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AGING CHARACTERISTICS OF GREEN-EMITTING Zn_2GeO_4:Mn ALTERNATING-CURRENT THIN-FILM ELECTROLUMINESCENT DISPLAYS

CHARAKTERISTIKY STÁRNUTÍ ZELENĚ SVÍTÍCÍCH Zn_2GeO_4:Mn TENKOVRSTVÝCH ELEKTROLUMINISCENČNÍCH PANELŮ

Abstract

Optical and aging characteristics of green-emitting Zn_2GeO_4:Mn alternating-current thin-film electro-luminescent (ACTFEL) displays are presented. Field-ionization of impact-excited Mn^{+2} luminescent impurities is found to give rise to positive space charge within the Zn_2GeO_4 phosphor, leading to unusual device behaviours such as conduction current delay, anomalous positive polarity transient luminance annihilation, transferred charge being comprised of mainly relaxation charge, and a decrease in the 50 Hz threshold voltage with increasing temperature. Low temperature aging experiments suggest that aging is at least partially due to hot electron-induced degradation. Although most Zn_2GeO_4:Mn ACTFEL devices exhibit a moderate amount of aging, certain devices are found to exhibit no measurable aging at 1 kHz when aged for 24 hours.

Abstrakt

Článek přináší studii optických vlastností a principů stárnutí zeleně svítících Zn_2GeO_4:Mn tenkovrstvých elektroluminiscenčních panelů. Pomocí ionizace pole způsobené dopadem elektronů na příměsi Mn^{2+} je v Zn_2GeO_4 vybuzen kladný náboj, což vede k neobvyklému chování součástek: zpoždění proudu ve vodivostním pásu, anomální anihilaci svítivosti způsobené kladnou polaritou přechodu, přenesený náboj je tvořen z větší části relaxačním nábojem, či k poklesu prahového napětí s rostoucí teplotou pro 50 Hz. Nízkoteplotní experimenty ukazují, že stárnutí je částečně způsobeno degradací indukovaných horkých elektronů. Ačkoliv většina Zn_2GeO_4:Mn ACTFEL panelů mění své vlastnosti s časem jen nepatrně, některé ze součástek vykazují měřitelné hodnoty stárnutí již po 24 hodinách při 1 kHz.

1 INTRODUCTION

Oxides were among the first and more extensively researched luminescent materials, and they comprise a substantial portion of important phosphors for electroluminescent lamp, cathode ray tube (CRT), and other applications [1]. Oxide phosphors are attractive because of their enormous number, large gamut of emission colours, and thermodynamic stability. Additionally, many historically important luminescent oxides, such as willemite (zinc silicate) and ruby (Al_2O_3:Cr), are naturally-occurring, and the manufacture of oxides is often relatively simple and safe. Research on alternating-current thin-film electroluminescence (ACTFEL) [2], however, has generally been focused on sulfide-based phosphor systems, particularly ZnS and SrS. Oxide phosphor materials have been thought to be poorly suited for ACTFEL applications because of their typically large bandgaps and their refractory nature. The last decade, however, has seen an increase in oxide thin-film phosphor research with several groups reporting success in manufacturing oxide-based ACTFEL devices [3].

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ACTFEL devices are made by using the standard noninverted structure on glass [4]. In this study, we extend this previous work by assessing temperature and aging characteristics of Zn_2GeO_4:Mn ACTFEL devices.

2 EXPERIMENTS

The ACTFEL device structure used is the standard metal-insulator-semiconductor-insulator-metal (MISIM) structure (Fig.1) consisting of a 200 nm thick layer of indium tin oxide (ITO) as the (transparent) bottom electrode, a 200 nm thick aluminium titanium oxide (ATO) bottom insulator layer, the phosphor, a 250 nm thick SiO_xN_y top insulator deposited via plasma-enhanced chemical vapour deposition, and a 150 nm thick top contact of Al; the ITO/ATO coated NEG glass substrates were provided by Planar Systems. The phosphor layer is composed of a thin film deposited by RF magnetron sputtering of a $Zn_{2x}GeO_4$:Mn_x target, where x = 0, 0.005, 0.01, 0.02, 0.04, or 0.06, i.e., undoped and 0.25-3 at %Mn relative to Zn sites [5].
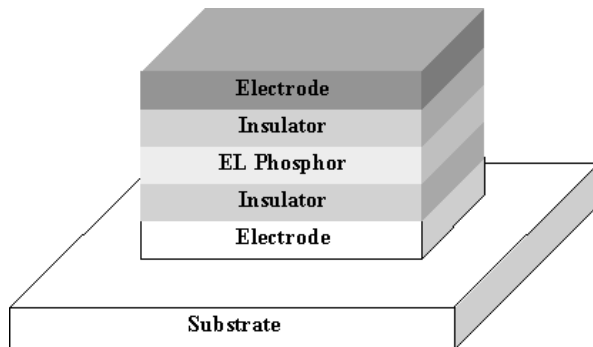
Fig. 1 ACTFEL thin-film stack

Note that in this paper the Mn concentration always refers to the atomic concentration in the target; the Mn concentration incorporated into the thin film phosphor may differ from that of the target concentration. These targets are prepared in-house from stoichiometric quantities of ZnO, GeO_2, and MnO powders that are reacted in air to form the germanate, cold-pressed into two-inch targets, and sintered in air at 1100°C for several hours to achieve densifition. The thin-film stack is furnace-annealed in air, typically for ~2 hours at ~680°C; films with bright photoluminescent emission are found to result from annealing at temperatures as low as 620°C.

All electrical measurements are taken by using our standard experimental setup, in which the ACTFEL device is placed in series with a resistor and a large sense capacitor [6]. Unless otherwise noted, all devices are driven by a bipolar trapezoidal waveform (from waveform generator Agilent 33220A in conjunction with a high-voltage operational amplifier 7265 DSP) consisting of 5 μs rise and fall times and a 30 μs plateau time, and applied voltage polarities are given in terms of the Al contact. An Ocean Optics PR-650 fiber spectrometer is used to measure luminance and emission spectra, while a Hamamatsu type R928 photomultiplier tube is used to record transient luminance waveforms using an Agilent 54621A digitizing oscilloscope. For variable temperature studies, a Delong Instruments cryostat chamber is also used.

3 OPTICAL CHARACTERISATION

The luminance-voltage (L-V) and luminous efficiency-voltage (η-V) characteristics of a 2 at % Mn device operated at 50 Hz are shown in Fig.2. $L_{40} = 10^5$ cd/m^2 and $\eta_{40} = 0.33$ lm/W are observed for the brightest device; other devices exhibit lower luminance levels ($L_{40} = 80$ cd/m^2) but better efficiency ($\eta_{40} = 0.45$ lm/W). These numbers can be compared to the brightest reported

saturated green ACTFEL phosphors, ZnS:Tb and ZnS:TbOF, which have 50 Hz L_{40} and η_{40} values of 90 and 100 cd/m^2 and 0.6 and 1.0 lm/W, respectively, and CIE coordinates of 0.30; 0.60. These ZnS:Tb EL phosphors, however, have been hindered by stability problems; four prominent emission peaks also limit color purity. Also, the use of $BaTa_2O_6$ as a top insulator material would double the insulator capacitance and therefore is expected to double the L_{40} value for the Zn_2GeO_4:Mn devices to $\eta = 200$ cd/m^2. [7]

The sharp step in the L-V curve shown in Fig.2 is the result of space charge in the device. Devices with low Mn concentrations tend to show exponential luminance increases with voltage until 40 V over threshold, at which point the luminance essentially saturates. This exponential luminance increase is also seen in devices with higher Mn concentrations, as well as in most sulfide devices, for a much shorter span of several volts, before the step in luminance noted above.

Additionally, some devices exhibit L-V curves that are basically step functions, with the luminance increasing from zero to on the order of a hundred cd/m^2 over the space of a few volts, then saturating at that level. This behaviour is accompanied by an extremely large amount of space charge generation, resulting in very high phosphor current densities that can reach instantaneous values well over 1 A/cm^2. This behaviour seems to be related to the "domain EL". These devices tend to be very unstable, usually burning out quickly, presumably as a result of the large current densities observed.
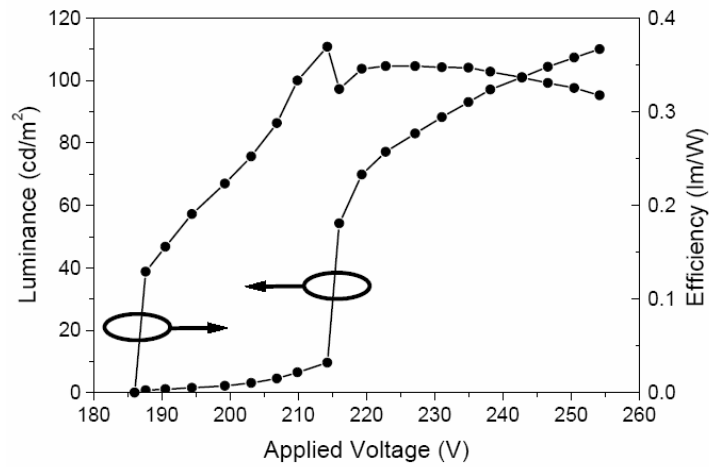
Fig. 2 Luminance-voltage (L-V) and efficiency-voltage (η-V) plots of a Zn_2GeO_4:Mn (2% Mn) ACTFEL device driven at 50 Hz. ($L_{40} = 10^5$ cd/m^2 and $\eta_{40} = 0.33$ lm/W)
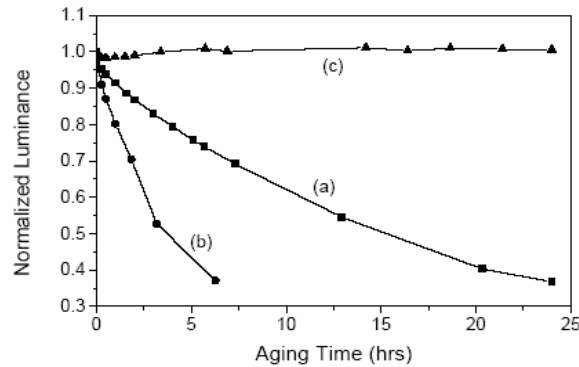
4   AGING TRENDS

One of the more important attributes of an ACTFEL phosphor material is its luminance stability.

Previous research indicated that Zn_2GeO_4 ACTFEL devices age very rapidly, essentially to zero luminance in a very short time [7]. The aging mechanism hypothesized involved rapid atomic diffusion through large, open 1-D tunnels present in the zinc germanate crystal structure.

Constant voltage aging behaviour typical of the devices manufactured during this study with the standard structure is indicated by curve (a) in Fig. 3, which shows the normalized luminance of a 3% doped Mn Zn_2GeO_4:Mn device operated at 40 V above the initial threshold voltage at 1 kHz as a function of time [8]. The luminance declines from 168 cd/m^2 to 62 cd/m^2 after 24 hours, while the threshold voltage is found to have shifted from 190 V initially to 212 V. The luminance at 40 V over the post-aging threshold of 212 V is 136 cd/m^2, indicating that most but not all of the luminance decrease is the result of the positive threshold voltage shift (i.e. p-shift aging). This type of p-shift

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aging is not perceived to be problematic since it may be accommodated via an initial 'burn-in' procedure.

To investigate the cause of the aging, a device adjacent to the device in curve (a) on the same substrate (which should be as nearly identical as possible) is aged at a reduced temperature of 125 K. At such low temperatures, processes that are strongly dependent upon thermal energy, including atomic diffusion, should be severely retarded, while the electron distribution should be significantly hotter since less lattice scattering of the carriers occurs. A hotter electron distribution could lead to accelerated aging as hot electrons break chemical bonds within the phosphor layer, or as they thermalise and recombine at the conduction band discontinuity between the phosphor and the insulator.

Fig. 3 Normalized luminance vs. aging time for three devices on two substrates, as described in the text. Devices (a) and (c) are aged at 300 K, while (b) is aged at 125 K.

The low-temperature aging trend of a Zn_2GeO_4:Mn device is shown as curve (b) in Fig.3. The initial 125 K luminance of 626 cd/m^2 is reduced to 232 cd/m^2 after only a little more than six hours, a degradation rate much faster than at high temperature; the luminance at 300 K was measured before and after aging and decreased similarly. Thus, it appears that hot electrons are responsible for some of the Zn_2GeO_4:Mn ACTFEL device performance degradation. This is in contrast to temperature-dependent aging experiments using evaporated ZnS:Mn ACTFEL devices, which showed more degradation after 15 min of aging at 300 K than occurred after 24 hours of aging at 125 K. Finally, curve (c) of Fig.3 corresponds to a device with a structure somewhat different from the other devices. The 300 nm thick bottom insulator of Y_2O_3 and the 1000 nm thick phosphor layer were deposited on ITO-coated glass and subjected to a 680°C furnace anneal in Ar/O$_2$. A 200 nm thick top insulator layer of SiON and Al contacts were deposited after a 650°C RTA in O$_2$. The device in curve (c) is aged at 50 V over threshold at 1 kHz and 300 K, and the initial luminance of 145 cd/m^2 is maintained over 24 hours of aging. This performance stability was verified for other devices on the same substrate.

In investigating the electro-optical characteristics of the device in curve (c), several atypical features stand out. First, when ramping up the applied voltage, only a small amount of negative transient offset of the electrical characteristics [7] is witnessed near threshold, whereas other devices usually display a large amount. This transient offset is thought to be due to a mismatch in the energy depths of traps responsible for sourcing transferred charge, with a negative offset corresponding to shallower top interface traps. The significant reduction seen in device (c) of this offset implies that the trap energies are more closely matched than in other devices. Second, luminescence is first observed roughly simultaneously for both applied voltage polarities, rather than the usual case in which the negative emission precedes the positive emission by several volts.

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Third, the nature of the emission itself is odd in that transient luminance annihilation is observed for both polarities at 1 kHz, rather than only for the positive pulse. Both polarities also exhibit strong trailing edge emission, so that the instantaneous luminance level at the end of either pulse is not diminished from the instantaneous luminance level at the beginning. Fourth, the phosphor field is more symmetric with respect to the voltage pulse polarity compared to other devices. Overall, the electro-optic behaviour of these very stable devices is much more symmetric, especially near threshold, than the behaviour normally observed in other devices.

However, the dependence Q_{max}-V_{max} trends of the very stable devices are found to be much more asymmetric than other devices. Specifically, the threshold step in the Q_{max}-V_{max} curves is found to be much larger and steeper for the negative applied voltage pulse; the derivative of these curves (transferred charge capacitance) show over four times as much overshoot for the negative pulse as compared to the positive, and a large amount compared to other devices in general. This is indicative that a much greater amount of space charge is being created during the negative pulse. At the same time, about 40% more charge is transferred per half-cycle during the negative pulse. These two facts, taken together, may explain the enhanced aging stability, assuming that hot electron damage to one of the insulator-phosphor interfaces is the dominant aging mechanism. The space charge asymmetry shown in the more stable device may act to reduce the field at the sensitive interface while it acts as the anode, or it may reduce the electron flux to the sensitive interface, thereby reducing aging. Additionally, the large phosphor thickness and space charge densities of this device reduce the average phosphor electric field, which may mitigate hot electron damage.

5 CONCLUSIONS

A study of aging characteristics of sputtered Zn_2GeO_4:Mn ACTFEL devices is presented. Although the electro-optic performance and aging behaviour of these devices is rather good, the luminous efficiency is currently not sufficient to justify commercialization of this phosphor. Future efforts to improve the luminous efficiency of this phosphor should focus on alternatives to field-ionization of impact-excited Mn^{+2} luminescent impurities as a means of introducing space charge into the phosphor. Perhaps this could be accomplished via co-doping or the use of alternative annealing procedures. Also, the use of luminescent impurities with shorter lifetimes could be advantageous since this would minimize transient luminance annihilation.

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