RBS analyses of transparent conductive oxides and high-k dielectric layers deposited using the Combinatorial PLD technique

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Flexible or transparent electronics are among the most intriguing potential applications for transparent conducting oxides (TCO) [1-4]. Oxide-based thin film transistors (TFT) are used in displays as switching components in the active-matrix over a large area and can be deposited at room temperature on plastic substrates. The best TCO for TFT are amorphous indium zinc oxide (IZO) [2,3], zinc indium tin oxide (ZITO) or indium gallium zinc oxide (IGZO) [3,4], which have the added benefit on using less In than ITO. The major basic materials science questions with these oxides are:

1) what are the best compositions (In/(In+Zn) or In/(In+Zn+Ga) values, type and concentration of dopants) of IZO and IGZO layers for displays or TFTs applications;

2) what are the best gate dielectrics for TFT fabricated using IGZO channels and IZO electrodes;

3) what is the effect of channel and dielectric composition and interface roughness on band offset or interface state density;

4) how the performance and stability of such devices is affected by low-temperature processing.

The objectives of this project are to answer these questions by fabricating using the combinatorial pulsed laser deposition technique IZO, IGZO, doped IZO and high-k dielectric layers that have various chemical compositions. The best layers will be incorporated into all-oxide transparent and flexible TFT devices that will be tested to improve their performance and increase their stability.

As mentioned before, the use of amorphous, transparent, and conductive oxide is key for the development of new thin film transistors and displays. Recently, indium zinc oxide (IZO) was shown to exhibit a very good transparency in the visible range and high mobility [1,2]. Since the properties and the cost of these films depend on the In/(In+Zn) values, an accurate measurement of this ratio is paramount for future developments and applications.

Combinatorial Pulsed Laser Deposition (C-PLD) technique will be used for controlled doping and synthesis of advanced libraries of IZO, IGZO, doped IZO and high-k dielectric layers, in a single-step process to facilitate the search for optimum dopants concentration values. The main difference with respect to conventional PLD, is that in the case of C-PLD the laser beam is divided into two beams (Fig. 1) by an optical beam-splitter. The two beams are separately directed by mirrors and focused by lenses inside the deposition chamber onto the surfaces of two or more targets. Accordingly, on the facing substrates we will obtain a perfectly controllable gradient of composition along the longitudinal direction from almost

100% of a material A (e.g. IZO) to almost 100% of a material B (e.g. dopant) over well-defined areas, by changing the separation distance (D) between targets, or the specific irradiation sites. Our expertise in this direction was mainly applied in case of IZO compositional libraries for tuning the structural, optical and electrical properties [5-7], in case of materials with complex stoechiometry like calcium phosphates doped with Ag for biomedical applications [8], but also for the synthesis of biopolymer compositional gradient thin films by Combinatorial Matrix-Assisted Pulsed Laser Evaporation (C-MAPLE) [9].

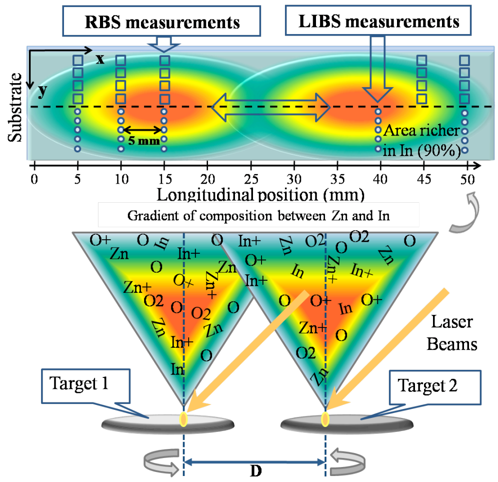

Figure 1. *Typical set up for Combinatorial Pulsed Laser Deposition*

The experimental conditions (laser fluence, number of pulses, repetition rate, target-substrate separation distance, ambient pressure inside reaction chamber, substrates's temperature) will be optimized in order to obtain the best quality coatings.

Preliminary results concerning the analysis of IZO thin films synthesized using a Combinatorial Pulsed Laser Deposition technique via laser-induced breakdown spectroscopy (LIBS) based on the calculation of the spectral radiance of the laser-produced plasma are presented in Figure 2. Several IZO thin films were irradiated with ultraviolet nanosecond laser pulses and the plasma emission spectra were characterized using time-resolved optical emission spectroscopy. The recorded spectra were then compared to the spectral radiance computed for plasmas in local thermal equilibrium. The metal fractions measured via LIBS were compared to values obtained by complementary measurements using energy dispersive X-ray spectroscopy (EDAX). The results obtained with both methods were found to be in good agreement independently of the relative fraction of indium and zinc that varied for our films from about 60 to 90 and 40 to 10%, respectively. The measurements accuracy was estimated to about 10 % and is mostly attributed to the uncertainties of spectroscopic data.

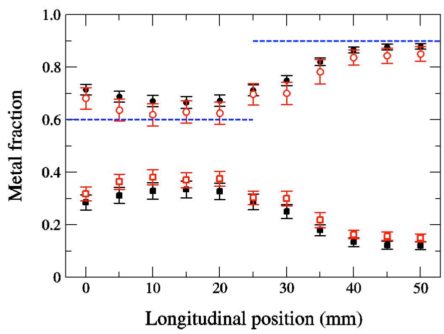

Figure 2. *Atomic fractions of indium (circles) and zinc (squares) measured by LIBS (empty red symbols) and by EDS (filled black symbols). The dashed lines represent the In/(In+Zn) fractions of the targets used for thin film synthesis by C-PLD.*

However, the precise investigation of the dopants concentration along the longitudinal direction of the samples as well as their 3D spatial distribution is mandatory. Since complementary characterization techniques suffers due to limited accuracy (EDAX), or very limited depth resolution (XPS), the chemical stoichiometry of the grown films is very important and must be achieved using a reliable technique such as Rutherford Backscattering Spectrometry (RBS) or non-Rutherford Backscattering Spectrometry (NRBS).

Rutherford backscattering spectrometry with light ions, typically 1–2 MeV ^{1}H or ^{4}He ions, is a often used technique for depth profiling of elements concentrations. Furthermore, under channeling conditions, the technique may be exploited to give information about the sample structure and lattice locations of impurities. Channeling is a powerful technique which is widely used for ordered samples characterization.

In the extensive use of elastic backscattering for materials characterization purposes, ^{4}He particles up to several MeV have been for long considered as most convenient projectile. This often gives sufficient mass and depth resolution. However, the case of more complex film structures, with compound materials, have put higher demands on both the mass and the depth resolution in the analysis.

The RBS technique has also its limitations. Mass resolution for heavy elements and sensitivity for light elements are poor, and, except for the surface, mass determination is not unambiguously possible. The analysis of light elements in a heavier matrix is often impossible, because of the energy overlap of the beam ions scattered by light surface atoms and by heavier bulk atoms deeper in the sample. Furthermore, small amounts of light elements are difficult to analyze, because of the Z^2 dependence of the Rutherford cross section.

It is well known that the mass and depth resolution, as well as the sensitivity may be improved by using heavier and more energetic ions. In particular, mass separation for medium and heavy elements is improved significantly by heavy ions RBS. The expression for the energy separation as a function of the projectile mass M_1, the projectile energy E_0 and the target mass M_2 can be written as:

$$\Delta E \cong \frac{2M_1E_0}{M_2^2}\left(1-\cos\theta\right) \qquad (1)$$

where θ is the backscattering angle. This is valid for $M_1/M_2 << 1$. The expression suggests the use of higher mass projectiles and higher bombarding energies. There are, however, some drawbacks, because the resolution of the silicon detector is worsened and, due to $1/E_0^2$ dependency of the cross section, the counting rate reduces. Subsequently, longer analyzing time has to be used if higher energies are needed. In order to avoid the worsened resolution of silicon detectors for heavy ions the measurement of backscattered ions energy using a time of flight spectrometer can be used.

A severe disadvantage of conventional RBS is low sensitivity for light elements. The Rutherford scattering cross section is proportional to the square of the nuclear charge of the target nucleus. Therefore, the scattering peaks from light elements such as C, N and O are superimposed on a relatively high background due to backscattering from heavy elements in the sample. In recent years, high energy ^{1}H and ^{4}H backscattering has been utilized to overcome this difficulty and to quantify the stoichiometry or to profile the light elements in the heavy bulk samples. In the high energy backscattering experiments, ^{1}H and ^{4}He ions of *3–9 MeV* (or even more) are used as incident projectiles. The elastic scattering cross section for light elements becomes a nuclear rather than a Rutherford interaction, called non–Rutherford backscattering or nuclear resonance elastic scattering. The non–Rutherford backscattering can be used to enhance the sensitivity for light elements. For example, at ^{4}He energies of *3.045*, *4.265* and *3.72 MeV* the elastic backscattering cross sections for O, C and N are 25, 150 and 6 times larger than their corresponding Rutherford cross sections, respectively.

We intend to use RBS and NRA techniques to characterize the thin layers of the above mentioned materials. Both RBS and NRBS with ^{4}He will be used. The measurements will be performed using a dedicated target chamber at the new 3 MV Tandetron accelerator. The energy of the ^{4}He beam used for measuremens will be calibrated. The method adopted for calibration of the accelerator consists simply of comparing the energies of alpha particles from a radioactive source with the energies of ^{4}He projectiles back-scattered into an silicon detector by thin carbon and gold layers. The ions scattered at 165^0 will be detected by a Si detector having 15 keV resolution.

We need 5 days (15 shifts).

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