Enhanced radiative efficiency in GaN nanowires grown on sputtered TiN$_x$

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GaN nanowires grown by molecular beam epitaxy generally suffer from dominant nonradiative recombination, which presumably originates from point defects. To suppress the formation of these defects, we explore the synthesis of GaN nanowires at temperatures up to 915°C enabled by the use of thermally stable TiN$_x$/Al$_2$O$_3$ substrates. These samples exhibit indeed bound exciton decay times approaching those measured for state-of-the-art bulk GaN. However, the decay time is not correlated with the growth temperature, but rather with the nanowire diameter. The inverse dependence of the decay time on diameter suggests that the nonradiative process in GaN nanowires is not controlled by the defect density, but by the field ionization of excitons in the radial electric field caused by surface band bending.

The recombination dynamics in GaN nanowires (NWs) synthesized by molecular beam epitaxy (MBE) is governed by nonradiative processes even at cryogenic temperatures. In fact, the typical decay times of the donor-bound exciton line in low-temperature photoluminescence (PL) spectra of GaN NWs with diameters between 30 and 200 nm range from 0.1 to 0.25 ns [1–4], i.e., they are significantly shorter than the radiative lifetime of the bound exciton in bulk GaN of at least 1 ns [5]. Obvious candidates for nonradiative recombination are the NW surface [6] and dislocations generated by NW coalescence [7, 8]. However, Hauswald et al. [3] showed that the decay time does not exhibit any obvious trend with either the surface-to-volume ratio or the coalescence degree and thus suggested that the nonradiative channel originates from point defects. This view was supported by subsequent work of Zettler et al. [9], who observed an increase of the decay time from 0.14 to 0.36 ns upon thinning NWs by partial thermal decomposition of a NW ensemble. This striking result was tentatively attributed to a reduction of the density of native point defects by the high-temperature (920°C) annealing of the thinned NWs obtained by sublimation.

The optimum growth temperature to minimize the point defect density in solids is a trade-off between the limited kinetics at low and the increasing entropy at high temperature and is expected to be close to half the melting point of the material ($\approx$1100°C for GaN) [10, 11]. Accordingly, Zettler et al. [12] proposed to push the growth regime for GaN NWs to far higher temperatures ($\gg$800°C). However, the authors only reached a maximum temperature of 875°C, at which Ga-induced melt-back etching of the Si(111) substrates was observed to set in, resulting in a substantial incorporation of Si into the GaN NWs. For GaN NW growth at even higher temperatures, a thermally and chemically more robust substrate is required. Wölz et al. [4] demonstrated the use of δ-TiN(111) films obtained by surface nitridation of a thick Ti layer deposited onto α-Al$_2$O$_3$(0001), but this layer was found to react with both the impinging Ga flux and the substrate, with the latter reaction inducing the incorporation of O into the GaN NWs at high growth temperatures [13]. Other groups have used Ti films on different substrates or thick Ti foils, but NWs always formed on a superficial TiN film obtained by nitridation prior to growth [14–17], leaving the substrate susceptible to reactions with Ga. Note that this interest in TiN as a substrate for GaN NWs has various reasons: besides its refractory properties, it is metallic in nature, and its chemical inertness results in a low nucleation density facilitating the fabrication of GaN NW ensembles virtually free of coalescence and the associated structural defects [8, 18].

In this Letter, direct sputtering of TiN$_x$ on Al$_2$O$_3$ is chosen as a new approach for preparing the GaN NW substrate. In contrast to Ti, TiN is stable against Al$_2$O$_3$ up to temperatures far exceeding those usable for the synthesis of GaN in MBE. The TiN$_x$/Al$_2$O$_3$ substrates allow us to fabricate GaN NW ensembles in a temperature range of 855–915°C. The bound exciton lifetimes of these ensembles are longer than any values reported previously for NWs with diameters between 30 and 200 nm, but do not exhibit the expected trend to get longer with increasing growth temperature. Instead, we observe a correlation with the mean diameter of the ensemble, pointing toward exciton dissociation in the radial electric fields in the NWs as the actual mechanism controlling the effective nonradiative lifetime.

The δ-TiN$_x$ films are deposited onto α-Al$_2$O$_3$(0001) wafers by reactive sputtering of a Ti target in a mixed Ar/N$_2$ gas environment. The stoichiometry of the films is controlled by tuning the Ar:N$_2$ gas composition [19] and the parameters selected are summarized in Table I. During sputtering, the substrate is heated to 300°C and, unless otherwise mentioned (see Table I), biased at 100 V relative to the target and chamber walls [20]. The 700 nm-thick sputtered films are subsequently transferred in ultra-high vacuum into the MBE chamber to prevent surface oxidation and contamination.

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TABLE I. Parameters for the synthesis of TiN₄ films and GaN NWs. A ramp between two values is indicated by ↗ and ↘.

| Samples | A    | B    | C    | D    |
|---------|------|------|------|------|
| TiN₄ films |      |      |      |      |
| \( \Phi_A (\text{scm}) \) | 13.5 | 13.5 | 13.5 | 12 ↗12.8 |
| \( \Phi_{N_2} (\text{scm}) \) | 1.5  | 1.5  | 1.5  | 3 ↘2.2  |
| Bias (V) | 100  | 100  | 100  | 0     |
| GaN NWs |      |      |      |      |
| \( T_{\text{sub}} (^\circ \text{C}) \) | 855  | 855  | 900  | 855 ↘915 |
| Ga/N flux ratio | 0.4  | 0.4  | 0.4  | 1.3 ↘0.4 |
| Growth time (min) | 90   | 120  | 220  | 120   |

In the MBE chamber, the growth temperature is measured by a pyrometer calibrated with the 7×7 → 1×1 reconstruction transition of a clean Si(111) surface occurring at 860 °C [21]. The emissivity of TiNₓ₋₁ is assumed to be equal to that of stoichiometric TiN, namely, 0.21 [22]. Prior to GaN growth, the TiN_{x} film is annealed at 955 °C under a N flux of 1.2×10¹⁵ cm⁻²s⁻¹ for 25 min. This annealing step results in a bright and streaky TiN, diffraction pattern as observed by reflection high-energy electron diffraction, indicating a smooth and well-ordered surface. NW nucleation is subsequently initiated by exposing the TiN film to Ga and N fluxes while ramping the growth temperature to the desired fluxes. All NW growth runs are performed with a N flux of 1.2×10¹⁵ cm⁻²s⁻¹.

The phase content of the TiN_{x} films is analyzed by symmetric triple-axis \( 0/20 \) x-ray diffraction (XRD) scans acquired with CuK\( \alpha_1 \) radiation. Their stoichiometry is estimated from the first-order transverse acoustic (TA) phonon energy in Raman spectra [23] measured in backscattering geometry using a laser wavelength of 473 nm. The radiative and nonradiative decay of excitons in the GaN NWs is probed by continuous-wave (cw) photoluminescence (PL) and time-resolved PL (TRPL) spectroscopy. In both cases, an excitation wavelength of 325 nm is used, with an intensity below 10 kWcm⁻² (10 Wcm⁻²) at 300 K (10 K) for the former and 200 fs pulses with a fluence below 0.1 µJcm⁻² for the latter.

Analogously to GaN NW growth on Si(111) substrates [24], the nucleation of GaN NWs on TiN_{x} is preceded by an incubation time during which no stable GaN nuclei form on the surface. On stoichiometric TiN, this incubation time exceeds 1 h already at a moderate growth temperature of 800 °C and a Ga flux as large as 1.2×10¹⁵ cm⁻²s⁻¹ (III/V ratio of 1). At higher temperatures, no GaN NWs form for any practical time span. The incubation time is found to drastically decrease on TiN_{x} films with a certain N deficiency. Specifically on TiN₀.₈₈, the incubation time is shorter than 5 min at a growth temperature of 855 °C and with a Ga flux of 0.5×10¹⁵ cm⁻²s⁻¹, which we adopt as the conditions for NW nucleation for the present samples A–D. The substrate temperature is increased during the NW elongation stage [25] for samples B and C. The enhanced thermal decomposition of GaN at 915 °C is partially compensated by a larger Ga flux for sample C. All growth parameters for samples A–D are summarized in Table I.

Figure 1(a) shows bird’s eye view secondary electron micrographs of the NW ensembles A to D. The increase in temperature from sample A to B to C results in shorter NWs and a reduction of the NW density from 2.5×10¹⁰ to less than 1.0×10⁹ cm⁻². The NWs are vertical due to a strict epitaxial orientation relationship with the single-crystalline TiN_{x} (111) film: the width of the out-of-plane and in-plane orientation distributions as measured by XRD \( \phi \) and \( \phi \) scans recorded for sample A (not shown here) are below 0.7°. The random orientation of NWs observed for sample D is again caused by an epitaxial alignment, but in this case the TiN film is polycrystalline due to the absence of a substrate bias during sputtering.

Figure 1(b) depicts the distributions of diameter \( d \) for samples A–D. The histograms are fit by a shifted \( \Gamma \) distribution yielding the mean diameter \( \langle d \rangle \). Also shown is the diameter distribution weighted by the NW volume, which is the relevant quantity for experimental techniques returning a signal proportional to the amount of probed material such as PL spectroscopy. Evidently, higher growth temperatures do not only decrease the NW density (see above), but also result in smaller mean diameters and narrower diameter distributions as a result of a reduced NW coalescence [18, 26]. Ensemble D is an exception in that it features a much narrower diameter distribution compared to sample A nominally grown under the same conditions. This difference stems from the random orientation of the NWs in sample D, which effectively inhibits their coalescence by bundling [27]. Ensemble D is thus essentially coalescence-free despite a relatively high NW density (5×10⁹ cm⁻²).

Figures 1(c) and 1(d) show Raman spectra and radial XRD scans, respectively, of samples A and D together with a representative Raman spectrum of an as-sputtered TiN_{x} film. For sample A, modes from the TiN_{x} film (TA, LA, TO, A+O) [23] and from the GaN NWs (A₁ and E₂) are visible. The TA mode shifts from 248 before to 242 cm⁻¹ after the NW growth, evidencing a reduction of the concentration of N vacancies due to the prolonged annealing during growth. The same spectral position, corresponding to \( x = 0.93 \) [23], is observed for samples B and C after growth. In the XRD profile of sample A (as well as for B and C), we detect a strong and sharp TiN 111 reflection as for stoichiometric TiN [28], but also two weak additional reflections. The angular position, intensity, and width of these reflections indicate that our TiN_{x} films contain nanoscopic inclusions of Ti and \( \varepsilon \)-Ti₂N with a total volume on the order of 1%.

Sample D is different in all these regards. First, the TA mode shifts from 248 to 200 cm⁻¹ after growth, the value for stoichiometric TiN [23]. Clearly, the polycrystalline nature of this TiN film expedites the annihilation of N vacancies. Second, the TiN 111 reflection for sample D is weak due to the polycrystalline nature of this film, and the NWs are barely detected because of their large orientational spread.

Figure 2(a) displays the PL spectra of our samples recorded...
under cw excitation at both 300 and 10 K. The energy of the respective emission band identifies the transitions as being due to the radiative decay of the free \( X_A \) and the donor-bound-bound \((D^0, X_A)\) exciton, respectively. However, the emission energy is diameter dependent and not identical to that of bulk GaN as usually observed for NWs with larger diameters, but exhibits on average a blueshift with decreasing diameter (see the respective insets). Several mechanisms have been identified that can shift the transition energy for thin NWs, namely, surface donor-bound excitons \([2, 29, 30]\), surface stress \([31]\), and dielectric confinement \([9]\). Since the shift depends on diameter, all of these mechanisms result in a broadening of the ensemble spectra as primarily observed here for samples B and D. In addition, NWs with a very small volume may not contain even a single donor \([32]\) so that the free-exciton transition may appear to be strongly enhanced in low-temperature ensemble spectra as seen here particularly for sample B.

PL intensity transients of the \((D^0, X_A)\) line obtained upon pulsed excitation at 10 K are shown in Fig. 2(b). The biexponential decay was shown to arise from a coupling of the exciton states \([33]\) with the initial decay time reflecting the actual lifetime of the \((D^0, X_A)\) state \([33]\) that so far remained mostly in the range from 0.1 to 0.25 ns \([3]\). For the present samples, exceptionally long initial decay times between 0.35 and 0.72 ns are observed, but not the expected correlation with the growth temperature. In particular, sample D features a decay time twice longer than the one of sample A grown at the exact same temperature. A comparatively clear trend is evident instead when correlating the decay time with the volume-weighted diameter \(\langle d_v \rangle\), as shown in Fig. 2(c), suggesting that the decay time increases with decreasing diameter. As a matter of fact, such a behavior was observed previously by Zettler \etal\ [9] and interpreted as an effect of NW annealing on the point defect density. Our results suggest that the key parameter is the NW diameter itself, calling for a reevaluation of the mechanism responsible for the nonradiative exciton decay in GaN NWs.

At this point, it is important to recall that band bending occurs in GaN NWs due to the presence of surface states at their oxidized \(\{11\overline{1}0\}\) sidewall facets \([34, 35]\). A reduction of the band bending was observed to enhance the intensity of the \((D^0, X_A)\) line \([36]\), suggesting that the electric field associated with the band bending triggers the nonradiative decay of the \((D^0, X_A)\) state, while the more strongly bound excitons remain unaffected \([37]\). These findings can be understood when taking into account that the actual nonradiative decay was shown to take place via the free exciton due to the strong coupling of free and bound exciton states \([3, 37]\). The nonradiative decay is thus initiated by the field ionization of the free exciton, i.e., the tunneling of an electron out of the Coulomb potential created by the hole \([38]\). Subsequently, holes are driven to the surface, recombine with filled surface states, followed by electrons filling the now empty states once more. These capture processes are rapid, and field ionization thus represents the rate-limiting step for nonradiative recombination.

For a continuous and homogeneous charge distribution and assuming the NW to be fully depleted, the electrostatic potential within the NW is parabolic \([39]\). The maximum electric
FIG. 2. (a) cw-PL spectra and (b) band-edge PL transients integrated (±15 meV) over the \( (D^0, X_A) \) line of samples (A–D). Measurement temperatures are given in the respective diagram. The insets in (a) show the peak energy vs. the mean diameter of the ensemble. The dotted lines in (b) are monoexponential fits of the initial decay times, which are also given in the figure. (c) \( (D^0, X_A) \) decay time versus the average NW diameter for samples A–D and samples from other experimental studies. Large filled circles with horizontal error bars correspond to \( \langle d_m \rangle \), whereas small filled circles refer to \( \langle d \rangle \). Diameters from other publications are not weighted and are overestimated in the particular case of Ref. 9. \( \tau_E \) is the calculated dissociation time of the free exciton in the electric field at the NW sidewall surface. The insets (i)–(iii) depict different band bending configurations for different NW diameters.

The insets (i) to (iii) of Fig. 2(c) illustrate the evolution of the radial band profile of a NW with its diameter. Below a critical diameter \( d_c \), the NW is fully depleted, resulting in \( F_m \propto d \). In sufficiently thin NWs (i), the decay time is thus not affected by the electric field, but represents the actual lifetime of the \( (D^0, X_A) \) state. The 0.72 ns decay time for sample D approaches the longest values measured for state-of-the-art GaN layers (1 ns), and even thinner NWs may thus help to settle the question whether this value represents the true radiative lifetime. With increasing diameter up to \( d_c \) (ii), a dead zone develops close to the NW surface, since the surface electric field becomes strong enough to ionize excitons virtually instantaneously. Radiative recombination can then only occur in the NW core, in which the radial field stays sufficiently small. For example, for a doping density of \( 8 \times 10^{10} \) cm\(^{-3} \), the electric field does not exceed 10 kV/cm (corresponding to \( \tau_E = 0.12 \) ns) within the inner 26 nm of the NW. For NWs with a diameter \( d > d_c \) (iii), the surface electric field is determined only by the doping level, and the space charge layer occupies an increasingly smaller portion of the NW. Field ionization of excitons is then limited by their diffusion toward the NW sidewalls, and the nonradiative lifetime becomes proportional to the NW diameter, resembling surface recombination. The resulting slowdown of nonradiative recombination with NW diameter is consistent with the long decay times of about 0.5 ns observed for NWs with a diameter of 400 nm [cf. Fig. 2(c)] [41, 42].

The mechanism detailed above also accounts for other experimental results. For example, the nonradiative lifetime in GaN NWs was observed to be essentially independent of both temperature (between 10 and 300 K) and excitation density (over four orders of magnitude) [3], which cannot be understood within the conventional framework of defect-mediated nonradiative recombination. When considering field ionization of excitons as the rate-limiting step, both findings are easily understood: first, the band bending in the NWs originates from the charge transfer from the bulk into surface states and is thus essentially independent of temperature. Equally important, the exciton binding energy in GaN is sufficiently high for excitons still dominating the spontaneous emission at room temperature. Second, the number of surface states in a NW is very high compared to that of point defects in its bulk, rendering the nonradiative channel hard to saturate.

Having identified the origin for the highly effective nonradiative channel for GaN NWs, the remedy becomes obvious. Since the nonradiative decay is mediated by the field ionization of excitons, the radial electric fields should be eliminated or at least reduced. This task can be achieved by either reducing unintentional doping or, perhaps more practical, by a suitable surface passivation [43, 44]. We finally note that the mechanism described in this work is not restricted to GaN NWs, but applies to NWs in general and may affect materials with lower exciton binding energy even more severely.

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