Inorganic Phosphors and ACTFEL Devices on Flexible Plastic Substrates

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INTRODUCTION

Interest in organic and polymer light-emitting devices (OLEDs and PLEDs) has exploded in recent years, in part because of the ability to create these devices on flexible plastic substrates. This is advantageous in producing wearable or lightweight displays, as well as utilizing low-cost roll-to-roll processing techniques. For the first time, we present crystalline refractory *inorganic* thin films, as well as alternating-current thin film electroluminescent (ACTFEL) devices, deposited on flexible plastic substrates.

EXPERIMENT

Our group has previously reported the preparation of crystalline oxide powders using a hyderthermal dehydration technique. [1] Hydroxylated, amorphous precipitates are heated in a sealed, Teflon-lined high pressure “bomb” reaction vessel (Parr Instruments) so that drying occurs under equilibrium conditions with concomitant crystalite nucleation and grain growth, resulting in anhydrous crystalline powders. Hydrothermal dehydration is also used to produce crystalline thin films of refractory oxide materials, such as ZrO_2, MnO_2, and Zn_2SiO_4. [2] Crystallization of suitable amorphous oxide thin films deposited via conventional techniques can be accomplished using a modification of the hydrothermal dehydration process in which water is added to the reaction vessel in addition to the sample. For example, we have reported highly crystalline thin films of the bright green emitting phosphor Zn_2GeO_4:Mn following the hydrothermal annealing of amorphous rf sputter-deposited films in this manner. [3]

A key advantage of hydrothermal dehydration and annealing is the ability to produce highly crystalline powders and films of refractory oxides at temperatures as low as 125 °C. This low processing temperature makes possible the creation of crystalline films on thermally unstable materials such as plastics. This may have important ramifications for the display industry because a large number of oxide materials are known to be luminescent, including several bright oxide ACTFEL phosphors. [4]

For the present work, amorphous thin films of Zn_2GeO_4:Mn are deposited by rf magnetron sputtering onto flexible, plastic substrates. These films are crystalized using the hydrothermal annealing method, possible due to the small solubility of Zn_2GeO_4 in water under the anneal conditions. The viability of various substrates are investigated and processes are developed for the fabrication of complete, operational ACTFEL devices on flexible substrates.

RESULTS AND DISCUSSION

The sputtered Zn_2GeO_4:Mn films show high crystallinity and bright photoluminescence (PL) following hydrothermal annealing at temperatures as low as 125 °C; for comparison, conventional furnace annealing requires a minimum of 625 °C to achieve PL; the PL intensity of films hydrothermally annealed at 200 °C for 2 h is about the same as for those annealed in a furnace at 680 °C for 2 h. Furthermore, film roughness can be controlled between tens of nm to approximately the entire thickness of the deposited film by varying the anneal parameters – temperature, time, and amount of water added.

The substrate material must be chosen with care. It must be able to withstand 150 °C, be flexible, must withstand short-term exposure to UV radiation and oxygen radicals during film deposition, and must withstand short-term exposure to high pressure in the presence of water during the hydrothermal anneal step. Most of the plastic films available fail to meet at least one of these criteria. These include the polyester (PET) films widely used as the basis for flexible substrates for OLED/PLED applications, which were found to exhibit severe dimensional instability under the hydrothermal annealing conditions. Other common plastic films are destroyed completely. However, several easily available plastic substrates of varying suitability have been identified.

Polypropylene (PP) is attractive due to its extremely low cost. Adhesion of the sputtered zinc germanate films to untreated PP is found to be poor, the PP is only marginally able to withstand the heating due to the sputtering process, and the hydrothermal anneal causes the PP to shrink significantly and become brittle and inflexible. However, the PP substrates may be initially treated to a hydrothermal treatment, which causes the dimensional stabilization of the substrates; the substrates are then unaffected during the sputter deposition. Following this initial hydrothermal treatment, the substrates are exposed to an rf glow discharge of 8% O_2 in Freon-14 (CF_4). This step results in very good adhesion of the subsequently sputtered zinc germanate film to the substrate. A second hydrothermal anneal results in bright green photoluminescence from a crystalline refractory oxide film on an inexpensive, lightweight plastic substrate. However, the post-anneal brittleness and opaqueness of the PP limit its attractiveness as a substrate for a display.

Kapton polyimide (PI) films from DuPont are also investigated as substrates. Adhesion of zinc germanate to these films is poor to marginal, depending on the type of Kapton, but becomes excellent when a thin layer of Ti is deposited before the Zn_2GeO_4:Mn; plasma treatment as with PP substrates is ineffectual. Hydrothermal annealing leads to bright PL from a high-quality film on a flexible substrate. For ACTFEL device fabrication, the dark amber color of the PI necessitates the use of an inverted structure. A thicker (50-100 nm) layer of Ti is deposited to serve as both adhesion layer and bottom contact. A 500 nm thick layer of Zn_2GeO_4:Mn is deposited and hydrothermally annealed. A 300 nm thick SiO_2 dielectric layer is then deposited via ion beam sputtering (IBS). This insulator is chosen as the best low-temperature (unheated substrate) dielectric process available; because the thermal coefficient of expansion is very high for the PI substrate, cooling after deposition of a thin film at an elevated temperature will result in compressive stress in the thin film and subsequent undesired warping of the flexible substrate. Finally, a 320 nm thick transparent top contact of indium tin oxide (ITO) is deposited via IBS to complete the ACTFEL device. The substrate and thin film stack may be moderately bent without cracking or buckling of the films. These devices are found to perform similarly to ACTFEL devices with hydrothermally annealed Zn_2GeO_4:Mn phosphor layers on glass previously reported [3], demonstrating electroluminescence (EL) of a few nits.

A third substrate material, cyclic olefin-based Appear 3000 from Promerus, is 92% transparent, obviating the necessity of using an inverted structure for ACTFEL device fabrication. Instead, IBS is used to deposit a thin Ti adhesion layer, 160 nm ITO bottom conductor, another thin Ti adhesion layer, and a 300 nm thick SiO_2 dielectric layer. A 500 nm thick layer of Zn_2GeO_4:Mn is then deposited and the device is hydrothermally annealed. Finally top contacts of Al are deposited. Note that an additional adhesion layer is necessary to prevent delamination of the SiO_2/Zn_2GeO_4:Mn layers following the phosphor deposition that was not necessary for the PI substrates, presumably due to the much higher coefficient of thermal expansion of the Appear 3000. At the same time, the lower tensile modulus of the Appear 3000 makes it more sensitive to warping due to accumulated stress. The finished ACTFEL devices perform similarly to those on PI.

CONCLUSION

For the first time, crystalline refractory oxide thin films have been deposited on flexible plastic substrates. Hydrothermal annealing of amorphous Zn_2GeO_4:Mn deposited via rf magnetron sputtering on a variety of substrates results in highly crystalline films exhibiting bright green PL. Complete single-insulator ACTFEL devices are fabricated and illustrate the ability to create displays on flexible substrates utilizing exclusively inorganic materials and very low processing temperatures. More work is required to incorporate better low-temperature dielectric materials, improve the EL performance of hydrothermally annealed Zn_2GeO_4:Mn films, and investigate the viability of other hydrothermally annealed oxide phosphors.

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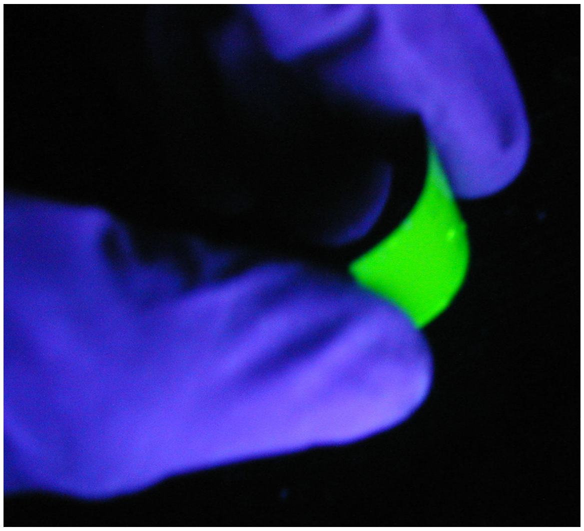

Figure 1: A 450 nm thick film of Zn_2GeO_4:Mn deposited on a flexible polyimide substrate shows bright green PL after hydrothermal annealing.

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