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Emission Stability of Semiconductor Nanowires

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Field emission of GaN and GaP nanowires, synthesized by thermal chemical vapor deposition, and their emission stabilities under oxygen and argon environments were investigated. The field emission current of GaN nanowires was seriously deteriorated under oxygen environment, while that of GaP was not. Both wires did not show any noticeable change under argon environment. The existence of oxide outer shell layers in the GaP nanowires was proposed to be a main reason for this emission stability behavior. Field emission energy distributions of electrons from these nanowires revealed that field emission mechanism of the semiconductor nanowires were different from that of carbon nanotubes.

Keywords : field emission, nanowire, GaN, GaP, oxygen, stability

After rapid progresses in carbon nanotubes (CNTs) [1], such as field emission displays [2-5], memories, and composites, other types of nanostructures are further investigated. Many types of nanowires, as an important structure among nanostructures, have been synthesized and their characteristics are under investigation [6-10]. Synthesis of numerous nanowires, especially compound semiconductor nanowires, has been reported [11,12]. Even superlattice nanowires in the axial or radial direction were recently reported [10]. Spontaneous light emission, photoluminescnece, and Raman scattering have been reported for nanowires. Nonetheless, many characteristics of nanowires are not yet known sufficiently--field emission is one of them. Investigation of field emission on nanowires is desirable, considering wide usage of field emission from CNTs and future possibility of nanowires as electron emitters. Small values of electron affinities in GaN and GaP may be of use in field emission. Here, field emission characteristics of GaN and GaP nanowires will be reported.

Several techniques have been developed for synthesizing nanowires, including arc discharge, pyrolysis, laser ablation, and chemical vapor deposition (CVD) [6-10]. Among these various methods, CVD has been known to be one of the promising methods for controlled and selective growth of nanowire. On an alumina substrate, NiO or CoO catalyst nanoparticles were evenly distributed, and the catalyzed substrate was put on the top of a quartz boat loaded with Ga/GaN or Ga/GaP powders. A tube furnace was used for nanowire growth as a tool of a thermal CVD. The details can be

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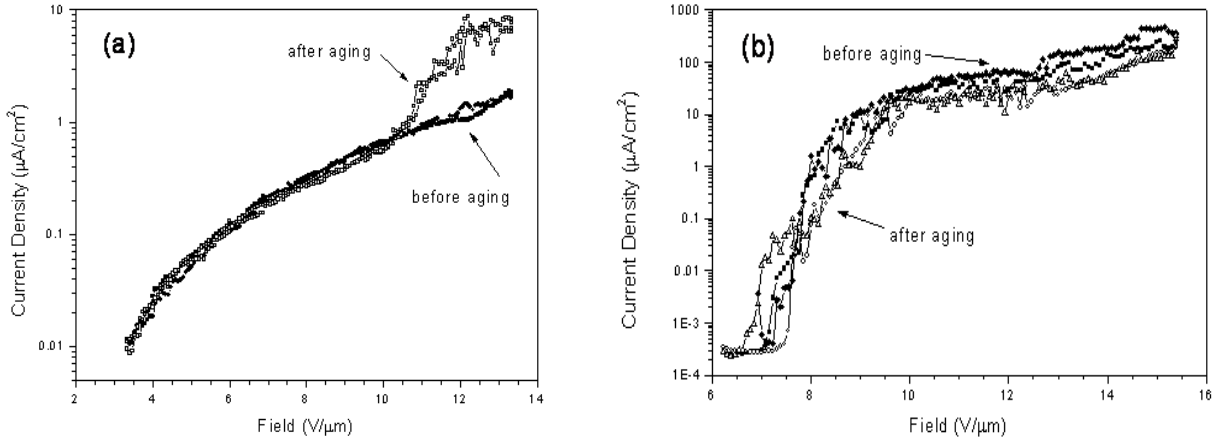

Fig. 1 Field emission characteristics of (a) GaN nanowires and (b) GaP nanowires. For GaN nanowires aging was performed during the field emission measurement (solid symbols: before aging, open symbols: after aging).

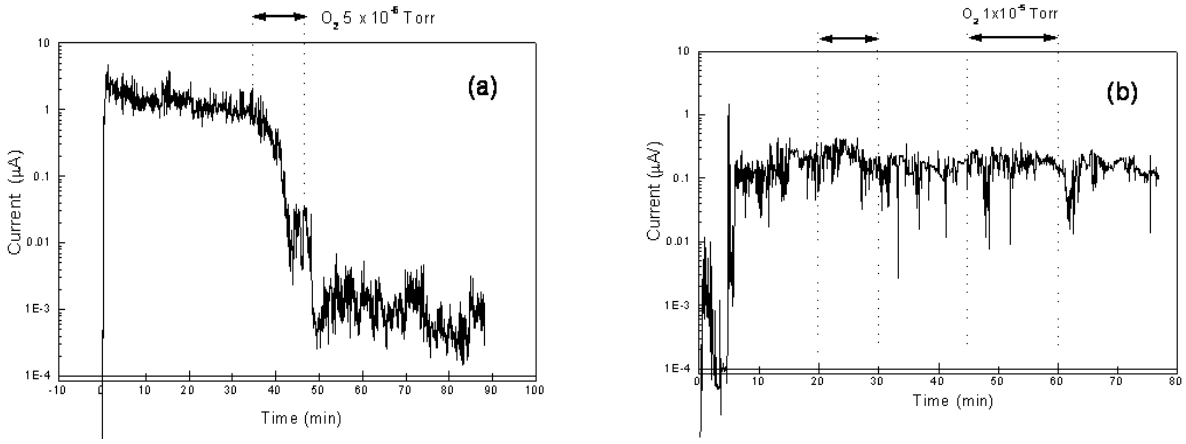

Fig. 2 Emission stability under the oxygen environment for (a) GaN (b) GaP nanowires. Only the GaN nanowires were severely influenced by an oxygen gas.

found in Refs. [6] and [7]. As-deposited products were characterized by scanning electron microscopy, transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX), and x-ray diffraction (XRD), which confirmed successful growth of single-crystalline GaN and GaP nanowires [6,7]. While GaN nanowires do not have any outer shell layer on the surface, GaP nanowires have outer oxide shell layers (See Fig. 4(c) of Ref. [6]). Actually, the shell layers were found to be double layers of orthorhombic structured $GapO_4$ and amorphous Ga_2O_3.

Nanowires were removed from the substrate by a knife and were dispersed in ethanol for field emission measurement. After sonification, several droplets of the nanowire-containing ethanol were dropped on a conducting substrate and dried in air. For electrical contact improvement, 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 Keithley 6517 pico-A meter. 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

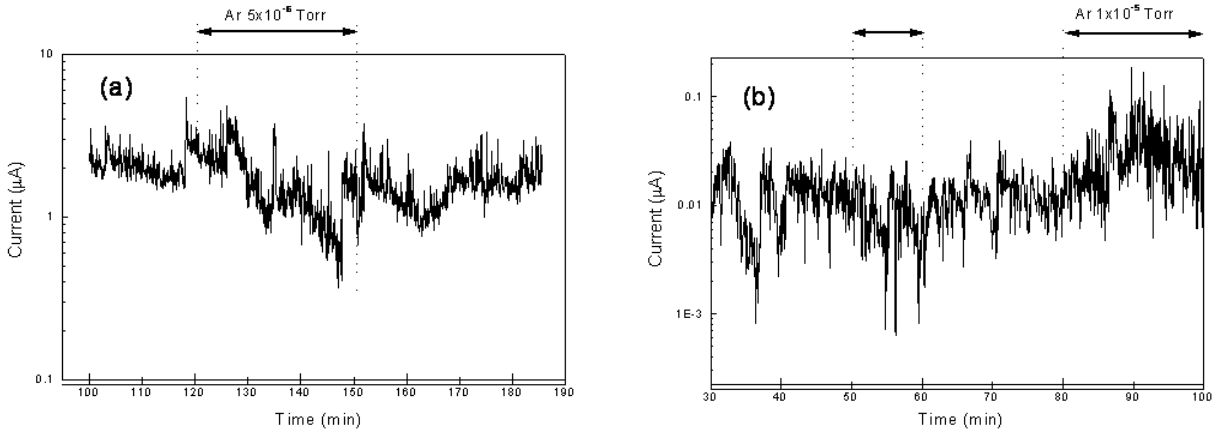

Fig. 3 Emission stability under the argon environment for (a) GaN (b) GaP nanowires. Both nanowires were not influenced by an argon gas.

from a cathode plate (150 for GaN nanowires, and 130 μm for GaP nanowires), where a small portion of electrons that escaped from the metallic mesh were 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 monitoring of the pressure of the chamber.

Field emission data clearly show that the turn-on fields (here, defined as a field required for the emission current density of 1 $\mu A/cm^2$) for the two nanowires were fairly higher than those of CNTs, that is, slightly higher than 10 V/μm for GaN and slightly lower than 10 V/μm for GaP nanowires, respectively (See Fig. 1). For comparison, the turn-on fields for CNTs are generally around 1~3 V/μm [13]. The mobilities of semiconductor nanowires are generally lower than their corresponding bulk partners [14]. Many native imperfections exist in the nanowires leading to poor mobility and photoluminescence, although TEM usually cannot image such imperfections. Consequently, poor field emission characteristics of nanowires might be occurred from this fact. Furthermore, the samples were prepared by dispersing nanowires on the substrates, leading to small density of nanowires and electrical contact problem between the nanowires and substrate [15]. Thus, there are a lot of rooms to improve the field emission characteristics of nanowires.

Generally, bulk GaN was poor in crystal quality due to many intrinsic imperfections, such as vacancies and unintentional doping [16,17]. Thus, the crystal quality of GaN nanowires is thought to be worse than that of GaP nanowires, which may lead to poor field emission characteristics of GaN nanowires. This can be confirmed by comparing the field emission enhancement factors—3500 for GaN, and 110 for GaP nanowires, respectively (The electron affinity for GaN (GaP) nanowires used in this calculation is 3.30 (1.96) eV) [18,19]. Field emission characteristics of GaP nanowires were almost the same before and after aging, while GaN nanowires clearly showed different behavior. Aging generally induces desorption of adsorbates on the field emitters [20,21]. GaP nanowires may sufficiently reduce the influence of adsorbates on the surface of nanowires due to native oxide outer shell layers. Since the oxygen-related absorbates mostly influence the field

emission characteristics [20,21], the oxide shell layer on GaP nanowires would reduce the emission change done by absorbates.

Figure 2 shows emission stability under an oxygen environment. GaN nanowires showed large current decrease upon the introduction of oxygen. After removing an oxygen gas, the field emission current for GaN nanowires failed to recover to the initial current. For GaP nanowires the pressure of oxygen gas was five times higher than that of GaN and an oxygen gas was introduced twice, however, the emission current did not show any noticeable change. The outer oxide shell layers protect GaP nanowires during this harsh environment. The initial 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 did not exhibit any significant current decrease (See Fig. 3). Thus, only GaN nanowires experienced large current reduction under oxygen that might attack nanowires chemically and physically. Since GaP nanowires have oxide outer layers, these layers are considered to play a key role in protecting nanowires from oxygen during field emission. The unvarying field emission current for GaP nanowires with a change of vacuum environment may be useful for fabrication of field emitters, since unprotected CNT field emitters were found to be severely deterioratedunder the oxygen environment [22].

The field emission energy spectra of GaN nanowires were not familiar shapes that are frequently observed for metallic emitters and CNTs (See Fig. 4(a)) [3]. The almost equal-sized two peaks were splitted around the Fermi energy. The left peaks seem to be originated from field emission through

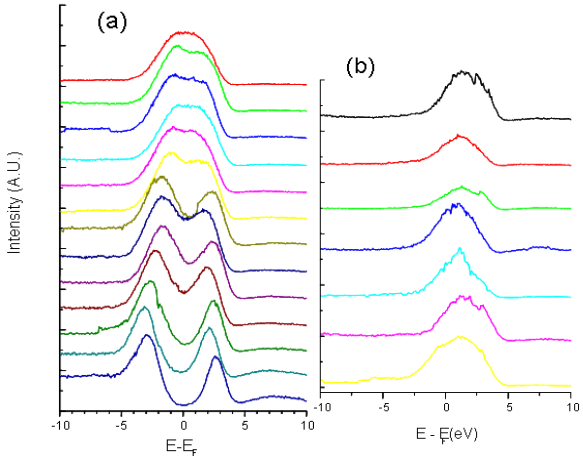

Fig. 4 Field emission energy distribution for (a) GaN (1820 to 2060 with 20 V interval from the top) and (b) GaP (1600 to 1700 with 20 V interval from the top except the bottom curve for 2000 V) nanowires.

semiconducting nanowires, since the peaks move to the lower energy with the increase of the applied voltage. The moving of the peaks was a strong evidence for the band bending due to the field penetration into the semiconducting nanowires. On the while, another peaks located higher than the Fermi level were found. Thermionic emission can be considered to be one of possible explanations. CNTs have been known to become very hot for a high field emission current by Joule heating due to a high electric field [23]. Considering the fact that semiconducting nanowires are more resistive than CNTs, nanowires may be hotter during high field emission. The possibility of being hot for nanowires may contribute to large intensity of right peaks. However, there may still exist other possi-bilities for the identity of these peaks.

GaP nanowires exhibited only one peakunlike 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 different energy shape behavior for GaP and GaN nanowires.

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 those of CNTs. The emission stability under the oxygen environment for GaP nanowire was better than GaN nanowires, possibly due to the protecting of nanowires by outer oxide shell layers, while no change for Ar environment for two wires. The field emission energy spectra of electrons from nanowires have been examined, which indicates different field emission mechanism for semiconductor nanowires from CNTs.

Acknowledgments

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반도체 나노와이어에서 전자방출 안정성

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열 화학기상법으로 만든 GaN와 GaP 나노와이어에서 전계 방출과, 산소와 아르곤 분위기에서 안정성에 대해 조사하였다. GaN 나노와이어의 경우 산소 분위기에서 전계 방출이 급격하게 줄었으나, GaP에서는 그렇지 않았다. 두 나노와이어 모두 아르곤 분위기에서는 큰 변화가 없었다. GaP 나노와이어의 외부에 존재하는 산화물 층이 전자 방출 안정성에 크게 기여한 것으로 생각된다. 나노와이어에서 방출된 전자의 에너지 분포를 통해 반도체 나노와이어는 탄소 나노튜브와 그 전계 방출 메카니즘이 다름을 유추할 수 있었다.

주제어 : 전계 방출, 나노와이어, GaN, GaP, 산소, 안정성

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