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Effect of Ozone Cleaning and Annealing on Ti/Al/Pt/Au Ohmic Contacts on GaN Nanowires

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We report studies on the effect of UV/ozone cleaning on n-type GaN nanowires prior to Ti/Al/Pt/Au ohmic contact deposition and the effect of annealing temperature on the total resistance of the contacted nanowires. The UV/ozone cleaning for periods of 1–5 min reduced surface carbon and oxygen contamination, as determined by Auger electron spectroscopy measurements and led to a specific contact resistivity of $1.8 \times 10^{-2}\ \Omega\cdot\text{cm}^2$ after annealing in the range 700–800°C. After subtraction of this contact resistivity from the total resistance of the nanowires, it was found that the ozone treatment reduced the apparent resistivity from 71 to $\sim 0.7\ \Omega$ cm. These results show the importance of surface cleaning in extracting the transport properties of GaN nanowires.

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Semiconductor nanowire device structures are expected to have potential advantages for improving carrier confinement over their thin-film counterparts.[1-19] For GaN nanowires, there are possible applications in low power and high density field-effect transistors (FETs), solar cells, terahertz emitters, and UV detectors. The high surface-to-volume ratio of nanowires means that if their surfaces are sensitive to external stimuli or can be functionalized to be sensitive to specific chemicals or biogens, then they are likely to be attractive for gas and chemical sensor arrays. GaN nanowires can be synthesized by a number of different techniques, including arc-discharge, laser-assist catalytic growth, and direct reaction.[19-27] The material is generally n-type, as is found with undoped GaN films, which makes it difficult to obtain p-n junctions. In some cases, logic gates have been fabricated using p-Si and n-GaN crossed nanowire junctions.[5] A key aspect of developing GaN nanowire technology is the achievement of high quality contacts and robust surface cleaning methods. Very little work has been done to examine the effect of annealing temperature and surface cleaning on the properties of ohmic contacts to GaN nanowires, whereas these are known to be important issues in their thin-film counterparts.[28] Surface effects should be even more important in nanowires, even in determining the measured resistivity, due to depletion regions caused by deep states associated with surface contamination.

In this paper we report on the ohmic contact and transport properties of single conically-shaped GaN nanowires measured as a function of both annealing temperature and UV/ozone cleaning time. The total resistance of the nanowires is extracted from the slope of total measured resistance as a function of surface/volume ratio. The UV/ozone cleaning is found to dramatically reduce the apparent resistance of the nanowires and is associated with a reduction in carbon and oxygen surface concentrations.

GaN nanowires were grown by catalytic chemical vapor deposition (CVD) on a Si wafer precoated with a 5 nm gold film by electron-gun evaporation. More details have been given previously.[21-24] In brief, the GaN nanowires (NWs) were grown by thermal chemical vapor deposition (CVD) following VLS mechanism. We used 3 g pure Ga metal and introduced 100 sccm ammonia gas to the tube chamber as the Ga and N sources, respectively. The GaN NWs were grown at about 900°C for 1 h. Figure 1 shows a field-emission scanning electron microscopy (FESEM) image of the as-grown wires. In each case the samples used for electrical measurements were examined by SEM to make sure only single wires were measured but not those with contacts on multiple wires. The conically shaped portion is mainly found at the very end of the wire. From the inset in Fig. 1, it is easy to see that the diameters of NWs between the contact ends are not too different. We used the average of the two diameters at the contact ends to estimate the resistivity. The wires were ~10 to 17 μm long, with typical diameters in the range 50–120 nm. Both transmission electron microscopy lattice images and selected area diffraction patterns (SADP) showed high quality single-crystal growth.[21-24] The *a*-plane lattice constant of the GaN was 0.3175 nm from these images. The nanowires were removed from the Si substrate by sonication and transferred to a SiN_X-coated Si substrate. Using a simple, commercially available copper grid as a shadow mask with square openings of 115 × 115 μm and spacing 10 μm, the ends of the wires were contacted by E-beam evaporated Ti/Al/Pt/Au (30/30/50/120 nm thicknesses) to form ohmic contacts. Prior to deposition of the metal, the nanowires were exposed to UV/ozone for 1–30 min at room temperature. These contacted structures were annealed from 25 to 900°C for 2 min under flowing N_2 ambient. The current-voltage (*I-V*) characteristics were measured using an Agilent 4156C parameter analyzer. The specific contact resistivity was extracted from a transmission line method (TLM) analysis.[29] In this method, both the resistivity of the nanowires and the associated contact resistance of the pad metallization contribute to the total measured resistance. We measured the total resistance of the nanowires as a function of the length/square of radius ratio. The measured total resistance, R_T, is given by the relation[29] $R_T = 2R_C + (\rho_S/\pi)(L/r^2)$, where R_C is the contact resistance, ρ_S is the sheet resistivity of the semiconductor, L is the length of the nanowire, and r is its radius. We have also examined by SEM each of the wires from which we took data and used only those with similar contact areas.

Auger electron spectroscopy (AES) of the UV/ozone exposed samples was performed in a Physical Electronics 660 scanning Auger microprobe. The electron beam conditions were 10 keV, 1 μA beam current at 30° from the sample normal. Charge correction was performed by using the known position of the C-(C, H) line in the C 1s spectra at 284.8 eV. The AES spectrometer was calibrated using a polycrystalline Au foil. The Au $f_{7/2}$ peak position was determined to be 84.00 ± 0.02 eV. The quantification of the elements was accomplished by using the elemental sensitivity factors.

Table I shows the near-surface composition of GaN nanowires

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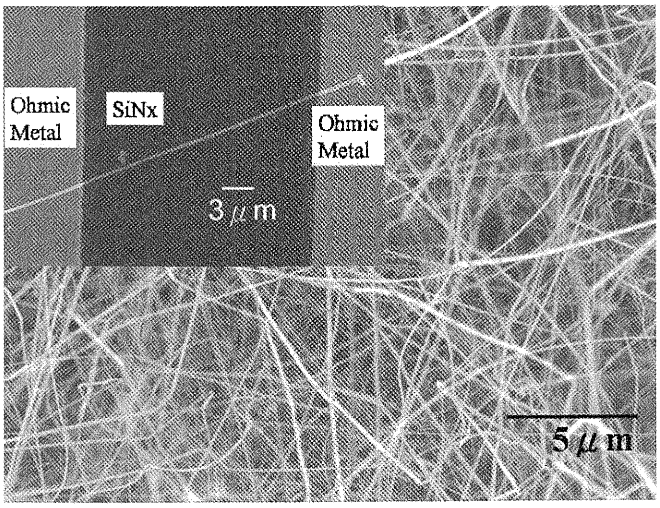

Figure 1. FESEM micrograph of as-grown GaN nanowires. The inset shows a two-terminal single wire device.

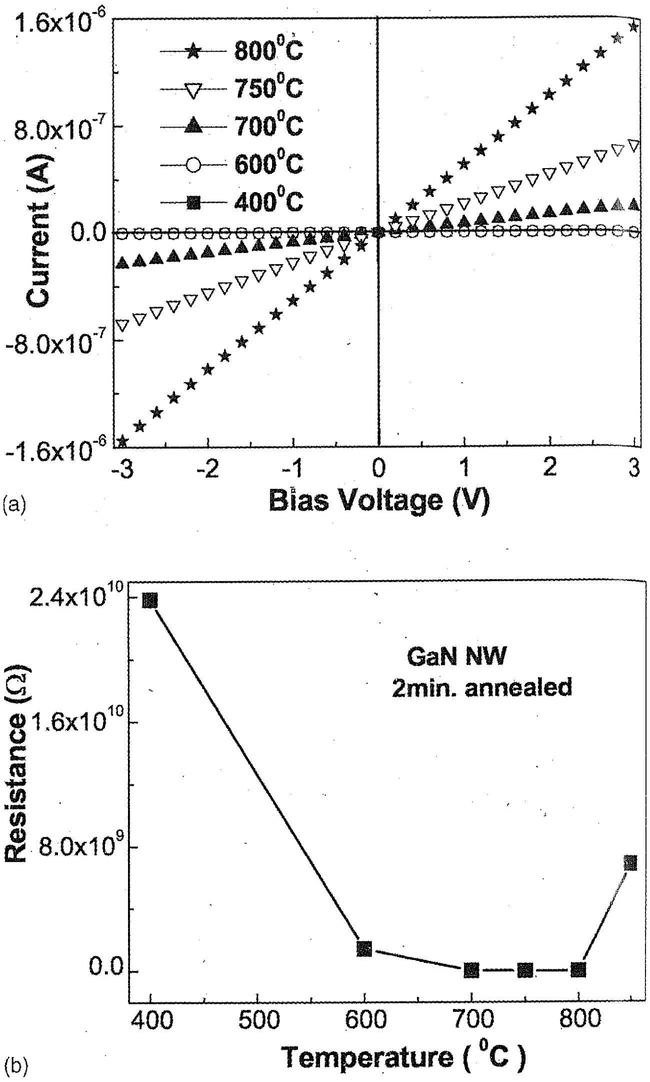

Figure 2. *I-V* characteristics from GaN nanowires contacted with Ti/Al/Pt/Au after UV/ozone exposure and 2-min anneal at different temperatures (a) and measured total nanowire resistance as a function of annealing temperature (b).

before and after UV ozone cleaning for 3 min. Similar results were obtained for exposure times in the range 1–5 min. Because nitridation of the Si substrate occurs when introducing the ammonia gas for GaN NW growth, the nitrogen signal obviously includes contributions from the Si-N bond, resulting in a N-to-Ga ratio much larger than 1 even after UV/ozone cleaning. Nevertheless, the UV/ozone exposure has effectively reduced the carbon and oxygen concentration near the surface and increased the Ga-to-C ratio. As is shown later, this has a strong effect on the measured resistance of the nanowires.

Figure 2a shows the *I-V* characteristics of the contacted nanowires as a function of annealing temperature from 400–800°C. In each case, these samples had been exposed to UV/ozone for 2 min. The unannealed wires show resistances >100 GΩ but the resistance decreased with increasing annealing temperature up to 800°C. At higher temperatures, the apparent resistivity increases, due in large part to the onset of the dissociation of the surface. Fig. 2b shows the extracted total resistance as a function of annealing temperature. The as-grown GaN nanowires are insulating but exhibit n-type conductivity upon annealing. The 700°C annealed nanowires showed a total resistance of 1.2×10^8 to 5.5×10^6 Ω in the temperature range 240–400 K. The temperature dependence of the conductance, G, of the annealed nanowires was thermally activated of the form $G = \exp(-E_A/kT)$ with an activation energy of 157 meV.[30]

To extract the contact resistance from the total resistance of the nanowires, we first made careful measurements of the length/diameter ratio of a number of nanowires using SEM. The length was corrected for the overlap of the contact area. Figure 3 shows the total resistance of samples exposed to UV/ozone for 5 min and annealed at 700°C, as a function of the length/(diameter)^2, which represents the surface-to-area ratio. For the samples exposed for 5 min, the intercept of the line (i.e., the extrapolation to zero length, where the contact resistance is the only contribution to the resistance) yields a specific contact resistivity of 1.8×10^{-2} Ω cm^2. This value is fairly comparable to that obtained on undoped GaN thin films with the same metallization and same annealing condition. Much lower contact resistances can be obtained on thin films at higher annealing temperatures (900–950°C), but we could not use those conditions because of surface decomposition of the nanowires. From Fig. 3, we fitted these three points linearly. When $x = 0$, the y value means the contact resistance. The fitting result shows that the contact resistance is $7.6 \pm 1.9 \times 10^6$ Ω. This value was the result after normalizing length and diameter of NWs.

Table I. Near-surface composition of GaN nanowires before and after UV ozone cleaning.

	Atomic percentage (atom %)				Ratio	
Substrate treatment	Ga	C	O	N	C/Ga	O/Ga
Reference sample	7.2	12.4	47.6	32.6	1.72	6.61
UV ozone for 3 min	14.9	11.5	30.4	43.2	0.77	2.04

Figure 4 shows the corrected resistivity of the 700°C-annealed nanowires after subtraction of the contact resistance from the total resistance, as a function of the UV/ozone exposure time. The UV/ozone exposure reduces the apparent resistivity from 71 to ~ 0.7 Ω cm for a 1 min treatment. This is likely due to reduced surface depletion effects as the carbon contamination is removed. Longer UV/ozone exposures are increasingly less effective in reducing the resistivity as the carbon is replaced by the oxidation of the GaN surface. The presence of various types of oxides on GaN is known to have a strong effect on the surface depletion of thin films.[31,32] Beyond 5 min exposure the contact resistance was not a

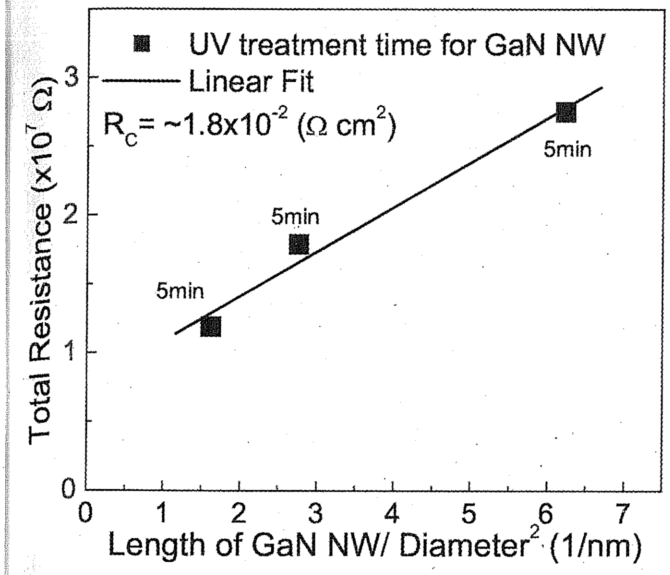

Figure 3. Total nanowire resistance as a function of surface-to-volume ratio for wires exposed to UV/ozone for 5 min prior to Ti/Al/Pt/Au deposition and subsequent annealing at 700°C.

strong function of exposure time, while the total resistance was dominated by the resistance of the nanowire itself as the surface became more oxidized.

In summary, GaN nanowires are insulating in the as-grown state and become conducting upon annealing. The contribution of contact resistance can be extracted from the total measured resistance to reveal the semiconductor resistivity. UV/ozone cleaning is found to strongly decrease the apparent GaN nanowire resistivity through a reduction in surface depletion effects.

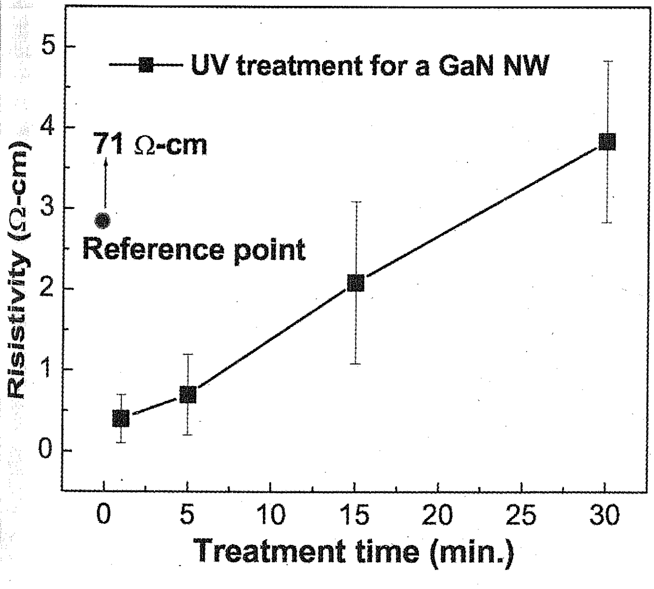

Figure 4. Resistivity of GaN nanowires corrected for contact resistance, as a function of UV/ozone exposure time.

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