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Origin of the unusually strong luminescence of *a*-type screw dislocations in GaN

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Based on luminescence studies and density functional theory calculations we identify the origin of the unusually strong luminescence of *a*-type screw dislocations in GaN. In contrast to previous models where only a localization of the holes was considered, density functional theory calculations show a localization of both electrons and holes in the dislocation strain field. This strain field causes a mixing of the *s*-type state at the conduction band minimum with the next highest state that has *p* character and is thus susceptible to the shear strain induced by the dislocation.

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Dislocations are linear defects that induce electronic states into the forbidden gap of semiconductors. Commonly deep states are assigned to the presence of dangling bonds along the dislocation core [1,2] while shallow states are allotted to the long-range strain field of the dislocation causing a shift of the band edges [3–6]. According to this generally accepted picture, charge carriers either recombine nonradiatively at the dislocation core or they may be bound in the form of excitons in one-dimensional bands split off from the valence and conduction bands due to the long-range strain field. These bound excitons can be measured by photoluminescence and appear there in the form of optical transitions redshifted from the band edges [7,8]. A particularly interesting case is the perfect screw dislocation in a direct band gap semiconductor. The core of a perfect screw dislocation has no dangling bonds and exhibits in first order a pure shear strain field. According to theoretical work based on effective mass theory and deformation potentials, the shear stresses will not affect the *s*-type conduction band minimum but only the *p*-type valence band maximum. Thus, such screw dislocations would bind exclusively holes [6,9]. Excitons then are formed by binding electrons to these bound holes by Coulomb interaction.

GaN is considered a model system for group III nitride semiconductors. Screw dislocations with *a*-type Burgers vector (Burgers and line vectors $b = \frac{1}{3}\langle 11\bar{2}0\rangle$ and $l = \frac{1}{3}\langle 11\bar{2}0\rangle$, respectively) are the most important threading dislocation in III-nitride heterostructures grown on nonpolar and/or semipolar substrates. Strained heterostructures with these orientations have recently attracted considerable interest in optoelectronic applications, since they allow us to reduce the quantum confined Stark effect and thereby to improve the efficiency of light-emitting devices [10,11]. In the present paper we will present a combined experimental and theoretical work on dislocation-bound excitons at individual *a*-type screw dislocations.

Our experimental analysis of *a*-type screw dislocations, freshly induced into semi-insulating GaN bulk crystals by scratching, show strong polarized luminescence at 3.34 eV. We further investigated the electronic structure of these defects by developing and applying a quasicontinuum approach that combines first-principles calculations with elasticity theory. Our analysis shows that, in contrast to previous calculations based on continuum approaches, *a*-type screw dislocations show bound states both for electrons *and* holes. Electrons are localized in a region close to the dislocation core and are related to the associated high strain field. We will show that this strain field induces a mixing of the *s*-type state at the conduction band minimum with the next highest state that has *p* character and is thus susceptible to the shear strain induced by the dislocation. The rehybridized band bends downwards and provides a confining potential well for electrons close or in the defect core.

Screw dislocations with *a*-type Burgers vector were produced by scratching the (0001) surface of a 500 μm thick semi-insulating GaN:Fe crystal with a diamond cone at room temperature [12]. The crystal, grown by halide vapor phase epitaxy (HVPE), has a dislocation density of 10^6 cm^{-2}. Electronic transitions at these freshly induced dislocations can be considered to be intrinsic and the effect of a possible "Cotrell atmosphere" of impurity atoms trapped by the strain field around the dislocation generally present at grown in dislocations can be excluded [13].

Figure 1(a) shows a spatially integrated photoluminescence spectrum close to the scratch. Besides the band edge luminescence at 3.489 eV, details of which will not be discussed here, a distinct peak at 3.346 eV and its 1LO phonon replica can be seen. A monochromatic cathodoluminescence map with the monochromator set to 3.346 eV is shown in Fig. 1(b). Straight bright lines aligned along $\langle 11\bar{2}0\rangle$ directions can be seen to extend about 30 μm to both sides of the scratch. Cathodoluminescence spectral maps confirm that the observed transitions appear exclusively at those positions where luminescent lines are observed in monochromatic maps. We do not reveal any qualitative difference in the band edge luminescence close to the positions of the luminescent lines and far from them. Contrast analysis by transmission electron microscopy of plane view samples shows these lines to be correlated with *a*-type screw dislocations lying underneath the surface. High-resolution transmission electron microscopy of cross-sectional samples reveals no splitting into partial dislocations; i.e., they are perfect screw dislocations.

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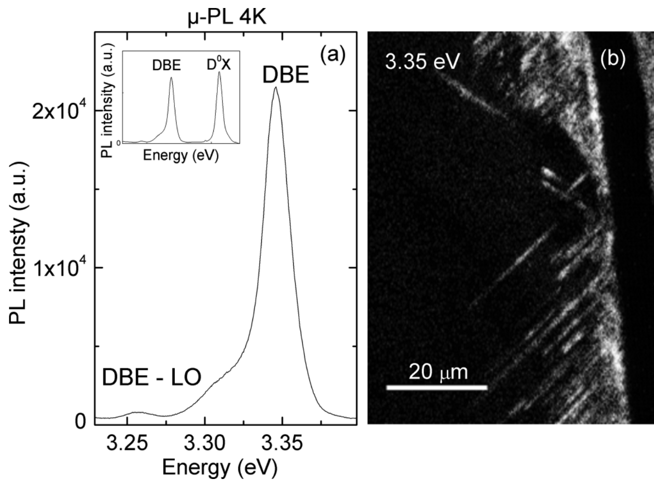

FIG. 1. Luminescence of *a*-type screw dislocations in GaN(0001). (a) PL spectrum of a single *a*-type screw dislocation from a micro-photoluminescence map in semi-insulating GaN taken at 4 K. The spectrum shows a main peak at 3.346 eV and the phonon replica of the main peak. The inset shows the donor-bound exciton (D^0X) and the dislocation-bound exciton in comparison. (b) Monochromatic cathodoluminescence map taken at an energy of 3.346 eV. Straight bright lines correspond to *a*-type screw dislocations aligned along $\langle 11\bar{2}0\rangle$.

To prove the excitonic nature of the transition, excitation and temperature dependent PL has been performed. Figure 2(a) shows the integrated PL intensity at 4 K as dependent on the excitation power. The PL increases linear with excitation power, as expected for an excitonic transition; no shift in the peak position is observed. From the relation of integrated intensity of the zero phonon transition (I_0) and the first phonon replica (I_1) according to $I_0/I_1 = S$ (see, e.g., Ref. [14]) we obtain a small Huang-Rhys factor of $S = 0.017$. The temperature shift of the dislocation transition follows that of the near-band-edge transition. The dislocation-related transition [Fig. 2(c)]

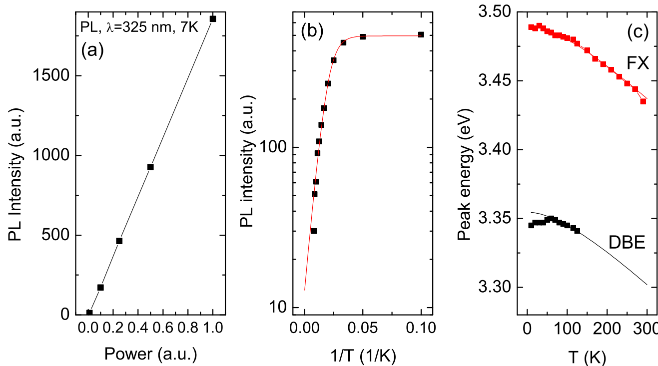

FIG. 2. (Color online) Phototoluminescence of the *a*-type screw dislocation in GaN. (a) Integrated intensity of the PL peak as dependent on excitation power shows a linear increase and no saturation. The line is a guide for the eye. (b) Integrated PL intensity as dependent on *T*. The fit shows a temperature quenching of the photoluminescence with a single activation energy of 16 meV. (c) PL peak position of the band edge luminescence and the dislocation luminescence as dependent on *T*.

quenches with an activation energy of 16 meV, essentially lower than that of free excitons. Polarization-dependent measurements show polarization along the $\langle 11\bar{2}0\rangle$ directions, i.e., collinear with the dislocation line direction; intensity ratios $I_{11\bar{2}0}/I_{1\bar{1}00}$ of 8 : 1 were measured for polarization along and perpendicular to the $\langle 11\bar{2}0\rangle$ line direction.

Our experimental observations of the luminescence properties are consistent with luminescence lines of structurally unknown origin reviewed by Reshchikov *et al.* [15]. In particular they identified a line close to 3.35 eV [16,17] (Y4 in their nomenclature) showing a linear increase in intensity with excitation power, a low Huang-Rhys factor, and no observable wavelength shift of the peak position with excitation power, very similar to ours. The authors assigned this line to a structural defect (dislocation, stacking faults, or inversion domain boundaries).

To get insight into the physical origin of the unexpected strong luminescence of the *a*-type screw dislocation in GaN we continue and model their electronic structure. *Ab initio* calculations would be well suited to calculate the electronic states of the core as well as of the strain field region. However, they may, due to the limited size of presently computable supercells, fail in correctly describing bound states due to the long-range strain field appropriately. Continuum approaches based on the effective mass approximation and deformation potentials (e.g., $\mathbf{k}\cdot\mathbf{p}$ calculations, or numerical solutions of the Schrödinger equation [6,9]) are appropriate to provide a reliable and accurate description of the bound states due to the long-range strain field. A major drawback of treating shallow states due to the long-range strain field by a continuum approach is the treatment of the high strain close to the dislocation core. Electronic states in this region may be affected by contributions that can no longer be represented by linear elasticity and deformation potential coefficients.

In order to tackle the above mentioned problem and provide an accurate description of the electronic properties of screw dislocations we follow a two-step approach: In a first step the electronic structure of the core is identified by calculating the electronic structure of a supercell consisting of 400 atoms. The electronic structure calculations are performed within density functional theory (DFT) using the local density approximation (LDA) and the projector augmented wave approach (PAW) [18,19]. The Ga semicore *d* states are treated explicitly as valence electrons and an on-site Coulomb interaction *U* for the aforementioned states has been included [20]. This approach yields a fundamental bulk band gap of 2.87 eV. The atomic positions are relaxed until the forces on each atom were smaller than 10^{-4} eV/Å. The supercell contains a pair of mutually compensating defects placing a quarter of a screw dislocation with the opposite Burgers vector at the edges of the cell (see inset of Fig. 3) [21,22]. This supercell corresponds to a dislocation quadrupole configuration and includes both the core region as well as elastically deformed material around the core.

To address the effect of the long-range strain field of the screw dislocation on the band edges we implemented an *ab initio*–based quasicontinuum approach that connects DFT computed deformation potentials with analytic as well as the DFT computed strain fields. Specifically, we computed the strain field of an infinite array of screw dislocations in the quadrupole configuration considering two scenarios:

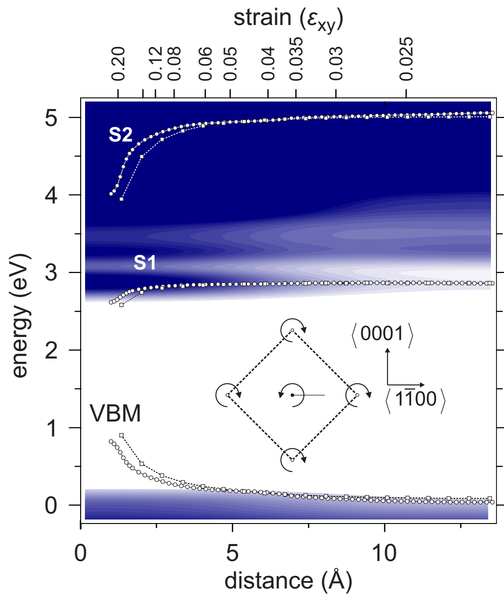

FIG. 3. (Color online) Spatially resolved DOS along the $\langle 1\bar{1}00\rangle$ diagonal of the supercell containing a pair of mutually compensating dislocations in the quadrupole configuration. Darker (lighter) colors correspond to larger (smaller) values, respectively. The energies of the highest occupied state (VBM) and the two lowest unoccupied states (S1 and S2) of bulk GaN are obtained from the quasicontinuum approach using two different approaches: analytical solution (circles) and a fully atomistic one where the strain field is extracted from the DFT supercell calculation (rectangles). Inset: Schematic representation of the supercell containing a pair of mutually compensating screw dislocations. Arrows indicate the sense of the screw dislocations. The horizontal line is the axis over which the DOS is plotted.

Using (i) anisotropic linear elasticity theory [23] and (ii) the strain field resulting from our DFT computed supercell with all atoms relaxed. In the next step we consider a series of bulk orthorhombic supercells consisting of 8 atoms and with their primitive vectors along the $\langle 1\bar{1}00\rangle$, $\langle 0001\rangle$, and $\langle 11\bar{2}0\rangle$ directions. These cells are used to sample all relevant strain states in our dislocation geometry and for this purpose placed at various positions in the computed strain field. For each deformation state the atomic coordinates have been optimized and the eigenvalues of the highest occupied and two lowest unoccupied states are then calculated. The relaxed core structure remains purely screw like, i.e., the strain around the dislocation has no hydrostatic component but is shear only. The alignment of the band structures has been performed using as reference the averaged electrostatic potential of each cell.

In the following we test whether the dislocation shows an attractive potential to electron and hole carriers at the band edges. We thereto compute the spatially resolved density of states (DOS) along the $\langle 1\bar{1}00\rangle$ line connecting the two a-type screw dislocations. The DOS is calculated by sampling the irreducible part of the Brillouin zone with 200 symmetry inequivalent k points and shown in Fig. 3 (contour plot). As can be seen in Fig. 3 both the bottom of the conduction band as well as the top of the valence band are bent towards the middle of the band gap; i.e., both electrons as well as the hole states are attracted by the dislocation consistent with our experimental observations of a dislocation-bound exciton. A closer inspection of the VB shifts at the dislocation gives a value of 0.15 eV while the downward bent of the CB is 0.05 eV. The resulting redshift of the transition energy of 0.2 eV corresponds reasonably well with the observed shift in the optical transition of 0.14 eV, within the accuracy of our DFT approach. Though the shift of the valence band has been found before and is well explained since it is formed of p-type orbitals, a shift of the conduction band formed of s orbitals is for symmetry reasons unexpected.

The impact the dislocation has on the hole states can be understood from the orbital character the top of the valence band has: It consists predominantly of a superposition of the N $2p$ states and is thus sensible to shear fields [24,25]. In contrast, the bottom of the conduction band is known to be s-like [24] and should thus in first order be insensitive to shear strain.

To understand this puzzling result of a strong shift in the conduction band we start by analyzing our results from the quasicontinuum approach. The results are shown in Fig. 3 and are depicted with the large and small balls for the strain fields derived from (i) anisotropic elasticity theory and (ii) the DFT relaxed supercell, respectively. As shown in Fig. 3 the two approaches provide identical results for the regions away from the cores indicating that the inner core region where continuum elastic theory is expected to fail is rather localized and well within the size of our DFT supercell. The lowest conduction band state S1 coincides with the CBM of bulk strain free GaN in the bulklike region between the two defects while the VBM is by ≈86 meV and ≈36 meV higher for the strain fields derived from elasticity theory and the DFT calculated supercell, respectively. As expected, close to and in the dislocation core the deviation between the two strain fields is considerable implying that in the core region the analytic solution of the displacement field breaks down.

Furthermore, we clearly observe that the shear stress induced by a screw dislocation causes an upward bending of the VBM towards the dislocation. The character of the deformed heavy hole bands consists of $p_{\langle 11\bar{2}0\rangle}$ and $p_{\langle 1\bar{1}00\rangle}$ orbitals with the former being stronger than the latter. This is in agreement with the polarization-dependent phototoluminescence measurements which show stronger polarization along the dislocation line (i.e., along $\langle 11\bar{2}0\rangle$). As can be seen in Fig. 3 the large shear strains in the vicinity of the dislocation core (i.e., for distances smaller than ≈5 Å) deforms substantially the CBM (state S1 in Fig. 3). Hence, like our DFT calculations the quasicontinuum approach shows the unexpected strong sensitivity of the (s-like) conduction band on shear strain. The fact that this effect is also observed when using the analytic strain field which is solely based on linear elastic theory implies that hydrostatic components, which could explain such a shift, are absent.

A closer inspection of the DFT calculations revealed that in the presence of large strain fields it is not sufficient to consider only the first conduction band. It turns out that the second highest unoccupied state at Γ (labeled as state S2 in Fig. 3) has a pronounced p character. In contrast to the s-like S1 state the S2 state is thus susceptible to shear strain. Going from unstrained bulk to the vicinity of the screw dislocation the calculated energy difference between states S1 and S2 reduces

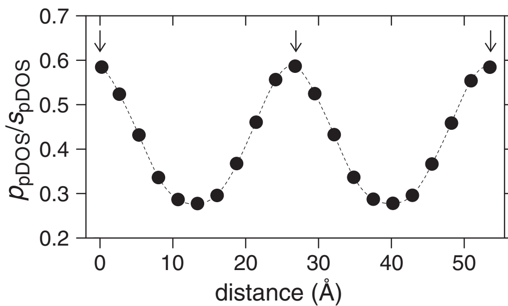

FIG. 4. Macroscopically averaged ratio between the atom-projected p DOS and s DOS along the $\langle 1\bar{1}00\rangle$ diagonal of the supercell. The arrows indicate the position of the dislocations.

from ≈2.16 eV to ≈0.95 eV at a distance of 1 Å from the defect line. This very strong dislocation-induced bending of the S2 state brings it close to the S1 state. This proximity causes a mixing between S1 and S2; i.e., the bottom of the CB becomes a mixture of s- and p-like orbitals with the consequence that it becomes susceptible to shear strain and bends downward.

A quantitative analysis of the sp hybridization (Fig. 4) shows how much p character the S1 CB state contains. The mixture between s and p character shown in this figure is the ratio of the p over s character of the macroscopically averaged atom-projected DOS (denoted $p_{\mathrm{pDOS}}/s_{\mathrm{pDOS}}$ [26]). Figure 4 clearly shows that the p character is strongly enhanced.

In conclusion we present experimental evidence for excitons bound to screw dislocations in GaN by photoluminescence and cathodoluminescence. This result is in stark contrast to what has been expected based on conventional band structure concepts according to which a strain field consisting of shear strain but without a hydrostatic component should not affect the position of the s-like conduction band edge in GaN. Based on a careful analysis of our DFT results together with a quasicontinuum approach we show that the conduction band is bent downwards consistent with our experimental observations. The unexpected and with previous concepts not understandable downward shift is shown to be a consequence of higher lying conduction bands that have p character and that are due to the huge strain fields around screw dislocations in GaN so strongly shifted that they hybridize with the band edge. The mechanism revealed here is likely to be present not only in GaN but also in other semiconductors and including it in theoretical concepts will thus help to better understand the impact of high strain defects on optoelectronic devices.

[1] W. T. Read, Philos. Mag. **45**, 775 (1954).
[2] W. Shockley, Phys. Rev. **91**, 228 (1953).
[3] R. Landauer, Phys. Rev. **94**, 1386 (1954).
[4] V. Celli, A. Gold, and R. Thomson, Phys. Rev. Lett. **8**, 96 (1962).
[5] P. R. Emtage, Phys. Rev. **163**, 865 (1967).
[6] Y. T. Rebane and J. W. Steeds, Phys. Rev. B **48**, 14963 (1993).
[7] Y. A. Osipyan, E. A. Shteinman, and V. B. Timofeev, Phys. Status Solidi **32**, K121 (1969).
[8] S. Myhajlenko, J. L. Batstone, H. J. Hutchinson, and J. W. Steeds, J. Phys. C: Solid State Phys. **17**, 6477 (1984).
[9] J.-L. Farvacque and P. Francois, Phys. Status Solidi B **223**, 635 (2001).
[10] P. Waltereit, O. Brandt, A. Trampert, H. T. Grahn, M. R. J. Menniger, M. Reiche, and K. H. Ploog, Nature (London) **406**, 865 (2000).
[11] A. E. Romanov, T. J. Baker, S. Nakamura, and J. S. Speck, J. Appl. Phys. **100**, 023522 (2006).
[12] M. Albrecht, H. P. Strunk, J. L. Weyher, I. Grzegory, S. Porowski, and T. Wosinski, J. Appl. Phys. **92**, 2000 (2002).
[13] M. Albrecht, J. L. Weyher, B. Lucznik, I. Grzegory, and S. Porowski, Appl. Phys. Lett. **92**, 231909 (2008).
[14] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).
[15] M. A. Reshchikov, D. Huang, F. Yun, P. Visconti, L. He, H. Morkoç, J. Jasinski, Z. Liliental-Weber, R. J. Molnar, S. S. Park, and K. Y. Lee, J. Appl. Phys. **94**, 5623 (2003).
[16] N. Grandjean, M. Leroux, M. Laügt, and J. Massies, Appl. Phys. Lett. **71**, 240 (1997).
[17] L. Eckey, J. C. Holst, P. Maxim, R. Heitz, A. Hoffmann, I. Broser, B. K. Meyer, C. Wetzel, E. N. Mokhov, and P. G. Baranov, Appl. Phys. Lett. **68**, 415 (1996).
[18] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[19] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[20] A. Janotti, D. Segev, and C. G. Van de Walle, Phys. Rev. B **74**, 045202 (2006).
[21] J. Li, C.-Z. Wang, J.-P. Chang, W. Cai, V. V. Bulatov, K.-M. Ho, and S. Yip, Phys. Rev. B **70**, 104113 (2004).
[22] L. Lymperakis, J. Neugebauer, M. Albrecht, T. Remmele, and H. P. Strunk, Phys. Rev. Lett. **93**, 196401 (2004).
[23] J. P. Hirth and J. Lothe, *Theory of Dislocations* (Wiley, New York, 1982).
[24] J. M. Wagner and F. Bechstedt, Phys. Rev. B **66**, 115202 (2002).
[25] Q. M. Yan, P. Rinke, M. Scheffler, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 121111 (2009).
[26] The $p_{\mathrm{pDOS}}/s_{\mathrm{pDOS}}$ ratio is calculated by deriving the on site, i.e., on atoms, and on angular momentum projected DOS. At each site the value of the ratio is the averaged ratio over all the atoms within a unit cell centered at this position. The lower and upper limits of the integration window are the middle of the band gap and the middle between states S1 and S2, respectively. We checked that the qualitative features of Fig. 4 are insensitive to the specific value chosen for as long it is below the S2 state.