Polarization-Induced Hole Doping in Wide–Band-Gap Uniaxial Semiconductor Heterostructures

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Impurity-based p-type doping in wide–band-gap semiconductors is inefficient at room temperature for applications such as lasers because the positive-charge carriers (holes) have a large thermal activation energy. We demonstrate high-efficiency p-type doping by ionizing acceptor dopants using the built-in electronic polarization in bulk uniaxial semiconductor crystals. Because the mobile hole gases are field-ionized, they are robust to thermal freezeout effects and lead to major improvements in p-type electrical conductivity. The new doping technique results in improved optical emission efficiency in prototype ultraviolet light-emitting–diode structures. Polarization-induced doping provides an attractive solution to both p- and n-type doping problems in wide–band-gap semiconductors and offers an unconventional path for the development of solid-state deep-ultraviolet optoelectronic devices and wide–band-gap bipolar electronic devices of the future.

The direct-gap III-V nitride semiconductor family and its alloys span the widest spectral range of band gaps (Eg) among all semiconductors, ranging from the infrared (InN, Eg = 0.7 eV) through the visible and the ultraviolet (UV) (GaN, Eg = 3.4 eV) to the deep UV range (AlN, Eg = 6.2 eV). This property is the basis for its applications in short-wavelength lasers (1, 2) and in light-emitting diodes (LEDs) for solid-state lighting applications (3, 4). In addition, the wide band gaps, availability of heterojunctions, high electron-saturation velocities, and high breakdown fields enable high-speed and high-power electronic devices. Compact short-wavelength, solid-state light sources will enable a wide range of applications such as high-density optical data storage, water treatment, sterilization of medical equipment, UV-enabled security marks on credit cards and currency bills, and biological and cellular imaging.

Currently, the III-V nitride semiconductors offer the most viable approach toward the realization of high-efficiency, deep-UV optical emitters based on semiconductors (2). A problem that has persisted since the early 1990s and is becoming increasingly troublesome is the high resistivity of p-type GaN and AlGaN layers. The activation energy Ea of the most commonly used acceptor dopant (Mg) in GaN is ~200 meV (5–7), several times the thermal energy kBT at room temperature (where kB is the Boltzmann constant, and T is temperature). The activation energy of acceptors increases with the band gap, reaching EA ~ 630 meV in AlN (7). For comparison, the donor (Si) activation energies are Ea~ ~ 15 meV for GaN and EaD ~ 282 meV for AlN (7). Thus, the thermal activation of holes is highly inefficient at room temperature for GaN and becomes increasingly problematic for higher-band-gap AlGaN and AlN layers. As a result, injection of holes is a severe impediment for light-emitting devices in

References and Notes

3. The blue continuum, in combination with residual host galaxy lines, explains the original erroneous classification of this object as a SN IIn on the basis of a noisier spectrum (22).
15. If our interpretation is correct, it would not be too surprising that the first SN Ia found would be unusually luminous, because such an object would be easier to find and to recognize as such.
19. Poisson statistics allow fractions in the range from 0.7 to 11% (10).

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Supporting Online Material

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SOM Text Figs. 51 to 54 Tables S1 to S3 References 9 September 2009; accepted 29 October 2009 Published online 5 November 2009; 10.1126/science.1181709 Include this information when citing this paper.
the UV and deep-UV spectral windows. High p-type resistance leads to excessive Joule heating of p-doped AlGaN layers for Al composition \( x_{\text{Al}} \geq 20\% \). Instead, p-GaN layers must be used and absorption losses incurred in the narrower-band-gap region. Furthermore, hole reflection and trapping at heterojunction valence-band offsets block hole injection into optically active AlGaN regions (2) and reduce the efficiency of such devices. An alternative strategy for efficient p-type doping and hole injection in wide-bandgap semiconductors is therefore highly desirable at this time.

The large ionic component of the Ga(Al)-N bonds, combined with the deviation of their equilibrium lattice structure from ideal wurtzite crystals, give rise to giant spontaneous polarization fields in III-V nitride semiconductors (8, 9). In addition, the strain-induced piezoelectric component of the fixed charge in the nitrides is the highest among all III-V semiconductors. At abrupt Al(Ga)N/GaN heterojunctions, the sharp discontinuity in the polarization field leads to the formation of a bound sheet charge \( \sigma_s \) at the heterointerface, captured by the Gauss law boundary condition \( \sigma_s = (\mathbf{P}_1 - \mathbf{P}_2) \cdot \mathbf{n} \), where \( \mathbf{n} \) is the unit vector normal to the heterointerface, and \( (\mathbf{P}_1, \mathbf{P}_2) \) are the polarization fields across the heterojunction. When wurtzite nitride crystals are grown along the [0001] orientation (metal or Ga-face), a positive bound polarization charge creates a high electric field and energy-band bending, such that a mobile two-dimensional electron gas (2DEG) forms at AlGaN/GaN heterojunctions without the need for intentionally introduced impurity dopants. The bound sheet-charge density can be as high as \( \sigma_s \sim 6 \times 10^{13} \text{ cm}^{-2} \) at pseudomorphic AlN/GaN heterojunctions, facilitating mobile 2DEGs with a very high charge carrier density. For example, in AlN/GaN semiconductor heterostructures, the mobile 2DEG concentrations are \( 4 \times 10^{13} \text{ cm}^{-2} \) (10). Such polarization-induced 2DEGs form the basis of nitride high-electron mobility transistors that have surpassed transistors made from any other semiconductor family in RF power performance (11).

The polarization fields have also been exploited to create parallel sheets of 2D hole gases in Mg-doped AlGaN/GaN multiple-quantum-well structures (12, 13). Although such parallel 2D hole sheets have high conductivity in the plane of the heterojunctions, they suffer from low conductivity perpendicular to the interfaces because of potential barriers in the valence band that require transport to occur through tunneling or thermionic emission processes. Even in short-period superlattice structures, the large effective mass of holes in minibands results in low mobility and high resistance (1). An alternate strategy for hole doping without potential barriers will facilitate higher conductivities.

If instead of sharp heterojunctions we grew a compositionally graded crystal, the bound polarization-induced sheet charge spreads to a bound 3D form in accordance with \( \rho_p(z) = -\mathbf{v} \cdot \mathbf{P}(z) \), where \( \rho_p(z) \) is the volume charge density in the polar (z) direction, and \( \mathbf{v} \) is the divergence operator. For [0001]-oriented Ga-face crystals graded from GaN to AlGaN, the polarization bound charge is positive and induces the formation of a mobile 3D electron gas. These 3D electron slabs are quite distinct from those formed by donor impurity doping: Because the carriers are created by effective electrostatic “field” ionization, they require no impurity incorporation, and thus exhibit virtually no freezeout at cryogenic temperatures as opposed to thermally ionized carriers in shallow, donor-doped layers (14). The resulting 3D electron gases have higher n-type conductivity than impurity-doped layers of comparable carrier concentration, because ionized impurity scattering is absent. The absence of freezeout and high mobilities made it possible to observe Shubnikov–de Haas oscillations (15). Polarization-induced field-effect transistors have also been demonstrated recently with this technique (16).

By the same measure, flipping the polarity of the crystal (growing along the N-face, which is

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**Fig. 1.** Schematic illustration of polarization-induced p-type doping in graded polar heterostructures. (A) Sheets of charge dipoles in every unit cell of the crystal. The net unbalanced polarization charge is shown in (B), which leads to the electric field in (C), and the energy-band bending in the valence band in (D) if holes are not ionized. Field ionization of holes results in a steady-state energy-band diagram shown in (E), which highlights the smooth valence-band edge without any potential barriers for hole flow. \( E_f \) is the Fermi level; \( E_c \) and \( E_v \) are the conduction and valence-band edges, respectively; and \( E_g \) is the band gap.
The [000̅1] direction) and compositional grading from GaN to AlGaN should result in mobile 3D hole slabs. The ability to do so without the introduction of Mg-acceptor dopants hinges on the propensity of the surface to act as a remote acceptor state. The surface of III-V nitride semiconductors freely provides mobile electrons, but not holes, and this difference has been attributed to the presence of deep-level traps that localize holes (17). Lowering of defect and trap densities may enable dopant-free p-type carriers, but intentionally introducing Mg-acceptor dopant atoms in the N-face graded AlGaN layer serves as the necessary source of holes. This work demonstrates the ability to use the polarization charges in N-face [000̅1] layers to generate polarization-induced, p-type graded AlGaN slabs that are highly conductive.

The mechanism of polarization-induced hole formation is illustrated schematically in Fig. 1. The total polarization (spontaneous plus piezoelectric) can be pictured as charge dipoles in every unit cell of the crystal (Fig. 1A). Because Al$_x$Ga$_{1-x}$N (where x is the Al mole fraction) has higher polarization than GaN, the sheet-charge dipoles in unit cells of the AlGaN layer are of a higher magnitude than in GaN, so the dipole strength increases linearly with the composition. When the composition of the layer is graded with increasing Al mole fraction, the net unbalanced bound polarization charge is negative (Fig. 1B), given by $\rho_p(z) = -\nabla \cdot P(z) \sim 5 \times 10^{13} \times (x_2 - x_1)/d \text{ cm}^{-3}$, where $x_1$ and $x_2$ are the Al compositions at the ends of the graded layer of thickness d (in centimeters). This bound charge creates a built-in electric field (Fig. 1C) and energy-band bending that would be greater than the band gap of the semiconductor layer if left uncompensated (Fig. 1D). To neutralize the bound, negative polarization charge, holes are consequently field-ionized from the deep Mg-acceptor atoms and form a high-density mobile 3D hole gas. The concentration of the 3D hole gas should then exhibit a weak temperature dependence and resist freezeout at low temperatures. In addition, the

Fig. 2. Structural and transport properties of p-type samples (A) Concentration of Al and Ga atoms in a compositionally graded AlGaN sample (sample d), with the measured concentration of Mg dopant atoms. The thickness of the graded layer is $d \sim 85$ nm, capped with a thin, heavily doped p++ layer for ohmic contacts. SIMS, secondary ion mass spectrometry. (B) Measured temperature-dependent resistivity for samples a to c, highlighting the polarization boost in p-type conductivity.

Fig. 3. Hall-effect temperature-dependent (A) hole concentration, (B) hole mobilities, and (C) hole concentration and mobility measured down to $T = 4$ K. The polarization-doped graded AlGaN p-type layers show higher hole concentrations and conductivities. Holes in polarization-doped layers are resistant to freezeout at low temperatures, and their mobility and concentration can be measured down to cryogenic temperatures.
smooth spatial variation of the valence-band edge (Fig. 1E) should further facilitate high-conductivity p-type transport in both lateral and vertical directions.

To test this concept of polarization-induced p-type doping, Mg-doped graded AlGaN layers were grown on top of semi-insulating N-face [000T] GaN substrates by plasma-assisted molecular beam epitaxy. A Mg-doped GaN sample \( N_a \sim 10^{19} \text{cm}^{-3} \), sample a; here, \( N_a \) is the acceptor concentration) was used as a control sample. Graded AlGaN samples doped with the same Mg concentration but linearly graded from \( x = 0 \) to 0.16 (sample b) and \( x = 0 \) to 0.3 (sample c) over \( d \sim 85 \text{nm} \) were grown. The sample structures and compositions were characterized by x-ray diffraction, in situ reflection, high-energy electron diffraction patterns and atomic force microscopy [see supporting online material (SOM) for a description of crystal growth and characteristic (18)]. Secondary ion mass spectrometry measurements were performed on a separate graded AlGaN sample \( (x = 0 \) to 0.4, sample d) as well as the control Mg-doped GaN sample to verify the incorporation of Mg atoms into the crystal and the linear grading of Al composition in the polarization-doped AlGaN layers (Fig. 2A). Samples a to c were subsequently processed for Hall-effect measurements, as described in the SOM (18).

The measured resistivities of the bulk p-GaN and polarization-doped AlGaN layers from \( T = 300 \) to 100 K are shown in Fig. 2B. The room-temperature resistivity of both polarization-doped samples b and c (\( \rho_a, \rho_c \sim 0.6 \text{ohm-cm} \)) is lowered by more than a factor of 2 compared with that of the control sample a (\( \rho_a \sim 1.22 \text{ohm-cm} \)). The resistivity of the control sample a increased monotonically by more than two orders of magnitude as the temperature was lowered from 300 to 100 K (Fig. 2B); this increase is expected from the freezeout of thermally activated holes. In comparison, the resistivities of the polarization-doped samples b and c actually decreased with temperature, which is indicative of metallic behavior. This decrease in resistivity can occur if (i) polarization-induced holes do not freeze out at low temperatures and (ii) the mobilities of polarization-induced holes increase when temperature is lowered from 300 to 100 K.

Temperature-dependent Hall-effect measurements performed at a magnetic field of 0.5 T confirmed the two hypotheses. The measured hole concentrations and mobilities are shown in Fig. 3, A and B. Compared with the exponential freeze-out (activation energy \( E_A \sim 170 \text{meV} \)) of mobile holes for the Mg-doped GaN control sample (a), the hole densities in the polarization-induced graded AlGaN samples (b and c) remain essentially independent of temperature, and are near the theoretical prediction \( [\rho_h = 5 \times 10^{13} \times (x_3 - x_1) / \text{cm}^3] \), as indicated by the thick gray lines in Fig. 3A. Polarization charges are atomic in origin and do not require thermal energy to be activated, so they enhance the hole concentration independent of temperature. In addition, because polarization charges are spatially distributed, the band-edge potential variations are smooth, and no abrupt potential barriers exist for the flow of holes along any direction. These properties are a major advantage and novelty of this method of p-type doping. Polarization enhancement of hole densities are \( 2^x \) and \( 6^x \) for samples b and c at room temperature and many orders of magnitude at lower temperatures.

The measured hole mobilities as a function of temperature in samples a to c are shown in Fig. 3B. Sample c has lower hole mobility because of increased alloy scattering. Although it was not possible to perform Hall-effect measurements for control sample a below \( T \sim 150 \text{K} \) because of carrier freezeout, we measured the polarization-enhanced hole concentration and mobility down to \( T = 4 \text{K} \) for sample b. As shown in Fig. 3C, the hole concentration showed a very small decrease with temperature, whereas the hole mobility increased to \( \mu_h \sim 65 \text{cm}^2/\text{Vs} \) at 30 K before decreasing, indicating competition between phonon and impurity scattering.

To test the effectiveness of such polarization-enhanced p-type layers as hole injectors in optical devices, a Mg-doped graded AlGaN layer \( (x = 0 \) to 30%, identical to sample c) was grown on a n-type doped N-face [000T]-oriented GaN substrate. A control p-n junction with a Mg-doped GaN p-type layer was also grown, and these structures were fabricated into light-emitting diode structures [see SOM for the fabrication procedure (18)]. These junctions serve as prototype LEDs, requiring electrical injection of holes and electrons into the depletion region where they recombine radiatively to emit photons. Under forward bias at room temperature, both devices exhibit electroluminescence in the UV spectral range (Fig. 4A). We observed characteristic sub-band-gap emission attributed to deep acceptor levels in nitrides (19). Furthermore, we note that the graded AlGaN p-layer structure showed much brighter optical emission (Fig. 4B), which we attribute to two factors: (i) improved p-type conductivity in the vertical direction due to polarization-induced hole doping and (ii) the existence of a built-in quasi-

![Fig. 4](https://www.sciencemag.org/content/sci/327/5976/63/F4.large.jpg)

**Fig. 4.** (A) Room temperature electroluminescence of the graded p-type AlGaN junction and the control GaN p-n junction at 40-mA drive current. Both samples have an area of 80 \( \mu \text{m} \) by 150 \( \mu \text{m} \). (Inset) Optical microscope micrograph displaying the blue part of the emission of the graded AlGaN junction. a.u., arbitrary units. (B) Relative output intensity with increasing drive current for the graded AlGaN p-n junction and the control bulk-doped p-n junction. The polarization-doped diode shows much brighter emission than the bulk-doped p-n junction. Schematic energy-band diagrams of a conventional (C) LED device and (D) a polarization-doped device. The graded AlGaN p-n junction uses the entire band offset \( \Delta E_v \) in the conduction band as an electron-blocking layer, resulting in enhanced electroluminescence. In comparison, a traditional electron-blocking layer (O) also blocks holes through a valence-band offset \( \Delta E_v \).

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Translocation of Single-Stranded DNA Through Single-Walled Carbon Nanotubes

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We report the fabrication of devices in which one single-walled carbon nanotube spans a barrier between two fluid reservoirs, enabling direct electrical measurement of ion transport through the tube. A fraction of the tubes pass anomalously high ionic currents. Electrophoretic transport of small single-stranded DNA oligomers through these tubes is marked by large transient increases in ion current and was confirmed by polymerase chain reaction analysis. Each current pulse contains about 107 charges, an enormous amplification of the translocated charge. Carbon nanotubes simplify the construction of nanopores, permit new types of electrical measurements, and may open avenues for control of DNA translocation.

This method of polarization doping should prove particularly useful for deep-UV optoelectronic applications where both p- and n-type doping of high Al composition AlGaN is a major challenge. The technique presented here could be applied to produce highly conductive p-type regions in wide-band-gap nitrides composed of high-Al composition AlGaN and in the more general AlInGaN material system with proper choice of the crystal direction of growth and management of strain within allowable limits. The doping scheme can be used to obtain desired hole or electron concentrations in spite of poor ionization efficiencies of deep-level dopants in any semiconductor crystals that possess sufficiently strong spontaneous and piezoelectric polarization (for example, in the ZnO material family).

References and Notes
17. Details of the growth and fabrication procedure are described in the supporting online material.
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22. Supporting Online Material
www.sciencemag.org/cgi/content/full/327/5961/60/DC1
Materials and Methods
Figs. S1 to S3
References
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