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Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Atomic and molecular layer deposition for surface modification

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ARTICLE INFO

Available online 8 December 2013

Keywords:

Adhesion
Atomic layer deposition
Hybrid
Inorganic
Surface treatment

ABSTRACT

Atomic and molecular layer deposition (ALD and MLD, respectively) techniques are based on repeated cycles of gas–solid surface reactions. A partial monolayer of atoms or molecules is deposited to the surface during a single deposition cycle, enabling tailored film composition in principle down to molecular resolution on ideal surfaces. Typically ALD/MLD has been used for applications where uniform and pinhole free thin film is a necessity even on 3D surfaces.

However, thin – even non-uniform – atomic and molecular deposited layers can also be used to tailor the surface characteristics of different non-ideal substrates. For example, print quality of inkjet printing on polymer films and penetration of water into porous nonwovens can be adjusted with low-temperature deposited metal oxide. In addition, adhesion of extrusion coated biopolymer to inorganic oxides can be improved with a hybrid layer based on lactic acid.

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1. Introduction

Atomic and molecular layer deposition (ALD and MLD, respectively) techniques utilize repeated cycles of self-limiting gas–solid reactions based on self-assembly chemistry. The precursor gases are pulsed into the reactor chamber alternately, separated by inert gas pulses to purge the reactor chamber from excess gaseous precursors and by-products. During such a cycle, only one molecular layer is deposited on the surface, enabling tailored composition in principle down to molecular resolution on ideal surfaces. These cycles are repeated until a layer with a specific thickness is achieved. This level of precision and resulting defect free conformal thin films have made ALD and MLD interesting techniques for applications such as microelectronics, displays, catalysis, solar energy and microelectromechanical systems [1], and diffusion barriers on polymers in general [2–10].

In this study non-ideal behavior of polymer substrate materials are studied in detail. The purpose is to demonstrate that low-temperature ALD/MLD can also be used as a tool to adjust wetting and adhesion characteristics of inorganic and non-ideal polymeric surfaces. In addition to conventional Al₂O₃ and TiO₂, we have been developing hybrid material based on the trimethylaluminum (TMA) and lactic acid.

Unlike with traditional solid substrates, such as silicon, glass and metals, small precursors can adsorb into near-surface regions

of the polymer substrate during the first deposition cycles depending on the polymer type, the precursors and the deposition temperature [11,12]. The precursors can react with the chemical groups on and within the polymers, and increasing the number of such groups before deposition leads to a more even film and enhanced film properties, especially with thinner films [8,12–20]. Different kinds of gas–solid reactions (ligand exchange, dissociation and association) are possible [21]. During this initial growth metal oxides start also to form clusters [11,19,22,23]. Surface roughness of polymer films can decrease after a few deposition cycles and increase thereafter [19].

Hyde et al. studied polypropylene and cotton fabrics [24]. The abrupt transitions in wetting behavior after ALD were explained by roughened surfaces and nucleation effects. Polypropylene fabric could be changed to a wetting state with Al₂O₃ depending on the deposition temperature and the number of deposition cycles, while cotton fabric indicated a strong and long lasting hydrophobic effect after the first TMA deposition cycles. This was explained by the stable Al–(O–C–)₃ groups on the cellulose with minimal number of hydrophilic Al–OH groups and carbon adsorption after deposition [25].

Relatively little has been published about further converting of ALD/MLD thin films. Inorganic oxide layers on polymer films in most cases require also an additional polymer layer to enable heat sealing and to protect the thin film from mechanical damages and exposure to liquids [20]. The sealant layer is typically applied with extrusion coating where a polymer melt is introduced and pressed onto the ALD surface. Adhesion of low-density polyethylene, polyethylene terephthalate, and polylactic acid on ALD Al₂O₃ were

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tested [26]. Good adhesion was achieved only with the low-density polyethylene. Interestingly, thin films of organic–inorganic hybrid materials based on unsaturated and saturated linear carboxylic acids and TMA have been developed [27,28].

2. Experimental details

2.1. Thin film deposition

For inkjet studies Al_2O_3 was deposited on commercial biaxially oriented polymer films. 40 μm thick polylactic acid (BOPLA; BI-AX 40-EV) film was obtained from BI-AX International Inc. and 50 μm thick polypropylene (BOPP; RayoFace C50) film from Innovia Films. These films were three-layer structures: a core layer sandwiched between two thinner skin layers. One side of BOPP film was corona treated. A polished silicon wafer (Si(1 0 0), MEMC St. Peters) was used as a reference substrate. All thin film depositions were carried out in a commercial SUNALE™ ALD reactor at 80 °C. The precursors for the Al_2O_3 depositions were TMA (SAFC Hitech, electronic grade purity) and water/ozone. High purity N_2 (99.9999%) was used both as the carrier and the purge gas in all three cases. Precursor dose and purge times were 0.1/12/0.1/12 s for TMA/ N_2 / H_2O / N_2 and 0.1/12/0.5/12 s for TMA/ N_2 / O_3 / N_2 , respectively. The number of cycles was 0, 5, 10, 15, 20 and 25.

The nonwovens used in this study were a 50 g/m² wet-laid fabric (50/50 viscose/cellulose) from Ahlstrom Inc. and an air-laid and pressed 60 g/m² cellulose nonwoven from McAirLaid Inc. (T070). TiO_2 coatings were deposited using titanium tetrachloride (TiCl_4 ; SAFC Hightech, electronic grade purity) and water as the precursors, and Al_2O_3 coatings using TMA and water as precursors. Deposition temperature was 100 °C. The cycle consisted of 0.2/12/0.2/12 s for TiCl_4 / N_2 / H_2O / N_2 and 0.1/12/0.1/12 s for TMA/ N_2 / H_2O / N_2 . ALD layers were deposited with 5, 15 and 25 deposition cycles. Thicker layers were also deposited as references.

Silicon wafers and cellophane film (NatureFlex 42 NP) from Innovia Films were used as substrates for the adhesion study. As a reference, 25 nm of Al_2O_3 was deposited using TMA and water onto these substrates in SUNALE™ ALD reactor at 100 °C. DL-lactic acid solution (~90%) was obtained from Sigma Aldrich and heated to 115 °C for deposition. The reactor temperature was 125 °C and the deposition cycle was 0.1/6/0.4/6 s for TMA/ N_2 /lactic acid/ N_2 cycle.

2.2. Characterization methods

Inkjet printing tests were initially performed with DWP (Digital Web Printer) with a solvent ink (Sun Jet Crystal UFX black from Sun Inc), a web speed of 6 m/min and a target resolution of 360 dots per inch (dpi). Later we utilized DMP (Digital Material Printer) with a dyed aqueous inkjet ink (Sensient Elvajet Magenta SK150 from Sensient) with the same dpi target. Print quality was estimated both visually and based on the number of dots obtained from the negative image of printed polymer films by using image analyses (Fig. 1).

Contact angles were measured using a CAM 2000 from KSV Instruments and the sessile drop method with 1–3 test liquids including water. The average value of contact angles measured on three to five locations on the sample was taken.

Thickness and refractive index of thin films on silicon wafers were determined with a single wavelength ellipsometry (SE400adv, Sentech Instruments GmbH) with angle of incidence of 70°.

Liquid wicking was determined with modified ISO 9073-6:2000E. Capillary rise of blue colored water was followed as function of time. Two to three parallel tests were performed.

Hybrid surface composition was analyzed with X-ray photoelectron spectroscopy (XPS) using an AXIS 165 electron

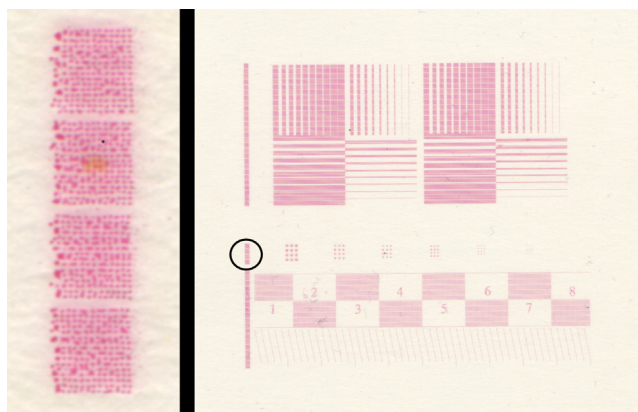


Fig. 1. Ink jet print layout with a resolution of 360 dpi used in this study. The part of printed image used for image analyses marked with a circle and magnified on the left. Size of each square approximately 1 mm times 1 mm. The maximum number of dots in the four printed squares 900.

spectrometer, monochromated Al $K\alpha$ irradiation at 100 W, a slot-M lens configuration and a charge neutralizer. Each sample batch was pre-evacuated and measured together with the lab-specified in-situ reference sample [29]. The analysis area was less than 1 mm², analysis depth less than 10 nm, and several data points were recorded for each sample. In data analysis, the C 1s high resolution signal was curve fitted with four symmetric Gaussian components (referring to carbon atoms with 0, 1, 2 or 3 bonds to oxygen neighbors). The binding energies were corrected using the C/C component of the C 1s peak at 285.0 eV [30].

Chemical composition of TMA/lactic acid hybrid films on silicon wafers were also measured by Fourier transform infrared spectrometer (FTIR). The reference samples were lactic acid spread as a drop on a silicon wafer and 25 nm of Al_2O_3 deposited on silicon wafer using TMA and water at 100 °C. The surface IR spectra were measured with 60° germanium ATR (attenuated total reflectance) crystal of VariGATR™ accessory attached to the Nicolet iS50 FTIR spectrometer. Spectra were collected by averaging 64 scans at a resolution of 4 cm⁻¹. ATR and baseline corrections were performed before spectrum interpretation. Three IR spectra were measured from each sample surface and an average spectrum was calculated of three parallel measurements. The surface spectra were then compared to the reference spectra.

Adhesion in extrusion coating was modeled with Kopp Labor-master HCT 3000 heat seal and hot tack tester. One jaw was kept at 30–50 °C and the other one at “polymer melt temperature” of interest (140–180 °C). Sealing time was 10 s and pressure 1.6 MPa. Cold tack was measured after 20 s at a peeling rate of 12 m/min. Two to three parallel measurements were performed for each test point.

3. Results and discussion

3.1. Inkjet printing onto polymer films

Initial printing tests were performed with a solvent inkjet ink. However, aqueous inks are more critical when it comes to the wetting characteristics of polymer surfaces. Fig. 2 demonstrates a set of images obtained from BOPLA samples with ALD Al_2O_3 and printed with an aqueous ink. The sample with 5 ALD cycles had clearly the highest number of dots. This indicated a strong hydrophobic transition with BOPLA after few TMA/water cycles—an effect similar to that suggested by Hyde et al. [24] and Lee et al. [25] for cellulose fabrics. As no significant effect was observed in contact angle measurements, the surface does not

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