A New Technique for the High Rate Deposition of EL Devices onto Plastic Substrates

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1. Introduction

The deposition of thin film EL structures requires the close control of multiple process parameters in order to achieve reliable, efficient devices. This paper describes a new technique referred to as High Target Utilisation Sputtering (HiTUS) for the deposition of thin film coatings. HiTUS offers a much larger parameter space than other conventional sputtering techniques and hence allows for the deposition of films with qualities that other techniques can not achieve. The luminance results of EL devices with the double insulating layer structure are presented, demonstrating the feasibility of low temperature deposition for flexible display, lighting and indicator applications. These devices have been deposited onto plastic materials with no substrate heating or post deposition annealing and comprise thin films of ITO, Y_2O_3 and ZnS:Mn all deposited using HiTUS.

2. High Target Utilisation Sputtering

The coating process utilises a remote, high density plasma (10^{13} ions cm^{-3}) that is generated in a side arm adjacent to the deposition chamber. See figure 1. This side arm is referred to as the plasma launch system (PLS). It consists of a quartz tube surrounded by a copper antennae coil. The antennae couples RF power into the argon gas at reduced pressure. Electromagnets at the exit of the PLS enhance and steer the plasma onto the target. Under these conditions the argon ions have insufficient energy (between 30 and 50 eV) to sputter. The application of a sufficient negative DC bias to the target results in a high current density over the full surface area of the target. This yields high rate, uniform erosion of the target surface. The HiTUS system used for this work accommodates four, 10.2 cm diameter, water cooled targets allowing for deposition of complete electroluminescence (EL) structures without needing to break the vacuum.

By using a remotely generated plasma, that is not driven from the target, we have independent control of the target voltage and plasma intensity. Of prime significance is the virtual elimination of target poisoning since the surface of the target is uniformly eroded. This not only results in a stable process but also enables very high rate deposition of ITO (70 nm/min), Y_2O_3 (30 nm/min) and ZnS:Mn (50 nm/min). This decoupling of the plasma density and target voltage also gives us more flexibility over deposition variables. It has been shown that by using this technique the structure of thin films of ITO can be influenced by variation of the RF power (independent of the target voltage), offering the possibility of depositing crystalline ITO without the need for any substrate heating (to be written up as part of a separate publication). This localised energy also offers advantages when depositing films onto flexible substrates since with careful control of the RF power, significant energy can be imparted to the growing film without heating the substrates. These polymeric materials are all immersed in a diffuse, high intensity plasma prior to deposition. Since they are not electrically biased, the impinging low energy argon ions remove any volatile species that may be present on the substrate surface without any deterioration of the plastic.

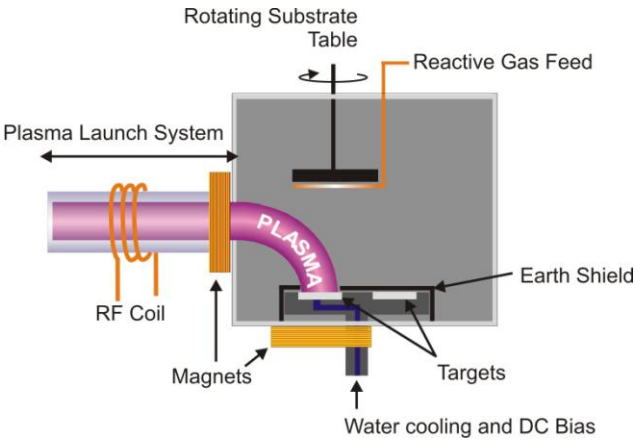

Figure 1. A schematic showing the HiTUS system

All the films discussed in this paper were deposited by reactively sputtering from a metallic target. In the case of ITO a 90:10 wt.% In:Sn target was used. For the ZnS:Mn coatings three different Zn targets were used with different concentrations of Mn (0.4, 0.5 and 0.6 wt.%). Oxygen and hydrogen sulphide (H_2S) were used as the reactive gases.

3. Photoluminescence Results

Single layers of ZnS:Mn, Y_2O_3 and ITO were initially deposited onto microscope glass slides and silicon wafers with no substrate

heating or post deposition annealing. This made the process directly transferable to plastic substrates.

3.1. ZnS:Mn

Prior to making a complete electroluminescent device using ZnS:Mn as the active, light emitting layer, individual films were first optimized for photoluminescence (PL). This was achieved by variation of several deposition parameters including the H_2S flow rate, target power and concentration of Mn in the Zn target.

3.1.1. Variation of H_2S flow rate for fixed target power

For a fixed DC power applied to the target, the flow rate of H_2S was steadily increased until the films became transparent and started to show intense PL. PL measurements using a pulsed nitrogen laser (337 nm) as the excitation source showed that the intensity of the light emission peaked at approximately 600 nm, characteristic of emission from the Mn phosphor. For good adhesion to glass it was necessary to deposit films at process pressures in excess of 8.5×10^{-3} mbar. Figure 2 shows the PL intensity for several films deposited with different H_2S gas flow rates. The target power in all cases was 500 W and the films were approximately 500 nm thick. The PL intensity improves up to a flow rate of 66 sccm of H_2S as the films become more transparent. Beyond this, an excess of sulphur within the material results in deterioration of the PL intensity. The reasons for this are currently being investigated.

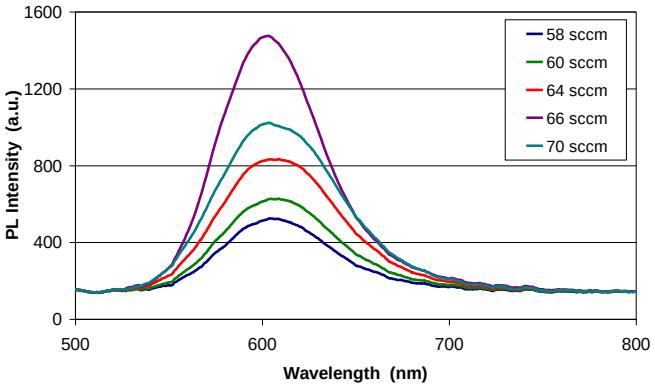

Figure 2. Variation of PL with H_2S gas flow.

3.1.2. Effect of target power on PL

Target power essentially controls the deposition rate. This has been seen to influence the quality of the ZnS:Mn coatings. For optimum PL the inclusion of Mn within the ZnS lattice must be carefully controlled. Both the concentration of Mn ions and their location determine how effective the ZnS:Mn will be as a light emitter. A small number of Mn impurities will result in very week emission whereas too many will result in non-radiative emission due to the overlap of neighboring electron states – the concentration quenching effect [1]. The energetically favorable position for the Mn ions is to substitute the Zn within the ZnS lattice. In this position they are active luminescent centers that contribute to the emission of light. If they sit interstitially within the host lattice they act as scattering centers for electrons. Figure 3 shows how the deposition rate affects the PL intensity.

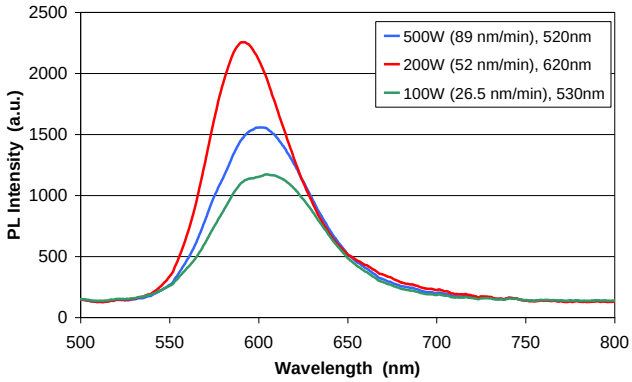

Figure 3. Variation of PL with target power

For optimum PL it is necessary to deposit the ZnS:Mn at an intermediate rate. It seems likely that excessively high deposition rates do not give the atoms arriving at the growing film time to find their energetically favorable position and hence this leads to a greater number of Mn impurities at interstitial locations. This is possibly something that could be addressed in future work by increasing the RF power. This has the effect of increasing the energy of the adatoms thus improving their mobility and could subsequently increase the probability of a Mn ion substituting a Zn atom during film growth. Slower deposition rates allow time for the growing film to incorporate more unwanted impurities thus deteriorating the film quality.

3.1.3. Effect of Mn concentration in Zn target

It has been shown that Mn doping at approximately 0.45 wt.% for RF magnetron sputter deposited ZnS:Mn results in an optimum emission for both optimum PL and EL excitation [2], which is consistent with the widely reported EL optimum of 0.4 – 0.5 wt.% [3, 4]. However, it is not correct to assume that a Zn target doped with 0.45 wt.% Mn will yield a film with the same concentration of Mn. Hence three Zn targets have been used with differing concentrations of Mn. Figure 4 shows the optimized PL intensity for ZnS:Mn films deposited from Zn targets with 0.4, 0.5 and 0.6 wt.% Mn. It is clear that the higher dopant levels yield the best PL.

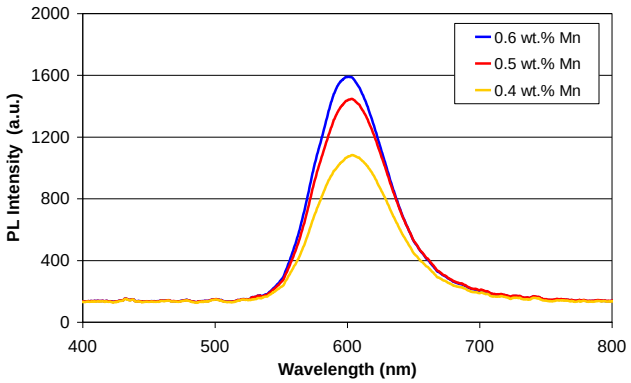

Figure 4. The effect of varying concentrations of Mn in the Zn target

3.1.4. Correlation between PL and film thickness

Thin films with a range of thicknesses from 200 nm up to 1 µm were deposited at a deposition rate of 90 nm/min. Figure 5 shows how the PL intensity improves with thickness. All the devices in this work were deposited with 800 nm of ZnS:Mn. Whilst thicker films exhibit brighter PL, they also require higher drive voltages making the electronics more difficult and costly to implement.

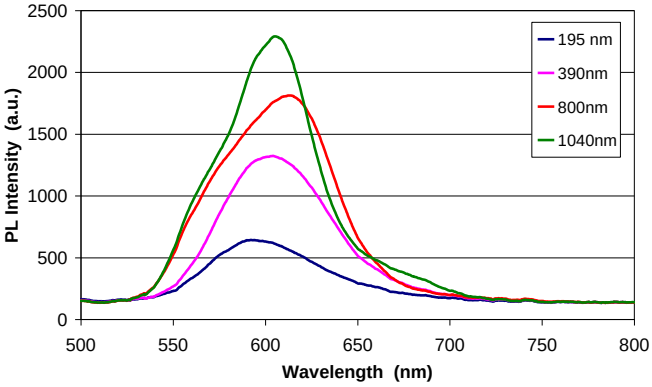

Figure 5. Improvement of PL intensity with increased film thickness

4. Electroluminescence Results

The PL measurements indicate that ZnS:Mn deposited using HiTUS should perform well as part of an EL device. The standard double insulating layer structure has been deposited onto Si wafers, glass and planarised PET substrate materials. A function generator with a frequency output of 1 kHz was used to drive the devices. Applied voltages of up to 700 V peak-to-peak were used with increments of 10 V every 5 seconds.

200 nm of ITO was deposited onto planarised polyethylene terephthalate (PET) as the back contact electrode. Earlier work on ITO deposited using HiTUS showed that this transparent conducting oxide can be deposited with very low resistivity (< 4.0 x 10^{-4} Ωcm) and high optical transparency (approximately 90%) onto flexible substrates [5]. The choice of dielectric material is essential to any EL device. It must have a breakdown strength high enough to support the additional field that is not dropped across the light emitting layer (approximately 1.5 x 10^{8} V/m) and should also be free from pin holes or any other kind of defects that might lead to shorting of the two electrodes. 300 nm of Yttria was used as the dielectric layer either side of the active, light emitting ZnS:Mn (800 nm). A further 200 nm of ITO was then used as the top contact. Figure 6 shows the transmission profile of a complete device deposited onto a glass substrate. The transparency at 600 nm is approximately 95%.

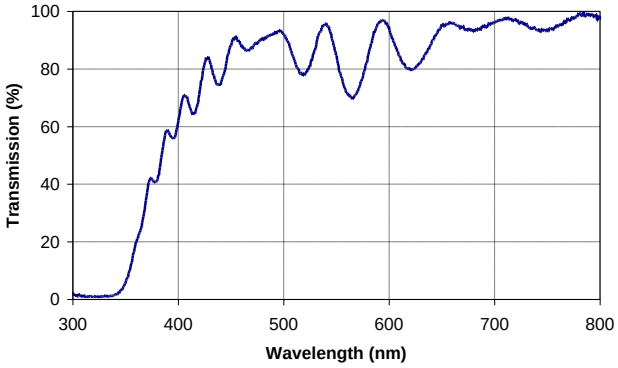

Figure 6. Transmission profile of a complete EL device with ITO-Y_2O_3-ZnS:Mn-Y_2O_3-ITO structure.

Figure 7 shows how the luminance changes with increasing applied voltage for devices deposited onto both glass and PET substrates. Both the devices were deposited with no substrate heating or post deposition annealing. A smooth increase in luminance is seen for voltages above 400 V peak-to-peak. The maximum luminance recorded was 25 Cdm^{-2} for both devices. These were the first EL devices deposited using the HiTUS technique and further work looking at the optimization of the layers within this structure is currently underway. This includes looking at the potential for combined HiTUS and laser processing [6] which could improve device performance and help to realize low temperature, high intensity EL devices for flexible device applications.

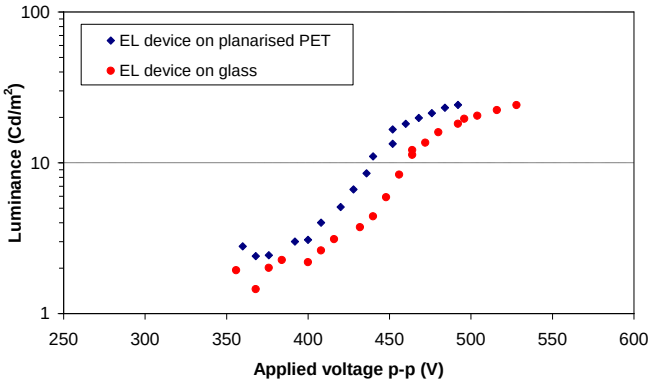

Figure 7. EL intensity as a function of applied voltage for a device deposited onto planarised PET at room temperature with no post deposition annealing.

5. Conclusions

EL devices with the double insulating layer structure have been deposited onto polymeric materials with no substrate heating or post deposition annealing using a new method of thin film deposition. ZnS:Mn has been used as the active, light emitting layer. PL measurements show that when these films are deposited using HiTUS, they emit high intensity light centered at approximately 600 nm. When deposited as part of a complete EL structure these devices are seen to exhibit stable electroluminescence for voltages in excess of 400 V peak-to-peak.

6. References

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