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Color tunable light-emitting diodes based on p^+ -Si/ p -CuAlO₂/ n -ZnO nanorod array heterojunctions

Bo Ling,¹ Jun Liang Zhao,¹ Xiao Wei Sun,^{1,a)} Swee Tiam Tan,¹ Aung Ko Ko Kyaw,¹ Yoga Divayana,¹ and Zhi Li Dong²

¹*School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798*

²*School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798*

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Wide-range color tuning from red to blue was achieved in phosphor-free p^+ -Si/ p -CuAlO₂/ n -ZnO nanorod light-emitting diodes at room temperature. CuAlO₂ films were deposited on p^+ -Si substrates by sputtering followed by annealing. ZnO nanorods were further grown on the annealed p^+ -Si/ p -CuAlO₂ substrates by vapor phase transport. The color of the p -CuAlO₂/ n -ZnO nanorod array heterojunction electroluminescence depended on the annealing temperature of the CuAlO₂ film. With the increase of the annealing temperature from 900 to 1050 °C, the emission showed a blueshift under the same forward bias. The origin of the blueshift is related to the amount of Cu concentration diffused into ZnO. © 2010 American Institute of Physics. [doi:10.1063/1.3459963]

As one of the most promising optoelectronic materials in the blue-UV region, ZnO has received great attention during the past decade and much effort has been dedicated to the growth of ZnO nanostructures owing to their unique properties compared to their bulk counterparts.¹ Among various potential applications of one-dimensional ZnO, light-emitting diodes (LEDs) based on ZnO nanorods/nanowires (NRs/NWs) have been studied.^{2,3} However, most commonly observed light emissions from ZnO based LEDs are defect-related emissions related to various parameters. This uncontrollable light emission hindered the practical application of ZnO in light-emitting devices. In view of the potential application of ZnO in full-color display, signal indicator, and illumination, it will be highly desirable if light emission can be tuned in one single LED by a facile and cost-effective fabrication process.

Conventionally, color-tunable LEDs were achieved by adopting phosphors, polymer dyes, inorganic quantum dots, and fluorescent microspheres.⁴ In this paper, we demonstrate all-inorganic phosphor-free LEDs based on p^+ -Si/ p -CuAlO₂/ n -ZnO NR arrays (NRAs) with a wide-range color-tuning by varying the annealing temperature of the CuAlO₂ layer.

The schematic of the LED structure is shown in Fig. 1(a). In our experiment, p^+ -Si(100) wafers (carrier density of ca. 10^{19} cm⁻³) cleaned by hydrofluoric acid were employed

as the substrates. First, CuAlO₂ films of ca. 50 nm were deposited by direct-current magnetron sputtering at room temperature.⁵ The postgrowth annealing of the films was conducted in air for 30 min ranging from 900–1050 °C followed by the deposition of a thin ZnO film (ca. 30 nm) by sputtering, which served as the seed layer for the ZnO NR growth. Vertically aligned ZnO NRAs were grown on the prepared substrates by vapor-phase transport method at 600–700 °C. Spin-on-glass (SOG) was chosen as the spacer layer to fill up the interspace of ZnO NRAs by spin coating.³ Au electrodes were also prepared by sputtering at both sides of the devices. The top cathode electrodes were patterned into circular shape using a shadow mask and the bottom anode electrodes were deposited directly on the back side of the Si wafers without any patterning. Figure 1(b) shows the cross-sectional view of the ZnO NRAs grown on a ZnO buffered p -CuAlO₂/ p^+ -Si substrate. The average diameter and the length of the nanorods are ca. 200 nm and 2.5 μm, respectively.

Figures 2(a)–2(d) represent the x-ray diffraction (XRD) patterns of the annealed CuAlO₂ films at different temperatures. When the annealing temperature of CuAlO₂ film ranges from 900 to 1000 °C [Figs. 2(a)–2(c)], the diffraction peaks can be indexed into three phases, i.e., hexagonal delafossite CuAlO₂ phase [Joint Committee on Powder Diffraction Standards (JCPDS) no. 35–1401], CuO (JCPDS) no.

FIG. 1. (Color online) (a) Schematic of the p^+ -Si/ p -CuAlO₂/ n -ZnO NRA LED. (b) Cross-sectional SEM image of the ZnO NRAs grown on a ZnO coated p -CuAlO₂/ p^+ -Si substrate.

^{a)} Author to whom correspondence should be addressed. Electronic mail: exwsun@ntu.edu.sg.

FIG. 2. (Color online) [(a)–(d)] XRD patterns and [(e)–(h)] corresponding AFM images of the CuAlO₂ film annealed at 900, 950, 1000, and 1050 °C.

05–0661), and CuAl₂O₄ (JCPDS no. 33–0488). However, when the annealing temperature reaches 1050 °C, the peak intensity of CuAlO₂ phase becomes more prominent with only two weak peaks from CuO phase [Fig. 2(d)]. This corresponds well with the thermodynamic data in the literatures that CuAlO₂ was more easily decomposed into CuO and CuAl₂O₄ under lower annealing temperature in air.⁶ Additionally, the full width at half maximum of the main peak CuAlO₂ (012) decreased from 0.65° to 0.37° with the increase of the annealing temperature from 900–1050 °C, indicating that higher crystallinity of CuAlO₂ can be obtained at higher annealing temperature. Figures 2(e)–2(h) show the atomic force microscopy (AFM) images and the calculated root mean square (RMS) of CuAlO₂ films annealed at different temperatures. It can be seen that the surface roughness of

the annealed CuAlO₂ films increases with the annealing temperature which should be ascribed to grains coalescence related to the recrystallization in the CuAlO₂ film. It is noted that the thickness of the CuAlO₂ film remains unchanged after annealing for all our samples.

The typical current-voltage (*I*-*V*) characteristics of the *p*⁺-Si/*p*-CuAlO₂/*n*-ZnO NRA heterostructured diodes are shown in Fig. 3. All the devices show diode like rectifying characteristics. In order to get an insight into the junction behavior in our devices, the contact behaviors of Si and ZnO sides were shown as insets in Figs. 3(a) and 3(b), respectively. The corresponding device configurations are schematically shown as insets in Figs. 3(c) and 3(d), respectively. The *I*-*V* characteristic of the Au/Si/CuAlO₂/Au junction [inset in Fig. 3(a)] shows a kinked straight line, which is primarily caused by the large band gap difference between Si and CuAlO₂, and the weak *p*-type of CuAlO₂.⁷ Inset in Fig. 3(b) shows the nearly linear *I*-*V* curve of the Au/ZnO NR/Au junction, suggesting the Ohmic-type behavior of our Au/ZnO NR contact. As a result, the rectifying behavior shown in our devices should be mainly ascribed to the *p*-CuAlO₂/*n*-ZnO junction. The turn-on and breakdown voltages differ from device to device and depend on the annealing temperature of the CuAlO₂ film. The turn-on voltages of CuAlO₂/ZnO LEDs are 0.5 V, 1 V, 2.2 V, and 3.2 V for samples annealed at 900 °C, 950 °C, 1000 °C, and 1050 °C, respectively. The breakdown voltage also showed the same tendency, i.e., it became higher with the increase of the annealing temperature. Considering that our ZnO NRs are grown at high temperature (600–700 °C), Cu will unavoidably diffuse into the ZnO side. As the crystal phase is less stable and the crystallinity is poorer in the CuAlO₂ film annealed at lower temperature, the Cu bonding in the lattice is expected to be weaker, which facilitates the Cu diffusion from CuAlO₂ into ZnO layer. Furthermore, Cu was reported to be easily diffused into ZnO lattice since the ionic radius of Cu²⁺ (ca. 0.73 Å) is very close to that of Zn²⁺ (ca. 0.74 Å).^{8,9} Therefore, the lower turn-on and breakdown voltages for the device fabricated with lower-temperature-annealed CuAlO₂ may be due to more Cu diffusion from CuAlO₂ side into ZnO side. The concentrations of Cu in the ZnO layer of each device were studied using energy dispersive spectroscopy (EDS) attached

FIG. 3. (Color online) *I*-*V* characteristics of the *p*⁺-Si/*p*-CuAlO₂/*n*-ZnO NRA LEDs with CuAlO₂ film annealed at different temperatures (a) 900 °C, (b) 950 °C, (c) 1000 °C, and (d) 1050 °C. Insets in Figs. 3(a) and 3(b) are contact behaviors of Si-CuAlO₂ (annealed at 900 °C) heterojunction and ZnO-Au contact, respectively. Insets in Figs. 3(c) and 3(d) are the corresponding device configurations for characterizing the contact behaviors in insets 3(a) and 3(b), respectively. The interspace between two Au contracts is 3 μm patterned by photolithography and the thickness of the SiO₂ layer is 500 nm.

FIG. 4. (Color online) RT EL spectra and the corresponding EL photos of p^+ -Si/ p -CuAlO₂/ n -ZnO NRA heterostructured LEDs with CuAlO₂ film annealed at different temperatures, i.e. 900 °C, 950 °C, 1000 °C, 1020 °C, and 1050 °C. Schematic band diagram of the p^+ -Si/ p -CuAlO₂/ n -ZnO NRA LED under (b) zero bias and (c) forward bias.

to SEM. All the EDS measurements share the same measurement parameters including accelerating voltage, spot size and magnification factor. It was found that the concentration of Cu decrease with the increase of the annealing temperature, which are 1.42%, 1.35%, 1.21%, 1.16%, and 1.07% for samples annealed at 900 °C, 950 °C, 1000 °C, 1020 °C, and 1050 °C, respectively. Cu doping normally forms defect-related impurity energy level above the valence band maximum of ZnO (Ref. 10) and the effective energy band gap of Cu doped ZnO becomes narrower.^{11,12} Since the turn-on voltages become higher from CuAlO₂/ZnO diodes with lower Cu doping concentration, less band gap reduction of ZnO was expected from higher temperature annealed samples. Figure 4 shows the room temperature electroluminescence (EL) spectra together with the emitting photos from the p^+ -Si/ p -CuAlO₂/ n -ZnO NRA heterostructured LEDs with various annealing temperatures for the CuAlO₂ layer. Both excitonic and deep level emission of ZnO can be detected under the forward bias. With the decrease of the annealing temperature from 1050 to 900 °C, the dominant EL peak redshifted gradually as the color of the emission changed from bluish purple, cyan, green, yellow to red emissions under the same forward bias of 20 V. It is worth mentioning that light emission spectra did not show significant shift for all devices when the forward bias was changed from 5 to 30 V. The light emission photographs taken from different devices are consistent with the corresponding EL spectra, indicating color tuning properties could be achieved by con-

trolling the annealing temperature of the CuAlO₂ in p -CuAlO₂/ n -ZnO NRA LEDs.

The possible mechanism responsible for EL tuning properties in ZnO is discussed as follows. The energy band diagrams of p^+ -Si/ p -CuAlO₂/ n -ZnO NRA at equilibrium and under forward bias according to Anderson model are shown in Figs. 4(b) and 4(c), respectively. The electron affinities of ZnO, Si, and CuAlO₂ were taken as 4.35 eV, 4.05 eV, and 0.15 eV, respectively.^{5,13} The band gaps of ZnO, Si, and CuAlO₂ were considered to be 3.37 eV, 1.12 eV, and 4.2 eV, respectively.^{5,13} It can be seen from Fig. 4(c) that the bands of Si will bend downward and those of CuAlO₂ will bend upward at the p^+ -Si/ p -CuAlO₂ interface. At the p -CuAlO₂/ n -ZnO interface, the bands of CuAlO₂ will bend downward under forward bias and the E_v of ZnO moves to higher energy and becomes closer to that of CuAlO₂. As a result, the holes was first injected from E_v of Si into that of CuAlO₂ and then injected into the valence band or Cu-related deep defect energy level bands in ZnO, resulting in UV and visible emissions from ZnO, respectively. With the incorporation of Cu, the deep defect levels in ZnO become complicated in view of its own intrinsic deep defect levels in as-grown ZnO.^{10,14} The gradual redshift in the EL spectra is related to the band gap reduction of ZnO, according to the previous reports both in theoretical calculation and experimental work.^{11,12}

In conclusion, color tunable all-inorganic p^+ -Si/ p -CuAlO₂/ n -ZnO NRA LEDs was fabricated by controlling the annealing temperature of the CuAlO₂ layer. With the increase in the annealing temperature from 900 to 1050 °C, the light emissions from the LEDs showed blueshift gradually from red, yellow, green, cyan, and to bluish-purple colors. The origin of the color tuning characteristics was attributed to the different amount of Cu diffused into ZnO from CuAlO₂ with various annealing temperatures.

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