Electroluminescence from \( n\)-In\(_2\)O\(_3\):Sn randomly assembled nanorods/p-SiC heterojunction

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Abstract: Room-temperature electroluminescence (EL) has been realized from Sn-doped In\(_2\)O\(_3\) (In\(_2\)O\(_3\):Sn) nanorods. Heterojunction light-emitting diode (LED) was formed by depositing a layer of randomly packed \( n\)-In\(_2\)O\(_3\):Sn nanorods onto a \( p\)-type 4H-SiC substrate. It is found that the emission intensity of the heterojunction LED under forward bias can be maximized by doping the In\(_2\)O\(_3\) nanorods with 3 mol. % of Sn. Furthermore, two emission peaks of the EL spectra are observed at \(~395\) and \(~440\) nm. These ultraviolet and visible peaks are attributed to the radiative recombination at Sn induced and intrinsic defect states of the In\(_2\)O\(_3\):Sn nanorods.

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References

1. Introduction

In$_2$O$_3$ is a wide band gap (i.e., direct band gap of 3.55 – 3.75 eV and indirect band gap of 2.6 eV) transparent conducting oxide semiconductor often used as transparent conductive electrode in optoelectronic devices such as solar cells, flat panel display, and light-emitting diodes (LEDs) [1]–[3]. Therefore, extensive studies had been concentrated on the electrical properties of In$_2$O$_3$ films [4], [5]. However, light-emitting properties of bulk In$_2$O$_3$ were seldom investigated due to its forbidden dipole transition. Recently, investigations have revealed that nanostructured semiconductors can demonstrate unexpected optical properties when compared to its bulk counterparts [6]. This offers tremendous opportunities to modify the undesired optical characteristics of dipole-forbidden semiconductors. Hence, different fabrication techniques such as vapor transport process, chemical vapor deposition, as well as electrochemical deposition and oxidization, have been proposed to fabricate nanostructured In$_2$O$_3$ [7]. Because of the size reduction, visible photoluminescence (PL) spectra were observed from In$_2$O$_3$ nanoparticles, nanobelts and nanowires at low temperature [8]–[12]. The corresponding emission mechanism was attributed to either the small dimension of amorphous In$_2$O$_3$ [8], [9] or the induction of oxygen vacancies [10], [11] in nanoscale. Ultraviolet (UV) emission, which is due to near-band-edge recombination, was also measured from In$_2$O$_3$ nanowires embedded in alumina template [12], [13]. Nevertheless, electroluminescence (EL) has neither been demonstrated from In$_2$O$_3$ films nor nanostructures.

In this paper, it is proposed to deposit a layer of randomly packed Sn doped n-In$_2$O$_3$ (n-In$_2$O$_3$:Sn) nanorods by vapor transport technique onto a p-SiC(4H) substrate to obtain heterojunction for the realization of EL at room temperature. In addition, it can be shown that the corresponding EL intensity can be maximized by doping the In$_2$O$_3$ nanorods with 3 mol. % of Sn.

2. Fabrication

Figure 1 shows the schematic diagram of the proposed n-In$_2$O$_3$:Sn nanorods/p-SiC(4H) substrate heterojunction LED. A p-doped 4H-SiC wafer (5 × 5 mm$^2$, purchased from Cree Inc) was chosen as substrate and hole injection layer of the heterojunction. This is because the p-doped SiC substrate has a high hole concentration (~1 × 10$^{19}$ cm$^{-3}$) and carrier mobility (~120 cm$^2$/Vs). Randomly packed In$_2$O$_3$:Sn nanorods of thickness ~1 μm were deposited onto the SiC substrate by a conventional carbothermal reduction method [14]. This was done by vaporizing a mixture of In$_2$O$_3$, SnO$_2$ (99.9%, Sigma-Aldrich) and graphite fine powders – source powder at the center of a horizontal tube furnace. Weight ratio of the precursors was set to SnO$_2$:In$_2$O$_3$:C = 0.3:0.7:1.0 so that the doping concentration of Sn in In$_2$O$_3$ nanorods can be about 3 mol. %. The 4H-SiC substrate, which polished (0001) surface was coated with ~3 nm thick of Au, was positioned at a distance 3 to 5 centimeters downstream from the source powder. A stream of pure Ar (99.99%) gas was maintained at a flow rate and pressure of 100 sccm and 30 mbar respectively inside the horizontal tube furnace. Process time was varied to control the thickness of the randomly assembled In$_2$O$_3$:Sn nanorods and temperature of the SiC substrate was kept at ~830 °C. For the purpose of comparison, randomly packed In$_2$O$_3$ nanorods of the same thickness were also deposited onto another p-SiC substrate.
Rough surface of the $p$-SiC substrates after cleaned by HF acid was deposited with a metal contact (size of about $2 \times 2$ mm$^2$), which consisted of a layer of ~25 nm thick Al film and a layer of ~150 nm thick Ti film, by using electron beam evaporation. The samples were subjected to rapid thermal annealing at 800°C in N$_2$ for 5 min in order to achieve a linear current-voltage dependence of the Al/Ti metal contact on the $p$-SiC substrate. It can be shown that the ohmic contact was formed on the $p$-SiC substrate by using Al/Ti metal and the corresponding resistance is less than 2 kΩ [15]. Room temperature electrical and optical characteristics of the heterojunction LEDs were measured by pressing an ITO coated quartz substrate onto the $p$-SiC coated with the randomly packed nanorods to form an ohmic contact. This configuration was used to avoid direct deposition of ITO onto the nanorods. This is because ITO may penetrate through the gap of the randomly packed nanorods into the 4H-SiC substrate during the deposition so that a small shunt resistance may be induced inside the heterojunction.

3. Results and discussion

Figure 2(a) shows the scanning electron microscopy (SEM) image of the In$_2$O$_3$:Sn (3 mol. %) nanorods deposited onto a $p$-doped 4H-SiC substrate. It is observed that the nanorods are closely packed together to form a thin film. In addition, the nanorods have average length and width of ~2 µm and ~100 nm respectively. X-ray diffraction (XRD) pattern of the as-grown In$_2$O$_3$:Sn nanorods is given in Fig. 2(b). All the relative sharp diffraction peaks, which illustrated the high crystallinity of the as-growth nanorods, can be indexed to a body-centered cubic structure. Furthermore, the growth conditions of In$_2$O$_3$:Sn nanorods (i.e., temperature, pressure and flow rate) were optimized such that the intensity and full-width half maximum (FWHM) value of the (222) peak is the highest and smallest respectively. These implied that the proposed growth conditions are the most suitable for the growth of In$_2$O$_3$:Sn nanorods with a good cubic crystal structure. Figure 2(c) indicates the composition distribution of In, Sn, and Au. (d) An SEM image of the In$_2$O$_3$:Sn (3 mol. %) nanorod given in Fig. 2(c). (e) EDS spectrum of the In$_2$O$_3$:Sn (3 mol. %) nanorod. (f) A HRTEM image of the In$_2$O$_3$:Sn (3 mol. %) nanorod and (g) the corresponding SAED pattern.

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selected area electron diffraction (SAED) pattern of the In$_2$O$_3$:Sn nanorod is shown in Fig. 2(g). The clear spots also prove that the nanorods are single crystalline structure. The SAED pattern confirms the $c$-type rare earth oxide cubic structure of the ITO nanowires and its uniphasic property consistent with the XRD results. It is also noted that the In$_2$O$_3$:Sn nanorods were randomly grown on the SiC substrate. However, it is observed from the XRD pattern that the growth direction was primarily along the <222> direction, perpendicular to the (0001) Si face of the SiC substrate.

![SAED pattern](image)

Fig. 3. Room temperature EL spectra of the (a) $n$-In$_2$O$_3$:Sn (3 mol. %) nanorods/p-SiC substrate and (b) $n$-In$_2$O$_3$ nanorods/p-SiC substrate heterojunction LEDs. The insets show the color photos taken from the LEDs under a forward bias voltage of 10 V and SEM image of In$_2$O$_3$ nanorods.

Figure 3(a) shows the EL spectra of the $n$-In$_2$O$_3$:Sn(3 mol. %) nanorods/p-SiC heterojunction LED biased at different forward voltages. The EL spectra were measured by connecting the cathode and anode of a rectangle pulse voltage source (with repetition rate and pulsewidth of 7.5 Hz and 80 ms respectively) to the ITO coating on the quartz substrate and Al/Ti metal contact on the $p$-SiC respectively. Light was collected from the uncoated side of the quartz substrate by an objective lens. The EL spectra show a broad emission bandwidth with FWHM equal to ~100 nm at 12 V and the emission peak is at wavelength of 400 nm. However, no light emission was observed from the heterojunction LED under reverse bias. The inset displays a color photo of the LED taken at forward bias at 10 V. It is noted that only the region below with metal contact gives intense white-light surface emission. This is due to the high electrical conductivity of the closely packed $n$-In$_2$O$_3$:Sn(3 mol. %) so that radiative recombination is dominated within the region sandwiched by the injection contacts. Figure 3(b) shows the EL spectra of the $n$-In$_2$O$_3$ nanorods/p-SiC heterojunction LED biased at different forward voltage. No light emission was observed from the heterojunction LED under reverse bias. In addition, the FWHM value and peak emission wavelength are found to be ~125 and ~425 nm respectively for the LED biased at 12 V. The inset of Fig. 3(b) shows a color photo of the LED taken at forward bias of about 10 V. White light emission is only observed at the region underneath the $p$-type metal contact due to the same reason as if the $n$-In$_2$O$_3$:Sn nanorods/p-SiC heterojunction LED. Furthermore, it is observed that pure In$_2$O$_3$ nanorods have similar size and crystallinity to that of the $n$-In$_2$O$_3$:Sn nanorods.

It is noted that the emission intensity of In$_2$O$_3$ nanorods is approximately 10 times less than that observed from the In$_2$O$_3$ nanorods doped with 3 mol. % of Sn under forward bias. Furthermore, it can be shown that the reduction of Sn mol. % decreases the EL intensity of the $n$-In$_2$O$_3$:Sn nanorods heterostructure LEDs. For In$_2$O$_3$ nanorods doped with 1 mol. % of Sn, the corresponding intensity of EL can be reduced by more than 50% when compared to that doped with 3 mol. % of Sn. However, Sn doping concentration higher than 3 mol. % is difficult to obtain due to the low solubility of Sn in In$_2$O$_3$ nanorods. Hence, $n$-In$_2$O$_3$ nanorods heterostructure LEDs doped with 3 mol. % of Sn provide maximum intensity of EL under forward bias. From Fig. 3, it is also noted that the introduction of 3 mol. % of Sn doping
blueshifts the entire EL spectrum by ~25 nm. This is because new defect states with energy higher than that of intrinsic defect states were induced by Sn dopant to support high-intensity UV radiative recombination.

Figure 4 plots the current-voltage ($I$-$V$) curve of the heterojunction LEDs with and without doping of 3 mol. % of Sn. The inset shows the corresponding light-voltage ($L$-$V$) curves of the heterojunction LEDs. It is observed that the heterojunction LEDs have a turn-on voltage of ~6 V. The introduction of Sn doping increases (decreases) the amount of injection current density of the heterojunction LED under forward (reverse) bias. This is because the resistivity of the nanorods decreases with the increase of Sn doping. In addition, it can be shown that the resistivity of In$_2$O$_3$ nanorods doped with 1 mol. % of Sn can be reduced by more than 60% when compared to that doped with 3 mol. % of Sn.

![Fig. 4. Room temperature current-voltage characteristics of $n$-In$_2$O$_3$:Sn (3 mol. %) nanorods/p-SiC substrate and $n$-In$_2$O$_3$ nanorods/p-SiC substrate heterojunction LEDs. The inset shows the light-current characteristics of the heterojunction LEDs.](image)

Figure 5(a) plots the fitting results of the EL spectra for the $n$-In$_2$O$_3$:Sn(3 mol. %)/p-SiC heterojunction LED at a forward bias voltage of 12 V. It is found that the emission spectra can be reconstructed by two Gaussian curves with peak wavelengths at around 395 and 440 nm. These two peaks can be considered as the energy levels of two radiative recombination centres of the In$_2$O$_3$ nanorods. The origin of 440 nm (2.82 eV) may be attributed to the intrinsic defect states inside the bandgap such as oxygen vacancies [10], [11], which induce new energy level within the bandgap, as amorphous layer has not been observed from the HRTEM image. Furthermore, the emission peak at 397 nm (3.13 eV) may be due to the Sn induced defect states. This is because the 1) emission energy is far away from the conduction band (different by ~0.57 eV) so that it cannot be considered as near bandgap emission [12], [13] and 2) emission intensity of the EL is dependent on the doping concentration of Sn.

Figure 5(b) plots the PL spectrum obtained from the In$_2$O$_3$:Sn(3 mol. %) nanorods deposited on p-SiC substrate under excitation of a 355 nm frequency tripled Nd:YAG pulsed laser (with 6 ns pulselength and 10 Hz repetition rate) at an excitation intensity of about 1 MW/cm$^2$. A spherical lens was used to focus a pump beam of 1 mm in diameter onto the surface of the nanorods. Emission was collected in the direction perpendicular to the surface of the randomly assembled nanorods. Fitting results of the PL spectrum are also shown in the figure. The emission spectrum can be roughly fitted by two Gaussian curves with peak wavelength at around 400 and 436 nm. These values are close to that obtained from the EL emission. This verified that there are UV and visible bands contributed to the radiative recombination of the In$_2$O$_3$:Sn nanorods.

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Fig. 5. Fitting results of (a) normalized EL spectrum obtained from the In$_2$O$_3$:Sn (3 mol. %) nanorods heterojunction LED at forward biased voltage of 12 V and (b) normalized PL spectrum of the In$_2$O$_3$:Sn (3 mol. %) nanorods deposited on p-SiC under 355 nm Nd:YAG laser with excitation power of ~1 MW/cm$^2$. The insets show the energy band alignment of the p-SiC/n-In$_2$O$_3$:Sn under forward bias and equilibrium. It is noted that the electron affinity and bandgap energy, $E_g$ of SiC (In$_2$O$_3$) are 4.05 (3.7) and 3.6 (3.6) eV respectively. In the energy band diagram, $E_C$ ($E_V$) represents conduction (valence) band. The discontinuity of conduction (valence) band is found to be 0.35(0.35) eV.

4. Conclusion

In conclusion, we have achieved EL from Sn doped In$_2$O$_3$ nanorods deposited on p-SiC substrate. It is found that the increase of Sn concentration in In$_2$O$_3$ nanorods increases the corresponding intensity of EL under forward bias. This is because high doping concentration of Sn dopants induced large amount of defect states to support intensive radiative recombination at UV wavelength. In addition, the electrical conductivity of In$_2$O$_3$:Sn nanorods increases with the doping concentration of Sn so that effective external injection of carriers can be achieved under forward bias. However, further increase of Sn concentration is not allowed due to the low solubility of Sn in In$_2$O$_3$ nanorods. 3 mol. % of Sn is the maximum amount of dopant that can be doped into In$_2$O$_3$ nanorods. On the other hand, due to the diffusion length of carriers, there should be an optimized aspect ratio of the In$_2$O$_3$ nanorods to maximize the corresponding electrical-to-optical conversion efficiency. Further investigation on this issue will be studied in our future publication. Two emission peaks were observed from the EL spectra of the In$_2$O$_3$:Sn(3 mol. %) nanorods/p-SiC heterojunction at around 395 and 440 nm under forward bias. By comparing with the corresponding PL spectrum, it is verified that the there are two emission bands contributed to two radiative recombination centers. In addition, these UV and visible emission peaks are related to radiative recombination at the Sn induced and intrinsic defect states of the In$_2$O$_3$:Sn nanorods.

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