

Fabrication of n -ZnO:Al/ p -SiC(4H) heterojunction light-emitting diodes by filtered cathodic vacuum arc technique

Clement Yuen, S. F. Yu,^{a)} S. P. Lau, Rusli, and T. P. Chen

School of Electrical and Electronic Engineering, Nanyang Technological University, Block S2, Nanyang Avenue, Singapore 639798

(Received 9 February 2005; accepted 10 May 2005; published online 8 June 2005)

We report the low-temperature ($\sim 150^\circ\text{C}$) fabrication of n -ZnO:Al/ p -SiC(4H) heterojunction light-emitting diodes by filtered cathodic vacuum arc technique. Diodelike rectifying current-voltage characteristics, with turn-on voltage of $\sim 3.8\text{ V}$ and low reverse leakage current of $< 10^{-2}\ \mu\text{A}$, were measured at room temperature. In addition, ultraviolet emission with peak wavelength of $\sim 385\text{ nm}$ and full width at half maximum of $\sim 20\text{ nm}$ are observed at a forward biased voltage of $\sim 7.4\text{ V}$. The ultraviolet electroluminescence from the heterojunction is originated from the exciton-exciton scattering inside the n -ZnO:Al film. © 2005 American Institute of Physics. [DOI: 10.1063/1.1947889]

Transparent Al-doped ZnO (ZnO:Al) films, which have metal-like electrical conductivity, are key materials for numerous applications, such as transparent electrodes for organic light-emitting diodes (LEDs) and flat panel displays¹ as well as its potential use in the conduction channel of transparent thin-film transistors.² However, it is difficult to achieve ultraviolet (UV) photoluminescence (PL) at room temperature (RT) from n type conduction ZnO:Al films grown on lattice-mismatched substrate.³ This is probably due to the oxidation of the Al during the growth process.⁴ On the other hand, n -ZnO:Al films have been employed as electron injectors in ZnO-based heterojunction LEDs,⁵ but only greenish-white electroluminescence (EL) has been observed. Hence, most of the successful ZnO-based active layer heterojunction^{6,7} and ZnO homostructural p - i - n junction⁸ UV LEDs have employed Ga-doped ZnO film as the electron injection layer. In fact, it is more desirable to use n -ZnO:Al films in the ZnO-based LEDs. This is because low-cost fabrication of n -doped ZnO films on lattice-mismatched substrate at a low substrate temperature ($< 150^\circ\text{C}$) can only be achieved by using Al as the dopant.⁹ In addition, the achievable resistivity ($< 8 \times 10^{-4}\ \Omega\text{ cm}$) and carrier concentration ($> 10^{21}\text{ cm}^{-3}$) of the n -ZnO:Al films are as good as that of the n -ZnO:Ga films.^{4,9} In this letter, we demonstrate the realization of n -ZnO:Al/ p -SiC(4H) heterojunction LEDs by a filtered cathodic vacuum arc (FCVA) technique at a low deposition temperature ($\sim 150^\circ\text{C}$). It is shown that the n -ZnO:Al-based active layer LED can exhibit RT EL with UV emission peak despite the use of lattice-mismatched p -SiC(4H) substrate.

Figure 1 shows the schematic diagram of the proposed p - n heterojunction LED. A p -doped single-side polished 4H-SiC wafer (with size of $5 \times 5\text{ mm}^2$) is chosen to be the substrate and the hole injection layer of the p - n heterojunction LED. This is because the p -doped SiC substrate has a high hole concentration ($\sim 1 \times 10^{19}\text{ cm}^{-3}$) and carrier mobility ($\sim 120\text{ cm}^2/\text{V s}$). On the polished surface (Si face) of the 4H-SiC, a ZnO:Al (3%) layer of thickness $\sim 100\text{ nm}$ was deposited by the FCVA technique, using a Zn target with 3

at % of Al. During the deposition, the substrate temperature and oxygen partial pressure were set to 150°C and $5 \times 10^{-4}\text{ Torr}$, respectively. ZnO:Al (3%) is preferred as the n -doped active layer due to its optimal level of carrier concentration ($> 1 \times 10^{20}\text{ cm}^{-3}$) and mobility ($\sim 7.2\text{ cm}^2/\text{V s}$).⁹ On the other hand, the rough surface of the 4H-SiC substrate was deposited with Al film of thickness $\sim 25\text{ nm}$ and followed by Ti film of thickness $\sim 150\text{ nm}$ (by using electron-beam evaporation). Then, this sample was stacked on top of another identical one. With the two ZnO:Al surfaces of the two samples touching each other (i.e., face to face), both underwent rapid thermal annealing (RTA) for 5 min in N_2 at 800°C . RTA was carried out to free the contacts from Schottky behavior, changing them to ohmiclike contacts. Figure 2 shows the current-voltage characteristics of the Al/Ti contacts (with size of $1 \times 2\text{ mm}^2$ and separation of 1.5 mm) on the p -SiC substrate before and after RTA. It is observed that linear current-voltage dependence of the Al/Ti metal contact on the p -SiC has been achieved. The face-to-face RTA method has another advantage of suppressing the defect-related deep-level emission while improving the near-band-edge emission in ZnO:Al films. In addition, the use of a face-to-face RTA method can maintain the low surface roughness of the ZnO:Al films during the annealing process.¹⁰ Finally, a ZnO:Al (7%) layer of thickness of

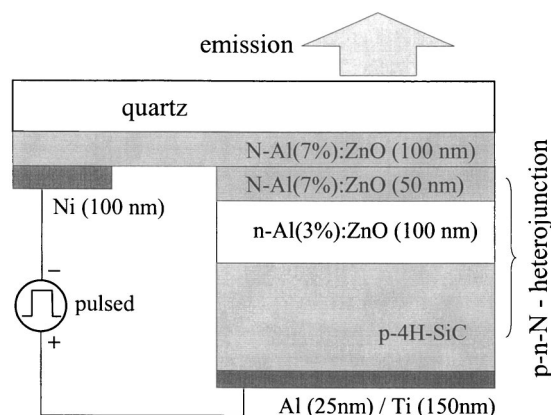


FIG. 1. Schematic diagram of the n -ZnO:Al/ p -SiC(4H) heterojunction LED structure.

^{a)} Author to whom correspondence should be addressed; electronic mail: esfyu@ntu.edu.sg

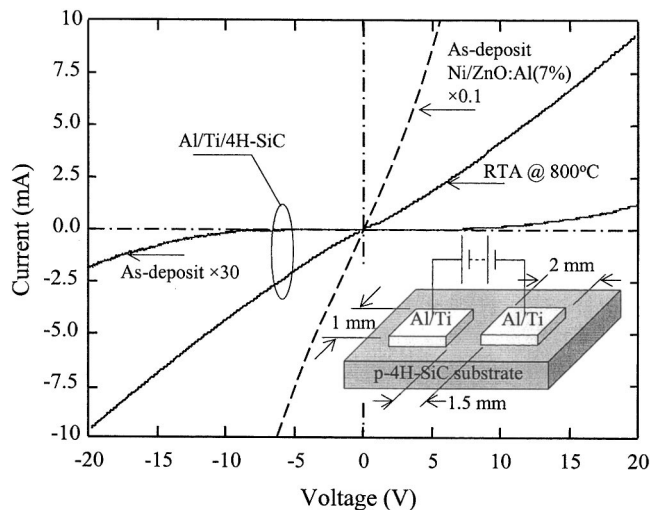


FIG. 2. Solid lines: Current-voltage characteristics of the Al/Ti metallization on *p*-SiC before and after rapid thermal annealing at 800 °C for 5 min. Dashed line: current-voltage characteristics of the Ni metallization on *n*-ZnO:Al(7%).

~50 nm was deposited on the ZnO:Al (3%) by the FCVA technique with the same deposition conditions. In this case, a Zn target with 7 at % of Al was used in the deposition process. Having lower resistivity ($<6 \times 10^{-3} \Omega \text{ cm}$), higher carrier concentration ($>1 \times 10^{21} \text{ cm}^{-3}$) and wider band gap ($> \sim 0.12 \text{ eV}$) than that of ZnO:Al (3%), the ZnO:Al (7%) serves the purpose as a transparent injector of electrons.

The RT optical and electrical characteristics of the *n*-ZnO:Al/*p*-SiC heterojunction LED were measured by contacting the *n* side of the LED to a ZnO:Al(7%)-coated quartz substrate as shown in Fig. 1. This configuration was used in order to avoid metallization on the ZnO:Al(7%) of the LED. Hence, the fabrication procedures can be simplified and the device can also be recycled for other experiments. The quartz substrate was coated with a ZnO:Al (7%) film of ~100 nm thick (by the FCVA technique with the same deposition conditions) and followed by a Ni film of ~100 nm thick (by using electron-beam evaporation). In this case, the ZnO:Al (7%) film acts as a transparent conducting layer and the Ni film forms an ohmic contact on the ZnO:Al (7%) film. Figure 2 shows that the ohmic resistance of the Ni metal contact on the *n*-ZnO:Al(7%)/quartz as compared with that of Al/Ti metal contact on the *p*-SiC is negligible. As for the biasing of the LED, the cathode and anode of a rectangle-pulse voltage source (with repetition rate and pulse width of 7.5 Hz and 80 ms, respectively) were connected to the Ni contact on the quartz substrate and the Al/Ti on the *p*-SiC, respectively. Light was collected from the uncoated side of the quartz substrate by an objective lens. Figure 3 shows the current-voltage (solid lines) and light-voltage (solid triangle) characteristics of the LED. It is evident that the current-voltage curve shows a rectifying behavior, with a turn-on voltage of 3.8 V. It is noted that if the electron and hole densities in *n*-ZnO:Al (3%) and *p*-SiC are greater than $1 \times 10^{19} \text{ cm}^{-3}$, the turn-on voltage should be closer to the corresponding band-gap energy. As the band-gap energy of ZnO and *p* SiC is approximately equal to ~3.3 and ~3.28 eV, respectively, the turn-on voltage will be around ~3.3 V. However, the measured turn-on voltage is larger than 3.3 V because of the high ohmic resistance from the Al/Ti metal contact on the *p*-SiC substrate. Besides, at low forward bi-

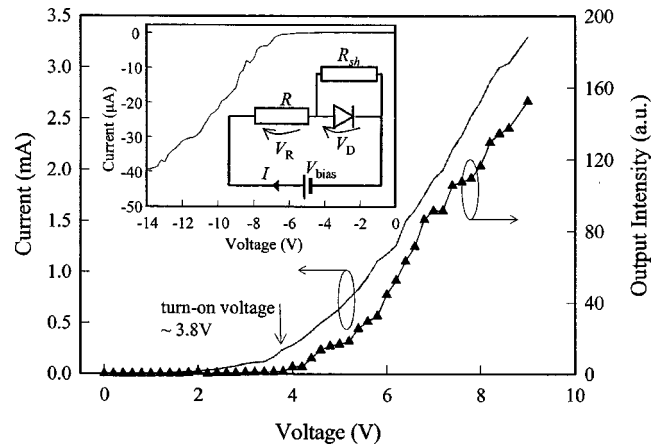


FIG. 3. RT current-voltage and light-voltage characteristics of the *n*-ZnO:Al(3%)/*p*-SiC(4H) heterojunction LED. The insert shows the enlarged current-voltage curve at reverse biased and the heterojunction model for the calculation of ideal factor.

ased ($<1.2 \text{ V}$), the correlation of the current density (J) to the applied voltage (V) shows a $\sim J-V^1$ relationship that indicated the influence of the large ohmic resistance. For forward biased greater than 1.2 V, the $J-V^1$ correlation changes to $\sim J-V^2$, which is expected for wide band-gap materials.⁶ The ideality factor, η , is calculated to be ~ 6 from the diode equation, $I = I_s[\exp(qV_D/\eta kT) - 1]$, where I_s is the saturation current, V_D is the diode voltage, and T ($=300 \text{ K}$) is the temperature, with the consideration of a series R ($\sim 1 \text{ k}\Omega$) and a shunt R_{sh} ($>50 \text{ k}\Omega$) resistance, see the insert in Fig. 3. R is introduced into the model because of the large ohmic resistance of the Al/Ti metal contact on the *p*-SiC. The presence of R_{sh} is probably due to the edge shunt of the device, which can arise from the inadequate edge isolation during the deposition processes. Moreover, when the sample is under reverse-biased condition, there is small leakage current ($<10^{-2} \mu\text{A}$) for reverse biased voltages up to $\sim 6 \text{ V}$. Hence, the measured current-voltage characteristics of our *n*-ZnO:Al/*p*-SiC heterojunction have indicated that our low-temperature deposition technique can produce diodes with performance compatible with those obtained from molecular-beam epitaxy and chemical vapor deposition.^{6,7}

Figure 4 presents the EL spectra of the device at different forward-biased voltages. It is observed that all EL spectra exhibit UV emission peaks at ~385 nm. The intensity of the UV peak increases with the increase of biased voltage. This indicates that the ZnO:Al films exhibit effective near-band-edge radiative recombination and the influence of the hetero-interface defect is negligible. The full width at half maximum (FWHM) of the UV peak at forward biased of ~7.4 V is ~20 nm. A peak at ~490 nm (stretches between ~430 to ~530 nm) is also observed from the EL spectra for forward biased greater than 6 V. Figure 5 shows the PL spectra from the layer of ZnO:Al (3%) deposited on a *p*-doped 4H-SiC substrate after RTA and a piece of bare *p*-doped 4H-SiC. Both samples were excited by a 355 nm pulse source (10 Hz, 6 ns) at $\sim 0.25 \text{ MW/cm}^2$. It is observed that the 4H-SiC sample exhibits no measurable light emission under the optical excitation. On the contrary, the PL spectrum of the ZnO:Al (3%) sample shows a strong UV peak at ~380 nm and a weak defect peak at ~490 nm. The narrow FWHM of the UV PL peak ($\sim 23 \text{ nm}$) shows that the presence of Al has

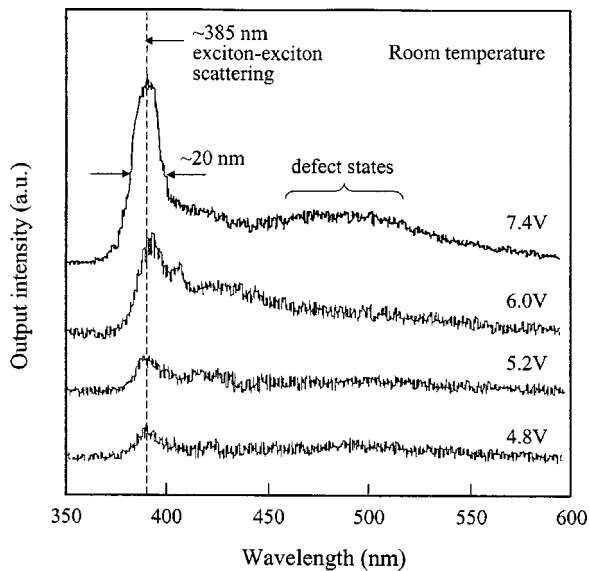


FIG. 4. RT EL spectra of the n -ZnO:Al(3%)/ p -SiC(4H) heterojunction LED at various forward biased voltage.

a negligible influence on the optical properties of the ZnO:Al films. The ~ 380 nm UV PL peak implies that the free-exciton recombination is the dominant mechanism inside the n -ZnO:Al(3%) film. A ~ 5 nm difference in the UV peak position between the EL and PL spectra indicates that the radiative recombination process has changed to exciton-exciton scattering under electrical excitation. This may be due to the lower efficiency of the electrical pumping when compared with that of the optical excitation. Furthermore, the x-ray diffraction (XRD) pattern of the n -ZnO:Al(3%) film deposited on SiC substrate at 150°C is inserted in Fig. 5. Only the ZnO (002) peak is observed at $2\theta \sim 34.5^\circ$, which indicates that the ZnO:Al(3%) film shows a good c -axis orientation and high-crystal quality.

There are two main reasons that account for the high-crystal-quality n -ZnO:Al films produced by the FCVA technique: (1) The ionized Zn-Al plasma was generated before the mixing with oxygen so that the reactivity of Al is suppressed, and (2) the double-bend design of the FCVA technique facilitated the generation of the energetic microparticle-free Zn-Al plasma in order to obtain ZnO:Al films with excellent optical properties at a low substrate temperature.¹¹ In conclusion, we have demonstrated the fabrication of n -ZnO:Al/ p -SiC(4H) heterojunction LEDs with a ZnO:Al-based active layer by the FCVA technique at a low deposition temperature. The EL spectrum exhibits a UV peak with a narrow FWHM indicating that the influence of non-radiative defects in n -ZnO:Al films is negligible. Hence, our

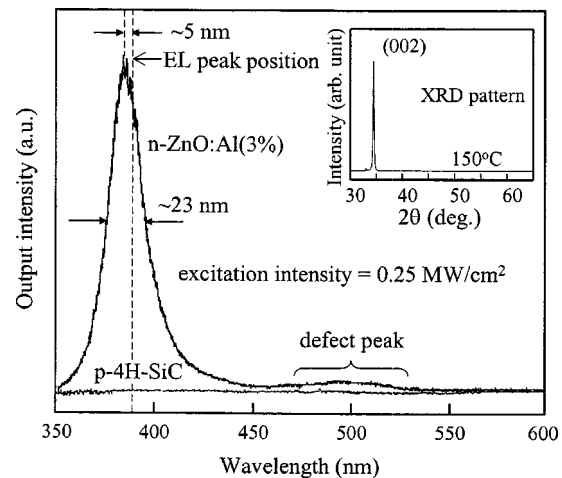


FIG. 5. RT PL spectra of an annealed ZnO:Al(3%)/ p -SiC and a bare p -SiC(4H) substrate under optical excitation by a frequency tripled Nd:YAG laser (355 nm) at pulsed operation (6 ns, 10 Hz). XRD pattern of the ZnO:Al(3%) film deposited on SiC substrate at 150°C is also included.

n -ZnO:Al films are well suited to be applied in ZnO UV LEDs, as well as diode lasers as the electron injection layer and active layer.

This work was supported by the Agency for Science, Technology, and Research of Singapore (Project No. 022-101-0033) and the Nippon Sheet Glass Foundation.

- ¹X. Jiang, F. L. Wong, M. K. Fung, and S. T. Lee, Appl. Phys. Lett. **83**, 1875 (2003).
- ²E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Concalves, A. J. S. Marques, R. F. P. Martins, and L. M. N. Pereira, Appl. Phys. Lett. **85**, 2541 (2004).
- ³M. Kumar, R. M. Mehra, A. Wakahara, M. Ishida, and A. Yoshida, J. Appl. Phys. **93**, 3837 (2003).
- ⁴T. Makino, Y. Segawa, S. Yoshida, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, Appl. Phys. Lett. **85**, 759 (2004).
- ⁵S. F. Chichibu, T. Ohmori, N. Shibata, T. Koyama, and T. Onuma, Appl. Phys. Lett. **85**, 4403 (2004).
- ⁶Y. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, Appl. Phys. Lett. **83**, 4719 (2003).
- ⁷A. Osinsky, J. W. Dong, M. Z. Kauser, B. Hertog, A. M. Dabiran, P. P. Chow, S. J. Pearton, O. Lopatiuk, and L. Chemyak, Appl. Phys. Lett. **85**, 4272 (2004).
- ⁸A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nat. Mater. **4**, 42 (2005).
- ⁹H. W. Lee, S. P. Lau, Y. G. Wang, K. Y. Tse, H. H. Hng, and B. K. Tay, J. Cryst. Growth **268**, 596 (2004).
- ¹⁰Y. G. Wang, S. P. Lau, X. H. Zhang, H. H. Hng, H. W. Lee, S. F. Yu, and B. K. Tay, J. Cryst. Growth **259**, 335 (2003).
- ¹¹S. F. Yu, Clement Yuen, S. P. Lau, Y. G. Wang, H. W. Lee, and B. K. Tay, Appl. Phys. Lett. **83**, 4288 (2003).