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Manganese Doped ZnS Grown by Plasma-Assisted MOCVD

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Fluorescent thin films with transparency, surface-flatness and high luminescence efficiency are potentially applicable to high-resolution vacuum fluorescent display (VFD) and electro-luminescent devices. Recently, the metalorganic chemical vapor deposition (MOCVD) technique attracts much attention to producing high-quality thin films of compound semiconductors. It is therefore interesting to know whether MOCVD is capable of fabricating practical device-quality materials of II-VI compounds. In this work, we have introduced an rf plasma decomposition in the MOCVD growth of ZnS, for which effective decomposition of the Mn compound source as well as reduction of the growth temperature are simultaneously achieved. As a preliminary step, the fabrication of VFD has been tried using ZnS:Mn deposited on the metal-coated glass substrate which acts as an anode.

Thin layers of ZnS:Mn were prepared by a plasma-assisted MOCVD using diethylzinc (DEZ) and H_2S as source materials, and tricarbonylmethylcyclopentadienyl manganese (TCM) as a dopant source. A selected area plasma (13.56 MHz) was introduced in the reactor, which was not in contact with substrate surface. TCM and H_2S were passed through the plasma, whereas DEZ was introduced separately, not being in contact with the plasma, and was considered only thermally decomposed. A smooth surface typically resulted when layer thickness was less than 1μm. Figure 1 shows typical

room temperature photoluminescence (PL) spectra of Mn-doped ZnS layers. It is apparent that the plasma enhances the decomposition of TCM, resulting in higher incorporation of Mn. Figure 2 shows the emission intensity of a VFD structure using ZnS:Mn films as a function of anode voltage for different layer thicknesses.
A uniform light emission has been observed from the preliminary devices, indicating that the film has smooth surface and is free from pinholes. Although it is well known that ZnS has naturally quite low conductivity, we can see fairly low threshold voltage for the VFD light emission when reducing the film thickness (Fig. 2). This indicates that the building-up of negative potential on the surface can be avoided when employing a sufficiently thin film. Possible higher-efficiency emission as well as lower threshold voltage include an optimization of the Mn concentration and an Al co-doping.

In conclusion, thin, uniform and high-quality ZnS:Mn films have been successfully grown at low substrate temperature by the selectively plasma-assisted MOCVD technique. A promising new application of the films to VFD devices has been demonstrated.

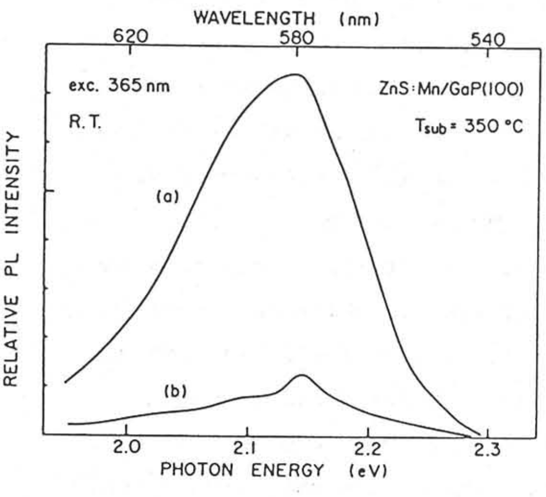

Fig. 1 PL spectra of ZnS:Mn grown a) with plasma and b) without plasma.

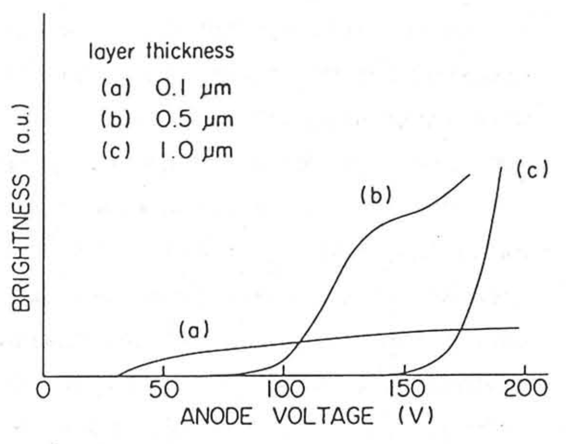

Fig. 2 Anode voltage dependence of VFD brightness.