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ABSTRACT

The iodide interplay with polar Zn\(^{2+}\) and O\(^{2-}\) induced nonpolar \([1\overline{1}0\overline{1}]\) ZnO nanowires is fabricated via a simple vapor phase transport at a temperature of as low as 250°C that is compatible with the nanodevice processing technique. As-fabricated nanowires exhibit single crystalline hexagonal wurtzite structures and grow along the \([1\overline{1}0\overline{1}]\) direction instead of the conventional polar \([0001]\) direction. The growth evolution can be explained by the synergy of the vapor–liquid–solid process and iodide direction-modulation. The electrical measurements demonstrate that the mobility of the PbI\(_2\)-induced \([1\overline{1}0\overline{1}]\) nanowires is significantly improved in comparison with that of the BiI\(_3\)-modulated \([1\overline{1}20]\) ones. These unique nonpolar nanowires are promising for improved high efficiency nanodevices.

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Nonpolar high quality zinc oxide thin films are of great interest since they give rise to weak internal electric fields and, subsequently, enhance the ZnO-based device performance.\(^{1-4}\) Alternatively, with the development of nanoscience and nanotechnology, there is recently an intense focus on low dimensional nonpolar ZnO nanostructures such as nanowires (NWs), which display improved properties in optoelectronics such as nano-light-emitting-diodes (nano-LEDs). Numerous preparation methods, including vapor phase transport (VPT),\(^{5}\) metalorganic vapor-phase epitaxy (MOVPE),\(^{6}\) thermal evaporation,\(^{7}\) and thermal decomposition,\(^{8}\) have been incorporated into making various ZnO nanostructures. In these routes, temperature is usually required to be over 400°C, which leads to a thermal drift and, thus, deteriorates materials' nanostructures and integration into the nanodevices. Hence, a low temperature VPT is highly desirable for preparation of high-quality nanostructures. Besides, the controllable growth of nonpolar ZnO nanostructures is beneficial for the tuning of electrical and optical properties. Iodide has been touted to impact on the growth directions and morphologies of nanostructures such as Au nanoprisms and nanorods\(^9\) because of deeply polarizable I\(^-\) and I\(_2\).\(^{10}\) Although some work has been done using iodides such as BiI\(_3\),\(^{11,12}\) the controllable and high yield fabrication of lateral nonpolar ZnO NWs in a low temperature VPT is greatly intriguing.

In this paper, ZnO NWs grown along the nonpolar \([1\overline{1}0\overline{1}]\) direction were obtained by a VPT around 250°C in the presence of the starting material, lead iodide. The electrical and optical properties of as-obtained nonpolar ZnO NWs were characterized, and the lateral growth evolution of nonpolar ZnO NWs along \([1\overline{1}0\overline{1}]\) was also suggested. Precursors of 3-g zinc (99.998%, 100 mesh, Aldrich) and 1-g lead iodide (99.999%, Aldrich) were blended in an agate mortar and ground for approximately 15 min by using a pestle. The homogeneously mixed powder was then transferred into an 8-cm-long alumina crucible. The oxidized surface silicon substrates downward were covered onto the crucible. The distances between the substrates are \(\sim1\) mm. An 80 SCCM flow of high-purity argon gas was fed, leading to a pressure of around 300 Torr after the covered crucible was loaded into the center of a quartz tube and, then, pumped to 95 mTorr. The quartz tube was naturally cooled down to the ambient temperature after the dwelling-growth process, and the white samples on the substrates were taken out from the quartz tube.
A scanning electron microscope (SEM) equipped with energy dispersive x-ray (EDX) spectrometry and JEOL–2010 high-resolution transmission electron microscopy (HRTEM) with an EDX was employed to investigate the surface morphology and microstructure of the samples. HRTEM samples were prepared on a carbon film supporting copper grid. A Rigaku x-ray powder diffractometer (XRD) was applied to characterize the crystal structure. An Agilent 4156C based semiconductor probe station was used to analyze the electrical properties. Photoluminescence (PL) excitation spectra were recorded at 10 K and 300 K, respectively, using source beams of 266 nm and 355 nm from a Nd:YAG laser with an output power of 10 mW.

The SEM image of the NWs on an oxidized silicon substrate is shown in Fig. 1(a). The NWs are very dense, high yielding, and stand-free, with an average diameter of ∼30 nm and length up to a few micrometers. The TEM image in the inset of Fig. 1(a) exhibits particles located at the tips of the NWs, an indicative of the vapor–liquid–solid (VLS) growth. The XRD pattern in Fig. 1(b) illustrates that the diffraction peaks of the NWs are similar to those of bulk wurtzite ZnO.

The TEM image of a single NW with a diameter of ∼30 nm is shown in Fig. 2(a). The lower left inset shows an EDX spectrum of the NW, confirming that the NW consists of Zn and O with an atomic ratio of 50.4–49.6, Zn exceeds O (Cu signal arises from the TEM grid), and the NW is Pb-free. The upper right inset of Fig. 2(a) is the selected area electron diffraction (SAED) pattern of the corresponding NW. The diffraction spots can be assigned to the single crystal hexagonal wurtzite ZnO structure with a zone axis of [0001], and no secondary phase diffraction spots were observed, in agreement with the above EDX analyses. The HRTEM image of the NW is shown in Fig. 2(b). The clear lattice fringes indicate that the NW is of high quality and low defects. The interplanar spacing of 0.278 nm corresponds to the (1010) plane. It suggests that the NW grows along [1010], which is nonpolar and different from the conventional polar ZnO NWs along [0001] in the absence of a catalyst as well as the nonpolar ZnO NWs along [1120] in the presence of BiI₃. The
lower right inset of Fig. 2(a) shows an enlarged segment of the NW with the grooves/stripes along the [10\overline{1}0] direction, implying a limited growth perpendicular to the [10\overline{1}0] direction. Similar features have been seen on m-plane and a-plane ZnO films. These grooves/stripes possibly originated from the anisotropic character of ZnO. Additionally, on the basis of EDX, SAED, and HRTEM investigation in Fig. 2, Pb\textsuperscript{2+} (ionic radius 0.119 nm) is not responsible for an effective donor substitution of Zn\textsuperscript{2+} (0.07 nm) in ZnO due to its larger diameter. Moreover, in this relatively low temperature VPT scenario, Pb\textsuperscript{2+} is even less possible to be incorporated into the ZnO lattice.

Accordingly, a series of experiments was conducted to clarify controllable lateral evolution of the nonpolar NWs. The Zn and PbI\textsubscript{2} first react at room temperature: Zn + PbI\textsubscript{2} ↔ Pb + ZnI\textsubscript{2}, PbI\textsubscript{2} ↔ 2Pb + I\textsubscript{2}, and ZnI\textsubscript{2} ↔ Zn + I\textsubscript{2}. After heating the furnace chamber up to the melting point of the Zn–Pb alloy (∼190 °C), ZnI\textsubscript{2}, PbI\textsubscript{2}, and I\textsubscript{2} begin to sublime and deposit onto the substrate. Interestingly, suppose that oxygen is intentionally not introduced during the deposition process, and only Zn(Pb)I\textsubscript{x} films are formed. When the temperature rises to 250 °C, Zn–Pb droplets initiate on the Zn(Pb)I\textsubscript{x} film. Introduction of oxygen into the furnace results in ZnO nucleation, which then solidifies from the droplets to develop the NWs now that ZnO is insoluble in the droplets.

The preference of the [10\overline{1}0] growth direction likely arises from the effect of \( I^- \) and \( I_2 \) on the liquid and the precipitation process, which is utterly different in NWs in comparison with nonpolar ZnO films in which the nonpolar films could be easily yielded by tailoring the lattice mismatch to the substrates. ZnO is generally regarded as a polar crystal with the positive Zn polar plane and the negative O polar plane. The oppositely charged ions yield a spontaneous polar plane. The oppositely charged ions yield a spontaneous polarization along the c-axis as well as a divergence in surface energies. The very polarizable \( I^- \) and \( I_2 \) preferentially absorb onto the ZnO (0001) plane and balance the surface charge, thus manipulating the evolution of [0001] NWs. In analog, effects of citrate ions, phosphate ions, and organic dye on the (0001) plane of ZnO suppress the [0001] growth direction, giving rise to the ZnO nanoplates. On the other hand, if CuI substituted PbI\textsubscript{2}, no NWs were acquired under identical conditions. The ZnO NWs are, hence, controlled by the interplay of VLS and direction modulation via iodide and/or iodine. Noteworthily, in the presence of BiI\textsubscript{3}, the ZnO NWs are grown along [11\overline{2}0] with traceable Bi dopants, which may induce strain and, subsequently, alter the growth direction of ZnO nanostructures.

To shed light on the electrical properties of nonpolar [10\overline{1}0] ZnO NWs, the photolithography techniques were used to fabricate Pt electrodes on a 1-μm-thick thermal oxide layer silicon substrate. The ZnO NWs were first dispersed into ethanol solution, then dropped onto the electrodes, and finally aligned onto the two Pt electrodes by means of dielectrophoresis. The aligned NW was bonded to the corresponding pair of Pt electrodes by focused ion beam (FIB). To minimize the Pt and Ga diffusion (Ga from FIB source), the current and time of the bonding were precisely set. A channel length of ∼2 μm and diameter of 60 nm have been achieved for an individual-NW based field effect transistor (FET), as shown in the lower right inset of Fig. 3(a). The NW source–drain current (\( I_{ds} \)) as a function of the bias voltage (\( V_{gs} \)) and the gate voltage (\( V_{sd} \)) was measured in a clean room at room temperature.

Figure 3(a) plots the current vs drain–source bias (\( I_{ds} \)) curves under the gate voltage stepping from −6 V to 6 V. The asymmetric response of the two-terminal \( I_{ds} \) curves implies the Schottky contacts because of the work function difference between Pt electrodes (5.68 eV) and ZnO (4.3 eV). At a certain \( V_{ds} \), \( I_{ds} \) increases (decreases) with an increase in positive (negative) \( V_{gs} \), verifying n-channel-ZnO-NW-FET. Figure 3(b) depicts the transfer characteristics of the nonpolar ZnO-NW-FET under a bias from −2 V to +2 V. The gate response \( I_{ds} \) curves further validate the n-type nonpolar ZnO-NW-FET. However, the on/off ratio is lower, which was also observed in MoS\textsubscript{2} and graphene FET.\textsuperscript{19,20} Probably due to the high conductivity caused by O insufficiency and/or Pt/Ga diffusion.

The NW charge carrier concentration, \( n \), can be defined by \( n = (V_{gs}/e) \times [2\pi\epsilon_0/(ln(2h/\tau))] \),\textsuperscript{21} where \( V_{gs} \) is the threshold gate voltage from transconductance, \( \tau \) is the relative dielectric constant of the oxide layer SiO\textsubscript{2}, \( h \) is the gate oxide layer thickness, and \( r \) is the NW width.

![FIG. 3. (a) Room temperature \( I_{ds} \) curve at different gate voltages. The inset lower is the SEM image of an as-fabricated FET. The inset upper is the energy diagram of the Pt–ZnO contact. (b) Transconductance of the NW under \( V_{gs} = 2, 1.5, 0, −1.5, \) and −2 V bias voltages.](https://scitation.aip.org/content/aip/journal/adv/10/3/10.1063/1.5130653)
TABLE I. Electrical properties of [0001], [10-10], and [11-20] films/nanorods/NWs.

| Sample                  | Conduction type | Carrier concentration (cm$^{-3}$) | Mobility (cm$^2$/V s) |
|-------------------------|-----------------|----------------------------------|-----------------------|
| [0001] ZnO nanorods$^a$| n               | $1.4 \times 10^{18}$            | 17.2                  |
| [10-10] ZnO film$^b$    | n               | $5.0 \times 10^{19}$            | 12.0                  |
| [11-20] Bi–ZnO NW$^c$   | n               | $2.7 \times 10^{19}$            | 1.5                   |
| [10-10] ZnO NW$^d$      | n               | $7.5 \times 10^{18}$            | 8.1                   |

$^a$Reference 22.
$^b$Reference 23.
$^c$Our previous work, Ref. 21.
$^d$This work.

radius. Substituting r of 3.9, h of 1 μm, and r of 30 nm into the above formula, $V_{gt}$ can be obtained from Fig. 3(b) to be approximately $-28$ V. Accordingly, the calculated charge carrier concentration is $\sim 2.1 \times 10^{18}$ cm$^{-3}$, and the volume concentration is, therefore, extrapolated to be $7.5 \times 10^{18}$ cm$^{-3}$, which is consistent with those observed data.\(^22\) The mobility ($\mu_e$) of the back-gated nonpolar ZnO NW FETs can also be estimated by $\mu_e = \frac{g_m L \ln(2h/r)}{2\pi \varepsilon \varepsilon_0 V_{sd}}$, where $g_m = \frac{dI}{dV}$, $V_{sd}$ as 2 V, the value is calculated to be 8.1 cm$^2$/V s, which is almost half as much as the reported ZnO nanorods.\(^22\)

Table I concludes the electrical measurements of [0001] ZnO NWs, [10-10] thin films and NWs, and [11-20] NWs. The results of this work are different from the previous reports on [0001] ZnO nanorods,\(^22\) [10-10] ZnO films,\(^23\) and [11-20] Bi–ZnO NWs.\(^21\) The mobility of the [0001] ZnO nanorods is 17.2 cm$^2$/V s, which is higher than that of [10-10] NWs (8.1 cm$^2$/V s). The difference of mobility between polar [0001] ZnO nanorods and nonpolar [10-10] ZnO NWs is large. The defect concentration that reduces electron mobility is higher in nonpolar ZnO than in polar [0001] ZnO. Besides, the anisotropy of ZnO may also result in the large electron mobility difference between nonpolar [10-10] ZnO and polar [0001] ZnO.

Compared with the [10-10] films (12 cm$^2$/V s), the [10-10] NWs have a relatively lower mobility probably due to a defect density difference. The [10-10] ZnO films are grown on closely lattice-matched GaN substrates by chemical vapor deposition at 800 °C, whereas the [10-10] ZnO NWs are fabricated by VPT at 250 °C. It is conceivable that the former has a higher quality than the latter. In comparison with [10-10] NWs, the [11-20] ZnO NWs were prepared similarly except for using BiI$_3$ instead of PbI$_2$. Traced Bi was incorporated into ZnO NWs, leading to an enhanced carrier concentration of $2.7 \times 10^{19}$ cm$^{-3}$ and a low electron mobility of 1.5 cm$^2$/V s as similarly observed in Ref. 17.

The PL spectra of the ZnO nanowires at 10 K under excitation by laser beams of 266 nm and 355 nm were recorded in Fig. 4(a). The PL spectrum of the ZnO NWs by the 266 nm excitation exhibits weak narrow UV emissions at 378 nm (3.28 eV) and a strong broad green emission band around 510 nm (2.43 eV). The PL spectrum of the ZnO NWs by the 355 nm excitation depicts a strong narrow UV emission at 374 nm (3.32 eV) and a weak broad green emission band around 508 nm (2.44 eV). As observed from the above results, the PL intensity and peak position depend on the excitation wavelength. In both 266 nm and 355 nm excitation sources, there are clearly two emission bands in the spectra, implying that PL emissions come from the [10-10] ZnO NWs.

ZnO nanostructures usually possess two emission centers: one is the UV emission, which is closely related to near band edge (NBE) emission by the radiative annihilation of excitons,\(^24\) and the other is the deep level (DL) green emission, which can be assigned to oxygen vacancy or Zn interstitials.\(^25,26\) With regard to the [11-20] Bi–ZnO NWs at 10 K, there are no donor bound (D$^+$X) peak and

![FIG. 4. (a) PL spectra of ZnO NWs grown on an oxidized Si substrate. The excitation was done with 266 nm and 355 nm lights. (b) Room temperature PL spectra of the ZnO NWs before annealing and after annealing at 350 °C and 550 °C for 1 h under the excitation of 355 nm light.](source)(source)
doping related peak around 3.24 eV, demonstrating that no Pb doping occurs and more defects exist. Moreover, the enhanced NBE may be associated with the higher quality of the [1010] NWs.

The room temperature PL spectra of the samples subjected to different annealing/oxidation processes under the excitation of 355 nm light are shown in Fig. 4(b). The unannealed sample exhibits strong UV emission and weak DL green emission. The ratio of intensity of DL green emission to UV emission ($I_{G}/I_{UV}$) is ~0.66. The intensity of DL green emission increases with the annealing temperature. At 350 °C for 1 h, $I_{G}/I_{UV}$ is ~5.5; at 550 °C for 1 h, $I_{G}/I_{UV}$ is ~18. The observed differences in the PL spectra following air annealing are most likely related to the increased content of oxygen after air annealing at an elevated temperature. The nonpolar [1010] ZnO NWs ($I_{G}/I_{UV} = 18$ at 550 °C) incorporate more oxygen vacancies than [1120] ZnO NWs ($I_{G}/I_{UV} = 2$ at 550 °C).

In conclusion, low temperature PbI$_2$ induced nonpolar ZnO NWs have been fabricated. The NWs are single crystalline and preferred along the nonpolar [1010] direction instead of the polar [0001] direction. The growth mechanism could be elucidated by a combined effect of VLS and iodine direction-modulation. The mobility of the PbI$_2$-induced [1010] NWs is higher than that of the Bi$_2$I$_3$-modulated [1120] ones. Meanwhile, photoluminescence manifests that the postgrowth annealing processes can modify the level of oxygen deficiency. The nonpolar ZnO NWs are of significance for potential usage in nano-LEDs.

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