Semiconductor Nanowires: Their Emission Stability and Energy Distribution

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Abstract
Ga-based semiconductor nanowires (GaN, GaP) were synthesized by the reaction of Ga metal and GaN/GaP powder with a NH_3/Ar gas using thermal chemical vapor deposition. The field emission and emission stability under oxygen and argon environments were investigated. Field emission energy distributions of electrons from these nanowires revealed that field emission mechanism of the semiconductor nanowires were different from carbon nanotubes.

1. Introduction
A number of potential applications for carbon nanotubes (CNTs) have been proposed, after the discovery of CNTs [1]. Field emission is one of the most promisings among them, due primarily to the rapid progress in areas such as successful demonstrations of CNT-based field emission displays [2,3] and field emission based lamps. These days, nanostructures other than nanotubes, which have one shell or multiple shells with the center core empty, i.e., nanowires, have been synthesized and their characterizations are under investigation [4-8]. Furthermore, these nanowires are also considered to be important materials for nanoscience and nanotechnology together with nanotubes. Nonetheless, their characteristics are still unknown, for example, field emission. In this paper, field emission characteristics of nanowires, mainly GaN and GaP nanowires, will be reported.

Synthesis of numerous nanowires such as GaN, GaP, GaAs, SiC, SiO_2, Cu_2S, [9] and etc, has been reported. Lieber group have been reported even semiconductor superlattice nanowires [8]. Core-shell Si-Ge two-layered radial superlattices were also reported recently. Spontaneous light emission, photoluminescnece, and Raman scattering have been reported for nanowire. However, few results on field emission characteristics of nanowires have been reported. Intensive investigation of field emission on nanowiers is much desirable, considering wide usage of field emission from CNTs and future possibility of nanowires as electron emitters.

2. Experiments
Several techniques have been developed for systhesizing nanowires, including arc discharge, pyrolsis, laser ablation, and chemical vapor deposition (CVD) [4-8]. Among these various methods, CVD has been known to be the most promising method for the controled and selective growth of GaN nanowire.

NiO catalst nanoparticles-coated alumina substrate (10 mm x 5 mm in size) was employed for the growth of gallium nitride nanowires. After dropping a nickle nitrate/ethanol solution onto the substrate and subsequent drying, the substrate was put downward on the top of a quartz boat loaded with Ga/GaN powders. The substrate was transferred to a tube furnace. The temperature was increased to preset reaction tempeature (1000 C) and kept at that temperature for 60 min under a constant flow of NH_3.

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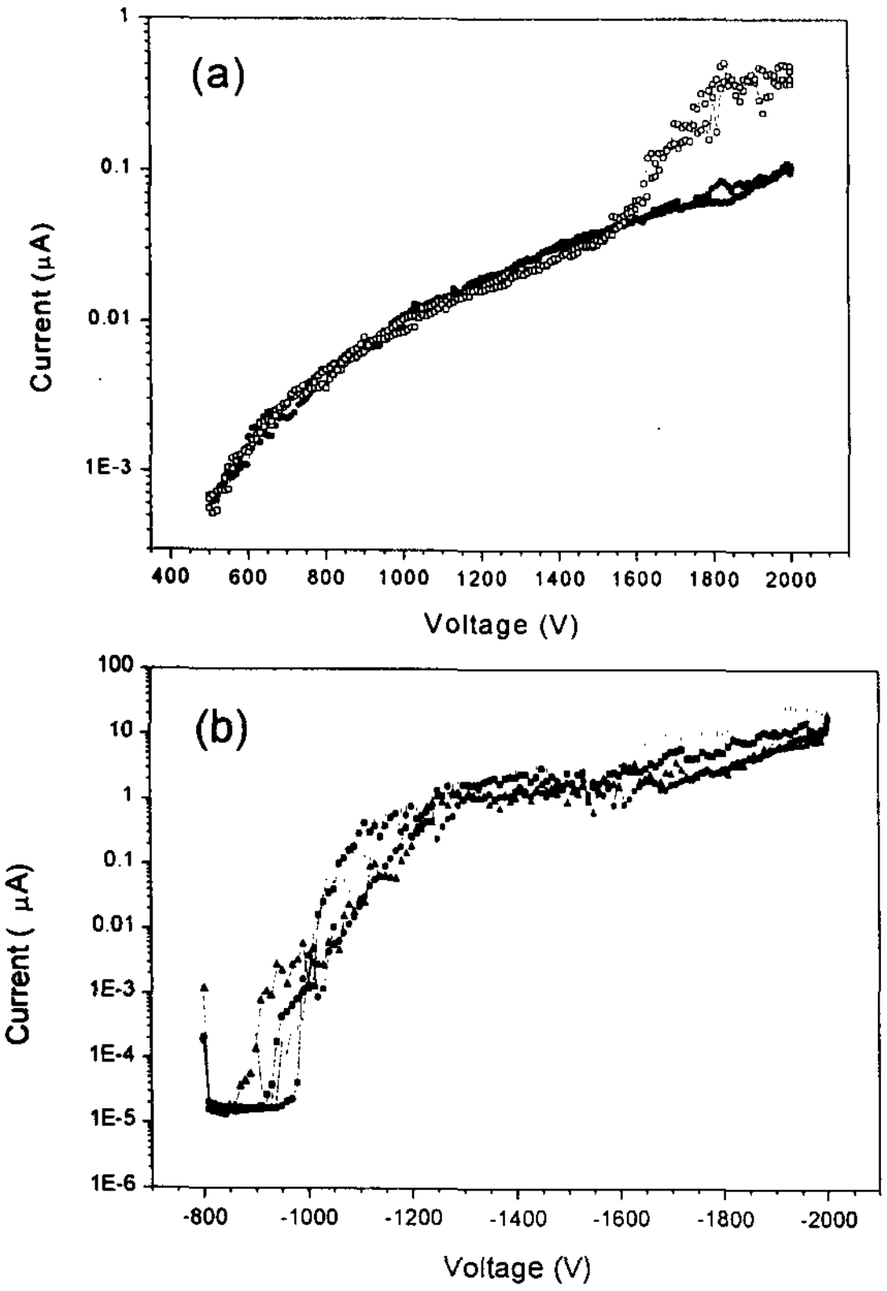

Fig. 1. Field emission characteristics of (a) GaN nanowires and (b) GaP nanowires. The distance between the sample and the anode is 150 (130) μm for GaN (GaP) nanowires. For GaN nanowires aging was perfomred during the field emission measurement (solid symbols: before aging, open symbols: after aging).

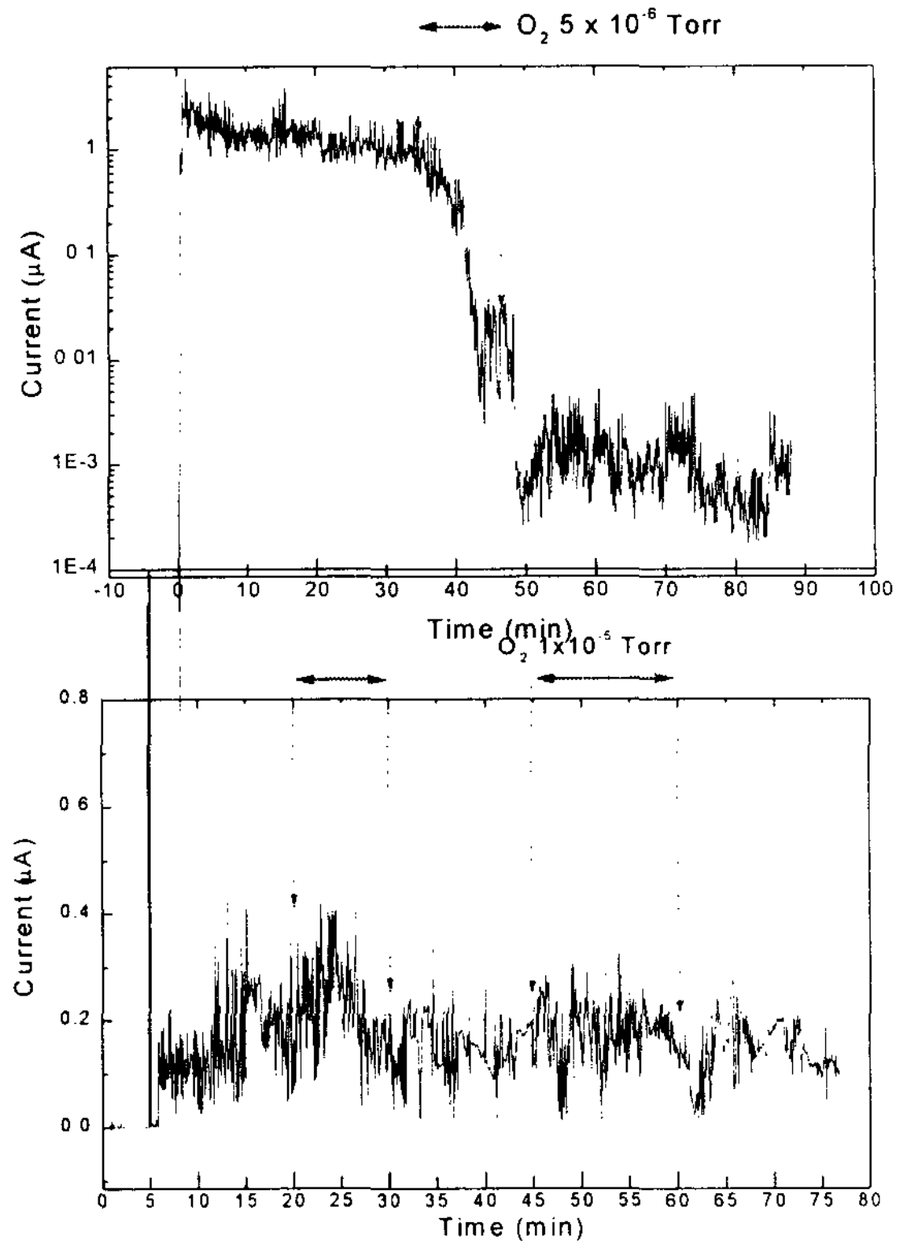

Fig. 2. Emission stability under the oxygen environment. Left (right) plot is for GaN (GaP) nanowires. Only the GaN nanowire is severely influenced by an oxygen gas.

For cubic zinc blend gallium phosphide, Ga/GaP powders were used at 850-1000 C under a flow of argon. The as-deposited products were characterized by scanning electron microscopy, transmission electron microscopy, energy-dispersive x-ray spectroscopy (EDX), and x-ray diffraction (XRD), which confirmed successful growth of single-crystalline GaN and GaP nanowires. While GaN nanowires do not have any outer shell layer on the surface, GaP nanowires have outer oxide layers. Actually, the shell layer was found to be double layers of orthorthombic structured $GaPO_4$ and amorphous Ga_2O_3 [4,5].

Nanowires were removed from the substrate by a knife and were dispersed in the ethanol for field emission measurement. After ultrasonification, several dropplets of the nanowire-containing ethanol was dropped on the conducting substrate and dried in air. For electric contact improvement, the samples were heated at 200 C for 2 hours in air. The field emission and the energy spectra were measured at room temperature in a vacuum chamber of low 10^{-9} Torr using a Keithley 2000 high voltage source and a Kethley 6517 pico-ameter. A hemispherical energy analyzer (VG Science, Clam IV) in the constant retarding ratio mode with the ratio of four was used for field emission energy distribution. A grounded metallic mesh used as an anode was separated from the cathode plate (150 for GaN nanowires, and 130 μm for GaP nanowiers), where a small portion of electrons that escaped from the metallic mesh was detected by the analyzer. For field emission stability of nanowires, an oxygen or argon gas was introduced via a leak valve to the vacuum chamber under the monitoring of the pressure of the chamber.

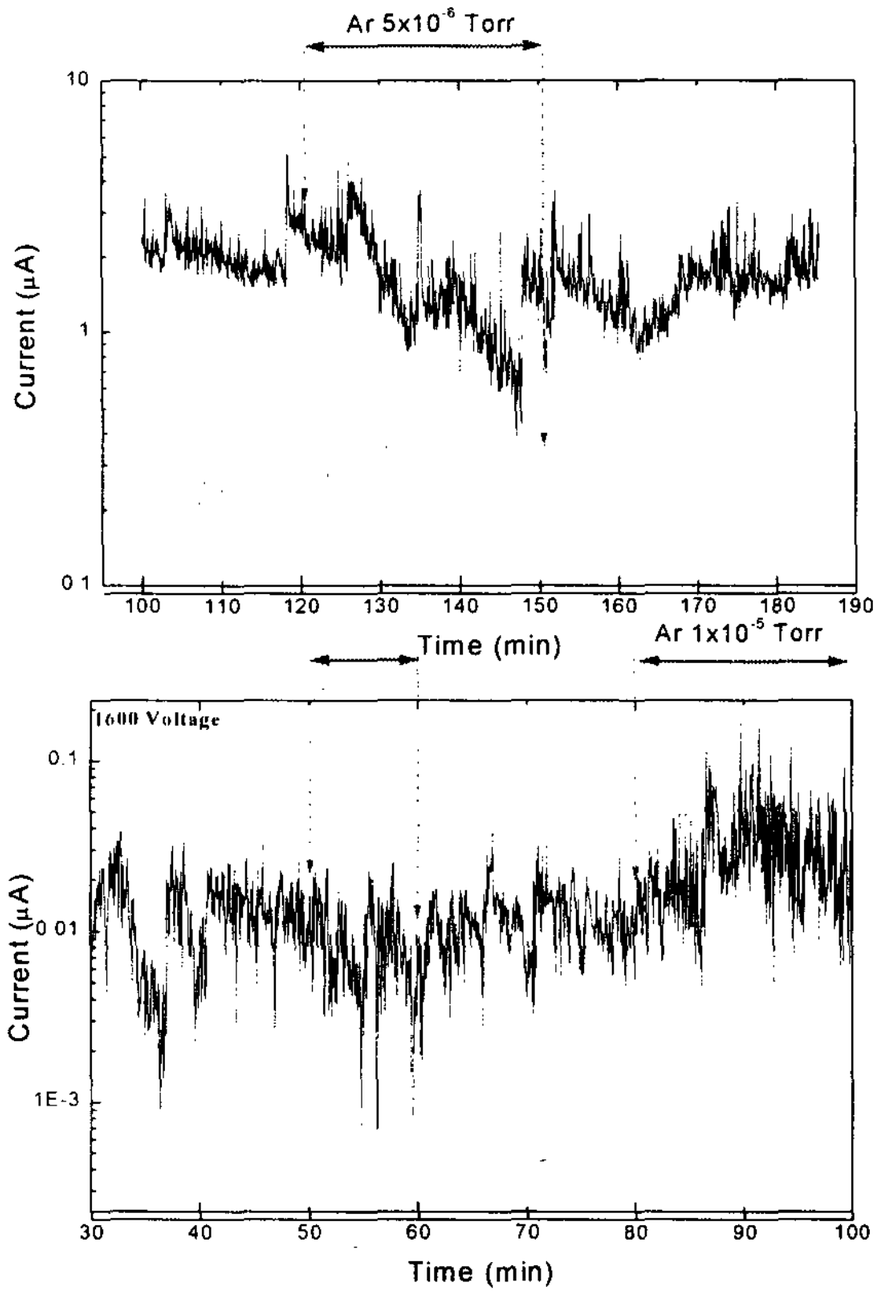

Fig. 3. Emission stability under the argon environment. Left (right) plot is for GaN (GaP) nanowires. Both nanowires are not influenced by an argon gas.

3. Results and Discussion

Field emission data clearly show that the turn-on fields for the two nanowires are fairly higher than CNTs, that is, higher than 10 V/μm (See Fig. 1). Normally CNTs exhibit around 1 V/μm. However, it is too early to say that nanowires are inferior to CNTs. Nanowires with less impurities may have low turn-on field. Furthremore, the samples were prepared by dispering nanowires on the substrates leading to very small density of nanowires and poor electric contact between the nanowires and substrate.

Figure 2 show emission stability under an oxygen environment. GaN nanowires show large current decrease upon the introduction of oxygen, while GaP nanowires do not. The inintial sudden change of the current was arisen from the sudden turn-on the applied voltage, which should not be regarded as experimental data. However, for the Ar gas environment both two wires do not exhibit any

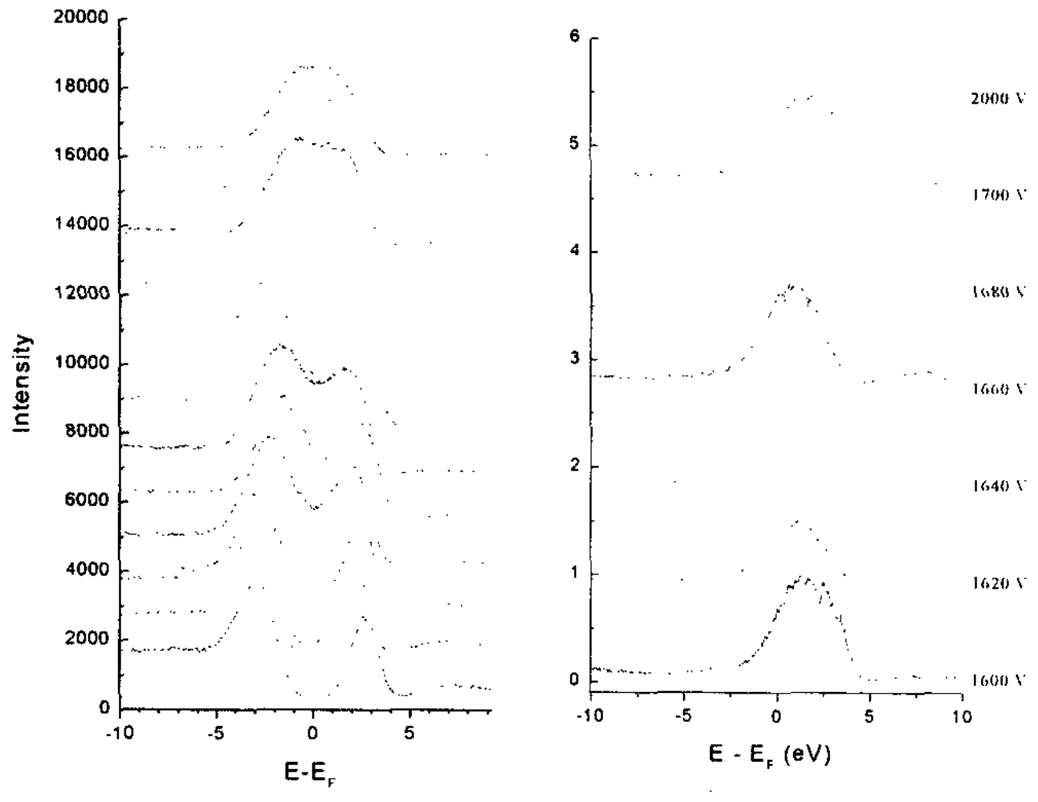

Fig. 4. Field emission energy distribution for GaN (left plot, 1820 to 2060 with 20 V interval from the top) and GaP (right plot, 1600 to 1700 with 20 V interval from the bottom excep the top of 2000 V) nanowires.

significant current decrease (See Fig. 3). Thus, only GaN nanowires experience large current reduction under oxygen which might attact nanowires physically and chemically. Since GaP nanowires have oxide outer layers, these layers are considered to play a key role in protecting nanowires from oxygen ions during field emission. The invariance of field emission current for GaP nanowires may be useful for fabrication of field emitters based on this nanowire, since CNT field emitters were found to be poor under the oxygen envrionment [10].

The field emission spectra of GaN nanowires are not familiar shapes which are frequently observed for metallic emitters and CNTs (See Fig. 4). The almost equal-sized two peaks are splitted around the Fermi energy. The left peaks seem to be originated from field emission through semiconducting nanowires, since the peaks move to the lower energy with the increase of the applied voltage. The moving of the peaks is a strong evidence for the band bending due to the field penetration into the semiconducting nanowires. On the while, the right peaks located higher than the Fermi level were not observed in CNTs. Thermionic emission can be considered to be one of possible explanations. CNTs have been known

to become very hot for an high field emission current due to high electric field [11]. Considering the fact that semiconducting nanowires are more resistive than CNTs, nanowires may be hotter during high field emission. The possibility of being at high temperature of nanowires may contribute to large intensity of right peaks. However, there still exist other possibilities for the identity of these peaks such as field emission through surface resonant states.

GaP nanowires exhibit only one peak unlike for GaN nanowires. Moreover, the peak position located slightly higher than the Fermi energy. The details of this behavior are still under investigation and the existence of the outer oxide shell layers may be one of reasons for this behavior.

4. Concluding Remarks

In this paper, field emission characteristics of GaN and GaP nanowires have been investigated. The turn-on fields of those two wires were found to be higher than CNTs. The emission stability under the oxygen environment for GaP nanowire was better than CNTs. The field emission energy spectra of electrons from nanowires have been examined, and possible explanation for two peaks behavior of GaN nanowiers was proposed here.

5. Acknowledgements

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6. References

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