Fabrication and electro-optic properties of a MWCNT driven novel electroluminescent lamp

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Abstract
We present a novel, cost-effective and facile technique, wherein multi-walled carbon nanotubes (CNTs) were used to transform a photoluminescent material to exhibit stable and efficient electroluminescence (EL) at low voltages. As a case study, a commercially available ZnS:Cu phosphor (P-22G having a quantum yield of 65 ± 5%) was combined with a very low (∼0.01 wt%) concentration of CNTs dispersed in ethanol and its alternating current driven electroluminescence (AC-EL) is demonstrated. The role of CNTs has been understood as a local electric field enhancer and facilitator in the hot carrier injection inside the ZnS crystal to produce EL in the hybrid material. The mechanism of EL is discussed using an internal field emission model, intra-CNT impact excitation and the recombination of electrons and holes through the impurity states.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Alternating current electroluminescent (AC-EL) lamps already occupy a segment of the high-resolution, flat panel display market. AC-EL displays in thin-film form are robust, possess long lifetimes, and offer high luminance with relatively low power consumption [1]. However, AC-EL lamps in thick-film form have attracted considerable interest for illumination and display applications, due to their substrate flexibility, simple fabrication process of large-area panels and low-cost fabrication avoiding requirement of vacuum processing [2–4]. Such AC-EL lamps consist of a phosphor layer, e.g. copper-doped zinc sulfide (ZnS:Cu), vertically sandwiched between two insulators that are contacted by electrodes. When a sufficiently high voltage is applied across the electrodes, electron charge carriers are injected into the conduction band of the phosphor, where they are accelerated to high energies by the field and energy transfer takes place via impact excitation of the luminescent centers and finally radiative relaxation results in the EL [5, 6].

Despite the simple fabrication processes of EL thick-film type lamps, their applications have been confined to backlight units in cellular phones due to deficient performance as low brightness and efficiency [7]. In spite of considerable efforts in improving the performance of AC-EL lamps, the fabrication of a simple and stable structure operated at low voltage and low frequency is still required and has been the greatest challenge to the scientific community [8, 9]. This paper reports the triggering of EL in a non-EL material with the use of commonly available multi-walled carbon nanotubes (CNTs) and it is anticipated that use of CNTs can improve the EL performance of AC-EL lamps. The mechanism to understand this unusual EL phenomenon has also been successfully explained.

The most investigated EL phosphor for conventional AC-EL lamps is copper-doped zinc sulfide (ZnS:Cu), wherein high doping of Cu ∼1000 ppm is present [10, 11]. It is well
known that excess doping of copper is a prerequisite for the phosphor to exhibit EL. This has the dual function of primarily forming electrically conducting Cu$_x$S needles inside the ZnS grain and secondly creating the required luminescent centers in the ZnS host lattice. When a high voltage is applied, the Cu$_x$S needles provide an enhanced local electric field in the ZnS grains [12, 13], thus producing EL, as represented in figure 1(a). However, the EL lamps fabricated from them have a serious operational problem with prolonged usage. With time, the sulfur diffuses into the lattice, resulting in the poor performance and drastic reduction of its lifetime.

In the current research, after rigorous experimentation and the development of many strategies of device fabrication, a novel idea of replacing Cu$_x$S conducting needles by commonly available multi-walled carbon nanotubes (CNTs) has been explored to produce smart EL. It is well known that CNTs are stable and outstanding field-enhancing materials due to their unique properties of high aspect ratio [14], excellent electrical [15] and thermal conductivities [16], mechanical strength [17] and chemical inertness. This makes them an ideal substitute for Cu$_x$S conducting needles, as shown in figure 1(b). The work was carried out in this direction, with an understanding that, when Cu$_x$S needles are replaced by CNTs, a high electric field region, called a hot-spot would necessarily be formed between the nearest placed CNTs within the ZnS grain, which can cause EL emission. For this purpose, a CNT-based AC-EL lamp was developed using a ZnS:Cu phosphor to check the concept, and smart EL was found to be triggered at very low operating voltages. (See the supporting information for the video clip available at stacks.iop.org/Nano/23/435704/mmedia.)

2. Experimental details

2.1. Sample preparation

A novel, cost-effective and facile technique is suggested, wherein a non-electroluminescent (non-EL) material is converted to exhibit stable and efficient EL at low voltages using CNTs. Commercial cathodoluminescent phosphor, ZnS:Cu (P-22G with quantum yield 65 ± 5%) having minimal (~50 ppm) Cu doping, procured from M/s Samtel Color Lab., India, was used as starting material. The multi-walled carbon nanotubes (CNTs) were grown by chemical vapor deposition technique in the Carbon section of CSIR-NPL, India. The weighing of lower amounts of CNTs with precision is a tedious job. Hence, we have dispersed a known weight of CNT in ethyl alcohol and ultra-sonicated rigorously for 2 h to make a suspension. This was further added to ZnS:Cu phosphor and allowed to dry at room temperature (~25°C). After complete drying the mixture was blended mechanically and annealed at 450°C under an inert N$_2$ atmosphere. The amount of CNT addition is found to be highly critical in our experiments. An admissible range to exhibit EL was only 0.005–0.03 wt%. However, ~0.01 wt% of CNT was found to be optimum and showed stable and bright EL from the ZnS/CNT hybrid material. Another important finding in our experiment is the addition of ~5 wt% of potassium bromide (KBr) as a chemical ‘additive’, which was mixed with the ZnS/CNT blend before annealing in order to diffuse CNTs into the ZnS lattice more effectively. This further helps in creating hot-spots inside the ZnS grain when there is an applied electric field, triggering smart EL as shown in figure 1. Afterwards, blends of ZnS and various concentrations of CNTs were prepared and annealed in the temperature range 400–600°C for 1–3 h and checked for their EL response. Stable and significantly good EL was found to be exhibited by the sample annealed at/above 500°C for 2 h. Hence, 500°C was fixed as a suitable annealing temperature for ZnS/CNT blend for further studies. The ZnS/CNT samples annealed at 500°C that were obtained were then characterized for various parameters as described in the following sections.

2.2. Sample characterization

For phase identification, the structural characterization was performed using x-ray diffraction (XRD; Rigaku: MiniFlex, Cu K$_\alpha$; λ = 1.54 Å). The surface morphology and microstructural characterization was carried out by scanning electron microscopy (SEM, model number LEO 440).
temperature steady-state luminescence characterization was done using a Perkin Elmer Luminescence Spectrometer (Model No. LS-55). The electro-optical characterizations of the samples have been performed using a home-made setup shown in figure 5 and discussed in the later sections.

A prototype EL lamp of size $15 \times 40 \text{mm}^2$ was fabricated at room temperature using ZnS:Cu phosphor and MWCNT hybrid material by a conventional spreading technique on indium tin oxide (ITO) coated conducting glass and screen printing of an aluminum electrode on the top. This enabled us to complete the final EL lamp structure.

3. Results and discussion

Figure 2 shows the photoluminescence (PL) spectrum of commercial ZnS:Cu (P-22G) phosphor as received from M/s Samtel Color Lab., India. It showed a bright green PL emission (quantum yield $65 \pm 5\%$) having peak maximum at 535 nm, when observed under an excitation wavelength of 335 nm (3.7 eV). The doped copper (Cu$^+$) ions form the required acceptor levels at $\sim 1.29$ eV above the valence band of the ZnS lattice [18]. The inset of figure 2 shows the energy band scheme for copper-doped ZnS phosphor, exhibiting its well-known band gap $\sim 3.6$ eV. This implies that excitation energies higher than the band gap could very well be absorbed by the ZnS crystal. A radiative recombination of electrons and holes occurs as the Cu$^+$ acceptor level emits the desired green (535 nm) light. It is important to note that ZnS:Cu phosphor in its as-received form did not exhibit EL in the ac range $10–1000 \text{ V}_{pp}$, which is due to insufficient doping of copper present in the crystal system. This may be attributed to the lack of conducting paths induced by Cu$_x$S needles inside the ZnS grain.

The phase analysis of the ZnS/CNT hybrid materials annealed at different temperatures is shown in figure 3. It is observed that the ZnS phosphor used in the current study exhibits a cubic nature with sphalerite structure. The presence of planes B1–[111]; B2–[200]; B3–[220]; B4–[311]; B5–[400]; B6–[331] confirm the zinc blende structure (JCPDS card no: 005-0566). The peaks have been identified and are indicated in the XRD pattern shown in figure 3. The XRD profiles did not show the peaks related to CNTs as they are present in nominal ($\sim 0.01$ wt%) amounts in any of the samples treated for high-temperature annealing cycles. This substantiates the fact that the original phase of the ZnS phosphor is retained even after annealing treatment.

The morphological studies of the ZnS:Cu phosphor, CNT, their mechanical blend and the annealed hybrid material were performed using a scanning electron microscope (SEM) and are shown in figures 4(a)–(d). The SEM image (figure 4(a)) of the representative ZnS/CNT hybrid material annealed at 500°C clearly shows that the CNTs have been diffused appropriately into ZnS particles due to heat treatment. The same has been marked in the images for convenience.

A schematic diagram of the EL device fabricated in the current study is shown in figure 5. A series of ZnS/CNT hybrid materials were prepared under various conditions of annealing and CNT concentrations. A prototype device
Figure 4. SEM images show the morphology of ZnS phosphor, carbon nanotubes, ZnS + MWCNT blend and ZnS/MWCNT hybrid material after annealing.

Figure 5. A schematic of the ZnS/MWCNT hybrid material-based AC-EL smart lamp structure.

for each hybrid material was fabricated and tested using the above scheme. Prior to the fabrication, the dielectric constant of the epoxy, used as dielectric medium in the device, was calculated by measuring the capacitance using an LCR meter and was found to $\varepsilon_r \sim 4.99$. In a typical fabrication process, the ZnS/CNT hybrid phosphor was mixed well with the dielectric medium ($\varepsilon_r \sim 4.99$) and coated onto the conducting surface of transparent ITO glass using a conventional spreading technique. The thickness of the phosphor layer was approximately 40 $\mu$m. After drying at 50 °C, another dielectric layer (thickness $\sim 10 \mu$m) was coated over the phosphor layer as a buffer to avoid shorting of the device. Finally, an aluminum (Al) metal layer was screen printed at the top, which served as back electrode. The electrical contacts were drawn out from ITO coated glass and Al metal. An ac voltage with varying amplitude and frequency was applied to the device through the contacts.

The observed EL was measured using a photomultiplier tube (PMT). The EL measurements for the entire representative devices were performed under similar conditions, such as distance of sample from the PMT and the active area of the device exposed to PMT, ambient conditions of temperature, atmospheric pressure, relative humidity etc, for relative comparison.

The dependence of EL brightness on the applied ac voltage ($B$–$V$ curve) for the hybrid material with varying CNT concentrations in the range 0–0.2 wt% is shown in figure 6. For the sample without CNT addition, EL emission was not observed up to 1000 $V_{pp}$ ac. However, with the introduction of CNT in a nominal quantity, EL was observed for very low applied ac voltages. In other words, the threshold voltages to drive the EL device decreased dramatically from unknown values to $< 100$ V ac upon the addition of CNTs. The measurable EL emission was observed for a sample having a CNT concentration of $\sim 0.01$ wt% and, in this case, the threshold voltage reduced to $\sim 50$ $V_{pp}$ ac. It is worth mentioning here that an $\sim 0.01$ wt% concentration of CNTs is found to be the optimum to exhibit stable and maximum EL brightness, as shown in figure 6. However, when the CNT concentration was $> 0.2$ wt% in the ZnS/CNT hybrid material, the device burnt out with sparking due to the high conductivity. Thus, the concentration of CNT in the ZnS/CNT hybrid material is critical for proper functioning of the EL device.

In view of this and the above-mentioned result, the concentration of CNT in the hybrid material was fixed at $\sim 0.01$ wt% for further studies. The inset of figure 6 shows the EL spectrum recorded for ZnS/CNT hybrid material having $\sim 0.01$ wt% CNT, indicating emission peak centered at 528 nm for 350 $V_{pp}$ and 2.65 kHz frequency. It is important to note here that the EL spectrum has been observed to blue-shift
Figure 6. Plot of the electroluminescent (EL) intensity versus the applied ac voltage across the lamp structure. Inset of the figure shows the EL spectrum of the lamp at a given ac voltage of 350 V<sub>pp</sub> at 2.65 kHz.

Figure 7. Plot of the EL response as a function of drive frequency at a fixed ac voltage 350 V<sub>pp</sub>. The inset shows a marginal (∼12 nm) variation of emission wavelength exhibited by ZnS/MWCNT hybrid material under various applied ac voltages.

by ∼7 nm when compared to the PL spectrum of ZnS:Cu phosphor, as shown in figure 2.

All the ZnS/CNT hybrid materials that show EL emission were found to obey the following empirical relation:

\[
B = \begin{cases} 
B_0 \exp \left( -\frac{b}{\sqrt{V}} \right) & 0 \leq V < 260 \text{ V} \\
B_0 \exp (V) & V \geq 260 \text{ V} 
\end{cases}
\]

where \( B \) is the brightness, \( V \) is the applied voltage, and \( B_0 \) and \( b \) are constants determined by the particle size of the phosphors, structure of the device and the exciting bias conditions [10]. The \( B-V \) relation in the range \( 0 < V < 260 \text{ V} \) implies the well-known phenomenon of EL in ZnS phosphors [19]. Usually the EL brightness of the device increases with an increase in the applied AC voltage and attains a saturation value. A typical increase of applied voltages beyond brightness saturation leads to a decrease in capacitance value and, hence, shorting of the device. The brightness–voltage relation could be explained using the above equation. In the first part, \( 0 < V < 260 \text{ V} \), the EL mechanism is responsible for the well-known process of tunneling of electrons as well as injection of hot electrons in the ZnS crystal [20]. However, the presence of CNTs seems to have modified the \( B-V \) relationship as represented by second part of the equation, \( V \geq 260 \text{ V} \), which may be due to efficient intra-CNT impact excitation by hot carriers and the development of hot-spots inside the ZnS grains [21].

The measurement of EL brightness with respect to frequency is another important feature of the EL study. The variation in EL brightness with frequency is shown in figure 7. The emission intensity was observed to increase with ac frequency initially, reaching to maximum at a frequency around 2.65 kHz and deteriorating afterwards. A possible explanation for this may be as follows: as the number of cycles per second increases, the energy supplied to the device also increases, reinforcing the EL brightness. When the frequency is further increased beyond the optimum, the extra energy starts dissipating as heat, leading to a decrease in brightness, and finally damage to the EL device [22].

The inset of figure 7 shows a marginal (∼12 nm) variation of emission wavelength exhibited by ZnS/CNT hybrid material under various applied ac voltages. With an increase in voltage the EL emission peak experiences a blue-shift. This may be attributed to the phonon-assisted EL emission by CNTs [23].

The EL brightness of ZnS/CNT hybrid material has been found to be influenced by the exciting input waveforms, as shown in figure 8. The sinusoidal wave delivered the optimum EL brightness compared to square and saw-tooth waves. The reason for this could be explained in terms of a distribution of voltages in different waveforms, thus leading to the injection of hot electrons into the device. The injection of hot electrons and extraction of hot holes in a sinusoidal wave is gradual, which in turn excites luminescent centers uniformly, thereby increasing the radiative recombination leading to an efficient EL. Although a saw-tooth wave also injects hot carriers gradually, the abrupt jump from positive to negative voltage reduces the excitation as well as the recombination rates, leading to a decrease in the EL brightness. The rapid jump from negative to positive (or vice versa) in a square wave causes a massive charge injection into the emitting layer, resulting in an unbalanced situation between much higher densities of charge of both polarities. This behavior also leads to a further decrease in the EL brightness [24].

An AC-EL device using ZnS/CNT hybrid material has been fabricated and analyzed for the first time, for photo- and electroluminescence and corresponding electro-optical properties; such as brightness–voltage, brightness–frequency and brightness waveforms. It was found that conducting paths induced inside the ZnS phosphor for effective electron and/or hole transport by the use of CNT was the main cause of realizing the low-voltage AC-EL device.

Figure 9(a) shows the photograph of the prototype device, depicting two spots, related to the intrinsic ZnS:Cu phosphor.
Figure 8. Plot of the EL response as a function of various input waveforms for a given bias conditions of 350 V$_{pp}$ at 2.65 kHz, which shows that the contribution of a sine wave is optimum.

and ZnS/CNT hybrid material respectively, operated at a threshold ac voltage $\sim$50 V$_{pp}$ and 2.65 kHz. It can be clearly seen from the photograph that the spot corresponding to the intrinsic ZnS:Cu phosphor does not show EL at all, while a very bright and stable green EL emission is seen from the ZnS/CNT hybrid material. The same has been marked in the photograph. Thus it can be concluded that a non-EL material has been transformed to exhibit EL by the introduction of a nominal ($\sim$0.01 wt%) concentration of CNTs.

The mechanism of EL is highly important to understand the working of the device. Figure 9(b) illustrates the energy band diagram for the ZnS/CNT hybrid material. When the voltage is applied across the device, CNTs produce high carrier mobility and local electric fields which lower the energy barrier at the contact aluminum electrode, facilitating efficient tunneling of electrons into the device. This process is known as internal field emission [21]. Due to the enhancement in local electric field at the ends of CNTs, some hot-spots are created between the nearest CNTs, within the ZnS grain, as shown in figure 1(b). These regions of high electric field promote charge carriers to be injected into ZnS:Cu phosphor, which get accelerated to higher energy and transfer their ballistic energy to luminescent centers. As a result, excitation of luminescent center takes place, and finally relaxation gives the EL emission.

4. Conclusions

Electroluminescence from the non-electroluminescent ZnS:Cu was successfully achieved with the introduction of CNT. This pilot study showed that a bright, stable and low-threshold EL can be obtained from ZnS/CNT hybrid material by a cost-effective and easy fabrication process. Electro-optical properties such as brightness–voltage, brightness–frequency and brightness waveforms were also presented. The phenomenon observed is new and has not been reported earlier. It is anticipated that the idea will be very interesting and useful in the field of AC-EL.

Figure 9. (a) A photograph of an EL lamp having intrinsic ZnS:Cu phosphor and ZnS/MWCNT hybrid material at an applied ac voltage of 50 V$_{pp}$ at 2.65 kHz. The phosphor without MWCNT did not show EL even at applied ac voltages greater than 1000 V$_{pp}$, whereas the ZnS/MWCNT hybrid material exhibited EL at threshold voltages as low as 50 V$_{pp}$ at 2.65 kHz. Both the materials are kept in a same lamp to compare the EL characteristics under similar conditions. (b) Role of CNTs in triggering the electroluminescence from ZnS:Cu phosphor. (c) Photographs of an actual EL lamp in room-light and dark conditions; exhibiting strong green EL emission operating at bias conditions of 350 V$_{pp}$ ac, 2.65 kHz and sine wave input.
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