On the film microstructure control by means of plasma enhanced chemical vapor deposition and plasma assisted atomic layer deposition.

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Abstract: The ultimate control on film growth represents a challenge in PECVD: interphase, film structure and surface roughness are affected by the surface energy, growth and ion fluxes and ion energy. Such control is desired for moisture diffusion barriers, where an irregular polymer surface and defects determine the performance. Routes for microstructure control in PECVD SiO₂ barrier layers are presented. The addition of ion bombardment to a remote plasma with a gradient in growth flux allows tuning the film microstructure during growth with the purpose of engineering an adhesive interphase and a dense SiO₂ barrier. The role of ion bombardment on the film microstructure is here investigated by means of ellipsometric porosimetry, which monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity can be determined. Recently, we have also explored atomic layer deposition (ALD) for a virtually ultimate control on film microstructure. Plasma can assisted ALD (Plasma-assisted ALD) by providing radicals, replacing one precursor (e.g., O radicals replacing H₂O in Al₂O₃ deposition). 20 nm-thick plasma-assisted ALD Al₂O₃ layers are characterized by water vapor transmission rates (WVTRs) as low as 10⁻³ g/m²day.

Keywords: Plasma-enhanced CVD, Film porosity, Monitoring (in situ).

1. Introduction

The control on thin film growth and microstructure in plasma deposition is a challenging issue. For example, in the case of an inorganic layer on an organic substrate (e.g., SiO₂ on polymers), the organic/inorganic interphase affects the bulk inorganic properties, such as adhesion and moisture permeation barrier performance. Within this framework, the ion bombardment-aided plasma deposition of SiO₂ layers [1-2], deposited from hexamethyldisiloxane/oxygen chemistry, is here reported. The purpose is to promote the densification of SiO₂-like layers deposited in a remote plasma configuration, the expanding thermal plasma, by means of an external rf bias applied to the substrate. The maximum mean kinetic energy of the ions arriving at the substrate is \(E_i = -e\cdot V_{DC}\), under the assumption that all the energy delivered to the system is used to accelerate ions without extra plasma generation and that the plasma potential is zero. Correspondingly, the ion flux impinging on the substrate is defined as \(\Gamma_{\text{ion}} = P_r / e \cdot A \cdot V_{DC}\), where \(P_r\) is the rf power and \(A\) the substrate area.

The growth flux, \(\Gamma_{\text{growth}}\), is calculated from the growth rate, under the assumption that the deposited films are stoichiometric SiO₂ layers. The control on the ion energy (via the delivered substrate bias), a graded growth flux, obtained by a gradient (e.g., a decrease) in the hexamethyldisiloxane flow rate during film deposition, is set up with the purpose of tuning the ion-to-growth flux ratio, therefore, the film densification. Initially, an adhesive porous layer is deposited, gradually shifting towards a highly dense barrier layer, due to the increase in the ion-to-growth flux ratio.

In literature, a comprehensive study on the densification mechanisms in SiO₂ films, based on molecular dynamics simulation and ion-assisted deposition experiments, was already carried out by Martinu et al. [3-4]. Here the role of ion bombardment on the SiO₂ film microstructure is investigated by means of ellipsometric porosimetry [5-6], which monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the layer.

Besides PECVD, presently, also atomic layer deposition is withdrawing considerable attention within the field of moisture permeation barriers for flexible electronics due to the following:

- ALD can deposit virtually defect-free layers due to the ultimate control on film growth, thus, overcoming the limits related to defects present in coatings deposited by means of PE-CVD and sputtering techniques;
- ALD can guarantee highly uniform and conformal barrier layer deposition necessary for 3D encapsulation of the OLED device;
- Superior barrier performances of ALD thinner (than PE-CVD and sputtered films) single layers can be expected, thus, paving the way towards...
have reached WVTR values as low as 1⋅10^-3 g/m²-day for very thin (10-25 nm) Al₂O₃ films on poly(2,6 ethylene-naphtalate) (PEN) deposited from sequential trimethylaluminum (TMA) and water exposures. Their study, however, was limited to deposits carried out at 120 °C in order to maintain a relatively short ALD cycle time (60 s). When Al₂O₃ deposition was attempted at lower temperature (33 °C), purging times as long as 180 s necessary to remove residual water (and suppress any CVD contribution to the ALD growth) were applied, thus, resulting in a total cycle time of 203 s.

In this contribution, we address the plasma-assisted ALD (PA-ALD) of Al₂O₃, where the water exposure is replaced by a remote O₂ plasma exposure, while the Al precursor is trimethylaluminum (TMA). The high reactivity associated to the plasma environment allows film deposition at room temperature without requiring long purging times. Moreover, the plasma chemistry can be easily tuned together with the film chemistry (e.g., towards AlOₓNy barrier films).

2. Experimental
The ETP set-up has already been described in detail in [9]. Briefly, the ETP is a remote plasma, i.e., plasma production, active species transport and deposition are geometrically separated. An Ar (ΦAr= 100 sccs) plasma is ignited at a constant arc current (IArc= 75 A) in a wall-stabilized dc cascaded arc at sub-atmospheric pressure. The arc consists of three cathodes, four cascade plates and an anode in which a nozzle is present. The thermal plasma expands supersonically through the nozzle into the deposition chamber kept at constant pressure (Pchamber= 0.3 mbar). The Ar ion and electron fluence (Ar⁺, e⁻) expanding from the arc is fully controlled by the plasma parameters, i.e., arc current and Ar flow rate, and measured by means of Langmuir Probe [10]. Co-precursors for SiO₂-like film deposition are O₂ and hexamethyldisiloxane ((CH₃)₃SiOSi(CH₃)₃, HMDSO), injected via the nozzle and via a ring placed at 5 cm from the nozzle, respectively. During the expansion the electron temperature is reduced to 0.3 eV in the downstream region and electron-impact dissociation path are unlikely to occur. Instead, molecule activation and dissociation are induced by charge exchange reactions between Ar ions and O₂ and HMDSO molecules, followed by dissociative recombination reactions with low energy electrons, as reported in [9, 10]. Because the charge exchange reaction constant for Ar ions-HMDSO is higher than for Ar ions- O₂ (4⋅10^16 m³/s vs. 6⋅10^17 m³/s), the consumption of Ar ions and, therefore, the ion flux arriving at the substrate, are mainly governed by the HMDSO addition.

The low electron temperature in the downstream region is also responsible for the negligible ion bombardment occurring at the substrate; therefore, ion bombardment studies are carried out by using an external rf (13.56 MHz) substrate biasing as delivered by an RFPP power supply with an L-type matching network. The substrate voltage and peak-to-peak voltage were monitored using a high voltage probe and an oscilloscope operating in DC mode. The depositions were carried out on (100) Si substrates and 100 µm-thick poly(ethylene 2,6 naphtalate), PEN (glass transition temperature Tg = 121 °C), substrates placed on a substrate holder at 60 cm of distance from the nozzle. The deposition temperature was fixed at 25°C and a He back-flow was used for thermal contact between the polymer and the substrate holder. An active N₂/O₂/ water cooling system guaranteed a constant substrate temperature.

The deposited layers were characterized by means of in situ spectroscopic ellipsometry in the 245-1000 nm range at an angle of 68° during film deposition. Further optical characterization aimed to identify the film porosity as affected by the use of ion bombardment and graded ion-to-growth flux ratio was carried out by means of ellipsometric porosimetry. This allows performing isotherm adsorption and desorption studies of a specific solvent (in our case, ethanol) in the open porosity of the layer as a function of the vapor partial pressure. Such studies were carried out in a vacuum chamber equipped with an ellipsometer which follows the changes in optical properties of the layer upon ethanol adsorption/ desorption at a constant substrate temperature of 14°C (ethanol saturated pressure= 40 mbar). The refractive index values were obtained by applying a Cauchy model to the SiO₂ layers. From the adsorption/ desorption isotherms and the presence of hysteresis, information on the porosity shape and dimensions can be obtained on the basis of the general definitions of porosity reported in [11]. Moreover, by means of the two component- (host matrix and pores) Lorentz-Lorentz relation, the open porosity of the layer could be determined.

Before being used to analyze the plasma- deposited SiO₂ layers, the system was tested as proof-of-principle on a known sample, i.e., a spun-on mesoporous silica layer with a porosity of 35%.

Thin Al₂O₃ films were deposited in a home-built deposition reactor by PA-ALD already described in [12] and depicted in Figure 1 from sequentially exposing the substrate to TMA vapor and a remote O₂ plasma. The deposition chamber was continuously purged by O₂ resulting in a pressure of 7.5 mTorr. The PA-ALD cycle consisted of 5x TMA dosing (1 s each) injected from a trapped volume, 5 s purge, 2 s O₂ plasma and 5 s purge. The plasma was ignited in an inductively couple plasma (ICP) source operated on the O₂ background gas at an rf power of 100W. In situ spectroscopic ellipsometry (241-1000 nm) was
used to determine the growth rate and refractive index of the Al₂O₃ films on Si. The depositions were carried out in a temperature range of 25-200 °C on c-Si substrates and up to 100 °C on PEN.

The moisture permeation barrier properties of the films were determined by means of the Calcium test [13], based on the change in transparency of 100 nm-thick Ca in a controlled environment (T = 21 °C and 60% relative humidity).

3. Results and discussion

Figure 1 shows the increase in film refractive index (at 633 nm) as monitored by means of in situ spectroscopic ellipsometry as a function of the DC bias voltage measured at the substrate for different HMDSO flow rate settings. At lower HMDSO flow rate the film densification process (n reaches values typical of thermal SiO₂) is a faster process because of the high ion-to-growth flux ratio available. An average ion energy of 40 eV per SiO₂ unit (as calculated from \( E_i \Gamma_{ion} / \Gamma_{growth} \)) is needed in order to promote film densification (n = 1.46). At high HMDSO flow rates, even high bias voltage values are not sufficient to promote full film densification, because of the limited ion flux arriving at the surface of the growing film.

In order to highlight the effect of the ion bombardment on the layer microstructure, specific studies by means of ellipsometric porosimetry have been carried out on 100 nm-thick SiO₂-like layers deposited in different conditions. Figure 2 shows a typical isotherm as a function of the ethanol partial pressure. In the absence of ion bombardment porous (n = 1.38) layers are characterized by an isotherm shape mimicking the structure of disordered mesoporous films (pore diameter in the range of 2-50 nm). The presence of hysteresis during the desorption process is usually associated with capillary condensation and its shape point out, in this case, a very broad distribution in pore size and shape, resulting in 20% open porosity. A progressive increase in substrate bias voltage leads towards film densification (n = 1.46) and induces a change in the isotherm: the ethanol uptake (i.e. the refractive index variation) is negligible and the adsorption/desorption process becomes reversible since only unrestricted ethanol multilayer adsorption can occur on the non-porous surface, see Figure 3. The open porosity is less than 1%.

PA-ALD Al₂O₃ layers characterized by a growth rate of 1.7 nm/cycle with a stoichiometry of Al₂O₃ = 2:3.2 and a refractive index of 1.65 at 633 nm have been deposited on PEN substrates at room temperature. Figure 4 shows the WVTR of the deposited layers as a function of the film thickness. It is observed that a 10 nm thick layer already shows very good barrier properties. The WVTR saturates for film thicker than 20 nm to the value of \( 5 \times 10^{-3} \) g/m²/day, which is a very good value for single layer barrier, especially in comparison with other deposition technique such as PECVD and sputtering. Possible explanations for the saturation behavior are that the layers are not completely pinhole free or that defects on the polymer surface are not conformally sealed by the ALD layer. More discussion can be found in [14].
Figure 4. WVTR of room temperature PA-ALD Al₂O₃ films on PEN as a function of film thickness.

4. Conclusions
In this contribution we have addressed the deposition of SiO₂-like layers by means of the expanding thermal plasma in the presence of an external substrate bias. The role of ion bombardment on the film microstructure is investigated by means of ellipsometric porosimetry. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity is calculated. The use of ion bombardment reduces the open porosity and slowly leads to full layer densification where only ethanol multi-layer adsorption can occur on the surface. When a gradient in growth flux is applied (results not shown here), both the isotherm and the hysteresis behavior exhibit the transition from meso- to microporosity (pore diameter less than 2 nm). Moreover, the use of a gradient in $\Gamma_{\text{ions}} / \Gamma_{\text{growth}}$ allows decreasing the open porosity of the deposited layer. We have also shown the feasibility of PA-ALD Al₂O₃ films at room temperature using short purging times in the order of seconds. PA-ALD of 20 nm-thick Al₂O₃ on PEN resulted in a very good WVTR of $5 \times 10^{-3}$ g/m²day.

References