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Electroluminescence from ZnO/Si-Nanotips Light-Emitting Diodes

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ABSTRACT

A new and general approach to achieving efficient electrically driven light emission from a Si-based nano p-n junction array is introduced. A wafer-scale array of p-type silicon nanotips were formed by a single-step self-masked dry etching process, which is compatible with current semiconductor technologies. On top of the silicon nanotip array, a layer of n-type ZnO film was grown by pulsed laser deposition. Both the narrow line width of 10 nm in cathodoluminescence spectra and the appearance of multiphonon Raman spectra up to the fourth order indicate the excellent quality of the ZnO film. The turn-on voltage of our ZnO/Si nanotip array is found to be ~2.4 V, which is 2 times smaller than its thin film counterpart. Moreover, electroluminescence (EL) from our ZnO/Si nanotips array light-emitting diode (LED) has been demonstrated. Our results could open up new possibilities to integrate silicon-based optoelectronic devices, such as highly efficient LEDs, with standard Si ultralarge-scale integrated technology.

Semiconductor nanomaterials have attracted worldwide interest because of their promising applications in many different areas, such as nanophotonics, solar cells, electrochromic displays, lasers, and light-emitting diodes (LEDs).[1−8] In particular, it has been shown that electrically driven light emission is possible in a heterojunction nanostructure, where carrier injection occurs across the p-n junction.[9−11] However, the p-n junctions in an individual nanoscale device can only provide a small injection current, which will greatly limit the resulting light intensity for practical applications. Moreover, owing to its indirect band gap, Si is not an ideal

material for efficient optoelectronic devices. Here, we demonstrate a new and general approach to generating sufficient carrier injection and efficient light emission from a Si nanotip array. We show that it is possible to fabricate nanotip LED arrays on a Si substrate operating with a very low voltage (~2.4 V). Our new approach for fabricating an efficient, large-area silicon-based nanotip LED array could pave the way for integrating Si ultralarge-scale integrated circuits with electro-optics to overcome the speed limitation of electrical interconnects and to add extra functionalities on silicon chips.[12−14]

The use of semiconductor nanowires as LEDs has been previously reported. However, poor crystalline quality, random entangled structure, and in particular limited scalability are issues that have to be overcome for practical device applications. Here, we use a novel approach to fabricating silicon nanotip arrays by self-masked dry etching (SMDE).[15,16] This SMDE technique is simple, cost-effective, and compatible with current semiconductor technologies. To overcome the difficulty of insufficient carrier injection in nanoscale junction and to avoid the compensation effect in homojunction material,[17] we have grown an n-type ZnO layer

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by pulsed laser deposition (PLD) on top of the p-type silicon nanotip arrays to form p-n heterojunctions. It has been shown that PLD can be used to coat nanowires with various kinds of materials despite a large lattice mismatch. [9] It is known that high-quality ZnO films can be readily grown by PLD. [18] Because of its high optical transmission in the infrared region, [19] ZnO was chosen as the n-type material for our infrared LED. The deposited ZnO layer is n-type with a carrier concentration of about 10^{16} cm^{-3}, [18] and together with the p-type silicon nanotips, it therefore forms a well-defined p-n junction essential for an electrically driven nanotip LED array.

Experimental Sections. SMDE is performed using a Seki high-density electron cyclotron resonance (ECR) plasma reactor. Uniform and high-density Si nanotips were generated in a regular array over a large area of up to six inches in diameter. The precleaning of the substrate by hydrogen (H$_2$) plasma, followed by simultaneous process of self-masking and reactive etching of the unmasked area for nanotip formation, was done in the reaction chamber in one step without interrupting the vacuum. Reactive gases comprising of argon (Ar), H$_2$, methane (CH$_4$), and silane (SiH$_4$) (10%, diluted in helium) with typical flow rates of 3, 8, 2, and 0.2 sccm, respectively, were activated by a microwave power of typically 1200 W at a chamber pressure of 5.8 mTorr, during the nanotip fabrication process. Silicon nanotip arrays were etched out from a bare untreated crystalline p-type silicon wafer with a carrier density of 10^{16} cm^{-3} at a temperature between 100 to 250 °C, as measured by a two-color optical pyrometer. A detailed description of the nanotips formation can be found elsewhere. [15] The morphology of Si-nanotips was characterized by scanning electron microscopy (SEM) (JSM 6500, JEOL). Cathodoluminescence (CL) measurements were performed using the same SEM system under an acceleration voltage of 5 kV.

Having explained our SMDE technique for fabricating Si nanotip arrays, we now describe the procedures for growing ZnO layers by PLD. A ZnO film was grown in a high-vacuum chamber maintained at a pressure of 3×10^{-8} Torr by a turbo molecular pump. A diode-pumped solid-state laser (355 nm wavelength, 15 ns pulse width) running at 10 kHz was used to ablate the ZnO target, which was maintained at a distance of 50 mm from the substrate. The energy per laser pulse was fixed to 200 mJ, and the laser beam scanned over the target surface was tightly focused so that the energy was maintained at approximately 2 J/cm^2. The films were grown at a rate of approximately 4 nm/min over a wide range of substrate temperatures from 600 to 900 °C. Atomic oxygen was introduced into the chamber during the growth using an RF atom source operated at 300 W, while the oxygen pressure was maintained at 1×10^{-5} to 3×10^{-4} Torr. The characterization of the optimized films grown at the substrate temperature of 800 °C and oxygen pressure of 1×10^{-5} Torr can be found elsewhere. [18] Here only the electrical properties should be mentioned; ZnO films grown by our PLD system achieve a high mobility up to 100 cm^2/V s at 300 K with a carrier concentration in the range from 2 to 5 $\times 10^{16}$ cm^{-3}. Transparent indium-tin-oxide (ITO) film served
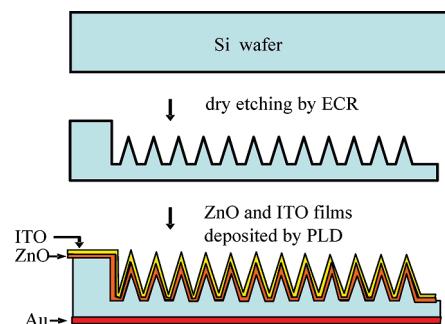

Figure 1. Schematic diagrams showing the fabrication technique of our ZnO/Si-nanotips LED array.

as the electrode on the n-doped face which was deposited using the same PLD system with ITO as the laser target. (Optimization yielded a substrate temperature of 600 °C and oxygen pressure of 1×10^{-4} Torr as the growth parameter for this step.)

To fabricate an electrode on the p-type Si nanotip array, Au was sputtered on the back side of Si as p-electrode and then the sample was annealed at 450 °C for about 3 min to form ohmic contact. Finally silver paste and gold wire were used as the contacts to both the p and n electrodes for our measurements. Figure 1 shows schematic diagrams describing the procedures for fabricating nanotip LED arrays with ZnO/Si-nanotips as the p-n heterojunction materials. Photoluminescence (PL) spectra were performed by excitation from a 325 nm He−Cd laser. The radiative emission was dispersed by a Spex 0.85 m double-grating monochromator and detected by a cooled photomultiplier tube. Crystal quality of ZnO/Si-nanotips was investigated by Raman scattering spectroscopy using a 325 nm He−Cd laser beam (Renishaw). Electroluminescence spectra were measured at room temperature under cw operation without cooling using a monochromator from a circular area of 2 mm diameter.

Results and Discussions. Figure 2a shows an SEM image after depositing ZnO on the nanotips. The average length of the fabricated nanotips is about 5 μm and the density of the tips reaches $10^7 \sim 10^8$/cm^2, which is the most suitable density according to electrostatic calculation[20] to maximize the emitted current density. Evidently, the ZnO film coverage is quite good throughout the whole silicon nanotip arrays. To confirm whether the ZnO film was uniformly coated on the whole silicon nanotips cross-section, we have performed CL measurements in a region indicated by a square in Figure 2a. Figure 2b shows the obtained CL spectrum. Both of the very narrow half-width (∼10 nm) of the band gap emission at ∼378 nm and the very weak defect emission at about 500 nm indicate that the ZnO film is of very good crystalline quality. Transmission electron microscopy (TEM) image indicates that the ZnO layer coated on silicon nanotips is about 80 nm in thickness as shown in Figure 2c. A selective-area electron-diffraction (SAED) pattern obtained from the square region marked in Figure 2c is shown in Figure 2d, which indicates that the ZnO coating is polycrystalline. The d-spacing calculated from the electron diffraction spot is estimated to be around 2.47 and 1.62 A, which are corre-
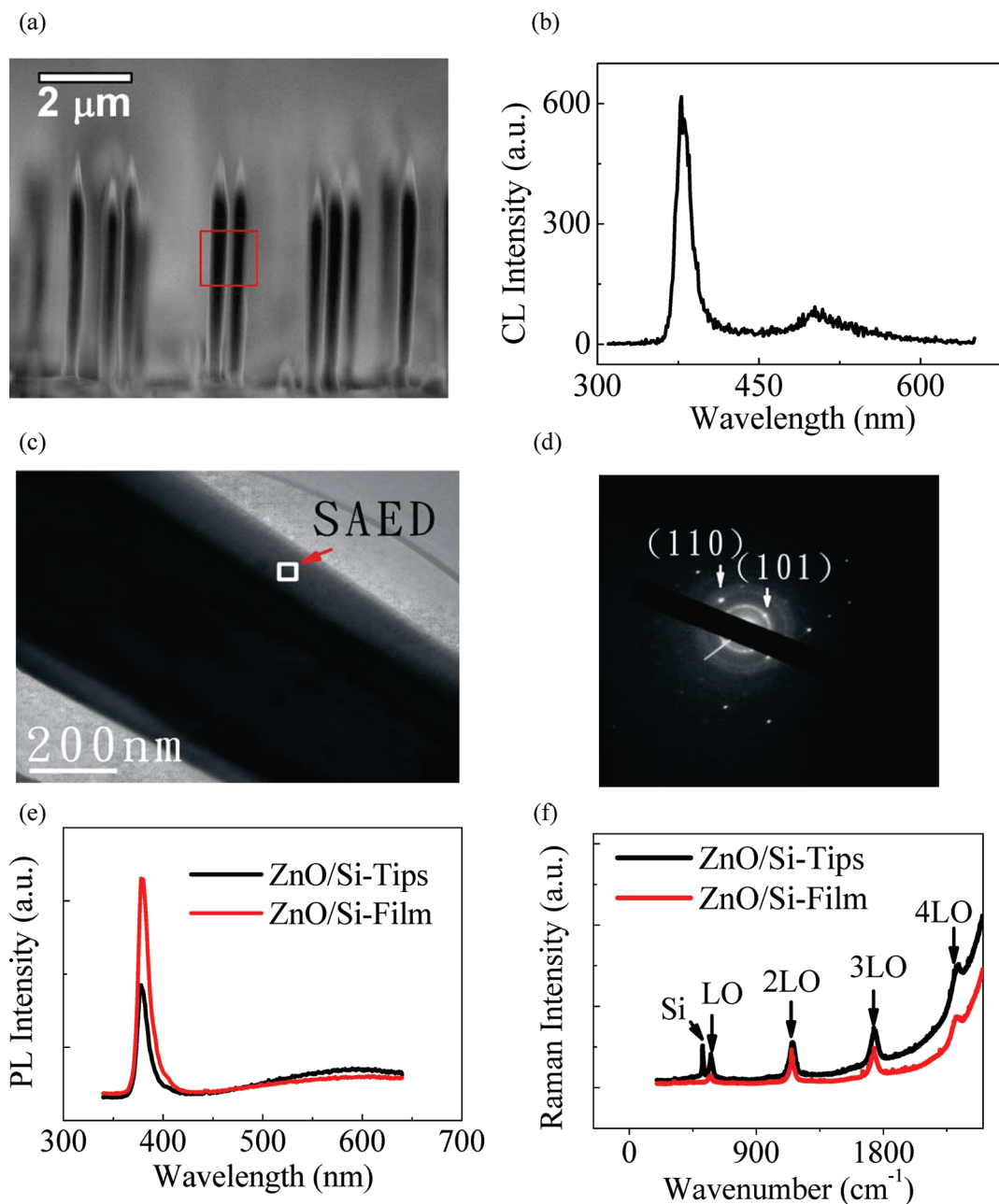
Figure 2. (a) SEM picture of silicon nanotips after coating ZnO using pulsed laser deposition. (b) CL spectrum taken from the square region drawn in the middle of the nanotip array as shown in Figure 2(a). (c) TEM image of ZnO/Si-nanotips and (d) SAED pattern taken from the square region drawn in the middle of the nanotip array as shown in panel c. (e) PL spectra and (f) multiphonon Raman spectra of ZnO film coated on silicon nanotips and flat substrate.

sponding to (101) and (110) lattice planes of ZnO, respectively.

To compare the quality of the ZnO film deposited on silicon nanotips with that on flat surface, we have also performed PL measurements as shown in Figure 2e. We can see that PL linewidths of both of the ZnO films on flat substrate and tips are very narrow (about 10 nm) and the intensity of the yellow defect band at around 500 nm is quite small, similar to that of cross-section CL spectrum as shown in Figure 2b. This indicates that both of the ZnO films are similar in quality. However, after a more careful check one can find a blue shift in the ZnO/Si-nanotips sample. It might be attributed to the strain effect or the surface effect due to

the increased surface-to-volume ratio.[21] To further characterize the quality of the ZnO film coated on silicon nanotips, we have performed micro-Raman scattering measurements as shown in Figure 2f. The multiphonon resonance Raman scattering spectrum again indicates that the crystal structure of the ZnO film coated on silicon nanotips is as good as that of the film on flat surface. Quite interestingly, we were able to detect the LO phonon mode up to fourth order, which can serve as an excellent signature for the good crystalline quality.[22,23] One can also see that the LO mode of the ZnO/nanotip sample has a blue shift compared to the film coated on the flat surface. This can be attributed to changes in the surface structure of the coated materials due to surface strain
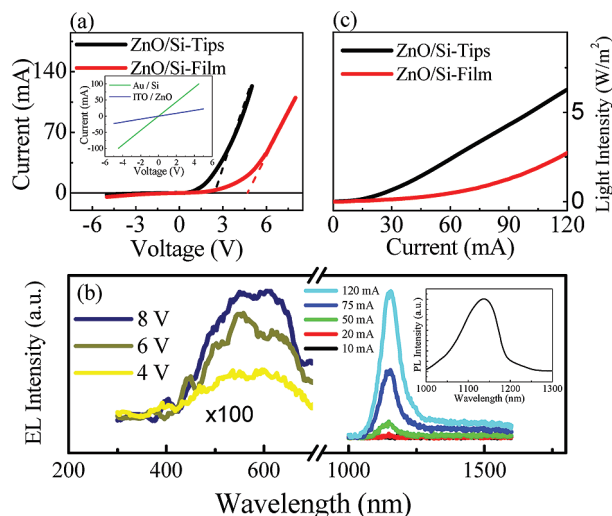
Figure 3. (a) Transport measurement of n-ZnO/p-Si-nanotips in comparison with n-ZnO/p-Si-film. The inset shows that the contacts to both p-Si nanotip and n-ZnO film are ohmic. (b) Electroluminescence spectra from n-ZnO/p-Si-nanotips. The inset is an infrared photoluminescence spectrum showing a similar infrared peak position as obtained from EL. (c) Light intensity (L) as a function of injection currents for both n-ZnO/p-Si-nanotips and n-ZnO/p-Si-film.

and was reported together with a broadening of the Raman peaks.[24] Raman and PL measurements therefore indicate that it is possible to grow good quality ZnO film on silicon nanotips.

Figure 3a shows the transport measurement with the n-ZnO film as the cathode and p-Si nanotip as the anode. The inset demonstrates that the contacts to both p-Si nanotip and n-ZnO film are ohmic. The current−voltage (I−V) relationship demonstrates that the rectifying behavior of the p-n junction ZnO/nanotips is much better than that of ZnO/flat surface. Under an identical forward voltage, the current of the sample with silicon tips is much larger than that of the silicon film. The turn-on voltages of our diodes are defined by extrapolating the linear fits in the high current regimes to $I = 0$ as indicated by the red and black dashed lines. We can see that the turn-on voltage of our ZnO/Si nanotips diode is estimated to be ~2.4 V, which is about 2 times smaller than that of its thin film counterpart (~4.8 V). Furthermore, the leakage current is smaller for the p-n junction with ZnO film on silicon tip. To have a meaningful comparison between the two different device structures we conducted an in depth investigation of film thickness and quality of both. SEM images show that the thickness of the ZnO film on flat Si was ~60 nm, which is smaller than on the nanotips (~80 nm). This is expected to increase the field across the structure at a given voltage, thus lowering the turn on voltage, and cannot account for the opposite effect. Meanwhile the comparison of the peak positions in the PL measurement and relative intensity of the 3 LO and 2 LO peaks in the Raman measurements show that the ZnO films in both cases have similar doping levels. [25,26] Therefore, these observations can be attributed to the inherent nature of the geometry of a nanotip in which a strong field can be induced on top of a tip by a small external bias according to the fundamental

electromagnetic theory. This field enhancement effect is similar to the commonly observed phenomena of the ultralow turn-on voltage used in field emission devices.[27] Here, by the same token, under a small forward bias the current can also be increased rapidly in the p-n junction of ZnO film due to the existence of the strong electric field on Si nanotip. In addition, because the current flow is restricted to the narrow tip region where the strong field occurs, the leakage current is thus greatly reduced.

The most important result of our work is the demonstration of electroluminescence (EL) detected under a low external voltage as shown in Figure 3. Infrared EL spectra measured at room temperature were successfully obtained as shown in the right-hand side of Figure 3b. The peak position at ~1156 nm corresponds to the band gap energy of Si. To further clarify the origin of the infrared EL peak photoluminescence spectra were obtained from bare Si-nanotips as shown in the inset of Figure 3b. The infrared photoluminescence spectrum shows a similar infrared peak position as obtained from EL. Occurrence of longer wavelength contributions under a larger injection current is probably caused by a heating effect. As can be seen, the EL intensity increases with increasing applied current. The relative infrared output EL intensity versus injection current (L−I) curves are shown in Figure 3c. One can see that under the same current, the electroluminescence from ZnO/Si-Tips has a much higher light intensity than from ZnO/Si-film. Again, the reason for this can be attributed to field enhancement effect of silicon nanotips.[27] While the turn-on voltage (2.4 V) of our nanotip device is higher than that (~0.6 V) of the Si LED reported in ref 14 at the same current of 50 mA, the full width at half-maximum of the EL peak of our device is measured to be 100 nm, which is close to the reported value (80 nm) of their device. Meanwhile, in our case the restricted current flow occurs through a limited tunneling area that has fewer defects and thus, the device exhibits higher emission efficiency. At present, the energy conversion efficiency is ~0.02%. However, the conversion efficiency of the nanotip emitters is 10 times better than the comparable film devices and shows the potential of our approach. To obtain results comparable to reported values,[28] further optimization of the electrical characteristics of our diode and thus an increase in conversion efficiency will be attempted. The obtained high quantum efficiency (0.008) proves the feasibility of this goal.

Similar to other reports,[29,30] very weak EL in the visible range was obtained from our devices under reverse voltage as shown in the left-hand side of Figure 3b. This can be understood by inspection of the band diagrams of the constituents. Because of the comparable and low doping levels, in a reverse bias the extracted minority carriers from Si are expected to recombine with holes through defects and surfaces states on the interface more effectively than with holes from the band edge. As a result, luminescence in a broad visible range and very small UV range are expected. In forward bias, a much stronger infrared radiation is emitted when electrons are injected into the Si and recombine across the band gap. The strong infrared light emission under low applied voltage and well-behaved rectifying I−V relationship

demonstrate clearly that good electronic and optical characteristics can be achieved with our designed material system. Because the key concept in our approach is the geometric enhancement by fabrication of nanotips, it is anticipated that our strategy is applicable to many other material systems.

In summary, nanotip LED arrays based on the p-n junction of ZnO film grown on silicon nanotips have been fabricated. We demonstrate that our designed devices exhibit an electrically driven light emission under a low voltage. We point out that the combination of SMDE and PLD techniques provides an excellent route for the fabrication of well aligned nanotip LED with high efficiency. The techniques involved are simple, low cost, and compatible with current semiconductor technologies. The production of highly efficient nanotip LED arrays demonstrate that our approach could provide a possible route for integration of optoelectronic devices based on silicon material as well as various hybrid material systems.

References

(1) Guichard, A. R.; Barsic, D. N.; Sharma, S.; Kamins, T. I.; Brongersma, M. L. *Nano Lett.* **2006**, *6*, 2140–2144.
(2) Huang, Y. F.; Chattopadhyay, S.; Jen, Y. J.; Peng, C. Y.; Liu, T. A.; Hsu, Y. K.; Pan, C. L.; Lo, H. C.; Hsu, C. H.; Chang, Y. H.; Lee, C. S.; Chen, K. H.; Chen, L. C. *Nat. Nanotechnol.* **2007**, *2*, 770–774.
(3) Greytak, A. B.; Barrelet, C. J.; Li, Y.; Lieber, C. M. *Appl. Phys. Lett.* **2005**, *87*, 151103.
(4) Tian, B.; Zheng, X.; Kempa, T. J.; Fang, Y.; Yu, N.; Yu, G.; Huang, J.; Lieber, C. M. *Nature (London)* **2007**, *449*, 885–890.
(5) Balasubramanian, C.; Godbole, V. P.; Rohatgi, V. K.; Das, A. K.; Bhoraskar, S. V. *Nanotechnology* **2004**, *15*, 370–373.
(6) Wang, L.; Zhang, X.; Liao, X.; Yang, W. *Nanotechnology* **2005**, *16*, 2928–2931.
(7) Gudiksen, M. S.; Lauhon, L. J.; Wang, J.; Smith, D. C.; Lieber, C. M. *Nature (London)* **2002**, *415*, 617–620.
(8) Zhong, L. W.; Yi, L.; Ze, S. *Handbook of Nanophase and Nanostructured Materials*; Kluwer Academic: New York, 2003.
(9) Hayden, O.; Greytak, A. B.; Bell, D. C. *Adv. Mater.* **2005**, *17*, 701–704.
(10) Qian, F.; Li, Y.; Gradecak, S.; Wang, D.; Barrelet, C. J.; Lieber, C. M. *Nano Lett.* **2004**, *4*, 1975–1979.
(11) Chang, C. Y.; Tsao, F. C.; Pan, C. J.; Chi, G. C.; Wang, H. T.; Chen, J. J.; Ren, F.; Norton, P. D.; Pearton, S. J.; Chen, K. H.; Chen, L. C. *Appl. Phys. Lett.* **2006**, *88*, 173503.
(12) Kveder, V.; Badylevich, M.; Steinman, E.; Izotov, A.; Seibt, M.; Schröter, W. *Appl. Phys. Lett.* **2004**, *84*, 2106–2108.
(13) Leong, D.; Harry, M.; Reeson, K. J.; Homewood, K. P. *Nature (London)* **1997**, *387*, 686–688.
(14) Ng, W. L.; Lourenco, M. A.; Gwilliam, R. M.; Ledain, S.; Shao, G.; Homewood, K. P. *Nature (London)* **2001**, *410*, 192–194.
(15) Hsu, C. H.; Lo, H. C.; Chen, C. F.; Wu, C. T.; Hwang, J. S.; Das, D.; Tsai, J.; Chen, L. C.; Chen, K. H. *Nano Lett.* **2004**, *4*, 471–475.
(16) Chen, K. H.; Hwang, J. H.; Lo, H. C.; Das, D.; Chen, L. C. U.S. Patent 6,960,528 B2, Nov. 1 (2005).
(17) Eckey, L.; Gfug, U. V.; Holst, J.; Hoffmann, A.; Kaschner, A.; Siegle, H.; Thomsen, C.; Schineller, B.; Heime, K.; Heuken, M.; Schon, O.; Beccard, R. *J. Appl. Phys.* **1998**, *84*, 5828–5830.
(18) Lin, M. Z.; Su, C. T.; Yan, H. C.; Chern, M. Y. *Jpn. J. Appl. Phys.* **2005**, *44*, L995−L997.
(19) Matsubara, K.; Fons, P.; Iwata, K.; Yamada, A.; Sakurai, K.; Tampo, H.; Niki, S. *Thin Solid Films* **2003**, *431−432*, 369–372.
(20) Nilsson, L.; Groening, O.; Emmenegger, C.; Kuettel, O.; Schaller, E.; Schlapbach, L.; Kind, H.; Bonard, J-M.; Kern, K. *Appl. Phys. Lett.* **2000**, *76*, 2071–2073.
(21) Chen, C. W.; Chen, K. H.; Shen, C. H.; Ganguly, A.; Chen, L. C.; Wu, J. J.; Wen, H. I.; Pong, W. F. *Appl. Phys. Lett.* **2006**, *88*, 241905.
(22) Scott, J. F. *Phys. Rev. B* **1970**, *2*, 1209–1211.
(23) Zhang, X. T.; Liu, Y. C.; Zhi, Z. Z.; Zhang, J. Y.; Lu, Y. M.; Shen, D. Z.; Xu, W.; Zhong, G. Z.; Fan, X. W.; Kong, X. G. *J. Phys. D: Appl. Phys.* **2001**, *34*, 3430–3433.
(24) Xu, C. Y.; Zhang, P. X.; Yan, L. *J. Raman Spectrosc.* **2001**, *32*, 862–865.
(25) Wang, X. B.; Song, C.; Geng, K. W.; Zeng, F.; Pan, F. *J. Phys. D: Appl. Phys.* **2006**, *39*, 4992–4996.
(26) Zalamai, V. V.; Ursaki, V. V.; Rusu, E. V.; Arabadji, P.; Tiginyanua, I. M.; Sirbui, L. *Appl. Phys. Lett.* **2004**, *84*, 5168–5170.
(27) Lo, H. C.; Das, D.; Hwang, J. S.; Chen, K. H.; Hsu, C. H.; Chen, C. F.; Chen, L. C. *Appl. Phys. Lett.* **2003**, *83*, 1420–1422.
(28) Green, M. A.; Zhao, J.; Wang, A.; Reece, P. J.; Gal, M. *Nature (London)* **2001**, *412*, 805–808.
(29) Sun, H.; Zhang, Q. F.; Wu, J. L. *Nanotechnology* **2006**, *17*, 2271–2274.
(30) Chen, P.; Ma, X.; Yang, D. *J. App. Phys.* **2007**, *101*, 053103.

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