Exo-electron Emission effects in the PDP protective layer.

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1. Introduction

In order to timely trigger the addressing discharge, and reduce the addressing jitter, sufficient exoelectrons must be emitted from the MgO surface. Metastable ions are long dead at the moment of the addressing pulse, and therefore cannot be a source of priming electrons. In his patent US 6184848 on "Positive Column AC Plasma Display ", Larry Weber refers to the essential role of exoelectron emission from MgO, in order to generate a stable rampdown and rampup discharge. Nagorny et al. recently described the role of exoelectrons for the ramp discharge in more detail [1]

Already in 1985 Yasunori YANAGISAWA, Sushi KIYAMA and Ryoitiro HUZIMURA of Nara University (J) presented a paper on delayed electron emission in MgO [2]. They concluded that after electron irradiation of MgO-powder with an energy of 10-1500 eV, delayed exoelectrons are emitted, and that Auger type transitions play an important role in that process. They indicated that Auger-type of recombination of two electrons in an F-type center with a hole from a V-type center near the surfaces might possibly be responsible for this effect.

In a second paper Yanagisawa et al described the Thermally Stimulated Exo Electron Emission from MgO crystal powder, after bombardment with high energy ions [3]. The effect of UV irradiation on the MgO afterglow was published in a later paper [4]. The energy spectrum of the exoelectrons emitted after stopping the previous exposure to argon ions, was presented Tsujita et al in 2002, and published in 2005 [5]. Details on how to measure the exoelectron emission properties of MgO, can be found in patent WO2005020268 by Matsushita.

Another field of application of exoelectron emission is that of so-called "glow-starters" for fluorescent tubes. In these devices exo-electrons are created by blending crystalline powders of Al2O3, MgO, and Be with a binder, as described in the relevant patents. [6].

In this review paper we will first describe the different mechanisms that might be responsible for the generation of priming electrons in MgO. First we will consider shallow electron traps from which electrons can be emitted by thermal or field-induced effects. After that, we will describe possible Auger mechanisms that might play a role in exoemission. We will also discuss candidate-doping materials that might enhance the exoemission properties of MgO. We have to remark however that almost no experimental data is available on measured exoelectron emission. Most of the data is circumstantial evidence, hinting at the possibility of exoemission. On the other hand there is a wealth of information from the related field of TSEE, (Thermally Stimulated Exoelectron Emission), and the related field of host-lattice emission from undoped phosphor crystals, caused by STE, that is Self Trapped Excitons.

Most of these mechanisms will be briefly reviewed in order to possibly exploit these effects in the future, for the optimization of priming the addressing and ramp discharges in a PDP.

An earlier overview of the MgO properties, called "*MgO, Present & Future*", or "The da Vinci Code of Exo-Emission", was presented by the author at the 41st PDP International Forum, Takamatsu (J), 10 December 2005.

2. Priming by Exoemission – Recombination luminescence in the "crystal emissive layer"

For fast addressing in a PDP we want the emission of priming electrons from MgO, to be independent of thermal or field induced activation. Such a process exists and is called exo-electron emission. This is most probably also the effect occurring in pure MgO crystals, as used e.g. by Pioneer, sprayed on top of the normal E-Beam evaporated MgO; see eg. patent WO2005/031782.



Figure 1 Cathode luminescence (CL) emission of the Pioneer MgO single crystal, compared with that of evaporated MgO [patent WO2005/031782]

In order to understand the mechanisms involved, we will need to understand the relationship with CL-light emission at 235nm (5.3 eV) and jitter reduction. Later we will describe the CL emission process as a recombination luminescence in MgO. We will also look at the so-called "host-lattice" or Self Trapped Exciton

emission, found when exciting some other oxides by VUV photons. Self-trapped holes and excitons however do not occur in undoped MgO. We will explain that most probably V_{OH} centers play a major role in the 5.3 eV recombination emission of MgO. In these V_{OH} centers protons from hydrogen doping is not sitting inside an oxygen vacancy, but instead is associated with a magnesium vacancy. The V_{OH} centers act as a recombination center for electrons and holes.

Doping by other charge compensating impurities can strongly enhance the recombination emission, and therefore also the delayed emission of Auger electrons, needed for priming in a PDP addressing discharge.

3. The Oster & Haddad Auger Recombination model for Exo-Electron Emission (EE)

The mechanism of Exoelectron Emission (EE), also called Relaxation Electron Emission (REE), is described by L. Oster, J. Haddad in [7]. EE is the non-equilibrium, non-stationary emission of low energy electrons from the surface of solid during relaxation, after excitation /irradiation of the sample. In dielectrics energy is stored in the form of electrons/holes trapped in the energy gap. During the process of relaxation, this stored energy can be released both in the form of electron emission and photon emission. In this process, the energy, released at the recombination of charge carriers (e.g. mobile V_k holes with trapped electrons), is transferred to other electron traps, ionizes them and leads to EE.



Figure 2 The Oster-Haddad model of Auger-type Exo-Electron Emission

 $\begin{array}{l} E_G - \text{band gap} \\ \epsilon_m - \text{energy depth of the hole trap (eV)} \\ \epsilon_1, \ \epsilon_2 \ - \ \text{energy depths of different electron} \\ \textbf{traps (eV)} \\ \chi - \ \text{electron affinity (eV)} \\ CB - \ \text{conduction band} \\ FB - \ \text{forbidden band} \\ VB - \ \text{valence band} \end{array}$

Oster and Haddad describe three possible mechanisms of electron emission, that are relevant for priming in a PDP

(i) Electrons can be ejected thermally from shallow traps at a depth less than about 1 eV; the electron escapes the trap and goes to the conduction band due to the thermal energy, and electron acceleration from surface electric fields compensates for the energy loss on the penetration depth and on the overcoming electron affinity.

(ii) Alternatively the total energy, beginning with the delocalization of electrons, comes from the surface electric field. The surface charge resulting from secondary electron emission results in an electrical field, which enhances the electron emission, resulting in an after-emission. The maximum surface potential can be found from the emitted electron energy and is usually not higher than (5 - 15) eV. For a typical value of trap depth of $\varepsilon = 1$ eV then at room temperature the tunnel ejection can compete with thermal ejection at $E = 10^6$ V/cm. We can, therefore, expect tunnel ejection for MgO crystals of 100nm thickness in the case of local charging voltage differences of 10 Volt.

Another possible mechanism of electron exit (iii) into vacuum is due to Auger-recombination of holes and trapped electrons (hole-induced electron emission). Holes released by optical or thermal stimulation can recombine with electrons trapped in the trapping centers. The energy, released during the recombination, partially emits as thermo-luminescence (TL) and partially transfers to the populated electron traps, inducing electron emission into vacuum. The highest probability of Auger-emission is caused by "shallow" recombination centers and "deep" transmission centers, as is shown in the Figure. For wide-band dielectrics Auger-emission can be observed at room temperature only when associated pairs of shallow and deep traps have been created (at a distance of typically less than 3 nm).

4. Luminescence from oxygen vacancies (530nm and 380nm) and the role of [H⁻] hydride ions .

We will first analyze the simple case of the luminescence of MgO with oxygen vacancies (F-centers) and the effect of filling them with hydrogen. Hydrogen doped MgO can be used as a source of priming electrons for addressing. In MgO crystals, formed at high temperature, hydrogen is always present, while during PDP panel processing, a large amount of water is bound at the surface of the MgO. During the subsequent panel firing and aging, oxygen vacancies are filled with [H⁻] hydride ions, consisting of a proton with two electrons occupying the oxygen vacancy site (see also figure 6)

When exposed to UV light or bombarded with highenergy electrons, MgO yields blue and green cathodeor photo-luminescence light at 3.2 eV (530nm), and 2.3 eV (380nm). The 2.3-eV cathode luminescence emission from MgO shows an initial relatively fast transient decay, which is followed by a long-lived

second-order process. [8,9]. The behavior is consistent with the model, that [H⁻] ions act as meta-stable traps for electrons optically excited from F centers (forming F^+ centers); the 2.3-eV emission results when these electrons recombine with the F^+ centers, following thermal release from meta-stable [H²-] ions.

Electrons released from $[H^{2-}]$ ions can either return to the positively charged anion vacancies (F⁺ centers), resulting in the 2.3-eV emission, or be captured by other positively charged [H⁻] centers, thereby further delaying the inevitable return to the anion vacancies. A relatively high [H⁻] concentration implies a high probability for successive captures by [H⁻] ions, thereby resulting in a long-lived phosphorescence.

The complete process of excitation of the oxygen vacancy F and F^+ centers by 5.0 eV photons and deexcitation is shown in figure , as described by Rosenblatt, et al.[10].

The hydride trap level is very shallow, about 0.6 eV below the conduction band. Therefore in a PDP, the electrical field can easily excite electrons into the conduction band. At high panel temperatures a large amount of priming electrons will be released, resulting in a small addressing jitter. At low panel temperature on the other hand the jitter is very large, because of lack of priming electrons.



Figure 3 Schematic representation of the trap and defect levels accounting for the F and F+ luminescence [8]

At a high panel temperature however, there is a serious loss of wall charge. This is undesirable, because it increases both the minimum sustain voltage and increases the addressing voltage pulse needed.

In conclusion, we see that the [H⁻] or hydride ions, can trap electrons at an energy level just below the conduction band. They are responsible for the longlived phosphorescence of the F center (oxygen vacancy containing two electrons) in MgO. They are probably also responsible for the thermal and field-induced generation of priming electrons in a PDP addressing discharge. Instead of doping by hydrogen, silicon doping can be used; in this case the electron trap is somewhat deeper, and more stable over time. The temperature related problems however are still a major concern.

It is interesting to note that hydrogen doping in MgO does not directly lead to conduction of the MgO, contrary to hydrogen doping of other oxides, like tinoxide (SnO2), as shown in figure 2. This can be understood by applying the methodology of A. Zunger, as described in [11]



Figure 4 Position of the hydrogen pinning level (horizontal thick lines) in MgO, ZnO, CdO, and SnO2 . The CBM and VBM band edge energies relative to the vacuum level are given in parenthesis. [11]

5. Surface electron and hole traps.

Electrons generated inside bulk MgO have to travel to the surface, before being emitted into the vacuum. Not much is known about the mean free path of energetic electrons. However, as long as the energy is below the bulk bandgap value, a mean free path value of at least 10 - 100 nm is expected.

An alternative electron emission mechanism however could occur at the surface of MgO, where electrons and holes, are trapped at kinks, corners, steps, etc of the MgO surface. The group of Peter Sushko has analyzed these effects in detail; an overview is given in [12] Because surface excitons can be excited at a lower energy than that of the bulk bandgap, these processes might become especially relevant when using MgO at high xenon concentrations, creating a large fraction of 173 nm (7.4 eV) radiation, with a photon energy smaller

6. Electron-hole recombination – Host-Lattice excitation Emission – Self-Trapped excitons (STE)

than that the bulk energy gap value of 7.8 eV.

Self Trapped Exciton (STE) are mostly found in ionic crystals like the alkali halides. It is directly related to the so-called host lattice emission, where UVC light (200-290nm) is emitted by the lattice of phosphor crystals, when exposed to VUV light. [13,14]. When doped with one of the rare earth ions, the UVC photons are further down-converted into visble light. In the case of undoped BAM, excited by VUV radiation of 147 and 173 nm, broadband UVC photons are emitted at 250nm with a very high efficiency. When doped with europium (Eu), all of the 250nm host-lattice emission is then transferred into visible blue light.

Another example of a the host-lattice emitter is undoped Y2O3, with a band gap edge (maximum absorption) of 208nm, and the host-lattice emission at 370nm. Contrary to the other PDP phosphors, Mn doped ZnSiO4 itself is a host lattice emitter; the green light is not emitted by Mn, but instead directly by the host-lattice, strongly Stark shifted. The resulting green emission is very broad banded, characteristic for hostlattice emission.

In undoped MgO self-trapped excitons do not occur [15]; nevertheless we observe a broadband CL and photo-luminescence that appears to be similar to that in the case of host-lattice emission. In order to understand this process we will describe the role of magnesium vacancies in MgO, forming so-called V-centers.

7. V-Centers

The V⁻ center in MgO is a magnesium ion vacancy with one hole trapped on a neighboring oxygen ion. The term V center however is also used generically to denote a hole trapped at a Mg^{2+} vacancy, including those associated with impurities, e.g., V_{OH} , V_A , as well as the unassociated V⁻ center. A review of defect centers in simple oxides including a discussion of the V⁻ center and impurity-associated hole centers is given by Hughes and Henderson. [16]

The conductivity of MgO single crystals doped with Al^{3+} , Fe^{3+} , or Sc^{3+} is directly proportional to the trivalent doping concentration. The activation energy for ionic conduction equals 202 kJ/mol (corresponding to a bonding energy of 2.0 eV), independent of the specific trivalent doping used [17].

Photon excitation of the positively charged anion vacancies (F⁺ centers) at 5.0 eV or higher energies releases holes that are subsequently trapped at V-type centers, which are cation vacancies, charge-compensated by impurities such as Al3⁺ and OH⁻ ions, often present as impurities in MgO [18]. The resulting defects, referred to as V_{A1} , or V_{OH} centers, have the following linear configurations: Al³⁺-O²⁻-[Mg vacancy]-O⁻ and Mg²⁺-OH⁻-[Mg vacancy]-O⁻ ;here the O⁻ represents an O²⁻ ion with a trapped hole.

The trapped holes at these centers are metastable and have a half-life of several hours at room temperature.

8. Recombination emission in undoped MgO

Figure 8 shows the delayed cathode luminescence of undoped MgO crystals at 78K, when exposed to 500-keV electrons, with values of time delay between the excitation and detection, measured by Williams, Williams, Turner and Lee (WWT&L) [19]. In addition to the strong 3.3 eV (380 nm) F⁺-center emission peak, they also find a broad emission peak at an energy varying from 5.3 - 4.9 eV, depending on the pulse delay. (Note: the emission peak is always referred by WWT&L to as the "4.9 eV" luminescence).

Lee and Crawford already demonstrated that crystalline MgO shows a CL emission at 4.9-eV, which luminescence is correlated with the concentration and thermal stability of the V-type centers i.e., holes trapped

at magnesium ion vacancies, acting as acceptors [20]. The 4.9-eV luminescence in MgO crystals is strongly increased by doping with hydrogen, and also by prior γ irradiation.





The nature of this so-called "4.9 eV" emission peak was studied in detail by WWT&L, and they conclude that the "4.9 eV" luminescence is the result of the tunneling recombination of an electron with a hole located on an oxygen ion, which is adjacent to a Mg^{2+} vacancy, rather than direct capture of a conduction electron by the V center.

In their un-doped MgO a hydrogen like donor was found to be associated with an electron trap, with an activation energy E = 0.06 eV. The thermal ionization of this trap controls the thermal decay of 4.9 eV luminescence.

Thermal ionization of the hydrogen-like donor is competing with radiative recombination. Thermal ionization of the donors, on a time scale faster than radiative recombination, can quench the 4.9-eV luminescence, whereas on a slower time scale the effect may be to enhance the 4.9-eV luminescence (glow peak) by redistributing electrons along the available donor sites.

Doping by transition metals (like scandium) was found to quench the 4.9eV recombination luminescence, presumably by competing with the V-centers as hole traps.

9. Effect of unintentional doping by impurities and hydrogen.

As discussed earlier, most MgO crystals contain hydrogen to a greater or lesser extent. The hydrogen in MgO:H doped crystals can be present in different forms, and is described in by Chen and Gonzalez et al. [21,22]. MgO- crystals with a large hydrogen content were produced by presoaking the starting MgO powder with water.

In case of processing of MgO with both oxygen vacancies and magnesium vacancies, and by exposing it to either hydrogen or water vapor, protons will fill both the oxygen vacancy and the magnesium vacancy, as shown in figure 4 [23]. The filling of the double negative oxygen vacancy by a proton results in a [H-] hydride ion, which has a positive charge; in figure 4 it is indicated as both p^+ and as [H⁻]⁺. The presence of [H⁻]⁺ ions can be seen from three sharp lines at 1024, 1032 and 1053 cm-1, corresponding to the fundamental vibrational frequencies in MgO, while OH- ions in the form of Mg(OH)2 precipitates show up as a 3700 cm-1 band. The presence of the V_{OH} defect is also exhibited by a characteristic optical-absorption band in the visible region at 2.3 eV (540nm) [23]

The filling of a magnesium vacancy by a proton on the other hand results in a V_{OH} center, which can be identified by the 3296 cm-1 infrared absorption band. The V_{OH} center is a special case of a so-called V_K center, where a cathion (magnesium) ion vacancy has one hole trapped on a neighboring oxygen ion, with a negative charge.



Figure 6 Schematic view of the rock-salt crystalline structure of MgO crystals containing $[V_{OH}]^-$ and $[H^-]^+$ centres. [from Gonzalez Review paper, Ref.24]

10. Aging process in a PDP and the creation of the V_{OH} type of defects.

External radiation at 5.0 eV induces a diffusion process, which involves the displacement of protons in the H-configuration and their relocation elsewhere in the crystal as hydroxil (OH) ions. In fact any form of ionizing radiation, such as γ rays, X-rays, or electrons, produces the V_{OH} type of defect, and an important effect of the aging process in a PDP.

The hydroxyl configuration is observed to be relatively stable at room temperature. The V_{OH} defect decays at room temperature with a half-life of a few hours, but disappears almost instantly at T=400 K.

Protons do not diffuse below T < 800K, and therefore the OH⁻ ion configurations are stable. However the OH⁻ ions become mobile during ionizing radiation at room temperature, resulting in the displacement of protons [Gonzalez Topical review, Ref 24]; this is probably happening in a PDP during sustaining

At high temperature crystallization, protons are randomly distributed throughout the MgO crystal and freeze in their substitutional sites during fast cooling, thus forming V_{OH} centers. However, if the crystal is cooled slowly the protons will move around and have ample opportunity to aggregate in Mg(OH)2 precipitates. These effects are relevant when comparing the properties of pure crystals made at high temperatures, with E-Beam evaporated MgO, where some of the original properties present in the MgO crystals are lost in the evaporated layer, depending on the deposition speed and substrate temperature.

11. Doping by impurities.

Si-doped MgO

Doping by silicon is one of the oldest methods used to reduce the address delay time jitter; see JP2005005086(A), US2004/0070341 and EP1408529(A2). The effect on the addressing jitter is shown in figure 10.

 SiO_2 is an oxide, with the Si^{4+} ion in the orbital shape of a Neon atom (completely filled 2s and 2p orbitals, i.e. completely spherical electron distribution), just like the case for Mg²⁺ inside MgO, making Si much more electronegative than Mg. (Note: electronegativity is a measure of the ability of an atom or molecule to attract electrons).

The defect chemistry of silicon doping unfortunately has not been described adequately. The impact will depend on the amount of oxygen and magnesium vacancies, and needs further study.

In the simple model, silicon acts as a shallow trap just below the conduction band, from which electrons can be released, either thermally or by locally strong electrical fields, as described by the Oster-Haddad exoelectron emission processes of type (i) and type (ii), described in section 3.

This behaviour is similar to the donor role of the [H⁻] hydride ions, discussed earlier; the Si-doping however will not change over the lifetime of a PDP, contrary to that of hydride ions.



Figure 7 Addressing discharge jitter as a function of Si-doping in MgO. Ref: LGE patent applications US2004/0070341 or EP1408529(A2)

Park & Kim of Hongik Un (K) investigated the effect of silicon doping of MgO, including the relationship with CL luminescence [25]. Using Si doping in MgO "pellets" they found very strong emission peaks at 250nm, as shown in figure 11; this CL peak wavelength differs from the 235nm CL emission peak of undoped submicron MgO crystals, used by Pioneer. The 250nm CL emission peak of MgO:Si was found to disappears after E-Beam evaporation.



Figure 8 CL spectra of MgO pellets doped with Al, Si, or Be at room temperature; [reproduced from Ref. 25 by Park & Kim, Hongik Un.]

Ca-doped MgO

Although self-trapping of holes and excitons is absent in MgO (and possibly also in CaO), calcium doping of MgO is very interesting. According to the Tartu group in Estonia, the presumed $Ca^{2+}O^{-}$ center in MgO (a hole trapped near an impurity calcium cation) is probably the closest analogue to a self-trapped hole in MgO. Doping by Ca strongly enhances the recombination luminescence of MgO at low temperatures, while shifting the energy from 5.5 to 6.8 eV at low temperatures (4K). The emission of MgO:Ca however disappears at room temperature.[27]

Be + H

The addition of BeO can also be used to create acceptor levels in MgO. There are a number of hole trap options. The most noticeable and the most investigated among them are the neutral V_{OH-Be} centers (the linear defect Be2+-O⁻-Vc-OH⁻), (where in this case Vc is the magnesium vacancy) and the positively charged [Be]⁺ centers, that is Be²⁺-O⁻, a hole trapped by an impurity Be2+ ion. [26]

In addition to these type of hole centers, $V_{\rm OH}$ centers are also present in such a material, that is the linear combination

 O^-Vc-OH^- . The V_{OH} centers however are only stable at room temperature, rapidly decreasing in number at a temperature of 70C. V_{OH-Be} centers on the contrary are stable at temperatures upto 400K [See Dolgov, 2002].

Park and Kim [25] found that PDP panels with hydrogen stabilized MgO:Be have a very small addressing jitter; unfortunately the use of BeO is not permitted by the industry.

In the case of hydrogen processed MgO:Be the electron donor and the hole centre might be physically close enough, to allow tunneling recombination, resulting in the emission of hot Auger electrons, according to the Oster-Haddad mechanism of type (iii). Direct measurement of the exoelectron current, emitted from pure single crystals is needed to confirm this possible effect.

Sc + Si and Sc+Ca

Another candidate for hole-type of doping is scandium. This type of doping has been patented both by LG and Mitsubishi Materials Company. See WO 20061006633,filed by MMC on 19.01.2006) and EP 1 679 732 A2 and US2006145614(A1), filed by LG on 05.01.2006.

Using either a high scandium doping level, or by codoping with SiO2, the MgO response time is strongly improved at low panel temperatures, as shown in figure 9.







The effect of a scandium doping depends on the nature of the defect it introduces. In case it would replace Mg^{2+} , it is expected to act as an electron trap and thermally excited donor, just like silicon. In combination with a magnesium vacancy however, it will be a V-type of hole trap, acting as a recombination center.

The table in figure 12 shows the impact of different doping levels for different combinations of materials. For all panel temperatures, from -20C up to +60C, doping by more than 500 ppm of scandium gives very low jitter values.

As we discussed earlier, a high level of scandium doping makes the MgO conductive at higher temperatures, thereby reducing the address voltage margin, similar to the effect of a high level of silicon doping. The address voltage margin is even negative, and therefore pure scandium doping should not be used.

The voltage margin was found to be improved by codoping the MgO:Sc with calcium, and therefore this might be the best compromise today. The effect of codoping with Ca however is not understood at all.

12. Conclusions

Two approaches are found to be effective to reduce the addressing jitter in a PDP. The first approach is the use of hydrogenated MgO crystals, containing a large amount of both oxygen and magnesium vacancies. In such a material electron-hole recombination can occur between electrons trapped at V_{OH} centers, and holes trapped at an adjacent magnesium ion vacancy. This probably results in the recombination emission of both 5.3 eV photons and of hot exo-electrons, needed for priming the addressing discharge.

The second approach is the use of polycrystalline materials, with extrinsic doping elements like Be or Sc, in addition to hydrogenation; the Be or Sc doping stabilizes the V-type of hole traps. The increased hole conductivity however reduces the wall charge collected. Therefore in its current form these types of materials do not result in both a small addressing jitter and a good addressing driving margin at the same time.

It is proposed that by using physically isolated submicron size crystals, on top of an isolating regular MgO layer, that the semi-conductivity of the crystals in both approaches can be avoided, resulting in a stable operation of the PDP, with a wide addressing margin.

We also emphasized the importance of aging to create a high density of V_{OH} centers. We did not discuss the dynamics of the possible recombination processes, but it will be clear that adequate pumping of the electron and hole traps is needed in order to maximize the non-radiative recombination and the emission of Auger electrons, as exo-electrons.

Finally it will be clear that much more experimental data are needed, for a better understanding of the different possible mechanisms in MgO, described in this paper.

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