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Automated reactive thermal evaporation system for transparent conductive coatings

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Abstract — **This work presents a fully automated plasma-enhanced reactive thermal evaporation system (rf-PERTE) that can be used for the deposition of transparent metal oxide films with high reproducibility of their electrical and optical properties. The developed hardware/software platform enables the full control over the critical deposition conditions such as mass flow of oxygen, process pressure, current flowing through crucible and rf-power. For indium oxide films on glass substrates a resistivity of 9×10^{-4} Ω-cm and a transmittance of 90% in the visible spectral range were achieved without substrate heating. The system is also suitable for the deposition of transparent conducting coatings on a wide range of plastic substrates, for applications in the field of flexible sensors or solar cells. In particular, we have successfully deposited indium oxide on PEN (polyethylene naphthalate) sheets with electrical and optical properties approaching the ones of the films deposited on glass substrates.**

Keywords: TCO, Deposition, Transparent Electronics.

I. INTRODUCTION

Transparent conducting oxide (TCO) layers on polymeric substrates are an important component of flexible electronics [1]. Substrate materials such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) are being considered for opto-electronic devices due to their high transparency and low cost [2]. The technological challenge is that TCO coating should be deposited at low temperatures, desirably below the glass transition point for these plastics. Several vacuum techniques such as dc and rf sputtering, ion beam-assisted evaporation, and arc-discharge ion plating have been used for deposition of indium-tin oxide (ITO) on polymeric substrates [3-6]. However, the properties of low-temperature amorphous ITO on plastics are substantially inferior in comparison to crystalline ITO grown on glass substrates at high temperatures. To overcome the limitation on growing TCO films with satisfactory electrical and optical properties on plastic substrates, we have developed a radio-frequency plasma-enhanced reactive thermal evaporation (rf-PERTE) technique [7]. This work reports on an automated rf-PERTE system, which is suitable for deposition of In_2O_3 based coatings on unheated polymeric substrates.

II. DEPOSITION SYSTEM

Fig. 1 shows a general design of the rf-PERTE system. The system is based on a bell jar type vacuum chamber with a diffusion and mechanical pump vacuum pumping group. The typical configuration for thermal evaporation is used, with a distance between the tungsten boat and the substrate holder of 32 cm. For plasma assistance, an rf-electrode in the form of a copper ring is placed at half-way between crucible and substrate holder. An electrically-driven shutter placed about 15 mm below the substrate holder, shields the substrate from oxygen plasma and impurities from the starting of the evaporation process. The oxygen injection into chamber is controlled by a SmartTrak 100 Series mass flow controller. A GenesysTM series programmable regulated power supply and a CesarTM Generator, Model 136, are used as dc and rf power sources, respectively.

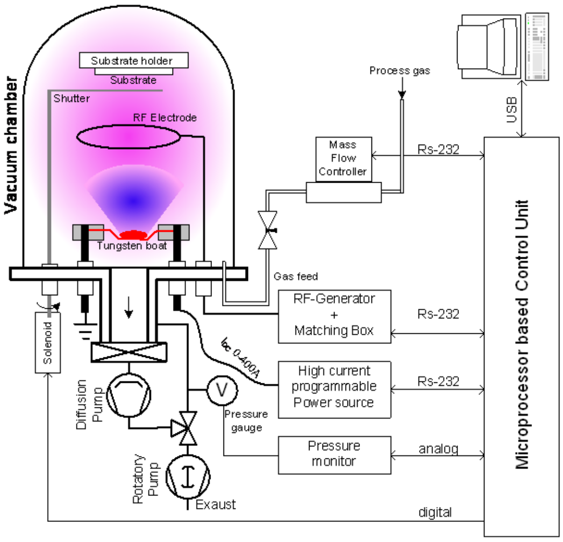


Fig. 1. General overview of the evaporation system

A. Controller Hardware

All electronic units and electrical parts are linked to a microprocessor based control unit either through analog, digital or communication (RS-232) ports. The control unit is connected to a personal computer through USB interface that enables the system control using dedicated software. In order to keep the controller board as simple as possible, the analog to digital converter (ADC) included in the microcontroller was used. As seen in Fig.1, an analog input is used for the measurement of the pressure signal coming from a Pfeiffer PKR251, the 10 bit resolution of the existing ADC was not sufficient for the determination of the process pressure with enough precision in the range of interest. To overcome this issue, without having to add an external higher resolution ADC, a two-step subranging architecture, similar to a pipelined ADC, was implemented using two inputs of the existing 10bits converter [8].

In the implemented architecture, depicted in Fig. 2, the pressure signal is converted by the microcontroller´s ADC in a two-step sequence with the aid of a differential amplifier. In the first step, the voltage from the gauge is measured on one ADC input, then this value minus a fraction is subtracted from the pressure signal and amplified 64x. The residue amplifier is fed with an analog signal generated using pulse width modulation technique and a low pass filter. The amplified residue is then captured on the second ADC input and the pressure valued calculated from the two ADC values.

With this simple method the resolution achieved enables the accurate control of the pressure during the process.

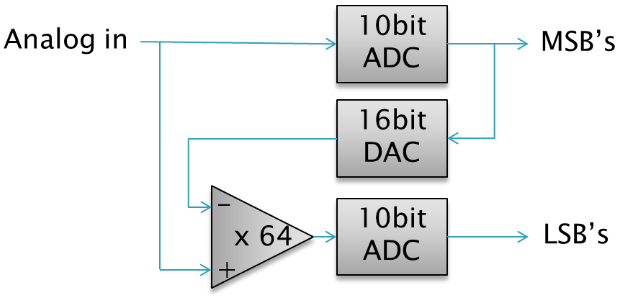


Fig. 2. Two-Step Subranging architecture used.

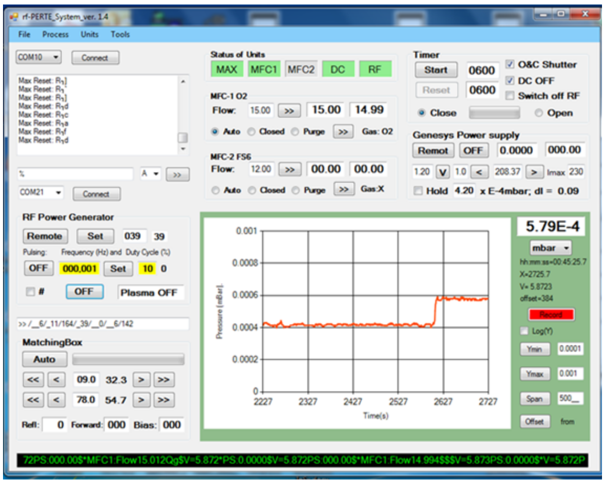
B. Software

The control software was developed targeting the following tasks: the programmed control of all electronic units; real time monitoring of all process variables and their recording for post-analysis and documentation; automated control of critical process parameters; and the use of recipe files for process reproducibility.

The user interface is intuitive and self-explanatory, with the functional blocks for each piece of equipment, in a way that a rapid look is sufficient to get information about system status. A view of the user interface is presented in Fig. 3. A pressure chart is also shown and updated in real time allowing the user to follow the pressure variations.

In a typical deposition sequence, when the initial values of the process parameters are reached, the program enables deposition in full-auto mode by starting a timer, and then a dedicated subroutine opens the shutter, holds the process pressure at a given value and adjusts the evaporation rate by varying the current through the tungsten boat. When the time has run out, the shutter will be closed and with some delay dc- and rf-values will be set to zero to end the process.

Adjusting the deposition conditions such as pressure, gas flow rate, rf-power, and evaporation rate the deviation from stoichiometry δ in $In_2O_{3-\delta}$ can be varied in wide range thus producing conducting, semiconducting and insulating films [9,10].



COM10
Max Reset: R₁]
Max Reset: R₁
Max Reset: R₁]
Max Reset: R₁d
Max Reset: R₁c
Max Reset: R₁a
Max Reset: R₁f
Max Reset: R₁d

COM21

MFC-1 O2
Flow: 15.00 15.00 14.99
● Auto ○ Closed ○ Purge Gas: O2

MFC-2 FS6
Flow: 12.00 00.00 00.00
○ Auto ○ Closed ○ Purge Gas:X

Start 0600
Reset 0600
☑ O&C Shutter
☑ DC OFF
☐ Switch off RF
● Close ○ Open

Remot OFF 0.0000 000.00
1.20 V 1.0 < 208.37 > Imax 230
☐ Hold 4.20 x E-4mbar; dI = 0.09

Remote Set 039 39
OFF 000,001 Set 10 0
☐ # OFF Plasma OFF
>> /_6/_11/164/_39/_0/_6/142

Auto
<< < 09.0 32.3 > >>
<< < 78.0 54.7 > >>
Refl: 0 Forward: 000 Bias: 000

5.79E-4
mbar
hh:mm:ss=00:45:25.7
X=2725.7
V= 5.8723
offset=384
☐ Log(Y)
Ymin 0.0001
Ymax 0.001
Span 500

```
72PS:000.00$*MFC1:Flow15.012Qg$V=5.872*PS:0.0000$V=5.872PS:000.00$*MFC1:Flow14.994$$$V=5.873PS:0.0000$*V=5.872P
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Fig. 3. Print screen of the user interface.

C. Results

To produce transparent and highly-conductive InO_x films, an optimal balance between the evaporated metal mass and absorbed volume of oxygen should be reached. This balance can be evaluated by measuring the pressure at steady oxygen flow, pumping speed, and RF-power. Fig. 4 shows that the pressure in the chamber decreases, when the evaporation of indium starts, and then stabilizes when the evaporation rate becomes constant. The deviation from stoichiometry in InO_x was found to be related to the difference between the initial pressure, P_{in}, and deposition pressure, P_{dep}, which is determined by the evaporation rate. The evaporation rate depends on multiple factors such as the dc power applied to the crucible, process pressure, amount of metal still in the crucible, etc. To stabilize the evaporation rate, the dc current through the crucible is automatically adjusted to keep the deposition pressure constant. This approach enables the reproducible deposition of metal oxide films with required stoichiometry simply by setting the differential pressure ΔP value.

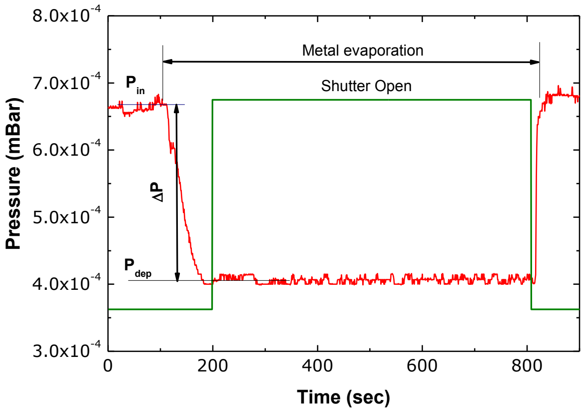

Fig. 4. Pressure in the chamber during the deposition.

A series of $In_2O_{3-\delta}$ films deposited on glass was obtained by varying the differential process pressure to study their electrical and optical properties. The films were deposited on 1-mm-thick borosilicate glass substrates at $P_{dep} = 4.1\times10^{-4}$ mbar with ΔP varying from 1.6×10^{-4} to 2.7×10^{-4} mbar. The oxygen flow rate and rf-power where kept constant at 15 sccm and 70W, respectively.

The transmittance spectra of the films are shown in Fig. 5. Here, one can see that the transmittance in the green-blue spectral range decreases with increasing ΔP, this effect can be ascribed to the growing number of atomic-scale defects as a result of oxygen deficiency.

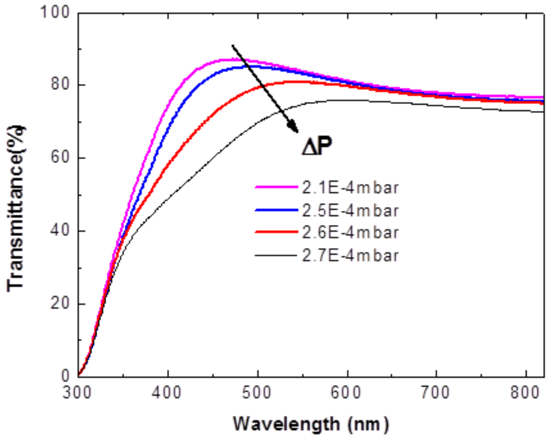

Fig. 5. Transmittance spectra of $In_2O_{3-\delta}$ layers deposited on glass at various differential process pressures.

To test the properties of the materials under low temperature deposition conditions, $In_2O_{3-\delta}$ films were also deposited on PEN (Q65FA-100 µm, Teijin-DuPont). The obtained material is highly conductive and transparent. A resistivity of 9×10^{-4} $\Omega\cdot$cm was achieved under optimized deposition conditions, in line with the literature [11]. The observed resistivity difference between the layers deposited on glass and on PEN substrates is within the range of the measurement error. For glass and PEN substrates with about 100 nm thick $In_2O_{3-\delta}$ coatings, the obtained peak values of visible transmittance were 90% and 85%, respectively (see Fig. 6).

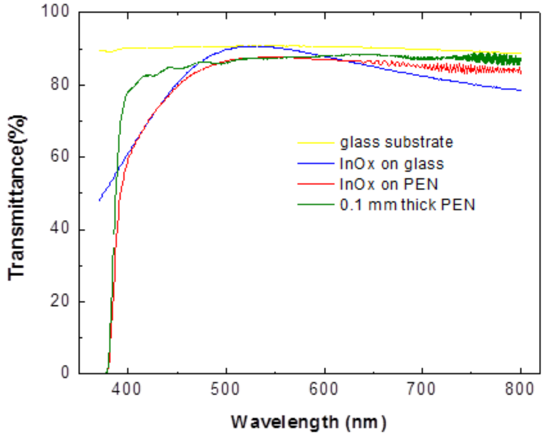

Fig. 6. Transmittance spectra of 104 nm thick indium oxide layers on glass and PEN substrates.

III. CONCLUSIONS

A simple technique for preparing undoped, conductive and transparent thin films of indium oxide has been developed using the rf-PERTE method. The resistivity of 9×10^{-4} Ω.cm was achieved for coatings on PEN and glass substrates. InO_x films on glass and PEN substrates show 90 and 85% peak values of transmittance in the visible spectral range, respectively. Process automation proved to allow stable deposition conditions and high reproducibility of the fabricated film characteristics

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