Decrease of the number of the isolated emission center Mn$^{2+}$ in an aged ZnS:Mn electroluminescent device


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We observed a decrease of the number of effective emission centers Mn$^{2+}$ in the aged ZnS:Mn electroluminescence (EL) devices compared to the fresh EL devices using the electron-paramagnetic-resonance technique. Such phenomena can take place during the operation of the EL device, since the isolated Mn can easily diffuse into another site and forming cluster. Another possible explanation is that Mn$^{2+}$ changes into Mn$^{1+}$ or Mn$^{3+}$ by transferring the electronic charge of the isolated Mn$^{2+}$ to the neighboring Mn ions via sulfur and/or sulfur vacancy. As a result, luminescence is lowered due to the decrease in the number of efficient emission centers of isolated Mn$^{2+}$. © 1995 American Institute of Physics.

I. INTRODUCTION

Reports on aged electroluminescent (EL) devices (ELD) have concentrated on the aging characteristics and mechanisms as well as the process modification to improve performance$^{1-4}$ of ZnS:Mn ELD. These have been concentrated on mostly change of characteristics of the phosphor-insulator interface as a function of operating time. However, none of those works has investigated any change of the emission center itself even though the luminescent properties such as luminance intensity, emission wavelength, and decay time could be controlled by the properties of the emission center Mn. Recently, Muller reported an experimental result showing that the decrease of the concentration of the active dopants is one of the specific degradation mechanisms of the alkaline-earth sulfide-based color ELD.$^{2}$ Therefore, it is interesting to investigate the change of the active dopants or the emission centers associated with the aging phenomena which influence the luminescence and efficiency of ZnS:Mn ELD. Recently, it has been recognized that the properties of the emission center can be obtained from electron-paramagnetic-resonance (EPR) measurements of powder or thin-film phosphor.$^{5}$

In the present work we report the behavior of the emitting center Mn$^{2+}$ in the aged ZnS:Mn ELD. We consider that this study is unique in the sense that the aging characteristics are evaluated in terms of the change of the isolated Mn$^{2+}$ emission centers using EPR and photoluminescence (PL). EPR spectrum of the $S$-state ion Mn$^{2+}$ has provided a wealth of information about the local atomic environment of Mn in EL host material. This is because the spectrum is readily observable even at room temperature and reveals information about both the fine structure, which is determined by the magnitude and symmetry of the local electric field, and the covalent bonding with surrounding atoms, which is very sensitive to the changes in wave functions of 3$d$ electrons of Mn$^{2+}$. In this study EPR and PL experiments have been measured on the fresh and the aged Mn-doped ZnS ELD. Finally, the relationship between the change of the site symmetry and the number of isolated emission centers in both cases is discussed to understand a possible origin of the aging phenomena.

II. EXPERIMENTAL PROCEDURE

Mn(0.5 wt %)-doped ZnS powder was prepared from finely ground mixtures of high-purity (99.999%) ZnS powder and a trace of MnCl$_2$. The doping concentration was kept at 0.5 wt % to avoid line broadening due to the dipole-dipole interaction as well as to obtain maximum luminescence of the ELD. The mixtures were placed in an alumina crucible and fired for 1 h at a temperature about 1000 °C under N$_2$ flow of the rate of 5 l/min. The fired powder was pressed into the pellets to deposit ZnS:Mn thin films by electron-beam evaporation. We used a Hoya NA-40 glass substrate and the substrate temperature during the deposition was 180–220 °C. The upper insulator was deposited by the rf magnetron sputtering using 3 in. hot-pressed ceramic target (99.9% purity, Cerac Co.) under 10 mTorr of Ar+25% N$_2$ or O$_2$ at room temperature. Annealing was performed at 450 °C for 1 h in another vacuum chamber before the deposition of the upper insulator. Cautions were taken to avoid any extrinsic effects, i.e., adsorption of moisture, O$_2$, or CO$_2$. The resulting ac thin-film ELD consists of an evaporated ZnS:Mn active layer sandwiched between the sputtered BaTa$_2$O$_6$ insulator and Si$_3$N$_4$ interlayer. Aluminum- and Sn-doped In$_2$O$_3$ (ITO) electrodes were employed as row and column electrodes for matrix driving. The experiment was performed using ELD with X-Y matrix-type pixels. The aging duration in this test was chosen 200 h using the 5 kHz sine wave form with a voltage of $V_{\text{threshold}}+40$ as a driving source.

We have measured EPR signal of Mn center, and PL emission, and excitation spectrum. The equipment used for the EPR measurements was a Bruker X-band EPR spectrom-
S-state ion. The hyperfine structure results from the interaction between the nuclear spin of $^{55}$Mn and its electronic spin. The experimental results of the resonance fields can be analyzed with the usual spin Hamiltonian

$$H = \beta g \mathbf{B} \cdot \mathbf{S} + AS \cdot I,$$

where the first and second terms are the Zeeman interaction and the hyperfine interaction, respectively. $\beta$ is the Bohr magneton, $\mathbf{B}$ is the external magnetic field vector, $g$ is the spectroscopic splitting constant, $S$ is the effective spin vector, $I$ is the nuclear spin vector, and $A$ describes the hyperfine interaction.

The normal hyperfine interaction constant $A$ can be obtained by the first-order perturbation of the Zeeman term. The $A$ and $g$ factor are found to be $74.7 \times 10^{-4}$ cm$^{-1}$ and 2.005 at 300 K, respectively. These values are similar to those of the $^{55}$Mn$^{2+}$ ion in previous work on the cubic ZnS:Mn thin film. Since the hyperfine structure results from the interaction between the nuclear spin of $^{55}$Mn and its electronic spin, the experimental results of the resonance fields can be analyzed with the usual spin Hamiltonian,

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Therefore, of 12 possible nearest-neighbor sites to which the Mn atom is able to jump or diffuse, six will contribute to randomize the Mn$^{2+}$ profile. According to reported results, the clustering of Mn centers with an anion (sulfur) vacancy as the first nearest neighbor, if they are really formed, has $C_{3v}$ symmetry and does not contribute essentially to the spectral properties of ZnS:Mn, but, the symmetry lowering or the electron delocalization produced by the clustering is consistent with the observed phenomena such as the emission shift to longer wavelength and large absorption in the UV or IR region. The isolated $(\text{Mn}_2-\text{S}_7)^{10-}$ cluster has $T_d$ symmetry. The $(\text{Mn}_2-\text{S}_7)^{10-}$ cluster, which is assumed in this article, consists of a pair of Mn ions as the first nearest neighbors (1 nn) in the cubic ZnS lattice.

At a glance Mn clustering seems to contradict the basic thermodynamic requirement for a statistical uniform impurity distribution in the host lattice. However, from a quantum-mechanical point of view, the substitution of Zn$^{2+}(d^{10})$ by a Mn$^{2+}(d^5)$ activator brings the electron deficiency. This electron deficiency can be resolved by delocalization of electrons via bringing the Mn ions closer in order to let them share the available electrons. If this is the case, then the orbital population and the symmetry restrictions should play a very important role in the clustering effect.

The total energy lowering of the system due to clustering makes it favorable for Mn ions to form clusters in the lattice and it is theoretically confirmed. The reasons for the clustering are as follows. Mn$^{2+}$ broadens the ZnS band gap by about 10% and the Mn$^{2+}$ states are located deep in the filled valence band. Hence, the electron redistribution may occur reducing the charge on Mn, making its orbitals more diffusive and ready for the electron delocalization. The clustering is expected to decrease the electron repulsion near Mn centers via electron delocalization and to enhance the competi-
tion for the sulfur orbitals which in turn will lower the Mn—S bonding parameter and thus reduce the d-orbital splitting.

Figure 5 represents the splitting of the energy level of Mn ion sited at various symmetries, and the emission and absorption processes. Lowered symmetry such as C₃ᵥ and C₈ due to clustering can result in the shift of transition to longer wavelength. Further evidence supporting the concept of clustering (pairing) is the result of the calculation on the statistical probability of presence of the isolated and the clustered Mn²⁺ in ZnS fcc lattice as a function of doped Mn concentration shown in Fig. 6. In our case, since the upper interface contains a high concentration of Mn, the possibility of Mn clustering seems to be very high.

If the clustering occurs, the most probable subsequent process in this cluster such as Mn²⁺−S−Mn²⁺ is the interaction between neighboring Mn ions. Then the electronic charges of the isolated Mn²⁺ can be transferred into the neighboring Mn²⁺ through bridging sulfur ligand or sulfur vacancies. One possible excitation most likely to occur is as follows:

\[ \text{Mn}^{2+} - S^2 - \text{Mn}^{2+} + \alpha(\text{Mn}^{1+} - S^2 - \text{Mn}^{3+}) \]

where \( \alpha \) is a small admixture coefficient. If this is the case, there must be EPR signals from Mn³⁺ and Mn¹⁺; however, no EPR resonance that can be directly attributed to Mn³⁺ has been observed in our measurements. Until now, there have been rare reports on the detection of an EPR resonance signal from Mn¹⁺. In our resonance spectrum, we could not detect any signal from the Mn¹⁺ or Mn³⁺ but only the decrease of signal intensity was observed.

The excited state energy can be estimated as a few eV from the ionization potential. Because the above model was based on the assumption of the presence of the Mn-rich region such as the upper interface, we assume that activation energy arises from electron dynamics at near interface. When highly energetic electrons are impinged against the conduction-band discontinuity between upper insulator and ZnS, they must dissipate a significant amount of energy to transit to the bottom of the phosphor conduction band and to be trapped at interface states. It is likely that the hot-electron transition energy near the upper interface is important in the charge-transfer process. In these cases, isolated Mn²⁺ concentrated at the interfaces can be changed into Mn¹⁺ or Mn³⁺. As a reference, we quote the report by Watkins who observed a decreasing EPR signal from isolated Mn²⁺ whenever visible light (2–3 eV) gave rise to a transition Mn²⁺−Mn³⁺. Also, we want to point out that on the contrary to the dramatic decrease of the number of isolated Mn³⁺ centers, the luminance of the aged ELD decreased just by a small amount. This result suggests that Mn clusters or pairs as well as isolated Mn²⁺ can act as a luminescent center in the aged ELD within the limited case. However, the main reason for the lowered luminance, although small, of the aged ELD with an e beam evaporated ZnS:Mn layer would be ascribed to the decrease in the number of an efficient Mn¹⁺ emission center.
V. CONCLUSION

In this work, we report for the first time a decrease of the number of isolated Mn in an aged ZnS:Mn phosphor layer, observed by EPR experiments. Such phenomena can be explained by the clustering of Mn ions, which is favored by both the quantum-mechanical aspect and lowering the system energy. Another possible explanation is that the electronic charge of the isolated Mn can be changed into Mn$^{1+}$ or Mn$^{3+}$. As a result, luminance of EL device is lowered due to the decrease of the number of efficient center of the isolated Mn$^{2+}$.

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