Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

Introduction of carbon nano-tubes into the phosphor to restrain the saturation behavior in low voltage cathodoluminescence

Chunyu Shang,* Jinxian Zhao and Xiuqin Wang

In order to restrain the saturation behavior in low voltage cathodoluminescence, a small amount of carbon nano-tubes (CNT) was introduced into the phosphor to form CNT-introduced phosphor material. In the specific working conditions in low voltage cathodoluminescence, field enhancement effect would be initiated in the CNT-introduced phosphor material, the local electric fields surrounding the tops of each CNT would be much stronger than the background electric field. The CNTs, with enhanced local electric fields surrounding the tops, play a key role in removing the electrons in the phosphor material, in which the CNTs act as convenient channels for the electrons to be removed in cathodoluminescence. By introducing a small amount of CNTs into the phosphor, the saturation behavior in low voltage cathodoluminescence was effectively restrained, having the similar effect as that in improving the conductivity of the phosphor material. The field enhancement effect in the CNT-introduced phosphor material may be activated and become more effective when the applied current density in cathodoluminescence is increased, and the dynamic performance of CNT-introduced phosphor material is favorable in low voltage cathodoluminescence.

1. Introduction

Field emission display (FED) is a promising technology, in which the fundamental principle is the low voltage cathodoluminescence. In FED, the high image quality of cathode ray tube (CRT) and the thin-thickness/low-energy consumption properties of flat panel display are combined.[1-4] Specifically, FED should be operated at a low voltage (<4kV), hence a large current density (10-100μA/cm^2) is required to guarantee a high output power.[5] However, operated at a low voltage, the saturation behavior is regularly exhibited in

School of Electronics and Information Engineering, Heilongjiang University of Science and Technology, Harbin 150022, China. Electronic mail: shang.chun.yu@163.com

cathodoluminescence when the current density is enlarged. The saturation behavior in low voltage cathodoluminescence means the decrease in efficiency with the increasing of current density. This is one of the most serious impediments hindering the development in FED. In our research, we have revealed in theory that the saturation behavior in low voltage cathodoluminescence is originated from the low conductivity of the phosphor material. The consistent viewpoints have been reported in literatures.[4, 6] In our research, a small amount of multi-walled carbon nano-tubes (CNTs), as a distinctive conductive component, was adopted to form CNT-introduced phosphor material. In the specific working conditions in low voltage cathodoluminescence, field enhancement effect is initiated in CNT-introduced phosphor material. The field enhancement effect plays a key role in restraining the saturation behavior in low voltage cathodoluminescence, having the similar effect as that in improving the conductivity of the phosphor material. In view of the favorable performances and the distinct mechanisms in cathodoluminescence, CNT-introduced phosphors may be identified to be a kind of advanced functional materials applied in low voltage cathodoluminescence.

2. Experimental

$Y_{1.9}Eu_{0.1}O_3$ sample was prepared in the sol-gel process. 35 g of Lanthanide nitrate $(Y(NO_3)_3 \cdot 6H_2O, Eu(NO_3)_3 \cdot 6H_2O)$ was dissolved in dilute nitric acid to form aqueous solution, then 170 g of citric acid $(C_6H_8O_7 \cdot H_2O)$, 200 mL of glycol $(C_2H_6O_2)$ and 10 g of polyethylene glycol $(HO(CH_2CH_2O)_nH$, molecular weight>20000) were added into the solution. The turbid suspension was stirred and heated at 90 ºC for 5h to form a gel, the gel was preheated at 300 ºC for 2h and then sintered at 600 ºC for 2h to form $Y_{1.9}Eu_{0.1}O_3$ sample.

In the preparation of multi-walled CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ sample, a certain amount of ethanol solution of multi-walled CNTs which had been sufficiently dispersed by powerful ultrasonic oscillation was added in the aqueous solution in the preparation of $Y_{1.9}Eu_{0.1}O_3$ sample in the sol-gel process. The last sintering process was performed in a nitrogen atmosphere. The adopted multi-walled CNTs have diameters of ~8nm and lengths of 10-30 μm, with an electrical conductivity of $\sim 1.5 \times 10^2 \, S/cm$.

In the resistivity measurements, each of the sample was made into a cylinder with diameter $2r = 13$mm and thickness $d = 2$mm under a pressure of 1.5×10^2 MPa. Electrodes were made by Al deposition on both sides of each sample. The resistance R was measured by a 769YP-24B megohmmeter and the conductivity was calculated by the formula,

$\sigma = d/\pi \cdot r^2 \cdot R$.

The crystalline phases of $Y_{1.9}Eu_{0.1}O_3$ phosphor and CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor were identified by Rigaku-D/max 2500 X-ray diffractometer using Cu Ka radiation ($\lambda = 0.15405$ nm). In the cathodoluminescence measurements, in order to achieve the comparability, each of the CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ samples (with CNT contents of 0wt‰, 1wt‰, 2wt‰, 3wt‰, and 4wt‰, respectively) was made into a thin layer of the same thickness on a metal substrate. The cathodoluminescence measurements were carried out in an ultra-high-vacuum chamber ($<10^{-8}$Torr), where the samples were excited at different current densities and a fixed voltage 2kV. The emission spectra were recorded using F-7000 spectrophotometer.

3. Results and discussion

3.1 Saturation behavior in low voltage cathodoluminescence owing to the low conductivity of the phosphor material

We have done much theoretical research work on the saturation mechanisms in low voltage cathodoluminescence.[2, 5] Herein, in order to carry out the discussions in this paper, the related theoretical conclusions must be referenced.

In the operation in low voltage cathodoluminescence, when the anode-cathode current is applied, the electrons would be emitted from the cathode and accelerated flying to the anode, the phosphor layer on the anode surface is then excited, giving out cathodoluminescence. Herein, three typical voltages are involved, having the relation, $V_0 = V_{acc} + V_{phosphor}$, where V_0 is the applied anode-cathode voltage, V_{acc} is the electron-accelerating voltage between the cathode and the phosphor layer, $V_{phosphor}$ is the voltage drop on the phosphor layer. Assuming the exciting area on the phosphor layer is a unit, the input power should be, $P_{input} = V_0 \cdot j$, and the exciting power on the phosphor layer should be, $P_{excite} = V_{acc} \cdot j$, where j is the applied current density. In the literature, the

3

average penetration depth of incident electrons in the phosphor layer is given to be, $\overline{X} = a \cdot V_{acc}^2 \cdot e^2$, where e is electron charge and a is a constant depending on the phosphor material.[7, 8] Owing to the randomicity in the penetration depth distributions of incident electrons with an average $\overline{X}$, the incident current density $J_{incident}(x)$, which is composed of incident electrons in the phosphor layer, should decrease gradually from j to 0 in the phosphor layer, having the relation, $\int_0^{x_d} J_{incident}(x) \cdot dx = \overline{X} \cdot j$, where x_d is the thickness of the phosphor layer. In the stable case, when an incident electron is emitted from the cathode, penetrating into the phosphor layer, there must be a relaying electron being transmitted successively to the anode to achieve the current continuity. When a certain current density j is applied in the low voltage cathodoluminescence, a certain distribution of negative charges, i.e., the space charge $Q(x)$, would be accumulated in the phosphor layer. Meanwhile, positive charges, i.e., the corresponding induced charges of the same quantity, would be simultaneously accumulated on the anode surface. The charge accumulations initiate a certain distribution of electric field $E(x)$ in the phosphor layer, promoting a relaying current density $J_{relay}(x)$ in the phosphor layer. The relaying current density $J_{relay}(x)$ should increase gradually from 0 to j, achieving the current continuity, $j = J_{incident}(x) + J_{relay}(x)$ in the phosphor layer; having the relation, $\int_0^{x_d} J_{relay}(x) \cdot dx = (x_d - \overline{X}) \cdot j$. The electric field $E(x)$ in the phosphor layer is determined by the space charge distribution $Q(x)$; meanwhile, it is proportional to $J_{relay}(x)$, given to be,

$$E(x) = \frac{1}{\varepsilon_0 \varepsilon_r} \int_0^x Q(x) \cdot dx = \frac{1}{\sigma} \cdot J_{relay}(x) \tag{1}$$

Where σ is the conductivity of the phosphor material. As a result, the voltage drop on the phosphor layer should be,

$$V_{phosphor} = \int_0^{x_d} E(x) \cdot dx = \frac{1}{\sigma} \cdot (x_d - \overline{X}) \cdot j \tag{2}$$

Based on formula (2) and the relations, $P_{excite} = V_{acc} \cdot j$, $V_0 = V_{acc} + V_{phosphor}$, $\overline{X} = a \cdot V_{acc}^2 \cdot e^2$, the exciting power in low voltage cathodoluminescence can be calculated to be,

$$P_{excite} = \frac{\sigma - \sqrt{\sigma^2 + 4a \cdot e^2 (x_d \cdot j - V_0 \cdot \sigma) \cdot j}}{2a \cdot e^2} \tag{3}$$

As presented in Fig. 1, for a fixed V_0, P_{excite} increases near-linearly at first with the increasing of j, and then it tends to saturate until it reaches its peak value

$P_{excite}^{max} = \dfrac{1 - \sqrt{1 - a \cdot e^2 \cdot V_0^2 / x_d}}{2a \cdot e^2} \cdot \sigma$ when $j = \dfrac{V_0}{2x_d} \cdot \sigma$, and then begins to decrease with the

increasing of j. In the operation, j should be smaller than $j_{th} = \dfrac{V_0}{2x_d} \cdot \sigma$. Consequently,

the saturation behavior in exciting power is what may happen actually.

For the typical phosphor materials applied in cathodoluminescence, a much lower conductivity σ is dominated in the order of $\sim 10^{-9} \, S/cm$. Consequently, under the normal current density j in low voltage cathodoluminescence (10-100μA/cm^2), the electric field $E(x)$ in the phosphor layer may be determined to be rather strong, with the maximum in the order of $\sim 10^5$V/cm. Taking into account the thickness of the phosphor layer, the voltage drop $V_{phosphor}$ on the phosphor layer should have considerable a magnitude, in the order of $10^2 \sim 10^3$V (indicated in formula 2). If σ were to be significantly improved, then the voltage drop $V_{phosphor}$ on the phosphor layer and its changing magnitude (with the changing of j) would be simultaneously decreased. In this case, V_{acc} would tend to be a constant approaching V_0, and the saturation behavior in exciting power P_{excite} is restrained. On the other hand, when $V_{phosphor}$ and its changing magnitude is simultaneously decreased, the average penetration depth $\overline{X}$ would no longer decrease with the increasing of j, tending to be the maximum, $a \cdot V_0^2 \cdot e^2$.

In the low voltage cathodoluminescence, electron-hole pairs would be generated with generation rate g_{e-h} in the phosphor layer owing to the energy input of incident electrons. The generated electron-hole pairs may transfer their energy with probability η_{et} to excite the ground-state activators. The excited activators may transit with radiation probability η_{rad} to the ground states. The output power, i.e., the output luminance flux in cathodoluminescence, is given to be, $P_{output} = g_{e-h} \cdot \eta_{et} \cdot \eta_{rad} \cdot hv$. Where hv is the photonic energy in cathodoluminescence.[5] The saturation behavior in low voltage cathodeluminescence is originated as follows: First, the saturation behavior of P_{excite} with the increasing of j leads directly to the saturation behavior of g_{e-h}, which is given to be, $g_{e-h} = P_{excite}/(\beta_g \cdot E_g)$, where E_g is the energy gap of phosphor material; β_g is the energy-losing factor, it ranges from about 2.7 to 5, depending on the phosphor material.[9] Second, the increase of P_{excite} and decrease of $\overline{X}$ with the increasing of j lead to the swiftly increase of excitation intensity, which is given to be, $I_{excite} = \dfrac{P_{excite}}{\overline{X}}$, as a result, the energy transfer probability η_{et} of electron-hole pairs is decreased. Third, the saturation behavior of exciting power P_{excite} means the loss of input power P_{input}, and the lost portion is the thermal consumption power in the phosphor layer, leading to an increased temperature of the phosphor layer, as a result the radiation probability η_{rad} of an excited activator is decreased. In view of these key factors, the saturation behavior in the output luminance flux should be the inevitable result. Summarizing the influences of σ on P_{excite} and $\overline{X}$, it is apparent that to restrain the saturation behavior in low voltage cathodoluminescence, the conductivity σ of the phosphor material were to be improved.

3.2 Distinct performances of CNT-introduced phosphor material in low voltage cathodoluminescence

According to the electrical percolation theory of composite conductive materials, a kind of suitable conductive fillers, as a separate component, may be introduced to improve the

conductivity of a composite matrix.[10-14] The electrical percolation theory indicates that when the conductive content increases to the electrical percolation threshold, a three-dimensional conductive network begins to be formed in the matrix and the conductivity of the composite conductive material begins to be dramatically increased. As for the formation of conductive network, the dominant mechanisms lie in the physical contacts between the conductive fillers. Meanwhile, the field enhancement effect and the quantum tunneling effect would play a role in the formation of conductive network when the size of conductive component is in nanometer magnitude.[10, 15]

In contrast to the conventional conductive components, CNTs are distinctive due to their unique properties. Consequently, distinctive performances may be expected for CNT-introduced composite materials. CNTs are rolled graphite sheets with diameters in nanometer magnitude and lengths in micrometer magnitude, possessing one-dimensional morphologies of rather larger aspect ratios (in the order of 10^3). CNTs can be classified to be single-walled CNTs and multi-walled CNTs, possessing remarkable mechanical strength, reliable chemical stability, high melting point and excellent electrical conductivity (in the order of $10^3\,S/cm$). In contrast to the single layer structure of single-walled CNTs, the structure of multi-walled CNTs is cylinders inside cylinders.[16-18]

Based on the electrical percolation theory, the conductivities of the phosphor materials may be improved to restrain the saturation behavior in low voltage cathodoluminescence. In the experiment, taking multi-walled CNTs as conductive component and $Y_{1.9}Eu_{0.1}O_3$ as the typical phosphor material, CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ was synthesized. Fig. 2 shows the XRD patterns of $Y_{1.9}Eu_{0.1}O_3$ phosphor and CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor (1.5wt%). The XRD patterns were all indexed to Y_2O_3 cubic phase, indicating that the crystalline phase of the phosphor has not been apparently distorted by the introduction of Eu^{3+} ions or CNTs. As shown in Fig. 3, the resistivity-CNT content relation for CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ is similar to those of conventional composite conductive materials, while the electrical percolation threshold of CNTs is rather low ($P_{th}\approx1.5$wt%), being at least an order of magnitude lower than the conventional conductive components (e.g., In_2O_3). In view of the relation presented in Fig. 3, it is apparent that when the content of CNTs is lower than the

electrical percolation threshold, the conductivity of $Y_{1.9}Eu_{0.1}O_3$ phosphor should not be effectively improved. However, as a kind of heterogeneous impurity introduced into the phosphor, an effective content (~1.5wt%) of CNTs is too much to keep the intrinsic luminescent performances of the phosphor material, even though the saturation behavior in low voltage cathodoluminescence may be restrained.

In the experiments, under a typical anode-cathode voltage (V_0=2kV) in low voltage cathodoluminescence, the emission spectra of CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor with different CNT contents were measured at different current densities. When the applied current density is higher (e.g., $80\mu A/cm^2$), the emission spectra of CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor becomes successively stronger with the increasing of CNT content introduced in the phosphor (e.g., from 0wt‰ to 4wt‰), as given in Fig. 4. For the different current densities, the integral cathodoluminescent intensities (CL) were obtained. Based on the discrete experimental data, the continuous curves indicating the CL-j relations were plotted for CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor with different CNT contents (0wt‰, 1wt‰, 2wt‰, 3wt‰, and 4wt‰), as shown in Fig. 5. In fact, the integral cathodoluminescent intensities stands for the output luminance flux P_{output}. Under a constant anode-cathode voltage V_0, the efficiency (f) in cathodoluminescence is proportional to the ratio between integral cathodoluminescent intensity and current density ($f \propto CL/j$). Consequently, the efficiency in cathodoluminescence would tend to be a constant in the linear region of CL-j relation which starts from j=0. As shown in Fig. 5, such a linear region of CL-j relation is extended and the corresponding linear degree is increased with the increasing of CNT content in $Y_{1.9}Eu_{0.1}O_3$ phosphor (0wt‰-4wt‰). Consequently, the saturation behavior in low voltage cathodoluminescence has been proven to be effectively restrained by introducing a certain amount of CNTs in the phosphor material.

It should be noted that the CNT contents in $Y_{1.9}Eu_{0.1}O_3$ phosphor (1wt‰-4wt‰) are much lower than the electrical percolation threshold (~1.5wt%) and hence the conductivity of the phosphor material has not been effectively improved when the saturation behavior in

low voltage cathodoluminescence has been proven to be effectively restrained. Consequently, there must be distinct mechanisms dominating the performances of CNT-introduced phosphor material in low voltage cathodoluminescence.

3.3 Field enhancement effect in CNT-introduced phosphor material in low voltage cathodoluminescence

When the CNT content in the phosphor material is much lower than the electrical percolation threshold (~1.5wt%), the conductive network of CNTs can not be formed and the conductivity of CNT-introduced phosphor material keeps at a low level. In this case the majority of the CNTs may be seen to be distributed separately in the phosphor material. Although the orientations of CNTs would be distributed randomly in the phosphor layer, each has a component paralleling to the electric field $E(x)$ given in formula (1). In the phosphor layer, under the stimulation of electric field $E(x)$, a much stronger local electric field would be initiated in the vicinities surrounding the two tops of each CNT owing to the field enhancement effect. The field enhancement effect involves distinct mechanisms in the operation in low voltage cathodoluminescence, significantly improving the performances of CNT-introduced phosphor material.

Herein, in order to throw light on the field enhancement effect, analogical discussions may be consulted.[19] When a CNT (with length l_0 and radius ρ_0) is located in and parallel to the background electric field $E_{background}$ between the two electrodes (with distance d) of a charged capacitor, and the CNT is erected on the negative electrode, the potential distribution surrounding the CNT is given in electromagnetic theory to be,

$$u(\rho,l) = E_{background} \cdot l - \frac{E_{background} \cdot l_0}{N_0(k\rho_0) \cdot \left[e^{kl_0} - e^{k(2d-l_0)}\right]} N_0(k\rho) \cdot \left[e^{kl} - e^{k(2d-l)}\right] \qquad (4)$$

Where N_0 is the zero-order Neumann function, ρ is radial coordinate ($\rho=0$ in the axis of CNT) and l is axial coordinate ($l=0$ in the initial end of CNT) in the cylindrical coordinate system; $k = 0.89/n\rho_0$, $n\rho_0$ is the least radial distance where the field enhancement effect is vanished.[19] Based on formula (4), the distribution of electric field

$E(\rho,l)$ surrounding the CNT may be obtained, the radial and axial components of $E(\rho,l)$ are given to be,

$$E_\rho = -\frac{\partial}{\partial \rho}u(\rho,l)= E_{background}\cdot\left\{kl_0\cdot\frac{N_0(k\rho)\cdot\left[e^{kl}+e^{k(2d-l)}\right]}{N_0(k\rho_0)\cdot\left[e^{kl_0}-e^{k(2d-l_0)}\right]}-1\right\} \qquad (5\text{-}a)$$

$$E_l = -\frac{\partial}{\partial l}u(\rho,l)= E_{background}\cdot\left\{kl_0\cdot\frac{N_1(k\rho)\cdot\left[e^{kl}+e^{k(2d-l)}\right]}{N_0(k\rho_0)\cdot\left[e^{kl_0}-e^{k(2d-l_0)}\right]}\right\} \qquad (5\text{-}b)$$

Where N_1 is the one-order Neumann function. Since the radius ρ_0 is in nanometer magnitude and the length l_0 is in micrometer magnitude, the local electric field surrounding the top of the CNT ($\rho \rightarrow \rho_0$, $l \rightarrow l_0$) may be quantitatively determined to be remarkably strong, and the field enhancement effect is significant. Herein, a field enhancement factor is involved, defined as,

$$\beta = \frac{E_{local}}{E_{background}} \qquad (6)$$

For the CNT, β may be much higher, it may be in the order of 10^3 approaching the top of the CNT.[20] Approaching the top, the local electric field is inclined to be vertical to the surface of the CNT; departing the top, the field enhancement effect is gradually weakened and the local electric field is gradually oriented to the background electric field. In addition, when the background electric field is increased, the local electric field would be substantially enhanced, and the spatial region it occupies would be expanded as well.

The above conclusions may be generalized to reflect the characteristics of field enhancement effect in CNT-introduced phosphor material in low voltage cathodoluminescence. In the background electric field $E(x)$ in the phosphor material, a CNT is an equipotential body owing to the high conductivity it presents.[20] The enhanced local electric field should be distributed in the vicinities surrounding the two tops of the CNT. The CNT, as an equipotential body, is a potential well of electrons in the phosphor material, the corresponding depth should be, $\phi' = \phi_0 - x'$, where $\phi_0 = E_0 - E_F$ (4.6eV) is the work

function of CNTs, E_0 is the vacuum level, E_F is the Femi level of CNTs and x' is the electron affinity of the phosphor material.[20]

As shown in Fig. 6, in the vicinity surrounding the initial top of the CNT (i.e., the top facing the cathode) in the phosphor material, the enhanced local electric field is oriented outward the surface of the CNT. When there is an electron in the conduction band of the phosphor material, presented in the enhanced local electric field (the CNT-phosphor interface is located at $x=0$; $x>0$ in the phosphor), its energy should be given to be,

$$E_C(x) = \phi_0 - x' + qE_{local} \cdot x \tag{7}$$

Where the enhanced local electric field E_{local} is simplified to be a constant. It can be seen that in the vicinity surrounding the initial top of the CNT, such an electron may be trapped by the enhanced local electric field, swept into the potential well (CNT). On the other hand, as shown in Fig. 7, in the vicinity surrounding the final top of the CNT (i.e., the top facing the anode), the enhanced local electric field is oriented toward the surface of the CNT. The energy of an electron in the conduction band of the phosphor material (the CNT-phosphor interface is located at $x=0$; $x>0$ in the phosphor) should be given to be,

$$E_C(x) = \phi_0 - x' - qE'_{local} \cdot x \tag{8}$$

Where the enhanced local electric field E'_{local} is simplified to be a constant. This means a potential barrier is formed on the CNT-phosphor interface, and its width x_0 may be adjusted by the local electric field E'_{local}. Owing to the remarkable field enhancement effect, an electron confined in the potential well (CNT) may penetrate the potential barrier, releasing out into the phosphor material by the quantum tunneling effect. CNTs have distinctive field emission properties, as reported in literatures.[1, 3, 21, 22]

3.4 Key role of field enhancement effect in restraining the saturation behavior in low voltage cathodoluminescence

As discussed in section 3.1 and indicated in formula 2, if the incident electrons penetrated into the phosphor layer or their relaying electrons were to be removed farther into the phosphor layer, i.e., if $\overline{X}$ were to be equivalently increased by a certain means, the

voltage drop $V_{phosphor}$ on the phosphor layer and its changing magnitude (with the changing

of j) would be simultaneously decreased, having the similar effect as that in improving the

conductivity σ of the phosphor material. Consequently, the saturation behavior in low

voltage cathodoluminescence may be restrained as well.

In the low voltage cathodoluminescence, the field enhancement effect would play a role

in removing the electrons in CNT-introduced phosphor material, in which the CNTs act as

convenient channels for the electrons to be removed. When an incident electron is penetrated

into the phosphor layer, a large number of electron-hole pairs would be generated (the

number should be, $V_{acc} \cdot e / (\beta_g \cdot E_g)$). The incident electron or one of the generated electrons

(act as the relaying electron) may be trapped by the enhanced local electric field surrounding

the initial top of a CNT, drifted along the CNT to the final top, and then released out into the

phosphor material in the field emission process. In this process the component of CNT in the

direction of background electric field is the equivalent distance the electron has been

removed. As the macroscopic effect, the incident electrons or their relaying electrons are

removed farther into the phosphor layer, the voltage drop $V_{phosphor}$ on the phosphor layer

and its changing magnitude (with the changing of j) are simultaneously decreased, and the

saturation behavior in low voltage cathodoluminescence is restrained. In essence, owing to

the participation of field enhancement effect in removing the electrons, the background

electric field $E(x)$ in CNT-introduced phosphor material should not be as strong and its

distribution should be shrunk toward the anode as compared to that in the pure phosphor

layer in the low voltage cathodoluminescence. As a result the voltage drop $V_{phosphor}$ on the

phosphor layer, given in formula (2), is decreased.

It should be noted that the dynamic performance of CNT-introduced phosphor material

is favorable in low voltage cathodoluminescence. With the increasing of the applied current

density j, the background electric field $E(x)$ in the phosphor material is increased, as a

result the local electric field surrounding the initial and final tops of a CNT become stronger

and the spatial regions it occupies are expanded. In this case, an incident electron or its

relaying electron may be easier to be trapped by the local electric field surrounding the initial top of the CNT. Meanwhile, such an electron in the potential well (CNT) may be easier to penetrate the potential barrier at the final top of the CNT, because the width x_0 of potential barrier is decreased due to an increased local electric field. This means the field enhancement effect may be activated and becomes more effective in removing the electrons in the phosphor material when the applied current density is increased. Consequently, the dynamic performance of CNT-introduced phosphor material is favorable in low voltage cathodoluminescence. Summing up the discussions above, the CNT-introduced phosphor may be identified to be an advanced functional material applied in low voltage cathodoluminescence.

3.5 Exceptional advantages of CNTs as conductive component in the phosphor material in low voltage cathodoluminescence

In contrast to the conventional conductive components, CNTs are distinctive due to their unique properties. The structural unit of CNTs is a six-membered benzene ring, which is composed of C atoms bonding by the sp^2 hybrid orbitals. As a result CNTs possess remarkable mechanical strength, which is the highest among all kinds of materials at present.[16-18] Consequently, CNTs are strong enough to be applicable in the specific working condition in the phosphor materials; they can not be damaged by the electron beam in low voltage cathodoluminescence. Meanwhile, owing to the unique net-like framework of CNTs which is composed of a single layer of C atoms, the electron beam may easily penetrate the CNTs, saving the kinetic energy of incident electrons in low voltage cathodoluminescence. On the other hand, CNTs possess reliable chemical stability and very high melting point (CNTs can not be decomposed at 1000ºC in a nitrogen atmosphere). Consequently, it is possible to introduce CNTs in the preparation processes of phosphor materials, forming CNT-introduced phosphor materials. In fact, there are various preparation processes for the typical phosphor materials (e.g., combustion process, sol-gel process, hydrothermal process, solid-phase process, precipitation process, etc.), in which different reagents and temperatures are involved, making it possible to achieve the compatibility of introducing CNTs. Consequently, by selecting a suitable preparation process for a certain phosphor material, the

corresponding CNT-introduced phosphor material may be obtained. In addition, it should be noted that as the conductive component, the multi-walled CNTs may be more suitable to be introduced into the phosphor materials than the single-walled CNTs. The reason lies in the fact that if the electric conductivity of the outer layer of a multi-walled CNT deteriorates in combining with the phosphor materials owing to the ultra-large specific surface area of the CNTs ($>500 \text{m}^2\text{g}^{-1}$), the inner layer may conduct independently, ensuring the conductive function of the CNTs.

4. Conclusions

The saturation behavior in low voltage cathodoluminescence is originated from the low conductivity of the phosphor material. In the specific working conditions in low voltage cathodoluminescence, a much stronger local electric field would be initiated surrounding the tops of CNTs in the CNT-introduced phosphor material. In the low voltage cathodoluminescence, an incident electron or its relaying electron may be trapped by the enhanced local electric field surrounding the initial top of a CNT, drifted along the CNT to the finial top, and then released out into the phosphor material in the field emission process. As the macroscopic effect, the electrons are removed farther into the phosphor layer, and the voltage drop on the phosphor layer and its changing magnitude are simultaneously decreased. When the applied current density is increased, the field enhancement effect may be activated and becomes more effective in removing the electrons in the phosphor material. Owing to the field enhancement effect, the saturation behavior in low voltage cathodoluminescence is effectively restrained, having the similar effect as that in improving the conductivity of the phosphor material. In addition, there are several exceptional advantages of CNTs as conductive component in the phosphor material in low voltage cathodoluminescence.

Acknowledgements

References

1 D. Lei, L. Y. Zeng, and W. B. Wang, J. Appl. Phys., 2007, **102**, 114503.

2 C. Y. Shang, J. X. Zhao, X. Q. Wang, H. Y. Xia and H. Kang, Physical Chemistry Chemical Physics., 2015, **17**, 9936.

3 S. C. Ray, U. Palnitkar, C. W. Pao, H. M. Tsai, W. F. Pong, I-Nan Lin, Abhijit Ganguly, L. C. Chen, and K. H. Chen, J. Appl. Phys., 2008, **104**, 063710.

4 J. Y. Kim, D. Y. Jeon, I. Yu, and H. G. Yang, J. Electrochem. Soc., 2000, **147**, 3559.

5 C. Y. Shang, X. Q. Wang, Z. Y. Cheng, Z. Y. Hou, and J. Lin, Journal of Applied Physics., 2013, **113**, 093101.

6 Sung Hee Cho, Seung Ho Kwon, Jae Soo Yoo, Chang Woo Oh, Jong Duk Lee, Kun Jo Hong, and Sang Jik Kwon, J. Electrochem. Soc., 2000, **147**, 3143.

7 Q. M. Yu, Z. S. Liu, and X. P. Jing, Chin. J. Liq. Cryst. Disp., 2005, **20**, 7.

8 C. Feldman, Phys. Rev., 1960, **117**, 455.

9 J. Y. Sun, H. Y. Du, and W. X. Hu, *Solid Luminescent Materials [M]*, Chemical Industry, Beijing, 2003.

10 C. Y. Shang, H. Kang, H. B. Jiang, S. P. Bu, X. H. Shang, and Yan Wu, Journal of Luminescence., 2013, **138**, 182.

11 S. H. Shin, Y. C. You, and S. H. Lee, J. Electrochem. Soc., 2004, **151**, 40.

12 H. Kominami, T. Nakamura, T. K. Sowa, Y. Nakanishi, Y. Hatanaka, and G. Shimaoka, Appl. Surf. Sci., 1997, **113**, 519.

13 S. W. Kang, B. S. Jeon, J. S. Yoo, and J. D. Lee, J. Vac. Sci. Technol. B., 1997, **15**, 520.

14 J. C. Souriau, Y. D. Jiang, J. Penczek, H. G. Paris, and C. J. Summers, Mater. Sci. Eng., B., 2000, **76**, 165.

15 D. D. Lu, Y. G. Li and C. P. Wong, J. Adhes. Sci. Technol., 2008, **22**, 815.

16 Z. Xu, W. Zhang, Z. Zhu, C. Ren, Y. Li and P. Huai, J. Appl. Phys., 2009, **106**, 043501.

17 K. Jeet, V. K. Jindal, L. M. Bharadwaj, D. K. Avasthi and K. Dharamvir, J. Appl. Phys., 2010, **108**, 034302.

18 Ji H. Lee, M. T. Kim, K. Y. Rhee and S. J. Park, Res. Chem. Intermed., 2014, **40**, 2487.

19 L. Q. Guo, D. Han, H. Ma, K. Y. SONG, H. N. Wu, and S. Wang, Journal of synthetic crystals., 2007, **36**, 847.

20 C. Y. Shang, J. X. Zhao, X. Q. Wang, H. Y. Xia and H. Kang, RSC Adv., 2015, **5**, 16993.

21 J. M. Bonard, J. P. Salvetat, T. Stockli, L. Forro and A. Chatelain, Appl. Phys. A., 1999, **69**, 245.

22 P. Verma, P. Kumar, S. Gautam and P. Chaturvedi, Fullerenes, Nanotubes, Carbon Nanostruct., 2009,
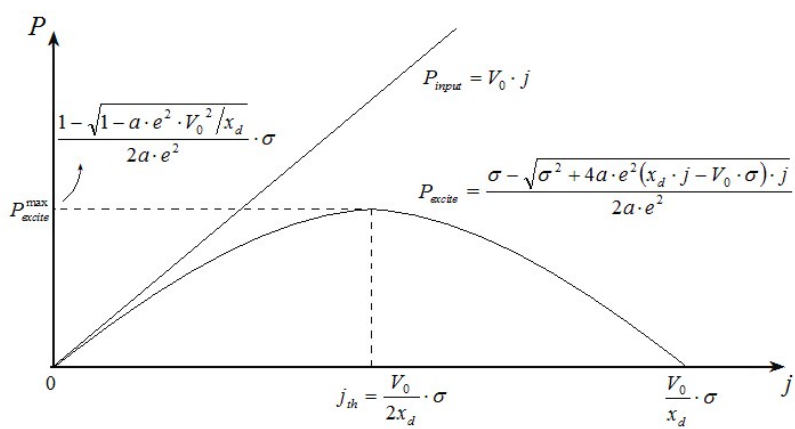
17, 249.

Figures:

$$P_{input} = V_0 \cdot j$$

$$\frac{1 - \sqrt{1 - a \cdot e^2 \cdot V_0^2 / x_d}}{2a \cdot e^2} \cdot \sigma$$

$$P_{excite} = \frac{\sigma - \sqrt{\sigma^2 + 4a \cdot e^2 (x_d \cdot j - V_0 \cdot \sigma) \cdot j}}{2a \cdot e^2}$$

$$P_{excite}^{max}$$

$$j_{th} = \frac{V_0}{2x_d} \cdot \sigma$$

$$\frac{V_0}{x_d} \cdot \sigma$$

Fig. 1 P_{input} and P_{excite} are depicted as the functions of j.

17
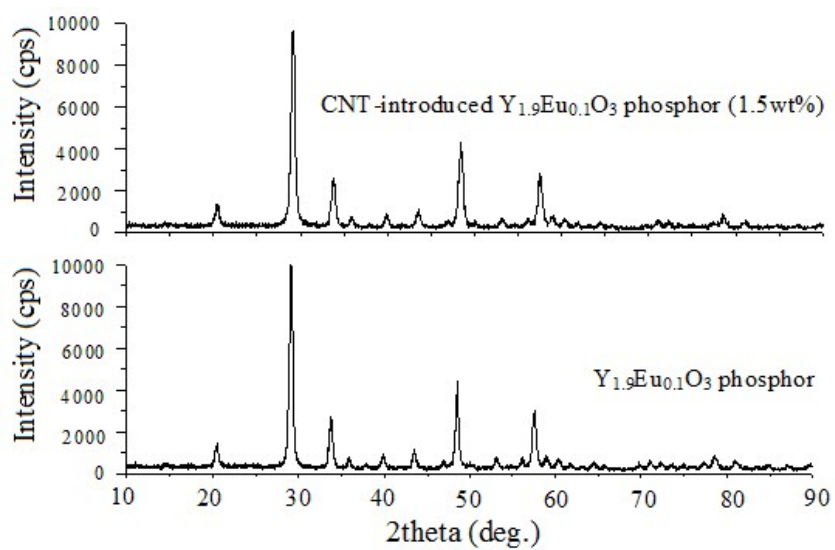
Fig. 2 XRD patterns of $Y_{1.9}Eu_{0.1}O_3$ Phosphor and CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ Phosphor with CNT content of 1.5wt%.
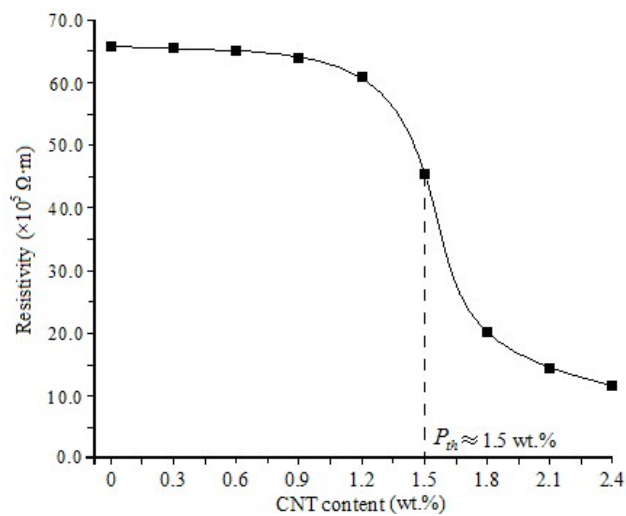
Fig. 3 Resistivity-CNT content relation for multi-walled CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor.
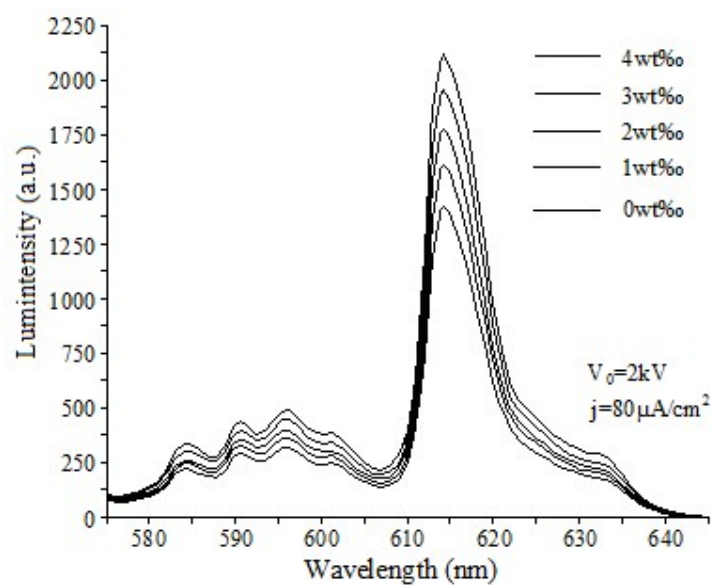
Fig. 4 Emission spectra of CNT-introduced $Y_{1.9}Eu_{0.1}O_3$ phosphor with different CNT contents.
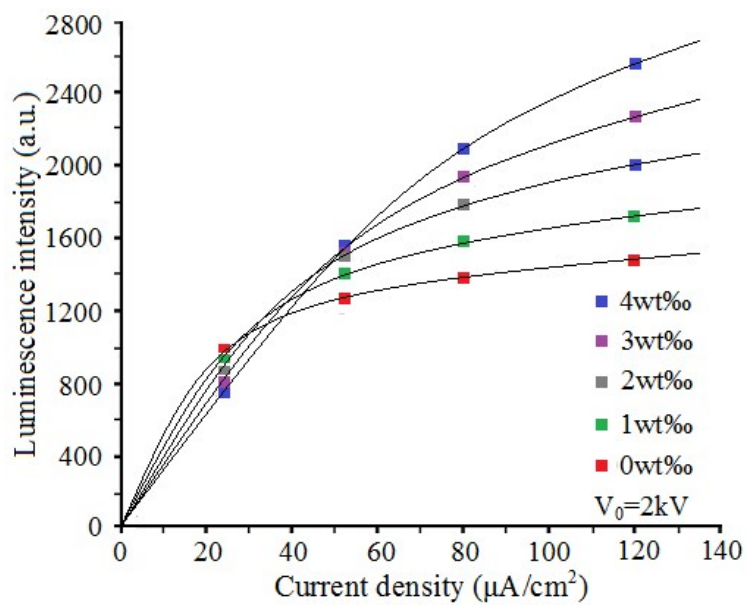
Fig. 5 Cathodoluminescent intensity-current density relations for $Y_{1.9}Eu_{0.1}O_3$ phosphor with different
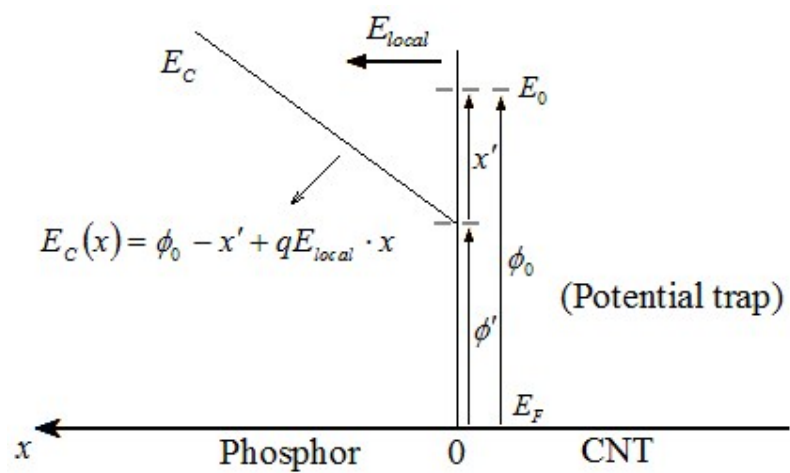
CNT contents at a fixed voltage of 2kV.

Fig. 6 Potential distribution of an electron around the CNT-phosphor interface at the initial top of the CNT (facing the cathode).

$$E'_{local}$$

$$E_0$$

$$x'$$

$$\phi_0$$

(Potential trap)

$$E_c(x) = \phi_0 - x' - qE'_{local} \cdot x$$

$$\phi'$$

Potential barrier

$$E_c$$

$$E_F$$

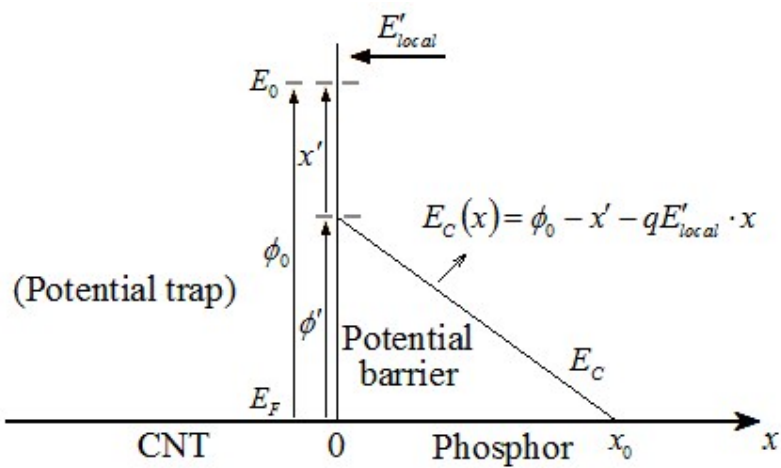CNT   0   Phosphor x_0 x

Fig. 7 CNT-phosphor potential barrier of an electron at the final top of the CNT (facing the anode).