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Thin Film Electroluminescence Displays

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High electric fields across thin films induce ballistic transport of electrons which in turn excite inner transitions of high luminescence. Electrical breakdown is readily controlled by distributed series capacitance.

Although it dominates the market, the CRT (cathode ray tube) display offering full colour, high resolution, good contrast and brightness is nevertheless bulky, heavy and not "solid-state". Consequently, for some years producers and designers of information displays have been looking for a substitute which is flat and light-weight. Liquid Crystal Displays (LCD) are the most promising candidates in conditions of high illumination, but light-emitting (active) displays are also demanded, and the 20 year old plasma panel, despite tremendous R & D efforts, stagnates on the market mainly because of its high price. According to a recent market forecast, all types of flat display will prosper in the coming years, the highest rate of increase being expected for thin-film electroluminescence displays (TFD).

Since the disappointments of the end of the 1960s over traditional electroluminescence, a new approach has evolved based on the principles:

— for large areas polycrystalline materials must be used;

— inner shell radiative transitions (of Rare Earths and Transition Metals) are little affected by polycrystallinity;

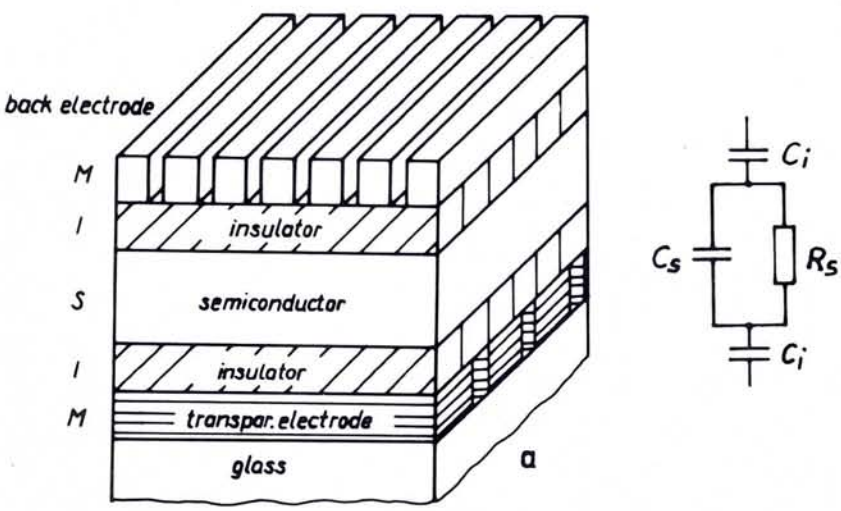
— inner shell transitions, even if dipole-forbidden, can be efficiently excited by electron impact;

— in some wide-gap semiconductors, electrons can be heated to a few eV by electric fields in the 10^6 V/cm range;

— destructive electrical breakdown can be avoided by distributed charge control much better than by current control.

One unique combination of host and dopant has so far proved successful in meeting all the requirements — ZnS:Mn which produces the well-known yellow colour, and a world-wide search has started to find other materials which would give full colour capability. If found, these could more easily be incorporated into the thin film design than into any other display concept. A tremendous variety of applications besides the simple replacement of the CRT are feasible and large new markets, can be expected to open up such as: the hand-held message display, traffic and time tables, home telephone directories, information displays of large sizes, hand-held electronic games, car dash-boards, aviation equipment etc.

Fig. 1 — Electrically the TFD is a capacitor which becomes leaky (and emits light) above a voltage threshold (highly non-linear R_s). Physically it is a stack of thin polycrystalline transparent films on a glass substrate. Economically it is the market runner of the nineties.



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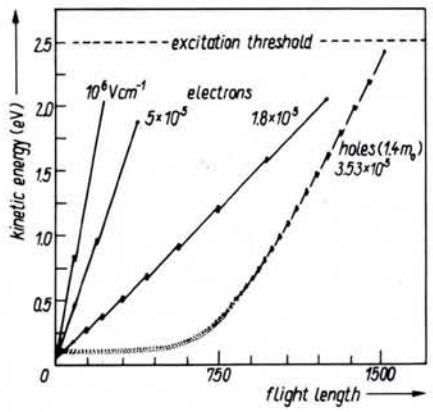


Fig. 2 — In ZnS with a medium electron-LO-coupling (Fröhlich type) in electric fields of 10^6V/cm only one or two phonons are emitted by an electron on a drift length of 250 Å so that it gains ≅ 2.5 eV on that distance, enabling it to impact excitation of Mn^{2+} on a cation site.

The New EL Concept

As always in the case of a successful development, it is difficult to follow it back to its earliest roots. It is however generally accepted that the inventor of the thin film EL display was T. Inoguchi of Sharp Co., Japan who gave a first talk on the new device at Palo Alto in 1974 and together with S. Mito wrote a first monograph on the subject in 1976 [1]).

The main insight was that polycrystalline materials are essential and, in contrast to powder devices, as much homogeneity as possible should be aimed for.

The second major innovation of Inoguchi was the replacement of the series resistive film for controlling the current, by a capacitative film (Fig. 1), so avoiding the resistance spreading that had previously been encountered. An additional advantage is that in production it is much easier to obtain a very low conductivity than one that is accurately controlled to a given value, and AC operation is not a problem.

Inoguchi's device relied on ZnS doped with the isovalent Mn^{2+} substituting on a cation site. Electric fields of about 10^6 V/cm gave rise to a lossless, so-called ballistic acceleration of electrons (Fig. 2), "heating" them to energies adequate to excite the fifth 3d electron of Mn^{2+} to its first excited state. Because of the very small lattice coupling, this returns radiatively to the groundstate with a probability of almost unity, in spite of the long lifetime of about 10^{-3} s.

Inoguchi's choice was well made, and it may not be possible to achieve higher efficiencies with single crystals even [3]). When the impact cross-section of Mn^{2+} was measured recently, it came out to be $\sigma = 4 \times 10^{-16}$ cm^2, even larger than the area of the electron wavefunction.

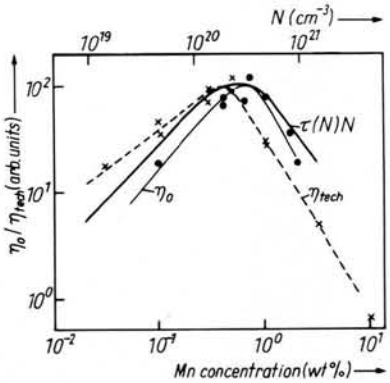
Minority carriers enter into the problem only indirectly. Following tunnel emission, electrons achieve the necessary 2.5 eV for excitation over an acceleration length l_a = 250 Å [2]). So it would seem wise to dope with a concentration N_d which would result in a similar cooling or impact length, l_i namely:

$$N_d = 1/\sigma l_i = 1/4 \times 10^{-16} \times 2.5 \times 10^{-6} = 10^{21}\ \text{cm}^{-3}$$

Unfortunately this turns out not to be the best choice because concentration quenching sets in at about 1.5×10^{20} cm^{-3}. Empirically, the optimum doping proves to be about 3×10^{20} cm^{-3} (Fig. 3), so only about 30% of the carriers strike their target at optimum energy; the others get hotter and give rise to multiplication, producing minorities as well as further electrons. In practice, each primary electron (originating at the cathode interface to the dielectric) has several chances of cooling down by either 2.5 eV (Mn excitation) or 3.8 eV (gap of ZnS) as the usual thickness of the ZnS film is about 30 times l_a. Minorities, being heavier, are rarely heated up to impact energies and, as is usual in II-VI compounds, are quickly trapped by native defects.

One very advantageous feature of the interface between the polycrystalline semiconductor and the (mostly) amorphous dielectric is that electrons are quickly trapped by relatively deep (1 eV) interface states on arrival at the anode. This prevents them from diffusing (drifting) back into the bulk at sign reversal of the applied voltage and gives rise to a polarization or overvoltage. Even more advantageous is the fact that they can only be released when the electric field has already reached the threshold for tunnel emission. Moreover, with an Al_2O_3 (dielectric)/ZnS (semiconductor) interface, the tunnel threshold E_t is itself higher than the loss-free acceleration

Fig. 3 — Below 10^{21} cm^{-3} Mn^{2+} concentration N, the electrons get more hot than cooled by exciting impacts, but above 10^{20} cm^{-3} energy transfer (concentration quenching) sets in reducing efficiency $\eta_o/(\eta_{techn})$.



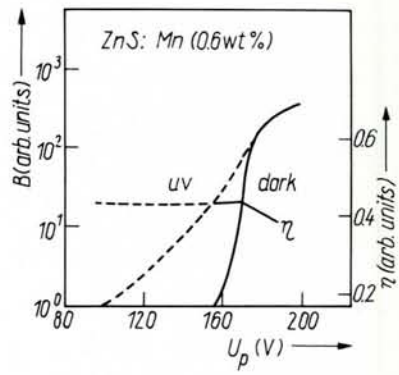


Fig. 4 — Two threshold processes are active in Al_2O_3/ZnS: Mn/Al_2O_3 TFDs, but the one with the higher voltage value dominates the brightness(B) - voltage(U_p) characteristics: tunnel emission supplies carriers at threshold. Under UV illumination, photoexcited electrons are accelerated at much lower voltages (dashed curve), proving that the acceleration threshold is the lower.

threshold E_a. Consequently, every electron emitted into the ZnS becomes hot (Fig. 4) which does not happen with other EL structures and even with the otherwise completely analogous Al_2O_3/ZnSe device [5]).

Operational Characteristics

Two thresholds are involved in the working of an MISIM-EL structure: tunnel emission and ballistic acceleration [2]) so it is not surprising that the brightness voltage *(B-V)* dependence is of a threshold character as seen in Fig. 5. If films are plane-parallel, crystallites small, and materials highly resistive, an extremely steep curve results: four decades of *B* within a 10 V interval are rather typical. This kind of threshold behaviour should please every LCD designer; it lends itself ideally to high multiplex rates in complex displays. Beyond the threshold region in the working regime, the brightness increases almost linearly with voltage (illustrated in the inset linear plot).

Brightness values depend also on the frequency of the applied voltage which in general is very high. Remembering that CRTs have a brightness in the range 50-80 ftL, a comparable performance appears easily attainable with a frame rate of 50-100 s^{-1}. The threshold voltage on the other hand at first sight appears to be inconveniently high: 150-200 V is hardly compatible with normal semiconductor electronics.

The next feature of interest in applications if of course the light conversion efficiency. The state of the art value is 3-8 lm/W or ~ 1% which may seem to be pretty low. Nevertheless it compares favourably with that of plasma displays (at least one order of magnitude lower) and is comparable with CRTs. From a user's point of view, efficiencies are not

a primary issue except in relation to cooling needs, limits to useful life, etc. With regard to heat development, 1% is just tolerable, and because the working voltage is so high the necessary 2×10^{-2} W to light a picture element (pixel) of 1 mm^2 to 50 ftL can be transported by a current of only 0.1 mA at 200 V without excessive loss over the transparent electrode stripe made of ITO (indium tin oxide). Problems to be overcome are wiring and/or reliability of the addressing electronics.

All that has been said so far on operational characteristics relates to ZnS:Mn and that means a broad yellow emission which can be shifted to some extent by optical interference. The thickness of the single films of the stack as shown in Fig. 1 are typically 0.7 μm for the semiconductor and about 0.3 μm for the dielectrics and the ITO. In consequence, the structure acts as an interference filter and this must be taken into account in any design.

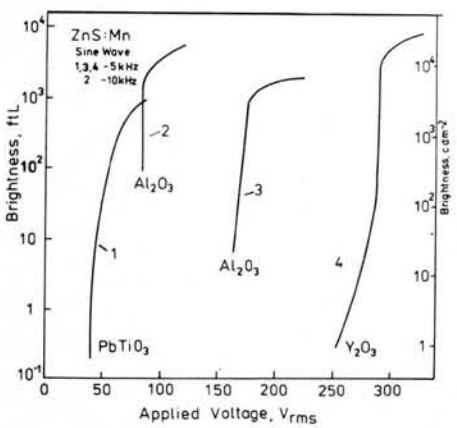
A TFD is essentially AC, so that all the operational characteristics given are time-averages over at least one period of the applied voltage. The device behaves up to threshold as a capacitor but above threshold an in-phase or dissipative current is drawn, during the rather small time near the voltage extrema (Fig. 6).

Yield

In the TFD the independent partial processes that can be identified [4] are:
- the heating of the carriers to excitation energies (> 2.5 eV),
- the excitation of Mn^{2+} by hot carriers,
- the radiative de-excitation of $(Mn^{2+})^*$,
- the outcoupling of generated photons from the structure.

However it is convenient to consider the first two processes together and ask how many of the transferred electrons

Fig. 5 — The most important feature for judgment of TFDs from a user's point of view is the brightness (B) - voltage (U_p) curve given in a lg-lin scale.



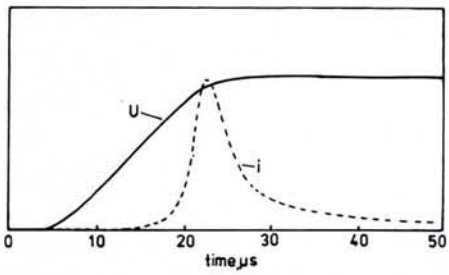


Fig. 6 — Even with long pulse or sinusoidal excitation, dissipative current is drawn only for a small time, necessary to transfer the voltage above threshold from the semiconductor film to the insulator film (capacitance).

are used for excitation, η_{exc}, as it is very difficult to measure the first alone.

The efficiency of de-excitation of Mn^{2+} radiatively (η_{lum}) has been known for a long time to depend strongly upon the Mn concentration, once this exceeds about 0.2 wt%. Only very recently has it been recognized that it also depends strongly on the concentration of excited Mn^{2+} ions, so the process of decay is highly non-linear. Independent measurements can be made *e.g.* by cathodoluminescence decay.

Optical outcoupling from an interference filter is not a simple problem, but an elementary approach is to average angles and wavelengths giving an approximation for a (thick) medium of index *n* into vacuum (which is not changed by inserting various other films in between):

$$\eta_{out} = 1 - (1 - n^{-2})^{1/2}$$
$$\cong 0.1 \text{ for ZnS when } n = 2.4$$

Practical numbers for the three factors for a 600 nm thick ZnS film sandwiched between Al_2O_3 films are $\eta_{exc} = 9$; $\eta_{lum} = 0.3$ which multiply to an overall yield of 0.27 photons/electron.

The technical efficiency is the ratio of emitted to used power into which one has to insert the ratio of photon energy to electron energy. We arrive at an inner efficiency of 5% and so an overall efficiency of 0.5%.

Different Colours

Such a good result can only be obtained with one combination of materials: ZnS as the host and Mn^{2+} as the dopant. The reason lies partially in the fact that Mn^{2+} has such a big cross-section for low energy electron impact and the solubility of Mn^{2+} in ZnS is high.

The only well-investigated alternative as a host is ZnSe [5]) and it suffers from two drawbacks: (i) the Mn emission (energetically the same as in ZnS) is temperature-quenched by a factor of 0.1 at room temperature and, (ii) the tunnel threshold of its interface to Al_2O_3 is slightly below the acceleration threshold, reducing the overall efficiency further. Heatability in ZnSe is as good as in ZnS.

Almost nothing is known about ballistic acceleration in other materials. From an applications point of view a multicolour display is highly desired and can be easily produced by simply stacking one colour MISIM above another; each is only about 1 µm thick and can transmit all colours. One early and easy choice to make colours other than yellow was to put rare earth ions into the ZnS. As there is practically no crystal field shift, at least of the 4f – 4f transitions, one can readily forecast the emission colour from the free ion spectral tables. These show visible emissions only for the RE^{3+} ion and so a lot of research work has been devoted to ZnS:RE^{3+} with RE = Tb, Sm, Tm, Er, etc. A green emission from ZnS:Tb^{3+} or ZnS:TbF_3 has been obtained and brightnesses up to 1000 ftL have been reported [6]).

The question completely unsolved at the moment is how the material, nominally doped with 1 wt% RE^{3+}, can stand this without decomposing. Because the yield is about one order of magnitude below the 1% of ZnS:Mn, very high power has to be put into the lattice, driving it to thermodynamic equilibrium which is a two - or multi-phase system with the REs withdrawn from the ZnS grains, down to their solubility limit. Several groups therefore have begun the search for other hosts. The most likely candidates for good heatability of the electrons are the alkaline earth sulphides: SrS, CaS, BaS doped again with Mn and REs [6]. It appears too early to judge their respective advantages.

Many insulators have been tried for EL devices, the most successful appearing to be Si(O,N), Al_2O_3 and Y_2O_3 but rather promising results have been reported on Ta_2O_5, TiO_2, a-$BaTiO_3$, $SrTiO_3$ and combinations of all the materials mentioned.

Conclusions and Perspectives

Large scale production of 240 × 320 pixel devices was started at Sharp Corp. in 1984. Planar Systems, (USA) was starting production of 256 × 512 devices last year and Lohja (Finland) is also ready.

In view of the potential market, which is forecast to reach the G$ level within the next decade, the level of research effort is surprisingly low in the thin-film EL area. And yet it has also other implications for physics. The device operates with one electrical breakdown per half period, but after 10^{10} breakdowns no irreversible changes have occurred. Consequently avalanche processes can be studied in a manner which has not been

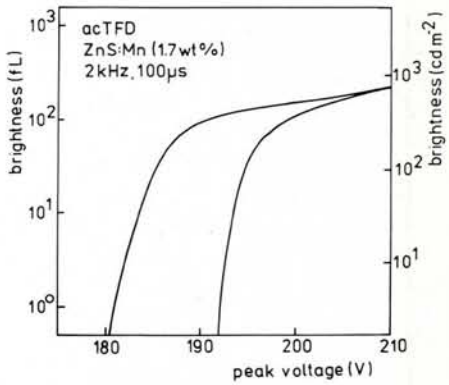


Fig. 7 — Hysteresis in the B-U_p characteristic would be a big advantage for addressing; relatively small amplitude pulses superimposed on a sustaining voltage can switch the brightness B on or off.

thought of before and by incorporating special dopants e.g. REs with a ladder of excitable levels, insight can be gained into the distribution function of electrons on their way to avalanching. Questions on the dependence of luminescence lifetime on Mn^{2+} concentration and excitation level are far from being answered and studies of the transfer to other dopants are only in their infancy.

Another phenomenon needing study is that of hysteresis (Fig. 7). Obviously this feature would greatly increase applicability and even the range of potential uses. The main problem is, that it shows a rather rapid degradation. It has been explained on the basis of a simulation model by Howard [7]) and depends on two prerequisites — a special interface structure and an adequate concentration of deep hole traps. The challenge is twofold: to find a recipe for preparing stable hysteresis characteristics and then to understand the nature of the hole traps which up to now seemingly can only be made by Mn^{2+}overdoping. The study of the interface between a-dielectrics and pc-semiconductors is a challenge in itself apart from its relevance to future hysteretic devices.

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