Substrate-Dependent Differences in the Crystal Structures and Optical Properties of ZnSe Nanowires

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The optical and structural properties of ZnSe nanowires directly grown on three different substrates, SiO$_2$, ITO, and graphene, were investigated. ZnSe nanowires grown on graphene and SiO$_2$ were found to have cubic structures, while ZnSe nanowires grown on ITO had a mixed cubic and hexagonal structure. The main peaks in the photoluminescence spectra of ZnSe nanowires grown on SiO$_2$, ITO, and graphene were located at 459, 627, and 627/460 nm, respectively. In addition, a field-emission light-emitting device was fabricated using ZnSe nanowires as a phosphor and graphene as an electrode. The device showed a red emission peak with Commission Internationale de L'Eclairage coordinates of (0.621, 0.315).

1. Introduction

One-dimensional single-crystal nanowires have large aspect ratios (length-to-width ratio) and exhibit a variety of interesting electrical and optical properties not observed in conventional bulk and thin film materials. These properties have led to the recent application of nanowires in conceptually new transistors, displays, lasers, photodetectors, and photovoltaic devices [1–3]. In particular, recent efforts to develop flexible and/or transparent displays have included research into developing light-emitting diodes (LEDs), field-emitting displays (FEDs), and electroluminescence (EL) devices with nanowires [4–6]. Indium tin oxide (ITO) and indium zinc oxide (IZO) are the materials currently being used for transparent electrodes, which are essential to the development of transparent displays. However, ITO and IZO materials have several limitations: they are available in limited quantities and their poor flexibilities lead to cracking, which deteriorates and reduces device reliabilities. To overcome these limitations, several studies have investigated transparent electrodes made from graphene thin films [7–9]. Graphene is a two-dimensional carbon nanomaterial. Recently, it has attracted increased attention as a possible electrode material for use in organic light-emitting diodes (OLEDs), solar cells, touch screens, and nanogenerators because of its outstanding properties, such as high electron mobility, transparency, conductivity, and flexibility [10–12].

ZnSe nanowires are excellent candidates for novel optoelectronic and electronic devices because they have a wide direct band gap of 2.7 eV at 300 K and large surface-to-volume ratios. ZnSe nanowires are particularly suitable for use in applications such as diode lasers, light-emitting diodes, and photodetectors [13–15]. Because of their numerous applications, the structural and optical properties of ZnSe nanowires grown on Si, Al$_2$O$_3$, and SiO$_2$ substrates have been previously investigated. Several studies have explored the growth of In$_x$Ga$_{1-x}$As, SiC, and In$_2$O$_3$ nanowires on...
graphene [16–18] but none has studied the direct growth of ZnSe nanowires on graphene. Thus, observations of the crystal and optical properties of ZnSe nanowires grown on graphene thin films are of particular interest. The advantage of growing nanowires directly on graphene is that it facilitates the formation of Ohmic contacts between the nanowires and graphene [17, 18]. In addition, hybrid graphene-ZnSe nanowire structures could be used in flexible and/or transparent displays.

This study presents a comparative analysis of ZnSe nanowires grown directly on graphene and those grown on SiO₂ and ITO. The crystal and optical characteristics of ZnSe nanowires grown on graphene were examined using photoluminescence (PL), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HR-TEM). In addition, a field-emission light-emitting device was fabricated using a ZnSe nanowire phosphor and transparent graphene electrodes to verify the luminescence properties of the ZnSe nanowires.

2. Materials and Methods

ZnSe nanowires were grown on three different substrates, SiO₂, ITO, and graphene, by chemical vapor deposition (CVD). SiO₂ was thermally grown to a thickness of 300 nm on a Si wafer. An ITO thin film (with a thickness of ~100 nm) was deposited on a quartz wafer using the radio frequency (RF) magnetron sputtering method. Graphene was grown on copper (Cu) foil (Sigma-Aldrich, 25 μm thick) and then transferred to a quartz wafer. Graphene was grown by placing the Cu foil in a CVD chamber with 100 sccm of H₂ gas and held at 1020°C for 90 min. 20 sccm of CH₄ gas was then passed through the chamber for another 30 min. The temperature of the CVD chamber was reduced at a rate of 150°C/min. Poly(methyl methacrylate) (PMMA) was then coated onto the graphene grown on the Cu foil and the Cu was removed using a wet-etching process. Subsequently, the graphene/PMMA was transferred to a quartz substrate and 20 sccm of Ar gas was passed through the vacuum (∼7.7 × 10⁻² Torr) at 400°C for 20 min to remove the PMMA. By repeating the transfer process five times, a five-layer graphene thin film on a quartz substrate was obtained. Au seed dispersion was achieved by placing a drop of Au seed solution, diluted to a volume ratio of 15:1 (IPA: Au colloid), on each substrate, namely, SiO₂, ITO, and graphene. Au-coated SiO₂, ITO, and graphene substrates, together with ZnSe (Sigma Aldrich, 99.995%) powder, were placed in zones 1 and 2 of the CVD chamber. The temperatures of zones 1 and 2 were increased to 620°C and 920°C, respectively, and 90 sccm of Ar gas was passed through the chamber for 30 min to grow the ZnSe nanowires.

Low-temperature PL measurements were taken over a temperature range of 6–300 K by mounting samples on the cold-finger of a closed-cycle refrigerator. A 50 cm spectrometer equipped with a liquid nitrogen cooled charge coupled device (2048 × 512 pixels) was used to record PL spectra. PL emissions were observed across the entire spectral range using a 150 line/mm (resolution ~1.3 meV) ruled grating and in the band-edge region using a 1200 line/mm (resolution ~0.1 meV) ruled grating. A 325 nm He-Cd laser was used to excite the ZnSe nanowires.

Figure 1 shows field-emission scanning electron microscope (FE-SEM) images of ZnSe nanowires grown on SiO₂, ITO, and 5-layered graphene, as well as optical images of the light-emitting states of the ZnSe nanowires when illuminated by ultraviolet (UV) light (365 nm, 8 W). The ZnSe nanowires were successfully grown on the three different substrates, showing no signs of flakes or particles. The average diameters of the ZnSe nanowires were between 20 and 60 nm and the average lengths were greater than 5 μm. As shown in the optical images of the light emissions of the ZnSe nanowires grown on 1 × 1 inch substrates, under UV illumination ZnSe nanowires on thin film SiO₂ were not luminescent, whereas ZnSe nanowires on thin film ITO exhibited a reddish-orange luminescence. The ZnSe nanowires on graphene also showed a reddish-orange luminescence, which was restricted to the area of graphene covered in ZnSe nanowires.

To identify the crystallographic differences between the ZnSe nanowires grown on thin films of SiO₂, ITO, and graphene, XRD analysis was performed (Figure 2(a)). Figure 2(a) shows that the ZnSe nanowires on both SiO₂ and graphene had cubic structures (a = 5.66882). The main peaks of those nanowires were (111), (200), (311), (400), and (331), located at 27.2°, 45.2°, 53.6°, 65.8°, and 72.6°, respectively (JCPDS 37-1463). On the other hand, the ZnSe nanowires grown on ITO demonstrated peaks from both cubic (a = 5.66882) and hexagonal (a = 3.974, c = 6.506) structures. In addition to the peaks of the cubic-structured ZnSe nanowires seen in samples grown on SiO₂ and graphene, ZnSe nanowires grown in ITO demonstrated the (100), (101), (102), (103), (203), and (105) peaks of hexagonal-structured ZnSe nanowires at 25.6°, 29.0°, 37.7°, 49.2°, 69.1°, and 77.7°, respectively (JCPDS 80-0008). The (222), (400), (440), and (622) peaks observed at 30.8°, 35.7°, 51.4°, and 61.1°, respectively (not shown in this figure), match the peaks of the ITO substrate (JCPDS 6-0416).

Figure 2(b) shows HR-TEM images of ZnSe nanowires grown on thin films of SiO₂, ITO, and graphene. Similar to the XRD results, these images show that the ZnSe nanowires grown on thin film SiO₂ had a cubic structure and a growth direction of [111]. In contrast, the ZnSe nanowires grown on thin film ITO had both hexagonal structure characteristics, demonstrating a growth direction of [100], and cubic structure characteristics, demonstrating a growth direction of [200]. In other words, the ZnSe nanowires grown on ITO exhibited two different crystalline structures and growth directions, whereas the ZnSe nanowires grown on SiO₂ showed a single crystalline structure and growth direction. Although the ZnSe nanowires grown on graphene had a primarily cubic structure and [111] growth direction (similar to ZnSe nanowires on SiO₂), some areas of the sample showed a twinned structure.

Figure 3 presents low-temperature PL spectra measured at 6 K. As shown in Figure 3(a), at the band edge, blue luminescence (centered at 2.70 eV (459 nm)) dominated the red luminescence (centered at 1.98 eV (625 nm)) of the ZnSe nanowires grown on SiO₂. The most intense peak of the ZnSe
nanowires fabricated on SiO$_2$ was at 2.6981 eV and is associated with a donor-acceptor pair (DAP) transition. Lower-energy shoulder peaks, observed at 2.6668, 2.6355, and 2.6042 eV, correspond to longitudinal optical (LO) phonon replicas of donor-acceptor pairs (DAPs) and were spaced 31.3 meV apart. Figure 3(b) shows an expanded view of the higher energy side-peaks, wherein the $I_2$ and $I_1$ peaks, as well as the free exciton (broken arrow) peak that was observed as a small bump in the spectrum at 2.8014 eV, are resolved [19, 20]. It is known that $I_2$ lines, which are associated with excitons bound to neutral donors, can be found only in crystal of the highest quality [21]. An exciton bound to a neutral acceptor is responsible for the $I_1$ transition as well as its LO phonon replica ($I_1$-LO) at 2.7525 eV. Assignments of these sharp band-edge features were based on characteristics of a uniform and defect-free zinc-blende cubic structure [22, 23]. These assumptions were confirmed by the XRD and HR-TEM results shown in Figure 2. In the case of the ZnSe nanowires grown on ITO, the main peak was located at 1.977 eV (627 nm) and lacked any band-edge transitions. The broad spectral feature centered at 627 nm is associated with a self-activated emission due to donors and deep acceptor pair transitions resulting from Zn-vacancies or interstitial states [15, 24]. In our case, such vacancies or interstitial states may be the result of crystal interfaces between hexagonal and cubic lattices, as shown in Figure 2(b). Such mixed phases deteriorate crystal quality and prevent PL emissions from having sharp band-edge structures.

On the other hand, the main transition peaks of the ZnSe nanowires grown on graphene had two distinct regions, namely, a band-edge related peak at 2.695 eV (460 nm) and a broad feature at 1.977 eV (627 nm). Unlike ZnSe nanowires grown on ITO, ZnSe nanowires grown on graphene had a single-phase cubic zinc-blende structure. However, it also demonstrated a twinned structure, as shown in Figure 2(b). Comparable to the ZnSe nanowires grown on graphene here, twinned structure ZnSe nanowires grown on alumina and Si substrates have been shown to have strong red emissions and relatively weak band-edge emissions [25, 26].

In addition, we verified that ZnSe nanowires grown on graphene can be used in light-emitting devices. Analyzing the optical emission processes of ZnSe nanowires should facilitate the development of ZnSe nanowire-based light-emitting devices. Figure 4(a) presents field-emission current densities as a function of the electric field applied to the device. As illustrated in Figure 4(a), electricity started to flow when the electric field was 1.5 V/µm and the field-emission current density increased exponentially as the electric field was increased to 2.2 V/µm. When the applied field was equal to 2.2 V/µm, the emission current density was $\sim 30 \mu$A/cm$^2$.

The field-emission-current-voltage characteristics were obtained using the Fowler-Nordheim equation, $J = (A\beta^2 E^2/\Phi) \exp[-B\Phi^{3/2}(\beta E)^{-1}]$, where $J$ is the current density, $E$ is the applied electric field, $A$ is $1.56 \times 10^{-10}$ (AV$^{-2}$eV), $B$ is $6.83 \times 10^3$ (VeV$^{-3/2}$µm$^{-1}$), $\Phi$ is the work function of the ZnSe emitting material (4.84 eV) [27], and $\beta$ is the field-enhancement factor, which is related to emitter geometry, crystal structure, and spatial distribution of the emitting centers [28]. Note that $\beta$ was extracted from the slope of a $\ln(J/E^2)$ versus $1/E$ graph.
plot. The $\beta$ value was $\sim 7,250$, which is higher than those previously reported for ZnSe nanoribbons ($\sim 1382$) [29], ZnO nanoneedles on plastic substrates ($\sim 1134$) [30], and carbon nanotubes on polyamide ($\sim 850$) [31]. These results indicate that ZnSe FEDs with graphene electrodes could be used to fabricate novel FE devices. The inset of Figure 4(a) illustrates a schematic of a FED structure employing ZnSe nanowires grown on graphene. Carbon nanotube (CNT)/ITO and ZnSe nanowire/graphene materials were used as the emitter/cathode and phosphor/anode, respectively. Note that the sheet resistance of the graphene electrode was $\sim 2.0 \, \Omega$/sq.

The field-emission properties of the device were measured in a diode configuration, using a $500 \mu m$ gap between the anode and cathode. During measurements, the pressure was maintained at $\sim 1.5 \times 10^{-6}$ Torr.

Figure 4(b) shows the brightness of ZnSe nanowire/graphene as a function of emission current. Figure 4(b) shows that the brightness of the ZnSe nanowire phosphor emissions increased from 20 to 80 cd/m$^2$ when the emission current was increased from 20 to 100 $\mu A$. The luminous efficiency was 0.87 lm/W at 2.2 kV/mm, higher than that reported for SrTiO$_3$:Pr$^{3+}$ (0.4 lm/W) [32]. The insets in Figure 4(b) show
images of the light emissions of the device at each applied emission current, the size of the area imaged being ~10 × 20 mm. The emission spectrum of the ZnSe nanowires shows an emission peak at ~627 nm. The average corresponding Commission Internationale de l’Eclairage (CIE) coordinates for the device are (0.621, 0.315).

3. Conclusions

In summary, ZnSe nanowires of varying crystallinity and luminescent properties were synthesized on three different substrates, SiO₂, ITO, and graphene. XRD and HR-TEM analyses revealed that the ZnSe nanowires grown on SiO₂ and graphene by CVD, using Au catalyst, had single-phase, cubic structures. On the other hand, the ZnSe nanowires grown on ITO showed the presence of both cubic and hexagonal structures. Furthermore, PL results for ZnSe nanowires on SiO₂ and ITO exhibited remarkably high peaks at 2.701 eV (459 nm) and 1.977 eV (627 nm), respectively, whereas those of ZnSe nanowires on graphene showed red luminescence at approximately 1.977 eV (627 nm) and a blue peak at 2.695 eV (460 nm). A FED device was fabricated with light-emitting ZnSe nanowires on graphene. The fabricated FED device showed a red emission peak at ~627 nm with CIE coordinates of (0.621, 0.315). Based on these experimental results, it is highly probable that a hybrid device made from nanowires and graphene could provide an effective means for developing highly functional and efficient light-emitting displays.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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