Red electroluminescence from ZnGaS:Mn thin films

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We demonstrate color shifting from the yellow to the red in the electroluminescence from (ZnGa)S:Mn films. We observe threshold voltages down to about 35 V, extremely low for such devices. We discuss the materials characteristics of the phosphor films, and the potential for improvement of the luminous intensity of the devices. © *1999 American Institute of Physics.* [S0003-6951(99)01542-9]

Full-color displays based on alternating-current thin-film electroluminescent (ACTFEL) devices are desirable for many applications because of their high resolution, tolerance of temperature extremes, and wide viewing angle. Monochrome displays are based on ZnS:Mn, which emits in the yellow [Commission Internationale de l'Eclairage (CIE) coordinates $x=0.5$, $y=0.5$]. With luminance $L_{40}=5000\,\mathrm{cd/m^2}$ and luminous efficiency $E_{40}=2-4\,\mathrm{lm/W}$ at 1 kHz and 40 V above threshold, ZnS:Mn is the brightest known electroluminescent (EL) phosphor.[1] Use of the ''color-by-white'' method to filter the radiation to produce full three-color TFEL capability has met with moderate success,[2] but clearly new phosphors that emit pure red, green, and blue at the same intensity that ZnS:Mn produces yellow would be preferable. The search for full three-color TFEL capability has intensified recently with the demonstration of high intensity blue emission from SrS:Cu,Ag ($L_{40}=360\,\mathrm{cd/m^2}$ with CIE $x=0.18$, $y=0.3$, and $E_{40}=0.14\,\mathrm{lm/W}$ at 1 kHz).[3] There has also been a recent report of strong green emission from SrS:Cu,K (CIE $x=0.289$, $y=0.596$, $L_{40}=53\,\mathrm{cd/m^2}$, $E_{40}=0.97\,\mathrm{lm/W}$ at 60 Hz).[4] In the red region of the spectrum, CaS:Eu (CIE $x=0.68$, $y=0.31$, $L_{40}=12\,\mathrm{cd/m^2}$ at 60 Hz)[1] is the most promising candidate, although the best red luminance is still from filtered ZnS:Mn (CIE $x=0.65$, $y=0.35$, and $L_{40}=65\,\mathrm{cd/m^2}$ at 60 Hz).

Very recently, yellow-to-red color shifting in the photoluminescence (PL) of Ga-doped ZnS:Mn phosphor powders has been reported.[5] Li and Keszler showed that by tuning the Ga concentration in $Zn_{(1-3\delta/2)}Ga_\delta S{:}Mn_{0.01}$, the yellow PL emission from undoped ZnS:Mn (CIE $x=0.543$, $y=0.455$) shifts towards orange for $Zn_{0.7}Ga_{0.2}S{:}Mn_{0.01}$ (CIE $x=0.620$, $y=0.379$) through deep red for $Zn_{0.25}Ga_{0.5}S{:}Mn_{0.01}$ (CIE $x=0.656$, $y=0.344$). They obtained chromaticity values for $Zn_{0.55}Ga_{0.3}S{:}Mn_{0.01}$ (CIE $x=0.640$, $y=0.360$) that are extremely close to those of the Y_2O_3:Eu phosphor, often used as a commercial red standard.

The purpose of the work described in this letter is to demonstrate yellow-to-red color shifting of the EL in thin films of (ZnGa)S:Mn, to discuss the materials characterization of the phosphor films, and to present some of the ACTFEL device characteristics.

We thermally evaporated (ZnGa)S:Mn powder precursors from metal boats, often with additional Mn evaporated from a metallic source. We also experimented with coevaporation of ZnS powder, metallic Ga, and metallic Mn. We used baffled tantalum boats for the powders, an aluminum oxide crucible for Ga, and a flat tantalum boat for Mn. The evaporation system is a modification of one described previously,[6] and it is briefly reviewed here.

The evaporation rates from each source were monitored by independent quartz crystals; the system stability is about 40% for powders and 5% for metals. Evaporation proceeds at about 0.5 nm/s, achieving films $\leqslant$500 nm thick for a substrate temperature of 120 °C. All results reported here are for films deposited at 120 °C. Films evaporated at different temperatures can be expected to yield a different stoichiometry because the sticking coefficients and reaction rates of the constituent elements are different functions of the substrate temperature. The glass substrates were heated at 300 °C in vacuum ($\leqslant 6\times10^{-7}$ Torr) for about 60 min before the substrate temperature was adjusted to the appropriate value for deposition. The substrates were 1-mm-thick Corning 7059 glass coated with about 200 nm of each indium tin oxide and aluminum titanium oxide, which serve as the transparent conductor and first insulator, respectively, of the ACTFEL device.

Following deposition, the films were subject to rapid thermal annealing (RTA) for 2 min in argon at temperatures between 550 and 700 °C. In the range of substrate temperatures used (20–400 °C), post-production RTA provided no particular improvement to the microstructure as measured by x-ray diffraction (XRD), but markedly improved PL. The

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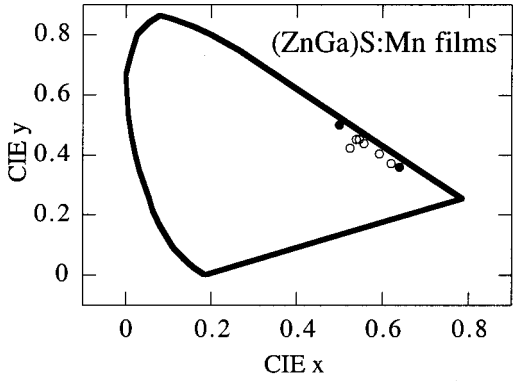

FIG. 1. CIE coordinates of electroluminescent emission from (ZnGa)S:Mn films in Table I on a chromaticity diagram. The dark circles represent the EL emission from ZnS:Mn (0.5, 0.5) and the PL emission from $Y_2O_3:Eu^{3+}$ (0.64, 0.36).

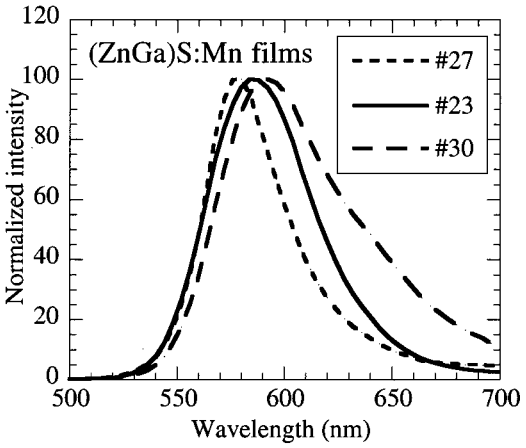

FIG. 2. Electroluminescence emission spectra of some of the (ZnGa)S:Mn films (see Table I).

phosphor films were made into TFEL devices by evaporating aluminum electrodes directly onto the phosphor. This is certainly sufficient to produce luminescence, but is not expected to produce optimized devices, which require a second insulator between the phosphor and metal electrode. The EL was observed by driving the system at 1 kHz with a system similar to that described by Keir and Wager.[7]

The main result of this letter is in Fig. 1, which shows the CIE coordinates of the EL emission shift from yellow through orange to deep red (see also Table I). The luminescence is quite variable, but in the better cases, the luminance is comparable to those quoted above for CaS:Eu (luminance scales directly with operating frequency in the ranges discussed here). In other cases, it is rather weak. We attribute this to the nonoptimized device structure, and all devices should be able to be improved to perform at least as well as the best devices presented here. Interestingly, the devices also exhibited extremely low threshold voltages down to about 30 or 40 V. The electric field in the phosphor at threshold, calculated with a simple parallel capacitor model with relative dielectric constants of 18.5 and 8.3 for aluminum titanium oxide and zinc gallium sulfide, respectively, is 0.6–0.8 MV/cm for the coevaporated films and 2–4 MV/cm for the films evaporated from powders. The difference appears significant, but is not understood in detail. A value of 1 MV/cm is commonly quoted as necessary for EL operation. These low voltages may represent a route to much lower-power consumption devices. However, it is also possible that such low-voltage devices are inherently limited because the hot tail of the distribution of tunnel-injected electrons responsible for the impact excitation of the Mn is much less populated at these lower voltages. The issue of the low threshold voltage of the EL devices could be related to Ga being incorporated as a shallow donor rather than being properly alloyed. Compensation by a shallow acceptor such as nitrogen might resolve the problem.

Figure 2 shows the EL emission spectra from selected devices listed in Table I. These were all coevaporated from ZnS powder, Ga metal, and Mn metal under the same conditions except for the percentage of Ga. As more Ga is included, the shift in the central EL emission peak shifts to larger wavelength, just as in the PL spectra from powders.[4] The asymmetric shape and the broadening of the emission also follow the same pattern. The stoichiometry, as measured by wavelength-dispersive electron probe microanalysis (EPMA) at 15 kV, does not reflect the relative evaporation rates, but it should be noted that the EPMA composition is an average one; there is no information about segregation. Also, one of the coevaporated films does not fit into the pattern. The difficulty with Ga control was also reflected in the films evaporated from the (ZnGa)S:Mn powder precursors; the concentration of Ga relative to Zn in the films was higher than in the precursors, sometimes by more than a

TABLE I. Characteristics of EL emission from (ZnGa)S:Mn ACTFEL devices. All films were deposited at a substrate temperate of 120 °C, and parameters measured with the device operating at 1 kHz.

Film No.	Precursor	Thickness (nm)	Composition	CIE x	CIE y	λ_{max} (nm)	V_{th} (V)	f_{th} (MV/cm)	L_{40} (cd/m^2)
32	$Zn_{0.925}Ga_{0.05}S:Mn_{0.01}$ powder	160	$Zn_{0.35}Ga_{0.49}S:Mn_{0.03}$	0.539	0.453	584	95	3.8	1.61
59	$Zn_{0.85}Ga_{0.1}S:Mn_{0.01}$ powder	480		0.557	0.438	592	140	2.5	9.71
27	ZnS powder, Ga metal 10 Å/s, 0.3 Å/s	660	$Zn_{1.04}Ga_{0.03}S:Mn_{0.003}$	0.525	0.423	578	60	0.80	1.58
23	ZnS powder, Ga metal 10 Å/s, 0.5 Å/s	450	$Zn_{0.36}Ga_{0.44}S:Mn_{0.03}$	0.546	0.452	585	31	0.57	170
33	ZnS powder, Ga metal 10 Å/s, 0.7 Å/s	500	$Zn_{0.37}Ga_{0.37}S:Mn_{0.08}$	0.620	0.372	639	47	0.80	1.15
30	ZnS powder, Ga metal 10 Å/s, 1 Å/s	600	$Zn_{0.31}Ga_{0.55}S:Mn_{0.005}$	0.593	0.405	592	45	0.65	13.9

factor of two. Efforts to improve the Ga control are underway. EPMA also revealed that the Mn content of films evaporated entirely from powder precursors was less than 0.01%, so we generally coevaporated Mn metal to produce about 1 at. % Mn. Rutherford backscattering analysis was also employed on some films. It confirmed the cation to sulfur stoichiometry obtained from EPMA, but it does not resolve Zn from Ga in this system.

XRD of the (ZnGa)S:Mn in the θ–2θ geometry revealed a strong peak at $2\theta = 28.5°$, indicating that the films are strongly textured, and not random polycrystalline. This peak corresponds to diffraction from the (111) planes in a cubic structure or from (0002) planes in the hexagonal structure for pure ZnS:Mn. None of our films showed any channeling in RBS.

Transmission through the (ZnGa)S:Mn films in the visible region of the spectrum is extremely good. Down to 500 nm, the transmission of the film and glass substrate is indistinguishable from the transmission of the substrate alone. The transmission drops to about 80% at 400 nm, and the films are strongly absorbing below 350 nm.

Several authors have discussed the need for a sulfur overpressure to grow high-quality ZnS films.[8] Although this was not implemented in our system, we have found that our ZnS films are nearly stoichiometric (with even a slight sulfur excess), are strongly oriented with the (111) plane parallel to the substrate surface, and are highly resistive at dc and low fields. Also, EL devices made from similar ZnS films doped with a few percent of Mn^{2+} luminesce with about 50% of the intensity of much thicker, optimized devices with a sputtered phosphor layer. The main drawback appears to be that the evaporated films are very thin ($<$500 nm from about 2 g of starting material) and this contributes to the weaker EL. It appears that an ALE-type mechanism is at work in that the low sulfur sticking coefficient is rate limiting.

Chromaticity control of PL and EL is possible in TFEL (ZnGa)S:Mn devices. The color coordinates indicate that saturated red can be obtained. The potential for useful devices needs to be further evaluated. The threshold voltage in most of the devices is below 50 V, which bodes well for low power drives, but this may also be responsible for low luminance. Thermal coevaporation is a useful method to make good quality, highly transparent phosphor films, and the Ga doping can in principle be controlled continuously without need to produce many sputter or laser ablation targets of particular stoichiometry. In practice, Ga control is difficult, and the system can be improved by incorporation of additional sulfur sources.

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