

DOI: 10.1002/sml.200500166

A Printable Form of Single-Crystalline Gallium Nitride for Flexible Optoelectronic Systems**

Keon Jae Lee, Jaeseob Lee, Heedon Hwang,
Zachary J. Reitmeier, Robert F. Davis, John A. Rogers,
and Ralph G. Nuzzo*

Printable semiconductors have recently gained widespread attention due to the potential they engender in enabling the fabrication of revolutionary new forms of lightweight, mechanically flexible circuits.^[1–4] A primary attraction of these materials resides in the fact that they can be deposited in patterned forms onto various substrates, including low-cost plastics and even paper, by using intrinsically low-cost means of fabrication. This ability, and the novel form factors of the devices they serve to enable, may lead to new opportunities in broad areas of commercial electronics technology.^[5–7] However, the inherent properties, notably the mobilities of carriers in materials that have been explored most extensively, serve to limit the range of these applications. Small-molecule and polymeric semiconductors^[8] can be used to form transistors whose mobilities typically fall in the range of 0.1–1 cm²V⁻¹s⁻¹. Nanowire and nanoparticle semiconductors,^[9] another printable class of semiconductor material, yield devices with mobilities of $\approx 1\text{--}3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Single-walled carbon nanotubes have exceptional intrinsic transport properties^[10] and, in the form of networks and

arrays, have been used to form devices with more promising mobilities, ranging from ≈ 10 to 40 cm²V⁻¹s⁻¹.^[11] Often, these nanowire- or nanotube-based devices show effective device mobilities that are too low for many classes of circuits, due primarily to the relatively low filling factor of semiconducting elements in the channel.^[6]

We recently described a complementary approach based on printable forms of single-crystalline inorganic semiconductors (Si, GaAs, InP), which we refer to as microstructured semiconductors ($\mu\text{-SC}$), for these types of applications. Here, micrometer-scale elements, which have some advantages compared to the types of nanometer-scale objects explored previously, are derived by patterning and etching high-quality, wafer-scale sources of the semiconductor.^[1] This “top-down” approach to printable inorganic semiconductors provides deterministic control over the resulting shapes of the objects—wires, ribbons, rectangles, etc.—and their spatial organization across the wafer.^[1,2] High fill factors, and correspondingly high effective device mobilities, can be achieved readily. This attribute enables a multitude of possibilities for new applications that use device substrates (e.g., plastics, paper, etc.) which are incompatible with the high-temperature steps that are generally required to grow and subsequently process these semiconductors.

Herein, we describe procedures suitable for generating and printing collections of microribbons of GaN, or $\mu\text{-GaN}$, onto plastic substrates.^[2,12] GaN is a material that is not generally available in the form of bulk single-crystalline wafers, the preferred forms of the semiconductors used in our earlier work. To fabricate $\mu\text{-GaN}$, we employ instead high-quality GaN thin films that are supported on sacrificial handle wafers, materials grown by using a metal-organic chemical vapor deposition (MOCVD) process. In this form, new processing methods were required to generate $\mu\text{-GaN}$ that was useful for printing. Methods useful toward this end are described.

The wide bandgap and thermal stability of GaN makes it an ideal materials choice for high-power and high-temperature field-effect transistors (FETs), and for blue light-emitting diodes and lasers.^[13,14] These same properties also make GaN an interesting material for use in new types of large-area, mechanically flexible circuits.^[15–18] Techniques for growing wafer-scale, single-crystalline films of GaN are advancing rapidly, and it is now possible to produce high-quality materials on Si, sapphire, SiC, AlN, and LiGaO₂ substrates.^[19] Other approaches can generate GaN in different forms. For example, GaN nanowires can be synthesized by laser-assisted catalytic growth,^[15] metal-catalyzed chemical vapor deposition,^[16] and other techniques.^[17,18] The effective mobilities of GaN nanowires prepared by these “bottom-up” approaches are reported to be as high as 650 cm²V⁻¹s⁻¹ for n-type materials.^[20] In principle, these wires could be used to fabricate GaN-based devices by casting solution-based suspensions onto a suitable substrate. However, the understanding of these materials—their purity, doping, crystallinity, and related properties that strongly impact device performance—is not as well developed as that of GaN thin films of the type currently finding widespread use in commercial applications.

[*] K. J. Lee, Dr. J. Lee, Dr. H. Hwang, Prof. J. A. Rogers, Prof. R. G. Nuzzo
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
104 S. Goodwin Avenue, Urbana, IL 61801 (USA)
Fax: (+1) 217-244-2278
E-mail: r-nuzzo@uiuc.edu

Prof. J. A. Rogers, Prof. R. G. Nuzzo
Department of Chemistry
University of Illinois at Urbana-Champaign
Urbana, IL 61801 (USA)

Dr. H. Hwang, Prof. J. A. Rogers, Prof. R. G. Nuzzo
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL 61801 (USA)

Z. J. Reitmeier, Prof. R. F. Davis
Department of Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695 (USA)

[**] This work was supported by the DARPA-funded AFRL-managed Macroelectronics Program and used the Center for Microanalysis of Materials and the Laser and Spectroscopy Facility of the Frederick Seitz Materials Research Laboratory, supported by the Department of Energy (DEFG02-96ER45439). K.L. thanks Prof. Jae Min Myoung in the Department of Materials Science and Engineering at Yonsei University for valuable information related to the processing of GaN thin films.

Herein, we report a procedure for fabricating useful forms of freestanding micro/nanoelements of single-crystalline GaN (μ s-GaN) and for printing them onto plastic substrates to produce simple types of flexible GaN devices. The protocol uses conventional photolithography and plasma etching of GaN thin films supported on Si(111) wafers to generate these structures, and a type of soft lithography process to print them onto a target substrate (see Figure 1).

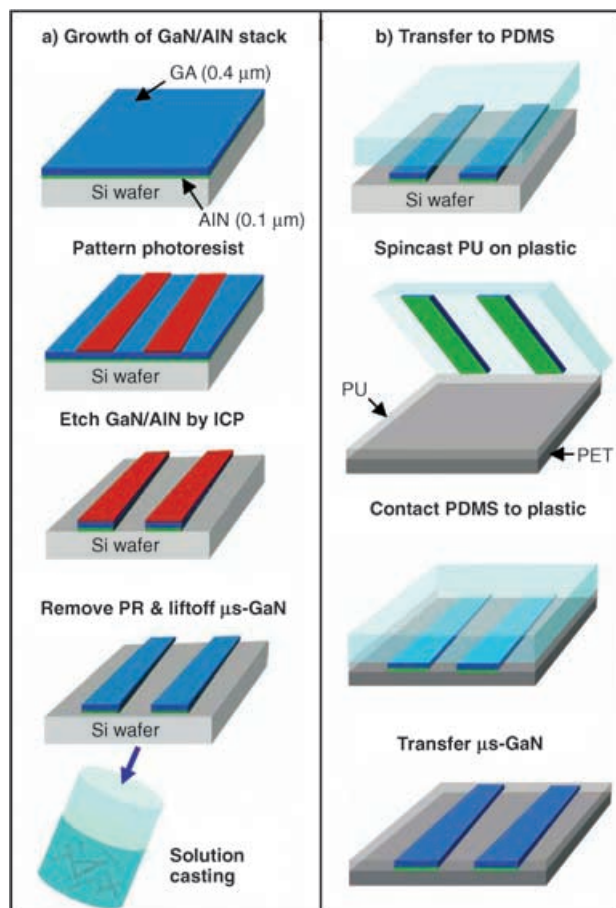


Figure 1. Schematic illustration of the steps used to generate and transfer print μ s-GaN onto plastic substrates: a) steps for fabricating the μ s-GaN; and b) steps for transfer printing the μ s-GaN onto a plastic substrate (poly(ethylene terephthalate), PET) coated with a thin layer of a photopolymer (polyurethane, PU). PDMS: polydimethylsiloxane; ICP: inductively coupled plasma; PR: photoresist.

The process starts with a high-quality thin film ($0.4 \mu\text{m}$ thick) of Si-doped GaN(0001) grown by MOCVD onto a Si(111) substrate bearing a $0.1\text{-}\mu\text{m}$ -thick AlN buffer layer.^[21] The buffer layer prevents meltback etching of the Si by Ga and also reduces the lattice mismatch between the GaN and Si layers.^[22] The photoluminescence (PL) spectrum (Figure 2a) shows a main peak with a photon energy of 3.382 eV and a full width at half maximum (FWHM) of 80 meV . Previous work has attributed such emission to an exciton bound to a neutral shallow donor.^[23] The spectrum also reveals a broad defect-related yellow luminescence, with maximum emission at about 2.25 eV .

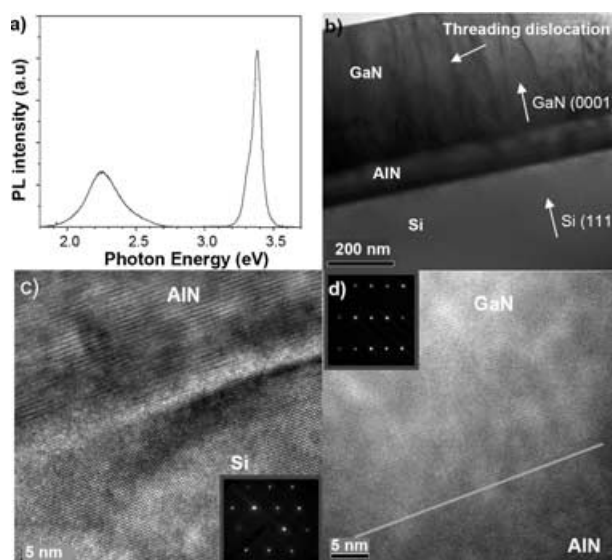


Figure 2. a) Photoluminescence (PL) spectrum of the GaN film on a Si(111) substrate at room temperature. A He–Cd laser excitation source (325 nm , 50 mW , room temperature) was used for these experiments. b) Cross-sectional TEM image of GaN/AIN/Si. c) HRTEM image of the interface between AlN and Si(111). d) HRTEM image of the interface between GaN and AlN. The insets in (c) and (d) are TEM diffraction patterns.

The lattice mismatch between the GaN and AlN-buffered Si substrate was observed to induce threading dislocations—lines of crystal defects that start at the substrate and propagate vertically up to the surface.^[19] Figure 2b shows a bright-field transmission electron microscopy (TEM) image taken under two beam conditions, which illustrates the nature and density of these dislocations. Figures 2c and d show high-resolution (HR) micrographs that reveal the interfacial microstructure of the as-grown material. The cubic Si lattice is imaged along the $[110]$ zone axis, and it can be seen that the AlN/GaN (with wurtzite structures) are along the $[11\bar{2}0]$ zone axes, as determined from the characteristic TEM diffraction patterns shown as the insets. These TEM micrographs indicate that the epilayers have a highly crystalline quality and that the GaN/AIN and AlN/Si interfaces are atomically flat.

To generate a printable form of μ s-GaN from these films, photolithography was used to define an etch mask of photoresist (PR) in the shapes desired for the μ s-SC objects. An inductively coupled plasma (ICP) was used to etch the unmasked regions of GaN/AIN through to the underlying silicon substrate. After stripping the PR, an isotropic wet etchant (a mixture of hydrofluoric acid (HF), HNO_3 , and deionized (DI) water) was then used to undercut the GaN/AIN and release it from the underlying Si. The resulting freestanding elements can be collected, suspended in solution, and used to form device components via casting or wet-printing methods (see Figure 1a). An attractive alternative approach uses a soft lithographic, dry-transfer method to place the μ s-GaN directly onto the substrate (see Figure 1b).^[4] To do so, the samples are etched in the Si wet etchant without agitation. Hence, the GaN ribbons do not float free from the wafer when the Si is undercut, but bond

weakly to it instead. A conformable polydimethylsiloxane (PDMS) transfer element is then used to contact the supported GaN elements. A strong van der Waals bond forms between the PDMS and the μ -GaN, which allows the μ -GaN ribbons to be lifted from the Si substrate when the PDMS is peeled away. This “inked” PDMS is then used to transfer the μ -GaN to the substrate, which in this case consists of a sheet of poly(ethylene terephthalate) (PET) coated with a thin film of polyurethane (PU) partially cured by exposure to a UV lamp. With the PDMS/ μ -GaN in contact with the PU-coated side of the sheet, a second UV exposure through the PET is used to fully cure the PU. Peeling back the PDMS results in the transfer of the μ -GaN elements to the plastic substrate.

Figures 3a and b present optical and scanning electron micrographs of freestanding μ -GaN after release from the

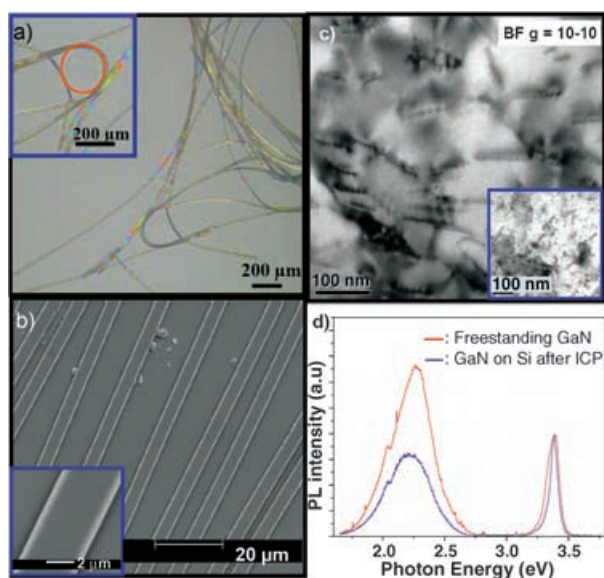


Figure 3. a) Optical microscopy images of freestanding μ -GaN objects transferred to a new Si wafer by solution casting. b) Scanning electron microscopy (SEM) images of μ -GaN ribbons transfer-printed onto a PU-coated PET substrate. c) A bright-field (BF) TEM image of the freestanding μ -GaN. Inset: a BF TEM image of a GaN thin film on a Si substrate prior to processing. d) A PL spectrum taken from the freestanding μ -GaN ribbons at room temperature.

Si carrier. Figure 3a shows optical microscopy images of ribbons deposited on a Si wafer by solution casting from a μ -GaN suspension in DI water. Note the mechanical flexibility of the 500-nm-thick μ -GaN ribbons observed in this image (bending radii as much as 100 μ m, corresponding to strains of $\approx 0.25\%$, see below). Figure 3b shows scanning electron micrographs of μ -GaN ribbons transferred by the dry-printing method onto PU/PET. The pattern transfer exploits the differences in adhesion that result from GaN contacts made with a fully cured PDMS stamp on the one hand, and with a PU resin (that is subsequently cured) on the other. The peeling force developed between the PDMS and μ -GaN (a value estimated to be $\approx 1 \text{ N m}^{-1}$ at a peel rate of 0.01 ms^{-1}) is sufficient to remove the etched μ -GaN from the handle wafer, whereas far stronger interactions (and probably cova-

lent bonding) of the GaN with the fully cured PU serve to transfer the μ -GaN from the PDMS to the plastic substrate.^[23] The misalignment seen in the pattern of GaN ribbons (4- μ m-wide stripes separated by distances of 6 μ m) is caused by a slight movement of the ribbons during the wet-etching step.

These results illustrate a useful aspect of the etching process developed here, namely, that it is possible to optimize the etching processes in ways that leave the etched μ -GaN objects weakly bonded to the handle wafer with minimal losses in registration. We do not fully understand the chemistry involved, but our belief is that it may be due to a hydrophobic contact mechanism that develops as a result of the adsorption of surfactants present in the etching solution. Additional steps can be added to prevent this movement but, to facilitate the processing, they were not included in this demonstration.^[12a] Figure 3c shows a plan-view, bright-field TEM image of the freestanding μ -GaN ribbons and a representative section of a GaN film on the Si carrier substrate before processing (inset). The densities of the dislocations, determined from quantitative analyses of the micrographs, were found to be about $3 \times 10^{10} \text{ cm}^{-2}$ in each case. This observation is consistent with negligible structural damage being inflicted during the fabrication processes. Figure 3d shows a PL spectrum measured for a collection of freestanding ribbons and reference data for a GaN film after etching by ICP. We believe the differences observed here are likely due to the contribution of ribbons that have the AlN side facing up; emission from the AlN/GaN interface related to point defects is expected to increase the yellow luminescence.^[24]

We tested the impact of mechanical flexure on the electrical properties of μ -GaN structures supported on a plastic substrate. Figure 4 shows the results of electrical measurements made using a simple a two-terminal diode device.^[2,25,26] The right-hand image of Figure 4a shows μ -GaN ribbons at a bending radius (R) of 2.5 cm. Figure 4b shows a series of current–voltage (I – V) curves obtained as a function of the bending radius. The corresponding I – V curves measured after relaxing the sample are given in Figure 4c. Although the currents are slightly reduced after the first bending cycle (the current was 16% smaller than that recorded from the device before bending), stable responses are seen after multiple subsequent bending cycles. The small differences among these I – V curves suggest that no ribbons were broken even when the bending radius of the substrate reached 2.5 cm (which corresponds to an approximate strain in the GaN of 0.36%). SEM images of ribbons taken during bending tests (Figure 4a) confirmed this conclusion. We believe the initial current reduction was caused by a slight change in the properties of the metal–GaN contacts.

In summary, we have demonstrated a “top-down” fabrication approach to generating high-quality GaN microstructures that can be printed by solution-casting or dry-transfer methods onto plastic substrates. Simple, two-terminal devices made with these GaN elements show electrical behavior that does not depend strongly on bending for the range of bending radii investigated here. The technology has the potential to offer device attributes that can complement those

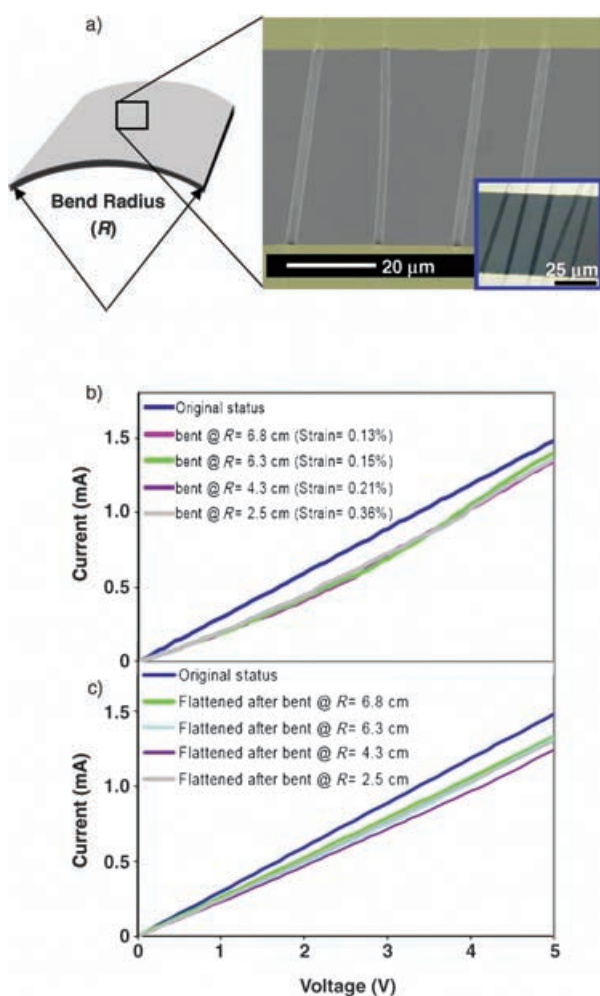


Figure 4. a) Schematic illustration of a bent μ s-GaN ribbon on a plastic sheet (left), and SEM image of a model two-terminal device at a bending radius of 2.5 cm (right). The metal area is artificially colored for ease of viewing. The inset on the right is an optical image of the unstrained device. Electrical contacts of Ti/Au (40 nm/10 nm) were used; the device channel was 50 μ m long. b) Current–voltage (I – V) curves recorded at different bending radii in normal dark conditions. c) I – V curves obtained when the plastic sheet was returned to its unbent condition after different bending radii.

achieved by nanowire-based approaches.^[27] In addition to the very simple devices shown here, the fabrication of high-performance transistors and LEDs should also be possible, a prospect that will be examined in future work. Our results suggest that the integration of μ s-SC materials of different types onto a single substrate may enable innovative opportunities for designing the next generation of lightweight displays, devices for mobile computing, and information-storage systems.

Experimental Section

Growth of GaN: The Si(111) substrate was dipped into a 10% HF solution for 10 min to remove the native oxide and blown dry with N_2 just prior to loading into a cold-wall, vertical-pancake-style, RF inductively heated MOCVD system. The 0.1-

μ m-thick AlN buffer layer and the 0.4- μ m-thick GaN film layer with carrier concentration of $2 \times 10^{18} \text{ cm}^{-3}$ were grown on a Si(111) substrate within the susceptor temperature ranges of 1080–1120 and 980–1020 $^\circ\text{C}$, respectively, at a total pressure of 45 torr. Triethylaluminum ($20.25 \mu\text{mol min}^{-1}$), triethylgallium ($23.29 \mu\text{mol min}^{-1}$), and NH_3 ($1.5 \text{ standard L min}^{-1} \text{ (slm)}$) precursors were used in combination with a H_2 (3 slm) diluent.^[21] Micrographic analyses were carried out using a JEOL 2010F microscope operating at 200 kV.

Fabrication and transfer of μ s-GaN: Photolithography (Shipley 1805, 3000 rpm for 30 s) was used to pattern the GaN by exposing the resist in the desired geometry followed by ICP etching (Plasmatherm, $Cl_2/BCl_3 = 18:2 \text{ sccm}$, pressure = 2 mtorr, DC power = 600 W, etch rate = 18 nm min^{-1} for 30 min) to remove the exposed GaN. After removing the photoresist with acetone, the underlying Si was etched away with a HF/ HNO_3 solution (HF/ $HNO_3/H_2O = 1:2:3$ for $\approx 2 \text{ min}$). A flat Sylgard 184 PDMS slab (Dow Corning) was then placed into conformal contact with the wafer to pick up the μ s-GaN. A PET sheet (180 μ m thickness, Mylar film, Southwall Technologies) was coated with PU (Norland optical adhesive 73) by spin-casting the prepolymer at 3000 rpm for 30 s and curing for 1 min using a UV lamp (home-built ozone-active mercury lamp, $173 \mu\text{W cm}^{-2}$). The PDMS stamp with the μ s-GaN was then brought into contact with the PU-coated side of the PET. A second UV exposure was performed for 1 min through the PET side. Finally, the PDMS was peeled from the plastic substrate, thus transferring the μ s-GaN to the flexible substrate.

Fabrication of a two-terminal μ s-GaN device on PET: The device structure was fabricated on a PET sheet. SU-8 5 (MicroChem) with 66 vol% SU-8 2000 thinner was spun onto the plastic sheet at 3000 rpm for 30 s. The SU-8 epoxy was then pre-cured at 60 $^\circ\text{C}$ on a hot plate for $\approx 1 \text{ min}$. Bringing the PDMS stamp with the μ s-GaN on its surface into contact with the epoxy layer for 30 s and then peeling back the PDMS led to the transfer of the μ s-GaN to the epoxy surface. The SU-8 epoxy was then fully cured at 115 $^\circ\text{C}$ for 2 min, exposed to UV/ozone (UVO) from both the front and the back of the plastic substrate for 10 s, and postbaked at 115 $^\circ\text{C}$ for 2 min. A Ti/Au layer (40 nm/10 nm) was then deposited by electron-beam evaporation and patterned with a photoresist (AZ 5214) by using photolithography. The exposed gold areas were then etched in TFA Gold Etch (Transene), and the titanium layer was etched by a 1% HF solution to form two electrical contacts. The strain values described in the text were calculated using Equation (1):^[28]

$$\text{Strain} = 100 \times \frac{(\text{Thickness of PET} + \text{Thickness of GaN})}{2 \times R_c} \quad (1)$$

where R_c corresponds to the radius of curvature. These calculations reflect two cases: the first for μ s-GaN supported on a PET substrate (total thickness $\approx 180 \mu\text{m}$); the second for μ s-GaN as a freestanding object (total thickness = 0.5 μm).

Keywords:

gallium · nitrides · optoelectronics · printing · semiconductors

- [1] a) E. Menard, K. J. Lee, D.-Y. Khang, R. G. Nuzzo, J. A. Rogers, *Appl. Phys. Lett.* **2004**, *84*, 5398; b) Z. Zhu, E. Menard, K. Hurley, R. G. Nuzzo, J. A. Rogers, *Appl. Phys. Lett.* **2005**, *86*, 133507.
- [2] Y. Sun, J. A. Rogers, *Nano Lett.* **2004**, *4*, 1953.
- [3] J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, P. Drzaic, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 4835.
- [4] N. A. Melosh, A. Boukai, F. Diana, F. Gerardot, A. Badolato, P. M. Petroff, J. R. Heath, *Science* **2003**, *300*, 112.
- [5] G. H. Gelinck, T. C. T. Geuns, D. M. De Leeuw, *Appl. Phys. Lett.* **2000**, *77*, 1487.
- [6] M. G. Kane, J. Campi, M. Hammond, F. Cuomo, B. Greening, C. Sheraw, J. Nichols, D. Gundlach, J. Huang, C. Kuo, L. Jia, H. Klauk, T. Jackson, *IEEE Electron Device Lett.* **2000**, *21*, 534.
- [7] H. E. A. Huitema, G. H. Gelinck, J. B. Van Der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, P. T. Herwig, A. J. Van Breemen, D. M. De Leeuw, *Nature* **2001**, *414*, 599.
- [8] *Thin Film Transistors* (Eds.: C. R. Kagan, P. Andry), Marcel Dekker, New York, **2003**.
- [9] X. Duan, C. Niu, V. Sahi, J. Chen, J. Parce, S. Empedocles, J. L. Goldman, *Nature* **2003**, *425*, 274.
- [10] A. Javey, J. Guo, Q. Wang, M. Lundstrom, H. Dai, *Nature* **2003**, *424*, 654.
- [11] Y. Zhou, A. Gaur, S. Hur, C. Kocabas, M. Meitl, A. Shim, J. A. Rogers, *Nano Lett.* **2004**, *4*, 2031.
- [12] a) K. Lee, M. J. Motala, M. A. Meitl, W. R. Childs, E. Menard, A. K. Shim, J. A. Rogers, R. G. Nuzzo, *Adv. Mater.* **2005**, *17*, 2336; b) M. A. Meitl, Z. Zhu, V. Kumar, K. Lee, X. Feng, Y. Y. Huang, R. G. Nuzzo, J. A. Rogers, *Nat. Mater.*, in press.
- [13] a) S. Nakamura, T. Mukai, M. Senoh, *Appl. Phys. Lett.* **1994**, *64*, 1687; b) S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, *Appl. Phys. Lett.* **1996**, *68*, 3269.
- [14] a) M. S. Shur, R. Gaska, A. Bykhovski, *Solid-State Electron.* **1999**, *43*, 1451; b) *GaN and Related Materials* (Ed.: S. J. Pearton), Gordon and Breach, New York, **1997**.
- [15] X. Duan, C. M. Lieber, *J. Am. Chem. Soc.* **2000**, *122*, 188.
- [16] Z. Zhong, F. Qian, D. Wang, C. M. Lieber, *Nano Lett.* **2003**, *3*, 343.
- [17] C. Chen, C. Yeh, C. Chen, M. Yu, H. Liu, J. Wu, K. Chen, L. Chen, J. Peng, Y. Chen, *J. Am. Chem. Soc.* **2001**, *123*, 2791.
- [18] J. C. Johnson, H. Choi, K. Knutsen, R. Schaller, P. Yang, R. Saykally, *Nat. Mater.* **2002**, *1*, 106.
- [19] L. Liu, J. H. Edgar, *Mater. Sci. Eng. R* **2002**, *37*, 61.
- [20] Y. Huang, X. Duan, Y. Cui, C. M. Lieber, *Nano Lett.* **2002**, *2*, 101.
- [21] a) Z. J. Reitmeier, R. F. Davis, *Mater. Res. Soc. Symp. Proc.* **2004**, *798*, 391; b) T. Weeks, Jr., M. Bremser, K. Ailey, E. Carlson, W. Perry, R. F. Davis, *Appl. Phys. Lett.* **1995**, *67*, 401.
- [22] H. Ishikawa, K. Yamamoto, T. Egawa, T. Soga, T. Jimbo, M. Umeno, *J. Cryst. Growth* **1998**, *189/190*, 178.
- [23] J.-M. Piau, G. Ravilly, C. Verdier, *J. Polym. Sci. B Polym. Phys.* **2005**, *43*, 145.
- [24] S. C. Jain, M. Willander, J. Narayan, R. Van Overstraeten, *J. Appl. Phys.* **2000**, *87*, 965.
- [25] *Group III Nitride Semiconductor Compounds* (Ed.: B. Gil), Clarendon, Oxford, **1998**.
- [26] M. Sakai, T. Egawa, M. Hao, H. Ishikawa, *Jpn. J. Appl. Phys.* **2004**, *43*, 8019.
- [27] M. C. McAlpine, R. S. Friedman, S. Jin, K.-H. Lin, W. U. Wang, C. M. Lieber, *Nano Lett.* **2003**, *3*, 1531.
- [28] *Elements of Strength of Materials* (Eds.: S. Timoshenko, D. H. Young), Van Nostrand, New Jersey, **1968**.

Received: May 13, 2005

Revised: July 22, 2005