Size-dependent impurity activation energy in GaN nanowires

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The effect of the surrounding dielectric on the conductivity of GaN nanowires is measured experimentally. The two following configurations are considered: bare suspended and SiO_2-coated nanowires. The measured conductivity is consistently fitted by two exponential terms with different activation energies, indicating multichannel conduction. The larger energy, attributed to activation of impurities into the conduction subband, shows essentially inverse dependence on nanowire radius, consistent with the dielectric confinement effect. This agrees with calculated values from finite element analysis. The smaller energy is independent of the nanowire radius, suggesting a surface conduction channel. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3115769]

Recent advances in growth techniques[1,2] have allowed the exploration of novel properties of nanoscale systems. In particular, the size-dependent[3,4] characteristics of semiconductor nanowires have resulted in new applications, such as optical, chemical, and biological sensors. The nanowire surface plays a key role in its electrical properties through confinement effects in two different regimes. (1) For radii much larger than the impurity Bohr radius, the induced surface charges due to the dielectric discontinuity at the surface of the nanowire tend to reduce the Coulomb screening in the material (the dielectric confinement effect[5,6]) and raise the binding energy of the impurity state. (2) For radii comparable to the impurity Bohr radius, quantum confinement from the nanowire size also becomes important. Furthermore, the conduction electron's activation energy, associated with the removal of the bound electron from its ground state to the lowest conduction subband state, increases due to the dielectric confinement effect because of the subband electron's interaction with the induced surface charge. A systematic investigation of the role of surfaces in determining the electrical properties is then essential for understanding nanowire devices.

The theoretical prediction of Delerue and co-workers,[7,8] for the activation energy in Si nanowires of radii less than about 10 nm, showed it to be inversely proportional to the wire radius. This result awaits experimental verification. Here we explore electrical conductivity of GaN nanowires in the context of dielectric confinement, as manifested through changes in the impurity activation energy. Two dielectric configurations are considered: one with bare nanowires freely suspended between metal contacts [Fig. 1(a) inset] and a similar device fully embedded in SiO_2 [Fig. 1(b) inset]. Our study suggests two distinct conduction channels in GaN nanowires. One conduction channel shows a strong nearly inverse variation in the activation energy with the wire radius, due in its entirety to the interaction of the dielectric interface with the impurity and the subband states. The other conduction channel shows relatively smaller activation energies (~1–5 meV) and almost no variation with the wire radius.

GaN nanowires were grown by chemical vapor deposition on silicon substrates using nickel nanoparticles as cata-

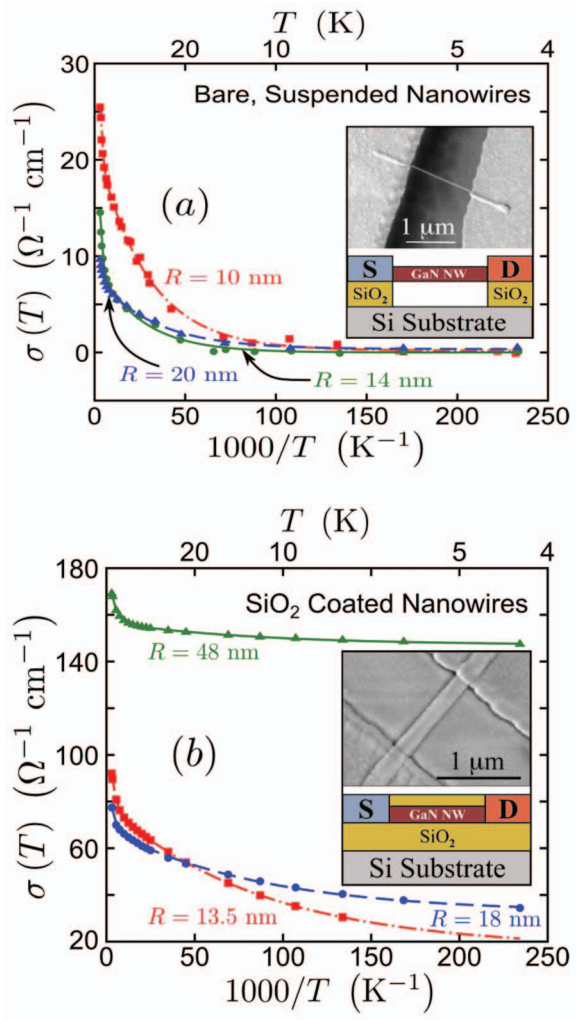

FIG. 1. (Color) The experimentally measured conductivity (points) and the fits to Eq. (1) (curves) for (a) bare suspended GaN nanowires with 10, 14, and 20 nm radii, and for (b) SiO_2 coated GaN nanowires with 13.5, 18, and 48 nm radii. Each inset shows an SEM image and schematic representation of the dielectric configuration.

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lyst. The crystal orientation along the wire axis was determined to be $[10\bar{1}0]$ through diffraction measurements. High resolution transmission electron microscopy (TEM) imaging confirmed single crystalline growth with a 1–2 nm amorphous oxide surface layer. After the growth, the nanowires were harvested by ultrasonic agitation in ACS/USP grade ethyl alcohol. A drop of the resulting solvent is then transferred to a degenerately doped $p++$ Si [100] wafer with 300 nm of thermally grown surface oxide. After locating suitable nanowires through an optical microscope, metal contacts were formed using electron-beam lithography. The titanium/gold contacts were deposited by thermal evaporation, after first removing residual polymer and oxide through 60 s of exposure to a 50 W O_2 plasma and by dipping them in 1–7 hydrogen fluoride/ammonium fluoride mixture for 3 s. The latter ensures Ohmic contact to the wires. The devices were reimaged with a field-emission scanning electron to determine their dimensions. The bare suspended nanowires were fabricated by etching the SiO_2 below the nanowire. The SiO_2 coated nanowires were achieved by sputtering SiO_2 onto a nanowire lying on the SiO_2 substrate. Conductivity measurements were then carried out in helium exchange gas at temperatures ranging from 4.2 to 300 K.

The experimental conductivity in GaN nanowires is plotted versus $1000/T$ in Fig. 1 for wires of three different radii, in each dielectric configuration. The activation energies[9] E_1 and E_2, were determined by fitting each set of conductivity data to

$$\sigma(T) = \sigma_0 + \sigma_1 \exp(-E_1/k_bT) + \sigma_2 \exp(-E_2/2k_bT). \quad (1)$$

The conductivity σ_0 represents a small degenerate (temperature independent) conduction channel, while the exponential terms represent alternate temperature-dependent conduction channels. The factor of 2 in the denominator of the second exponential term corresponds to weak compensation.[10] (This is confirmed by comparing E_2 to calculated values.) Additionally, we are neglecting the weaker temperature dependence of the mobility that is implicit in σ_1 and σ_2. The temperature dependence of the mobility has been investigated earlier with the results supporting this approximation.[11,12] Using a single exponential term, or well-known power laws[10] for σ_1 and σ_2, resulted in either a poor fit, or parameters that lacked recognizable trends. The double exponential fit of Eq. (1) is the only form which yields excellent fits and consistently meaningful parameters, which are shown in Table I (a) for suspended nanowires and Table I (b) for SiO_2 coated nanowires. The energy E_2 shows a strong dependence on the nanowire radius, while E_1 shows almost no radius dependence.

The finite element method[13] (FEM) provides a direct approach to calculating the shift in the activation energy E_2 for GaN nanowires as a function of the wire radius, the dielectric constants of the wire, and the geometry of the surrounding medium.[14] We use the concept of the dielectric constant for our analysis, since it continues to hold essentially as close as 1 nm of the surface as evidenced by microscopic calculations of the local electric field.[15] Our nanowires are considerably larger in radius, ranging over 10–50 nm and the surface induced charges can be very well approximated by a dielectric constant. The envelope function approximation is used to calculate separately the ground state of an electron bound to a hydrogenic impurity on the axis of the nanowire and the first conduction subband state. The FEM discretization was tested by reproducing the GaN bulk binding energy of $E_0 = 33.6$ meV, which agrees with reported values.[16] In the case of the impurity state, the electron screens the nucleus, thereby producing only a small amount of net surface charge. In contrast, the subband edge calculation involves only the electron state which induces a larger surface charge. Hence, the majority of the change in activation energy with wire radius comes from the subband edge shift. In Fig. 2, we show the close agreement between E_2 as obtained from the fit and from the FEM calculations as a function of $1/R$. We note that Delerue and co-workers[7,8] calculated the dependence of the activation energy on the wire radius in Si using the tight-binding (TB) approach. Computational limitations of the TB method restricted their investigation to nanowires

TABLE I. Fitting parameters for (a) bare suspended and (b) SiO_2 coated nanowires. The energies are in meV and the conductivities are in Ω^{-1} cm^{-1}.

(a) Bare suspended nanowires

R	10 (nm)	14 (nm)	20 (nm)
σ_0	0.2 ± 0.2	0.0 (fixed)	0.35 ± 0.08
σ_1	22.1 ± 0.5	9.4 ± 0.3	7.8 ± 0.2
σ_2	80 ± 0	66 ± 16	17 ± 5
E_1	3.1 ± 0.1	3.5 ± 0.2	2.7 ± 0.1
E_2	150 ± 30	130 ± 10	110 ± 20

(b) SiO_2 coated nanowires

R	13.5 (nm)	18 (nm)	48 (nm)
σ_0	17.13 ± 0.02	32.4 ± 0.8	147.1 ± 0.3
σ_1	61.66 ± 0.01	36.2 ± 0.7	9.8 ± 0.2
σ_2	50.12 ± 0.04	28 ± 4	30 ± 1
E_1	0.9875 ± 0.0005	1.0 ± 0.06	$1.04 \pm .09$
E_2	67.9 ± 0.05	58 ± 8	51 ± 2

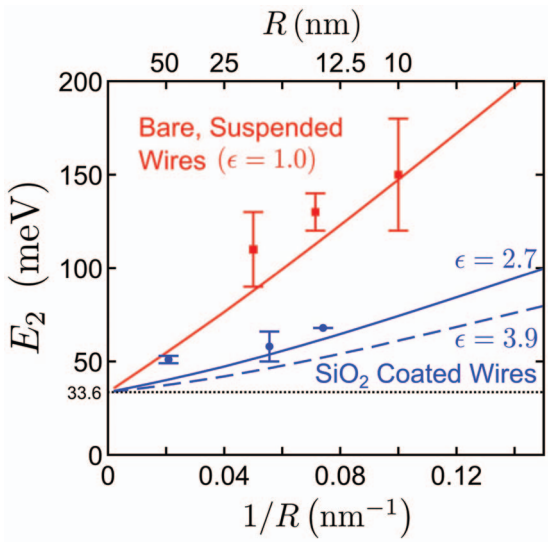

FIG. 2. (Color) The activation energies E_2 (points) from fitting $\sigma(T)$ with Eq. (1) for each nanowire vs the inverse wire radius, with the error in each energy. The curves are calculations from the FEM and were done with SiO_2 dielectric constants of 2.7 and 3.9 for comparison, as the coating was not thermally grown and hence could have a dielectric constant different from that of bulk SiO_2.

smaller than ~10 nm in radius, whereas dielectric confinement would be more important for thicker wires.

Conductivity measurements allowed the identification of impurity activation energy in GaN nanowires surrounded by dielectric media; two sets of activation energies were determined. The first E_1 was relatively small (~1–5 meV) and effectively independent of the nanowire radius, suggesting that it is associated with the surface of the nanowire. The second activation energy E_2 showed a nearly inverse dependence on the wire radius; for which the FEM calculations agree well with the experimentally determined values (Fig. 2), confirming the hypothesis that impurities in this channel are weakly compensated. The large change in E_2 suggests that when designing nanoscale devices, special attention must be paid to the surrounding dielectric since the induced surface charge significantly modifies the thermal activation energy for subband conduction.

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