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Letters

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Electroluminescence from AIN nanowires grown on *p*-SiC substrate

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Aluminum nitride (AlN) nanowires were prepared by the carbothermal reduction method. A heterojunction light-emitting diode (LED) was fabricated by depositing randomly aligned AIN nanowires onto p-type 4H–SiC substrate. When a forward bias voltage greater than 8 V was applied to the LED, a broad band emission peaked at 417 nm could be observed. The peak deconvolution revealed four emission peaks at \sim 400, 420, 468, and 525 nm. These emission peaks may be attributed to the radiative recombination between electrons from trap-level states and holes from the valence band of the AIN nanowires. © 2010 American Institute of Physics. [doi:10.1063/1.3513308]

Aluminum nitride (AlN), which has a wide band gap of ~ 6 eV, is a promising material for deep ultraviolet devices such as light-emitting diodes (LEDs).¹ Recently, extensive studies have been concentrated on the fabrication of nanostructured AlN by various chemical and physical deposition techniques.²⁻⁴ Investigations have revealed that AlN nanocones exhibited an emission band centered at ~ 481 nm.⁵ Cathodoluminescence from AlN nanorods revealed an emission peak centered at \sim 519 nm.^{6,7} On the other hand, two defect-related emissions at around 364 and 590 nm were observed from AlN nanotips, which were prepared by a vapor transport and condensation process.⁸ These emission peaks observed from AlN nanostructures were usually attributed to (i) radiative recombination of photon-generated holes with electrons occupying nitrogen deficiencies (V_N) and/or (ii) transition between shallow levels of $V_{\rm N}$ and deep levels of oxygen related impurities (O_N) such as Al vacancies (V_{Al}) complexes in AlN nanostructures. Typically, AlN nanostructures were grown on Si or sapphire substrates. Due to the close lattice match ($\sim 1\%$) between AlN and SiC, high crystal quality AlN nanowires could be formed on SiC.⁹ In this letter, we showed that a broad electroluminescence (EL) emission peaked at 417 nm can be observed from a heterojunction formed between AlN nanowires and p-SiC (4H) substrate. The peak deconvolution was performed to understand the emission nature of the EL spectrum.

AlN nanowires were synthesized by a conventional carbothermal reduction method.⁴ The experiment was carried out inside a horizontal tube furnace in which a mixture of AlN and MgCl₂ powders (with weight ratio of 2:1) was used as the source material. The mixture was loaded into an alumina boat, which was then placed into the center of an alumina tube of 3 cm in diameter. A clean p-doped 4H-SiC substrate (Cree Inc.) was placed on another alumina boat 2 cm away from the source material. The *p*-doped 4H–SiC substrate was chosen as the hole injection layer of the heterojunction because it has a high hole concentration (~ 1 $imes 10^{19}$ cm⁻³) and carrier mobility (~120 cm²/V s). In addition, the p-SiC substrate does not support radiative recombination at visible regime. The furnace was flushed with Ar until the temperature of the furnace reached 800 °C, then N₂ at 70 SCCM (SCCM denotes cubic centimeter per minute at STP) was introduced into the tube. When the temperature of the furnace reached 1200 °C, the flow rate of N2 was increased to 140 SCCM. The growth was maintained at 1450 °C for 2 h and a layer of randomly aligned AlN nanowires was formed on the surface of the *p*-SiC substrate. It is noteworthy that MgCl₂ is acted as a catalyst for the growth of AlN nanowires. Without MgCl₂ powder in the mixture of the source material, AlN nanowires cannot be obtained under the above growth conditions.

Figure 1(a) shows a scanning electron microscopy (SEM) image of the randomly oriented AlN nanowires. The magnified SEM image of a single AlN nanowire is shown in Fig. 1(b). It is observed that the nanowires, which have an average length of $\sim 6 \ \mu m$ and a diameter of $\sim 80 \ nm$, are closely packed together to form a thin film. Figure 1(c) shows the cross-sectional SEM image of the heterojunction. The AlN nanowires were grown on the surface of the SiC substrate. It is noted that the AlN nanowires exhibited good interfacial properties with the SiC substrate primarily due to its lattice match with SiC. Figure 1(d) shows a high-



FIG. 1. (a) A typical SEM image of the randomly packed AlN nanowires. (b) A magnified SEM image of a single AlN nanowire. (c) Cross-section SEM image of interface between AlN nanowires and SiC substrate. (d) A HRTEM image of the AlN nanowire and the SAED pattern.

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FIG. 2. (Color online) (a) Room-temperature I-V characteristics of AlN nanowires/p-SiC substrate. The inset shows the schematic diagram of the proposed AlN nanowires/p-SiC(4H) substrate heterojunction LED. (b) Room-temperature I-V curves of two ITO contacts deposited on a layer of randomly packed AlN nanowires. The inset shows the corresponding measurement setup.

resolution transmission electron microscopy (HRTEM) image of the nanowire and the inset indicates the corresponding selected area electron diffraction (SAED) pattern. It is verified that the nanowire is composed of AlN with a hexagonal structure. The lattice spacing of 0.493 nm in the growth direction corresponds to the [0001] plane of wurtzite AlN. No Mg and related compounds can be detected which suggested that MgCl₂ acted as catalyst for the growth of AlN nanowires.

The schematic diagram of the AlN nanowires/p-SiC heterojunction LED is showed in the inset of Fig. 2(a). The contact of the heterojunction was fabricated by depositing a metal layer of dimension about $2 \times 2 \text{ mm}^2$, which consisted of a layer of ~ 25 nm thick Al film and a layer of ~ 150 nm thick Ti film, onto the rough surface of the *p*-SiC substrates via electron beam evaporation. The sample was then subjected to rapid thermal annealing at 800 °C in N2 for 5 min in order to obtain an Ohmic contact on the p-SiC substrate, the corresponding contact resistance was less than 2 k Ω . The Ohmic contact of the AlN nanowires can be obtained by depositing a ~ 200 nm thick indium tin oxide (ITO) layer onto the surface of the randomly packed AlN nanowires via electron-beam sputtering at room temperature. Figure 2(a)plots the current-voltage (I-V) curve of the heterojunction at room-temperature. It is observed that the heterojunction has a turn-on voltage of 8 V. However, the heterojunction has a large leakage current under reverse bias. The large leakage current can be explained by energy band diagram of the heterojunction as shown later. In order to show that the I-Vbehavior is mainly due to the AlN nanowires/p-SiC heterojunction, I-V curves of two ITO contacts (separated at a distance, $d=200,500,800 \ \mu m$) deposited on the surface of randomly packed AlN nanowires were measured, see Fig. 2(b). It is noted that the relationship between I and V is roughly linear for the absolute voltage less than 15 V.

Figure 3(a) shows EL spectra of the heterojunction LED under bias at different voltages. The spectra were measured by connecting the cathode and anode of a rectangle pulse voltage source (with repetition rate and pulsewidth of 7.5 Hz and 80 ms, respectively) to the ITO and Al/Ti metal contacts, respectively, of the heterojunction. Light was collected from



FIG. 3. (Color online) (a) Room-temperature EL spectra of the AlN nanowires/p-SiC heterojunction. (b) Fitting results of the EL spectrum obtained from the LED at forward biased voltage of 15 V. (c) Fitting results of the PL spectrum of the AlN nanowires deposited on p-SiC.

the surface of the ITO by an objective lens. It was noted that at forward bias of 15 V, the corresponding emission spectrum has a full-wave-half-maximum of ~125 nm. The LED exhibited white-light emission. However, no emission was observed from the heterojunction LED under reverse bias. It is suggested that the AlN nanowires are unintentionally doped into *n*-type so that a heterojunction is formed between the AlN and *p*-SiC. The *n*-type conduction of the AlN nanowires could be related to defect levels associated with V_N , O_N , or V_{Al} . Due to the high growth temperature of the AlN nanowires (over 1400 °C) on Si (donor in Aln¹⁰) from the SiC could diffuse into the AlN nanowires and turned the nanowires was still too high to perform a Hall effect measurement.

Figure 3(b) plots the fitting results of the EL spectrum for the heterojunction LED at forward bias of 15 V. It is found that the emission spectrum can be fitted by four Gaussian curves with peak wavelength at $\sim 400, 420, 468,$ and 525 nm. Furthermore, the wavelength of the four peaks will not change by more than ~ 4 nm for the variation in bias voltage above the turn-on voltage. Hence, the AlN nanowires can be considered to have four radiative recombination centers. Figure 3(c) plots the photoluminance (PL) spectrum of the randomly packed AlN nanowires deposited on p-SiC substrate. The sample was pumped at an excitation intensity of ~ 1 MW/cm² by a 355 nm frequency tripled neodymiumdoped yttrium aluminum garnet pulsed laser (6 ns pulsewidth and 10 Hz repetition rate). A spherical lens was used to focus a pump beam of 1 mm in diameter onto the surface of the randomly packed nanowires. Emission was collected in the direction perpendicular to the surface of the randomly packed nanowires. The PL spectrum was fitted by four Gaussian curves with peak wavelength at \sim 398, 425, 470 and 525 nm. These values are closed to that observed from



FIG. 4. (Color online) Energy band diagrams for the AlN nanowires/p-SiC heterojunction under (a) equilibrium, (b) forward bias, and (c) reverse bias. E_{Def} represents the energy levels of the four trap-level states.

the EL spectrum. Hence, this verified that there are four emission bands responsible for the radiative recombination of AlN nanowires.

There is no clear consensus on the specific origin of the defect-related emissions in AlN. It is generally believed that the visible emissions from AlN nanostructures are originated from crystal defects that formed during growth. The two violet emissions (398 and 425 nm) are believed to be related to oxygen-related defects. The oxygen impurities will produce defects including oxygen point defects, $V_{\rm N}$ and $O_{\rm N}-V_{\rm Al}$ complexes to form the deep levels or trap-level states inside the band gap of the AlN nanostructures.^{11,12} The blue/green emissions (470 nm and 525 nm) can be associated with vacancies of N in AlN nanowires. Hence, the emission may result from the radiative recombination between electrons occupying $V_{\rm N}$ and holes in the valance band.^{13,14} It is also possible to have radiative transition between shallow levels of $V_{\rm N}$ and deep levels of $O_{\rm N} - V_{\rm Al}$ complexes.^{5,8} However, in order to explain the emission characteristics observed from both PL and EL spectra, it is necessary to have some traplevel states inside the band gap contributing to both electrical and optical excitation processes.

Figure 4 shows the energy-band diagram of the n-AlN/p-SiC heterojunction under the conditions of equilibrium, forward and reverse bias. As shown in Fig. 1(c), the AlN nanowires are in good contact with the *p*-type SiC substrate so that their vacuum levels can be roughly continued across the heterojunction. Electron affinity energies of AlN, χ (n-AlN), and 4H–SiC, χ (p-SiC), can be assumed to be ~ 0.25 eV and 4.05 eV, respectively.^{9,15} Furthermore, the band gap energy of AlN, $E_{\rm g}$ (AlN), is set to ~6.0 eV and that of the 4H–SiC, E_g (*p*-SiČ), is set to ~3.26 eV. It can be shown that the conduction band offset, $\Delta E_{\rm C}$ and valance band offset $\Delta E_{\rm V}$ of the AlN–SiC heterojunction are roughly equal to 3.8 eV and 1.06 eV, respectively. The Fermi level, $E_{\rm F}$, of p-SiC substrate, according to its high hole concentration and carrier density, can be estimated to be ${\sim}0.8~{\rm eV}$ above the valence band. For AlN nanowires, $E_{\rm F}$ of AlN is assumed to be ~ 2.8 eV below the conduction band (i.e., slightly *n*-doped due to unintentional doping). For the heterojunction at equilibrium and under optical excitation, radiative recombination can be obtained from the photogenerated holes at the valence band with the excited electrons occupying the four trap-level states, see Fig. 4(a). For the heterojunction under large forward bias, holes can be injected from the valence band of *p*-SiC into that of AlN. Hence, electrons excite to the conduction band of the AlN can be relaxed nonradiatively to the four trap-level states (with energies of E_{Def}) and then radiatively recombined with holes in the valence band of the AlN, see Fig. 4(b). Nevertheless, it is possible to have electrons radiatively recombined with holes in the trap-level states very near to the valence band. However, the similarity between EL and PL spectra suggests that holes in the valence band are dominated. Figure 4(c) shows the heterojunction under reverse bias condition. Although $\Delta E_C > \Delta E_v$, electrons can tunnel through the barrier of the conduction band of AlN so that high leakage current was observed under reverse bias.

The four trap-level states can be either $V_{\rm N}$ or $O_{\rm N}-V_{\rm Al}$ complexes, however, it is believed that V_N may be contributed to the trap-level states of the AlN nanowires. This is because the emission intensity of AlN nanowires can be significantly suppressed after thermal annealing at 900 °C for 1 hr in NH₃ as this annealing process can reduce the concentration of $V_{\rm N}$.¹³ In conclusion, a white-light AlN nanowires/p-SiC heterojunction LED was fabricated by depositing a layer of randomly packed AlN nanowires onto a p-SiC substrate. It was demonstrated that for the LED under forward biased, the corresponding EL emission spectra were observed with multiple peaks at \sim 400, 420, 468, and 525 nm. By comparing with the PL spectrum, it is noted that there are four trap-level states of the AlN nanowires contribute to the effective generation of light. The four trap-level states are related to $V_{\rm N}$ inside the band gap of the AlN nanowires. It is believed that the high concentration of V_N from the nanowires (i.e., arisen from the large surface to volume ratio) leads to the radiative recombination in visible regime.

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