})]$ vs $1/T$ is not strictly meaningful. Such a plot did yield a straight line with a correlation coefficient of 0.988 for four temperatures between 273 and 353 K with a slope corresponding to an activation barrier of 132 meV, using as the T_2^{-1}(no dynamics) limiting value the 180 K value measured in the same sample. We note that diffusion of atomic species or vacancies at room temperature in a solid such as GaN is not expected to occur; for hydrogen species, which might be expected to diffuse most rapidly, the theoretical activation barrier in GaN is from 500 to 1500 meV,[9] with the larger value agreeing with an experimental value.

Thus, the dynamical process is most likely *electronic* in origin. A dynamic equilibrium involving fixed un-ionized and ionized donors and electrons in the conduction band could produce the type of effects seen. Indeed, perturbed-equilibrium experiments in GaN (and other semiconductors) have demonstrated electron emission rates from traps on slow (ms to s) time scales.[2] Interestingly, we have also observed analogous behavior in the c-GaN sample, but at slightly higher temperatures. The novel NMR manifestations of dynamics resulting from semiconductor defects that we report here and attribute provisionally to electronic effects may also be observable in polycrystalline or nanocrystalline samples of other semiconductors possessing quadrupolar nuclei, as well as in film samples. They offer unique opportunities to characterize dynamical as well as structural aspects of defects in important semiconductors.

Supporting Information Available: Full experimental details, additional characterization data including SEM micrographs of GaN samples; ESR, Raman, and fluorescence data and additional ^{69,71}Ga and ^{14}N NMR data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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