Automated rf-PERTE system for room temperature deposition of TCO coatings

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Abstract

In this work we present a fully automated plasma-enhanced reactive thermal evaporation system (rf-PERTE) that can be used for the deposition of transparent metal oxide films without intentional heating of the substrate. The system and developed software enables the full control over critical deposition conditions such as mass flow of oxygen, process pressure, current flowing through crucible and rf-power. These parameters are automatically adjusted during the deposition thus keeping them in a narrow process window. This way, highly transparent and conductive coating can be deposited with a high degree of reproducibility of the optical and electrical characteristics. The resistivity of 9×10^{-4} Ω-cm and the peak transmittance of 90% in the visible spectral range were achieved for indium oxide films deposited on glass substrates. This technique is also suitable for the deposition of transparent conducting coatings in a wide range of plastic materials for flexible solar cells. In particular, we have successfully deposited indium oxide on PEN (polyethylene naphthalate) sheets with electrical and optical properties approaching the ones for films on glass

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1. 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.

2. Automated Deposition System

2.1. Apparatus design

Fig. 1 shows a block diagram of the rf-PERTE system. The system is based on a bell jar type vacuum chamber with a pumping group including diffusion and mechanical pumps. The typical configuration for thermal evaporation is used, with a distance between the tungsten boat and the sample holder of 32 cm. For plasma assisting, an rf-electrode in the form of a copper ring is placed in the half-way between them. An electrically-driven shutter is placed about 15 mm below the sample holder to shield the plastic substrate from oxygen plasma before the deposition starts. The oxygen injection into chamber is controlled by a SmartTrak 100 Series mass flow controller. A Genesys[TM] series programmable regulated power supply and a Cesar[TM] Generator, Model 136, are used as dc and rf power sources, respectively. 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.

2.1. Control 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 program was written applying the object-oriented programming concept and using VB.NET for the MS Windows platform. A print screen of the user interface form is shown in Fig. 2. The user interface here is intuitive and self-explanative, with the functional blocks for each piece of equipment, in a way that a rapid look is sufficient to get information about system status. The form also includes a pressure chart that allows the user to estimate the pressure variations. When the initial values of the process parameters are reached, the program enables deposition in full-auto mode by starting the timer. In particular, the dedicated subroutine opens the shutter, holds the process pressure at given value and adjusts the evaporation rate by varying the current through the tungsten boat. When the timer is run out, the shutter will be closed and with some delay dc- and rf-values will be set to zero to end the process.
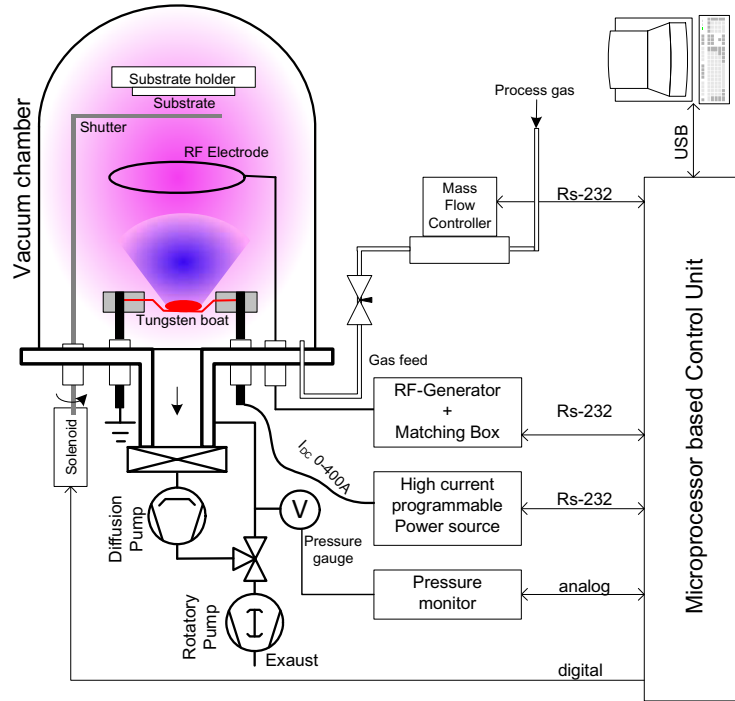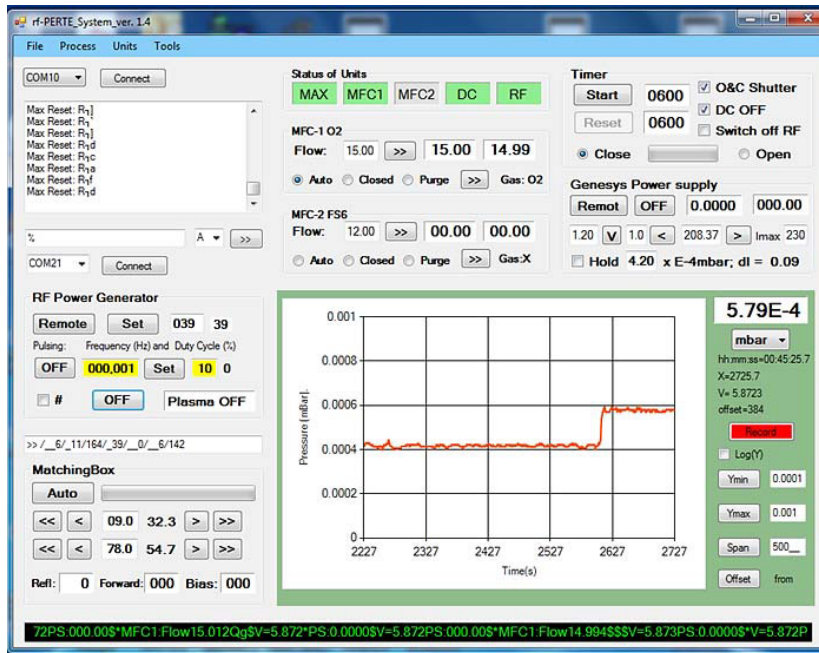
Fig. 1. Block diagram of the rf-PERTE system.

Fig. 2. User interface form of the computer program.

3. PC-controlled deposition process and material properties

The metallic atoms evaporated from the heated crucible may undergo collisions in the oxygen ambient during their transit to the substrate leading to formation of metal oxide molecules in the gas phase. The applied rf-power not only produces highly reactive oxygen plasma but also ionizes the metallic atoms. This is revealed by a blue light emitting cloud over the heated crucible (see Fig. 3). Using a Thorlabs' optical spectrum analyzer, the emission peak at 451.1 nm, which is the strongest line in the spectra of In, was detected [8]. Furthermore, the surface oxidation reaction on the growing layer also takes place due to the existence of intense oxygen ion bombardment. 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 [9-11].

To produce transparent and highly-conductive $In_2O_{3-\delta}$ 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 $In_2O_{3-\delta}$ is related to the difference between the initial pressure, P_{in}, and deposition pressure, P_{dep}, that 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.
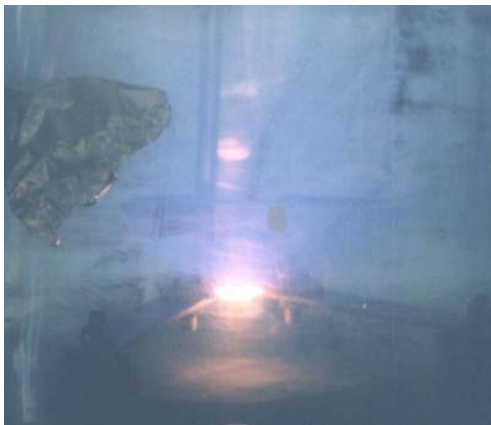

Fig. 3. Photograph of the chamber during the deposition process. The blue cloud above the incandescent crucible is due to ionized indium vapour.
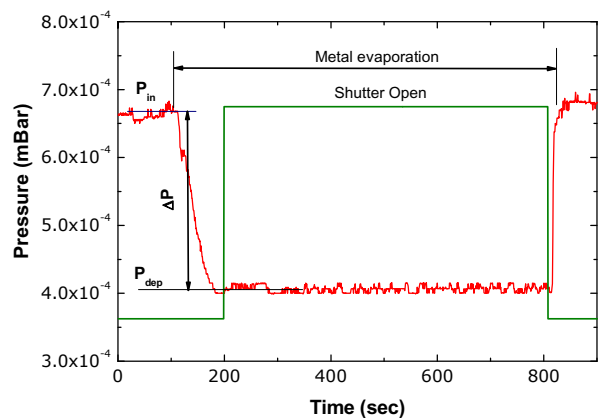

Fig. 4. Pressure in the chamber during the deposition process.

A series of $In_2O_{3-\delta}$ films 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 and ΔP varied from 1.6×10^{-4} to 2.7×10^{-4} mbar. The oxygen flow rate and rf-power was set to 15 sccm and 70W, respectively. The thickness of $In_2O_{3-\delta}$ layers was 111±6 nm at 10 min deposition time. Fig. 5 shows resistivity of $In_2O_{3-\delta}$ as a function of ΔP. The resistivity minimum is observed at $\Delta P = 2.5\times10^{-4}$ mbar when the optimum concentration of oxygen vacancies is reached. At larger ΔP values, the films are less conductive, due to ionized impurity scattering, and less transparent. Transmittance spectra of the films are shown in Fig. 6. Here, the transmittance in the green-blue spectral range decreases with increasing ΔP that indicates a growing number of atomic-scale defects as a result of oxygen deficiency. Cation interstitials and clusters are likely responsible for the observed excessive absorption [12].
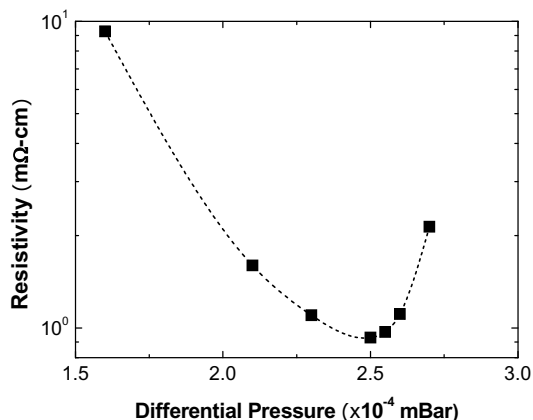
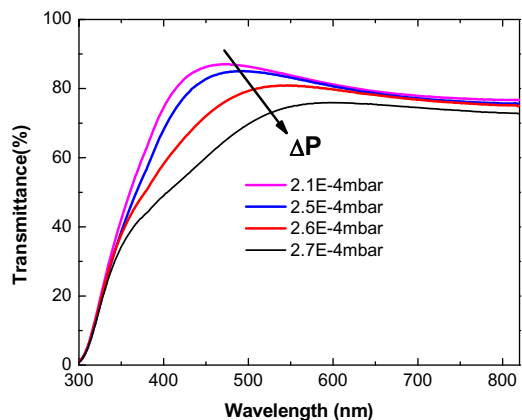Fig. 5. Resistivity of $In_2O_{3-\delta}$ as a function of differential process pressure.

Fig. 6. Transmittance spectra of $In_2O_{3-\delta}$ layers deposited on glass at various differential process pressures.

The highly conductive and transparent $In_2O_{3-\delta}$ films were also deposited on PEN (Q65FA-100 µm, Teijin-DuPont) and glass. The resistivity of 9×10^{-4} $\Omega\cdot$cm was achieved under optimized deposition conditions. The difference in resistivity of the layers deposited on glass and on PEN substrates were 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. 7).
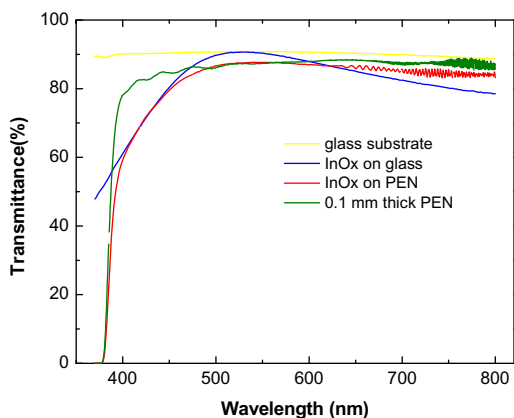

Fig. 7. Transmittance spectra of 104 nm thick indium oxide layers on glass and PEN substrates.

4. Conclusion

A simple technique for preparing undoped, conductive and transparent thin films of indium oxide at room temperature has been developed using the rf-PERTE method. It is demonstrated that the electrical and optical properties of $In_2O_{3-\delta}$ can be controlled by adjusting the differential process pressure ΔP that is a function of the metal evaporation rate at a constant oxygen flow rate. The resistivity of 9×10^{-4} $\Omega\cdot$cm was achieved for coatings on PEN and glass substrates. $In_2O_{3-\delta}$ 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.

Acknowledgements

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