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CRYSTALLINE STRUCTURE AND DOPING LEVEL OF THIN ELECTROLUMINESCENT ZnS:Mn LAYERS

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Abstract - Comparing electrooptic and microstructural properties of electroluminescent (E.L.) ZnS:Mn thin layers, we showed the increase of the luminance with the grain size; meanwhile the annealing under specific conditions induces two simultaneous effects: the E.L. threshold voltage is lowered and the Mn concentration in the depth of the active layer is modified.

High field ac thin film ZnS:Mn electroluminescent devices (ACTFEL) have been reported as having many useful and interesting characteristics for display applications [1], [2]. However the microstructure of the various layers in such devices have been scarcely studied [3],[4],[5]. As the electrooptic properties of the devices depend upon the growth and annealing conditions, this work tends to correlate them with the microstructural properties of the ZnS layer, deduced from STEM microscopy and microanalysis.

EXPERIMENTAL

A. Specimen growth and annealing method

We have used the conventional double-insulated structure of ACTFEL devices shown on Fig.1. The various layers are deposited under vacuum on a glass substrate by electron beam evaporation. The ZnS:Mn active layer is evaporated from a doped source material obtained by intimate mixing between ZnS powder and various Mn compounds (MnS, MnF2, MnCl2). During the ZnS evaporation, the substrate is either at room temperature or heated at approximately 150°C. In some cases a three hour annealing at 470°C is performed under various conditions given in Table 1.

B. Specimen preparation for transmission electron microscopy

To be observed by transmission electron microscopy ZnS:Mn layers have to be separated from the other layers and thinned from the side which is in contact with the HCl diluted etchant to a thickness of less than 100 nm. The usually observed side is the growth end side, but not exactly the top, because part of the ZnS layer (estimated to about 100nm) is taken away during these operations. Cross-sections are also observed. Specimen are thinned down to less than 50μm by grinding and mechanical polishing. Further thinning to less than 100nm is obtained by ion milling.

C. Microanalysis specifications

Microscopic study is performed on a dedicated scanning transmission electron microscope (STEM VG HB5) equipped with an energy dispersive XRay detector (KEVEX)
Quantitative microanalysis of the Mn distribution is possible taking into account the ionization cross-section, the fluorescence yield and the weight of line of the X ray peaks. Let us call:
x the mass concentration percentage of Mn in stoichiometric ZnS
I(E) the half width integrated X ray intensity of the X peak emitted by the element E
We can show that \( I(Mn)/I(Zn) = x \times 1.95 \).
We checked this result by comparing STEM averaged Mn concentration with atomic absorption measurements.
Absorption corrections are always negligible: in all our measurements the decrease of the \( I(S)/I(Zn) \) ratio as compared to its value without absorption is smaller than 20\%, which makes it sure that the absorption correction on the \( I(Mn)/I(Zn) \) ratio is smaller than 2.5%.
A usual counting time of 5 to 10 minutes and a typical x value of 0.4\% correspond to \( I(Mn) = 350 \text{ cts} \quad I(Zn) = 40000 \text{ cts} \)
The statistical uncertainty upon the Mn concentration is then:
\[ \Delta x/x = \sqrt{\frac{1}{350} + \frac{1}{40000}} \approx 6\% \]
With a thickness of about 50nm, the probe size at the specimen output remains smaller than 5 nm, the random movements of the probe on the specimen are usually smaller than 5 nm, so the spatial resolution of the microanalysis is better than 10 nm which is always smaller than the grain size.

D. Electrooptic measurements
Voltage, current and light output are measured on the devices driven with a 5 kHz sinusoidal waveform. In the following sections, the E.L. will be simply characterized by the threshold voltage and the saturation luminance as defined on the luminance versus applied voltage curve of Fig.2. More sophisticated measurements, taking into account the polarity, allow to distinguish the E.L. contribution of each \( Y_2O_3/ZnS \) interface.

RESULTS

A. Cristallinity
As shown on the transmission bright field micrograph of Fig.3, the ZnS layers are polycrystalline, with disordered grains of various shapes. The enlarged micrograph of Fig.4 shows within one ZnS grain a black and white strip contrast corresponding to microtwins parallel to \( (111) \) planes, spaced by 2 nm, characteristic of ZnS polytypism. They also appear on the cross-section micrograph of Fig.5, nearly parallel to the interface which indicates a \( <111> \) preferred orientation of the ZnS grains [4]. Fig.5 micrograph is reconstructed from several images corresponding to different exposures. We notice in the first 100 nm of the layer a granular structure (20 nm grains). Then a columnar structure appears: the columns grow nearly perpendicularly to the interface, their diameter increases in the first 2-300 nm and then reaches a mean va-
value of about 70 nm which remains steady up to the end of the growth. The average grain size at the end of the growth is independent of the Mn compound used for the source material, increases with the substrate deposition temperature from 30 nm at room temperature to 70 nm at 150°C. Usually grain size is not modified by annealing but sometimes an increase is observed. In both cases of deposition on a heated substrate and of annealing, a larger mean grain size always induces a higher saturation luminance. These results are partially shown on Table 1.

B. Manganese distribution (see Table 1)

As shown previously by Kun [6] best results are obtained at room temperature with ZnS:MnCl₂ source material. The dopant is homogeneously distributed in the layer (variations from center to edges in the same grain or between two grains are less than ±5%) and the luminance is relatively high and homogeneous on a macroscopic scale. With other Mn compounds MnS or MnF₂, the Mn insertion is much more difficult and its distribution becomes very inhomogeneous: variations from one part of the specimen to another reach 100%. This can explain the poor luminance level observed with these layers. However, ZnS deposition on heated substrate from MnCl₂ doped source yields a poorer homogeneity: local variations are now of ±20%.

Annealing does not change the Mn homogeneity parallelly to the layer but changes noticeably its distribution in depth as shown on Fig.6. Before annealing the Mn concentration is the same across the whole ZnS layer thickness: we did not notice neither the presence of Mn precipitates nor a Mn concentration gradient in the layer thickness as mentioned by Oppolzer [4]. After vacuum annealing with the ZnS layer as the external layer of the device, the Mn concentration decreases in a region laying between 100 and 200 nm from the external surface and increases.
near this surface. Correlated with the Mn concentration gradient near the second Y2O3/ZnS interface, one observes a decrease of 50 Vrms of the threshold voltage and a clear asymmetry in the electrical response of the device with the polarity of the applied voltage. None of these phenomena appears when annealing is performed after the second dielectric layer deposition, where no Mn migration is observed. However, in the case of annealing under nitrogen flow without the second dielectric layer, the results are intermediate and need further investigations: we observe a Mn migration, a small threshold voltage decrease (25 Vrms), an unusual low resistivity and no asymmetry.

CONCLUSIONS

This work corroborates the way of improving E.L. properties of ACTFEL devices. Luminance increases with Cl presence in the source material and with bigger grain size obtained by heating the substrate during deposition. High temperature (470°C) vacuum annealing before the deposition of the second Y2O3 layer induces a decrease of the threshold voltage, which is perhaps explained by the different electron injection conditions at this interface due to the Mn concentration increase. At the same time, poorer dielectric properties and undesired polycrystalline microstructure of the annealed Y2O3 layer have been observed. These two topics need further investigations as well from the microscopical point of view as from the electrical one.

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