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Low-voltage cathodoluminescent Characteristics of $ZnGa_2O_4$: Mn phosphors

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Abstract

Green-emitting $ZnGa_2O_4$: Mn phosphors were synthesized by a thermal method and their low-voltage cathodoluminescent characteristics were examined for the field emitter display (FED) application. Low efficiency of $ZnGa_2O_4$: Mn phosphors could be ascribed to the low penetration depth of incident electrons into phosphors, which might results in charge accumulation on the phosphor screen. For increasing cathodoluminesence of $ZnGa_2O_4$: Mn under low voltage excitation, wide band-gap oxide materials were added to the $ZnGa_2O_4$: Mn powder. It is found that the luminance can be increased by 20%. Measurement of leakage current on the phosphor screen shows that the enhancement of low-voltage cathodoluminescence by additive materials is mainly due to the consumption of surface charges on the phosphor.

I. INTRODUCTION

The great achievements that have been made in a vacuum microelectronic technology have led th the demonstration of field emitter displays(FEDs) [1]. Depending on the anode voltage, various types of display construction have been applicable and there is still adebate on the relative merits of various technology options to build the most efficient FEDs [2]. The low-voltage construction has some benefits over the other option. It neither needs an electrode for focusing the electrons on a pixel nor the columnar spacer within a cell of high aspect ratio which results in a fabrication complexity. Its drawback is luminance, since the efficiency of phosphor materials is increasing with higher anode voltage. So, the low-voltage construction of FEDs requires high current opration to compensate for the low luminescence. In this situation, charge accumulation on the phosphor screen becomes important issue. In fact, a large attention has been put on the preparation of conductive powder phosphors, for instance, by mixing In_2O_3 microclusters in phosphor powder [3]. shows that the conductivity of phosphor screen is related to the luminous efficiency of powder phosphor screen. An interesting phenomenon which is observed in low-voltage phosphors is the enhancement of cathodolu-minescent efficiency when they are mixed with wide band-gap materials [5]. We just ascribe this to the increased concentration of oxygen vacancy from the wide band-gap material. Note that the concentration of oxygen vacan cies in the sintered bodies is one of the important factors to determine their conductivites. However, a mechanism responsible for this luminescence property absolutely remains unclear.

In this work, $ZnGa_2O_4$: Mn powder phosphors were prepared and further treated by mixing a wide bandgap material such as WO_3 enabling us to control the optical characteristics of phosphor screen. Leakage current from the phosphor scr-een when excited in a vacuum chamber, resis-tivity of the phosphor screen, and SEM analysis were combined to understand the optical and electrical characteristics of phosphor screen under low-voltage excitation.

II. EXPERIMENTAL

Green-emitting $ZnGa_2O_4$: Mn phosphors are known to be one of the best candidates for FED applications [6] and their synthetic process has been well reported in articles [7, 8]. For the preparation of $ZnGa_2O_4$: Mn phosphors, a conventional method was used in this experiment. The raw materials, ZnO(99.999%), Ga_2O_3(99.99%) and $MnCO_3$(99.99%) were thoroughly mixed in the ball miller for 1hr, allowed to dry for 2hrs at 100℃, then fired in furnace at 1200℃ for 10hrs. After a light grinding and mixing step, the phosphor powders were annealed in a reducing atmosphere. The X-ray deflection curve from the synthesized samples were exam-ined to make sure that source materials should be converted to spinel-structured $ZnGa_2O_4$. Heat treatment time and temperature, reduction condition, and activator concentration were optimized to give the maximum intensity of photoluminescence(PL). To investigate the surface effects of a hosphor on the catholoIuminescence, a small quantity of WO_3 or(~a few weight %)was thoroughly mixed with the synthesized $ZnGa_2O_4$: Mn powder phosphors and they were deposited onto ITO glass by electrophoretic method [9], followed by annealing at 450℃ for 1 hr. WO_3 powders were obtained from commercial suppliers. Electron microscopy images show that particle sizes of WO_3 powders are distributed over~1㎛. They are known to provide oxygen vacancies which may govern the electrical conductivity of phosphor screen. While it was excited by thermionic electron gun(Kimball Physics Inc, ER-2X-1) in the vacuum chamber(4×10^{-7} torr), luminance., chromaticity, and electrical properties were characterized by cchromameter(Minolta CS-100), spectrum analyzer(Samsung OSMA-900), respectively and leakage current from the phosphor screen was measured by ampere meter.

Ⅲ. RESULTS AND DISCUSSION

Figure 1(a) shows the Scanning Electrion Microscope(SEM) image of the synthesized $ZnGa_2O_4$: Mn powders. Particle sizes were distrivuted over 1~2㎛. The contents of Manganese in $ZnGa_2O_4$: Mn host material were optimized to 0.1 atomic percent for the maximum PL intensity, followed by reduction process at 900 i for 3hrs. The body color was observed to change from week green to white. The Mn^{-4} *ions were known to be reduced to* Mn^{-2} ions and incorporated to $Zn_{1-x}Mn_xGa_2O_4$ lattice[10]. The screen thickness or deposition weight of $ZnGa_2O_4$: Mn phosphors was determined for the maximum CL intensity[11]. The optimum screen thicknes for $ZnGa_2O_4$: Mn is about 3~4㎛, which is corresponding to 1~2 particle layer. Typical CL intensity of phosphor screen according to the quantities of modifier are shown in Fig. 2. Obviously, small quantities of modifier enhance the luminescence of phosphor screen. Note that the CIE chromaticity of $ZnGa_2O_4$: Mn phosphors with midifier, WO_3 is the same as that without the midifier.

A question on a function of the modifiers, WO_3 in phosphor screen is arisen. We believed that the wide band-gap materials such as WO_3 could supply the oxygen vacancies to the $ZnGa_2O_4$: Mn phosphors screen and increase the electronic conductivity, which might result in the enhancement of cathodoluminescence under electron excitations with low-voltage and high density. Recent experimental results show that *green emission in ZnO : Zn phosphors is well*

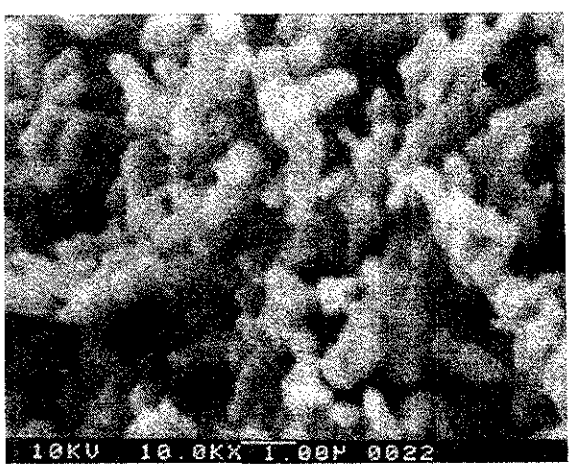

Fig. 1 Scanning electron micrograph of $ZnGa_2O_4$: Mn phosphors.

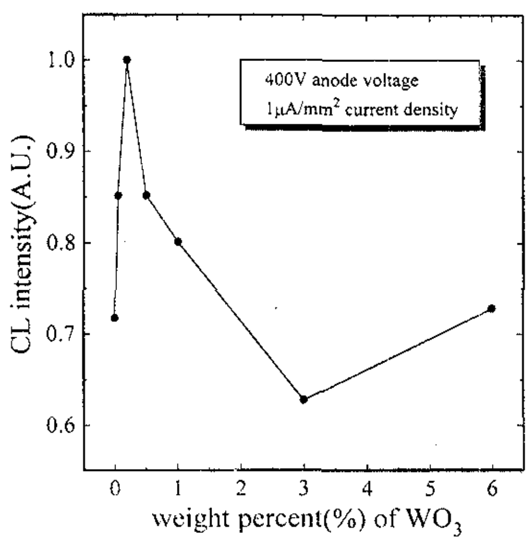

Fig. 2 Enhancement of CL intensity as a function of contents of WO_3 in $ZnGa_2O_4$: Mn phosphors.

correlated to the density of singly ionized oxygen vacancies[12]. At the moments, we do not know how much the oxygen vacancies in phosphor screen can be increased by adding WO_3. In order to investigate the effects of modifier on the cathodoluminescence, leakage currents from the phosphor screen were measured.

In ahigh vacuum chamber, leakage current from the phosphor screens was measured while phosphor screens were exciting. Figure 3(a) depicts the leakage current which is measured at the ITO-electrode as a function of injected current density on the phosphor screen. The injected dlectrons were measured by using Faraday cup of which lole area is 0.25 mm^2. Phosphor screen was grounded and leakage current is measured by ampere meter which is put between ITO-electrode of phosphor screen and grounded point. Comparing to the phosphor screen without WO_3, phosphor screen with modifier, WO_3, shows less leakage current. It reflects that more electrons are dissipated to the vacuum chamber or less charges are accumulated on phosphor screen in case of phosphor materials with modifier at a relatively low-voltage. It is important to understand why this phenomenon happen. It may be found in the existence of surface-bound electrons outside powder phosphors. The secondary electrons generated in the surface volume are ejected from the crystal leaving holes in the crystal. When a crystal holds the positive charge in the surface volume, the electrons outside the crystals are tightly bound with the holes inside the crystal. This, so called charge build-up phenomenon is getting pro- minent as the beam current density injected on the screen increases. Here, We presumed that the oxygen vacancies in modifier, WO_3, act as recombination centers for electron-hole pairs and remove electron cluds near the surface

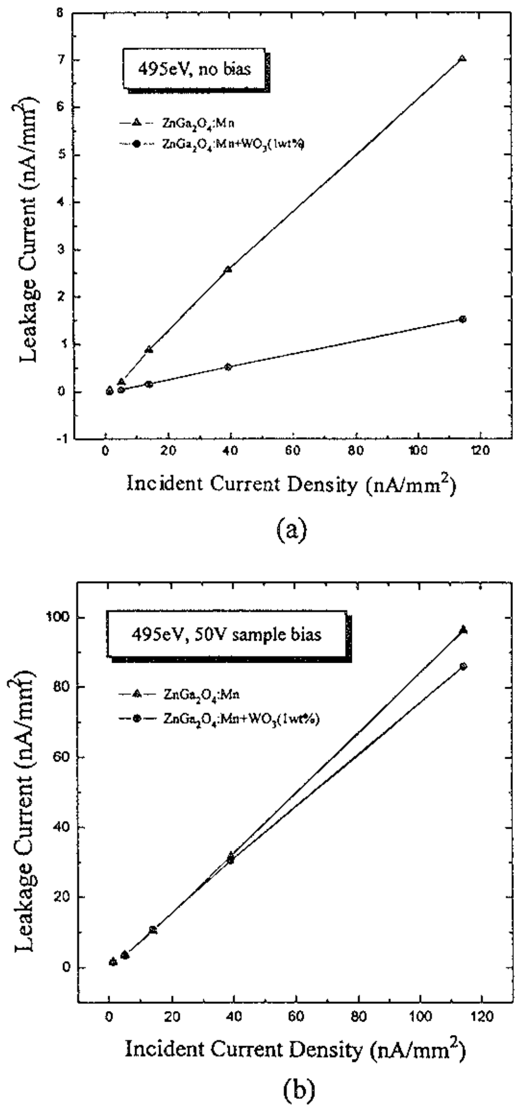

Fig. 3 Relationship between the incident electron density and leakage current in phosphor screen in case of electron energy of 495eV : (a) no bias; (b) positive bias of 50V.

volume of phosphor which reads to easy penetration of electrons into the phosphor and results in higher cathodoluminescence(Fig. 2). This may be proven by measuring the leakage current at phosphor screen when it is positively biased, as shown in Fig. 3(b). Based on the above exper- mental observation, it can hardly say that modifiers, WO_3 can increase the conductivity of phosphor screen but rather that they decrease charge accumulation on the phosphor screen. When the injected electrons are accelerated with high energy(1555eV), the influence of modifier on the leakage current is not critical as much as the case of low-voltage excitation(495eV), even though it is noticeable at higher current density(Fig. 4). This is due to the energy which the injected electrons have. Electrons which have energy high enough to penetrate through the electron shield outside the phosphor may reach the phosphor crystals and are effectively working for cathodoluminescence.

However, the ambiguity on the conductivity of phosphor screen still remains unclear. The oxygen vacancies which may supply donor levels in sintered bodies are usually responsible for the conductivity. It leads to the expectation that the leakage current from the screen with modifier will be larger than that from the screen without modifier. But, the results are contrary. We believe that the quantitative estimates of the resistance or conductance of phosphor screen are possible by biasing the phosphor screen of different thickness and measuring the leakage current. More expermental observations are needed for the quantitative analysis. However, our measurements

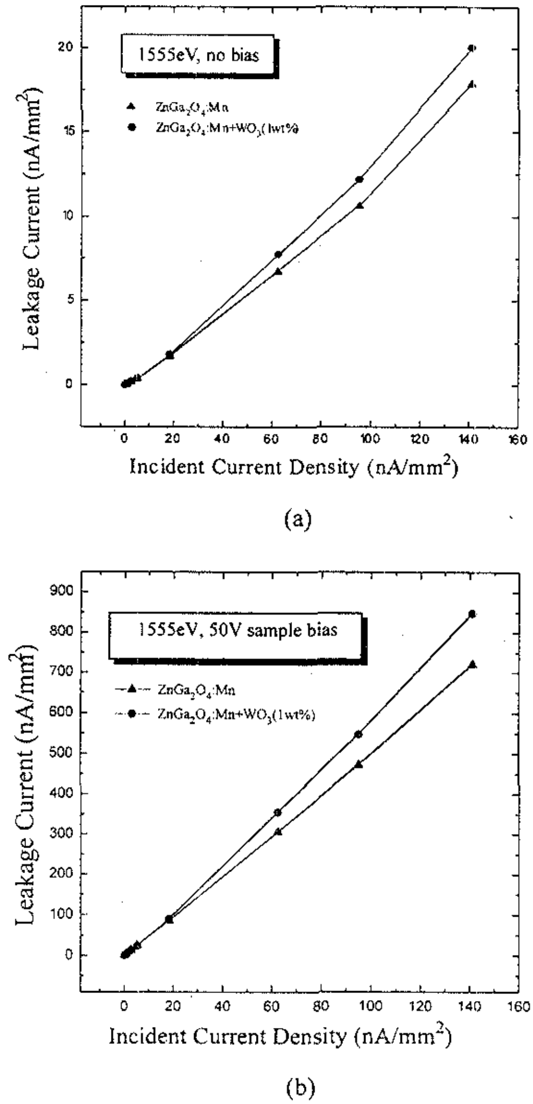

Fig. 4 Relationship between the incident electron density and leakage current in phosphor screen in case of electron energy of 1555eV : (a) no bias; (b) positive bias of 50V.

show that the removal of potential barrier on the surface of phosphor is more reasonable interpretation than the conductivity is for effective cathololuminescence. So, if we used modifiers in microcluster form and phosphors were coated by microclusters, the enhancement factor of our samples would be expected to be higher, and the optical properties are clearly correlated with the electrical properties. Our forthcoming experimental work will be published.

Ⅳ. SUMMARY

$ZnGa_2O_4$: Mn phosphors were synthesized by a combustion method. The luminance of phosphor screen which is electrophoretically deposi- ye on the ITO-glass is linearly increased to 110cd/㎡ at 500V and 1μA/㎟ with chromaticity of X=0.0341 and Y=0.6622. When a surface modifier, WO_3 was added to the phosphors, luminance was increased by 20 %. By examining the leakage current in phosphor screen. the primary reason for the enhancement of low-voltage cathodoluminescence is ascribed to the removal of electron clouds by surface modifier which may supply the recombination centers for electron and holes. But, more experimental data are needed for the quantitative presentation to express the effect of electrical resistance of phosphor screen on the cathodoluminescence.

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