PP-TOFMS Depth Profiling of ZnO Thin layers co-doped with Rare Earths for Photonic Materials

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Abstract

This note reports on an example of depth analysis by plasma profiling time of flight mass spectrometry of rare earth doped materials: codoped Eu and Tb ZnO thin layers developed for making white LEDs.

Key words
PP-TOFMS, fast depth profile, rare earths, thin films, photoluminescence, magnetron sputtering, photonics

Introduction

The rare earth elements (REEs) form a chemically uniform group and include yttrium (Y), lanthanum (La) and the lanthanides cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (they are highlighted in the periodic table shown in Figure 1). REE unique electronic, optical, luminescent, and magnetic properties have made them attractive for a variety of applications[1] (Figure 2). Recently, considerable research activity is being carried out on rare earth (RE) doped materials for photonics[2]. Among these materials, the optical properties of ZnO studied extensively for various applications in the photoelectrochemical cells, diluted magnetic semiconductors (DMS), field effect transistors, and photoluminescence devices may be tailored by RE doping for wide range electroluminescent devices (white LEDs). In RE-doped ZnO, the intra-ionic 4f transitions of RE ions form luminescent centers which generate narrow and intense emission lines at infrared and visible wavelengths.

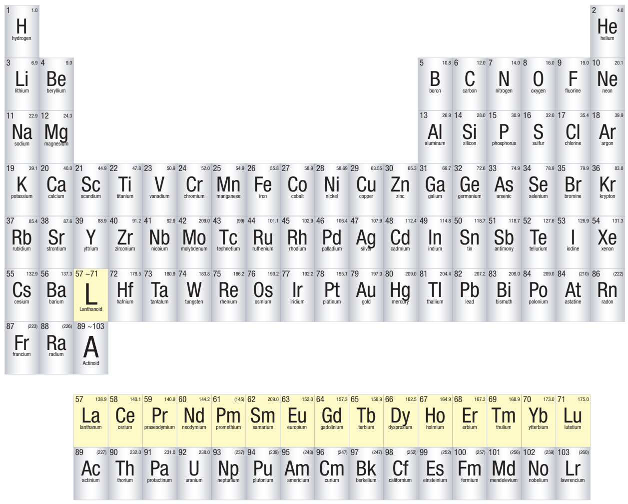

Figure 1: Periodic table

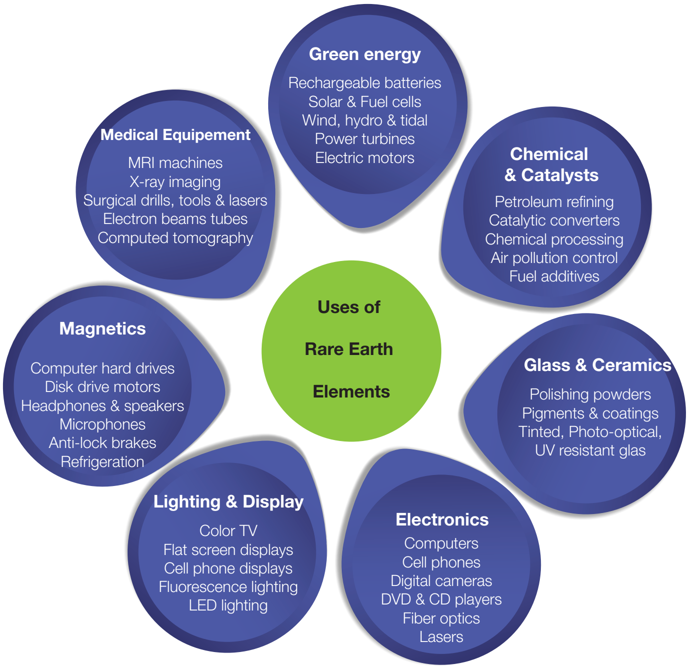

Figure 2: Use of REE

For rapid optimisation of thin film deposition processes, direct analysis techniques (with no sample preparation) are highly in demand. Plasma Profiling Time of Flight Mass Spectrometry (PP-TOFMS^{TM}) provides direct measurement of the chemical composition of materials as a function of depth, with nanometre resolution and the capability to measure both thin and thick layers. It consists in a pulsed radio frequency glow discharge plasma source fed with pure Ar and created under a pulsed RF potential coupled to a time of flight mass spectrometer (TOFMS). The instrument is shown in Figure 3 and schematically in Figure 4.

The key strength of PP-TOFMS is to record **a full and continuous spectrum over a flexible mass range at any depth point** (sampling as low as sub-nanometer/point). In addition the high mass range benefits from low background, which makes PP-TOFMS high mass sensitive. As a result, PP-TOFMS is well suited for measuring REE composition distribution in thin films. In this note, PP-TOFMS data on Eu-Tb co-doped ZnO layers are presented. PP-TOFMS profiles complemented with structural characterisation (XRD) allow for interpreting PL data for a better understanding of the emission mechanisms of the as grown and post-growth treated ZnO layers.

Figure 3: PP-TOFMS instrument

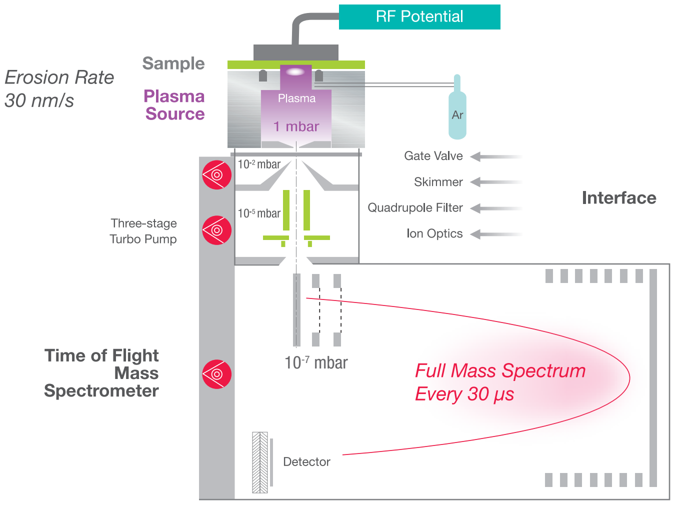

Figure 4: PP-TOFMS Principle

Experimental

Undoped ZnO, RE co-doped ZnO thin films and multilayer structures were grown on (100) silicon substrates by RF magnetron sputtering using a pure ZnO target (figure 5). Magnetrons make use of the fact that a magnetic field parallel to the target surface can constrain secondary electron motion to the vicinity of the target. As a result, trapped electrons enhance collision and thereby ionisation creating a more dense plasma in the target region for higher deposition rates. Eu and Tb codoping was achieved by arranging europium oxide (Eu_2O_3) and terbium oxide (Tb_4O_7) calibrated pellets on the target surface. Samples were post-growth annealed at 1200°C for 1 min under N_2 to optimise dopant distributions and activate dopants.

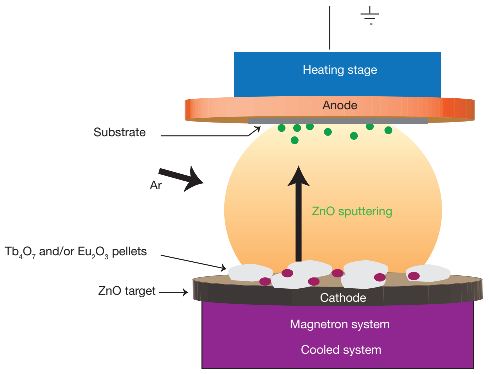

Figure 5: RF magnetron sputtering deposition system

Depth profile analysis was carried out with PP-TOFMS^{TM}. The erosion plasma was created between a cylindrical copper anode and the sample (used as cathode) fed with RF from its back surface. The initial sample dimension was 10 mm x 10 mm. The anode was 4 mm diameter creating a 4 mm diameter crater (probed region). The Argon pressure was maintained constant at 150 Pa; RF excitation (50 W) was pulsed with a pulse width and period of 1 ms and 4 ms, respectively. The transient ion signals of the pulsed plasma were recorded over 1.8 ms by 65 successive TOF mass spectra. The resulting "source profiles" were summed over 50 RF periods giving a point in depth profile every 200 ms. For each sample, thickness and refractive index n were determined using a UVISEL ellipsometer (1.5 - 4.5 eV range) (Figure 6). Photoluminescence emissions (PL and PLE) were collected by using a HORIBA Scientific Fluorolog spectrometer with a 450 W lamp as source excitation (Figure 7).

Figure 6: UVISEL 2 Ellipsometer

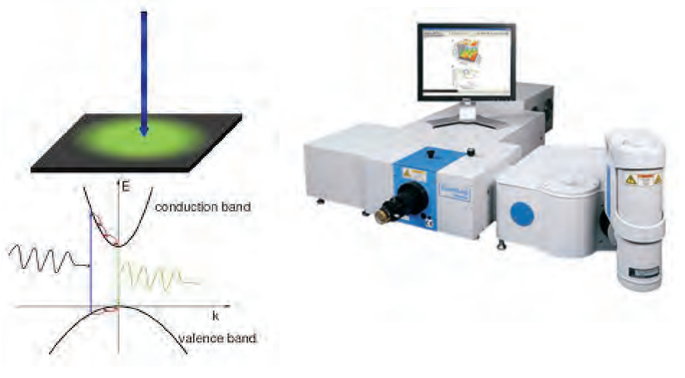

Figure 7: Fluorolog principle & Fluorolog PL

Discussion

Figure 8 shows the depth profile of an as-deposited ZnO thin film in which inputs of Eu and Tb co-dopants are varied within the layer (every 50 nm). Eu and Tb are shown as atomic % and major elements, namely, O, Zn, and Si are shown as raw signals in counts per extraction.

We have used the thickness determined by ellipsometry to convert the raw PP-TOFMS measurement time (X axis) to depth (in nm). Tb and Eu concentrations are obtained by simple calculation of ion beam ratio* **without any calibration.** IBR is the ratio between signal of a peak corrected for isotopic abundance of corresponding isotope and the sum of ion matrix signals corrected for isotopic abundance. Here, ^{30}Si, ^{67}Zn, and ^{16}O are used as matrix ions **.** It is important to note that this profile was obtained in **less than 1 min**.

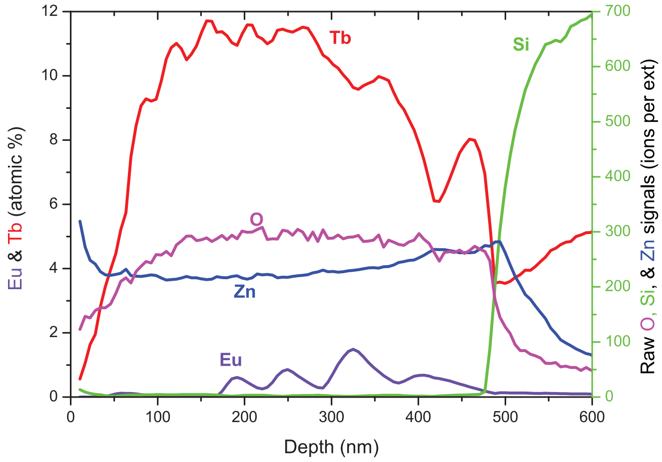

Figure 8: ZnO thin film depth profile

In this study, photoluminescence signal was detected on annealed samples whereas as-deposited samples were non-active (Figure 9). As shown in Figure 10 PP-TOFMS depth profiles of both as-deposited and annealed samples evidence the high Si diffusion in Zn upon annealing and formation of a new matrix. This study extends to several doped and undoped ZnO thin layers. More details may be found in reference [3].

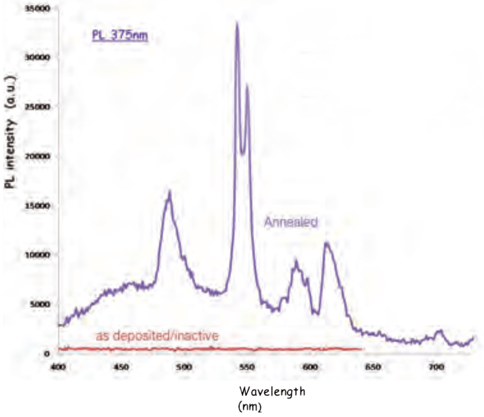

Figure 9: Photoluminescence of ZnO layer

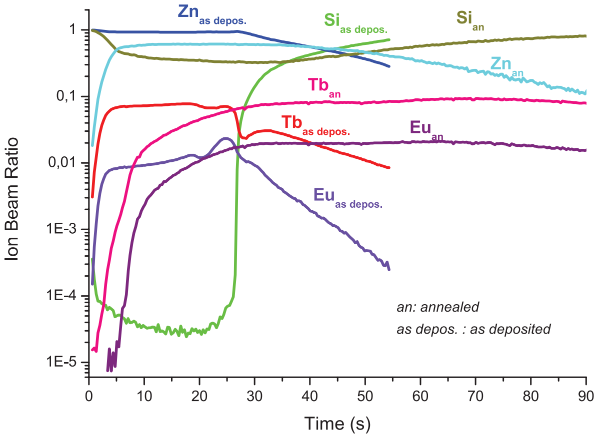

Figure 10: Depth profiles of as-deposited & annealed samples

The high PP-TOFMS sensitivity in rare earth elements is explained by the unique TOFMS capability of recording a complete mass spectrum every 30 µs and the ultra-low background for high mass elements. This is illustrated by the full mass spectrum taken from a single point of the depth profile (i.e. integrated over a 0.3 nm depth) shown in both linear and semi logarithmic scales in Figures 11 and 12. Below mass 50, ions such as C, O, OH_x, CO_X … are present.

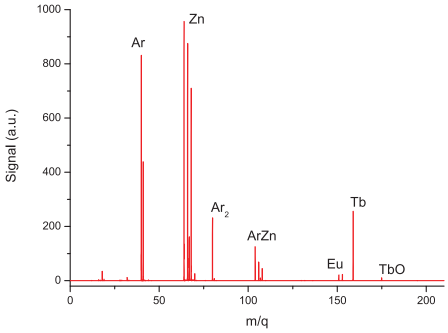

Figure 11: Mass elements spectrum (linear scale)

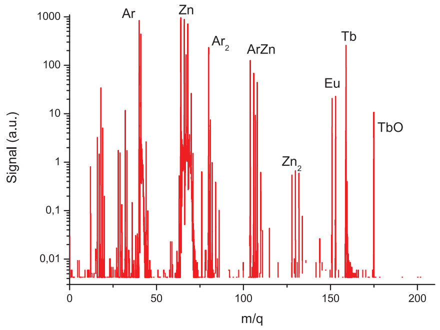

Figure 12: Mass elements spectrum (logarithmic scale)

The acquisition of a continuous full spectrum gives access to signals of all isotopes. The spectrum in Figure 13 zoomed on the two Europium isotopes shows perfect fit between ^{151}Eu and ^{153}Eu signals (violet line) and the natural isotopic distribution (green line) of Europium. Such isotopic abundance matching is readily checked with PP-TOFMS software and allows for picking non-interfered isotope.

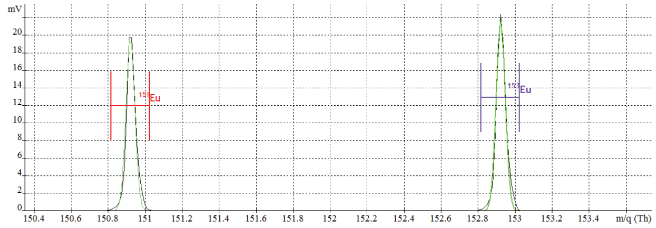

Figure 13: Europium isotopes

Conclusions

This example shows that PP-TOFMS is **a fast and reliable technique for depth profiling of rare earth doped ZnO thin films**. Tb and Eu profiles are obtained with high sensitivity and high depth resolution. **This type of information is typically provided by SIMS, RBS or depth profiling XPS but not as rapidly and readily and at a higher cost.** Such profiles turn out to be powerful complementary information to understand photoluminescence data.

This example extends to similar materials for photonics (lighting, display, solar energy industries) applications such as other wide bandgap semiconductors (SiC,GaN…), nitrides and oxynitrides layers, silicon nano-objects, glasses… doped with Yb, Y, Sm, Er, Nd, Pr, and Tm...

Definition of Ion Beam Ratio or IBR

$$IBR_x = \frac{I_x^i / A_x^i}{\sum_{k=1}^{N_m} I_k^i / A_k^i}$$

N: Number of all elements (ion peaks being investigated)

N_m: Number of main elements included in a matrix

I^i_j: Signal of an isotope i of an element j

A^i_j: Abundance of an isotope i of an element j

x: An element of interest

References

[1] *The Rare Earth Elements: Fundamentals and Applications*, David A. Atwood, John Wiley & Sons, 2013.

[2] Andries Maijerink, *Lanthanide Ions as Photon Managers for Solar Cells*, Material Matters, 6 (4) 113 (2011).

[3] A. Ziani, A. Tempez, C. Frilay, C. Davesnne, C. Labbé, Ph. Marie, S. Legendre and X. Portier, *Concentration determination and activation of rare earth dopants in zinc oxide thin films*, EMRS Fall 2013 Proceedings, physica status solidi

Close Applications

All materials containing rare earth elements: nanometer thick thin films at level down to 10^{17} atom/cm^3 and atomic ppb level in thicker films or bulk materials.

Examples: GaN, SiC, glass, hard coating, steels…

Check on other HORIBA techniques in this field

Structural properties: Raman Spectroscopy

Thickness and optical properties: Spectroscopic Ellipsometry

Purity determination: ICP-OES

Defect studies: Cathodoluminescence

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