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Liquid phase deposition methods monitoring techniques influence for solid substrates and thin metal oxide films properties

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Properties

ABSTRACT

Purpose: Liquid phase deposition (LPD) method is a useful method to create thin oxide films from aqueous solutions under ambient conditions. Deposition of ceramic layers on polymers is a technological challenge because of polymer sensitivity to chemicals and high temperature processing.
Design/methodology/approach: The work attempts to elucidate the role of the substrate during LPD of TiO2 films by using Kapton with different types of surface treatments.
Findings: Was found that small differences in pH, temperature, and solution composition can lead to dramatic differences in the film's crystallinity, adherence, and growth rate. Thin films are very smooth, uniform with small amount of cracks.
Research limitations/implications: Independent of technique and substrate, film thicker than a few hundred nm exhibited cracks, attributed to stresses that result during drying of the film.
Originality/value: Techniques for monitoring the surface chemistry of the solid substrate and the deposited ceramic film have been developed.
Keywords: Mechanical properties; Thin films; Deposition methods

1. Introduction

Techniques for synthesizing inorganic oxide thin films from low-temperature liquid solutions have received increasing interest in recent years. Lower temperatures allow films to be deposited on substrates that might not be chemically or mechanically stable at high temperatures. Liquid phase deposition (LPD) is an aqueous technique for deposition of oxide films that has been widely used for SiO_2 but is being studied increasingly as a method for films of other oxides such as Titania and others. LPD was first reported in a 1950 patent by Thomsen. In the 1980's Kawahara and co-workers patented a related method for coating glass with TiO_2. The distinguishing characteristic of LPD is the use of a solution of metal-fluoride complexes whose hydrolysis in water is modulated by adding boric acid (H_3BO_3) or aluminum metal. The fluoride ligand provides for a slower and more controllable hydrolysis, while the boric acid or the aluminum functions as F^- scavengers [1].

2. Experimental

2.1. Equipment

UV ozone cleaning of substrates was done using a UVOCS Model 10-X10/OES/E. Air-plasma cleaning of substrates was done using a PDC-3XG model. Solution pH was measured using a Metrohm model 691 pH meter.

Wetting properties were assessed by water contact angle measurements using a Rame Hart Model 100 Contact Angle Goniometer. External reflection FTIR microscopy spectra were collected on a Bruker Model Vector 22 FTIR spectrometer using the A691 microscope reflection accessory with an internal A690/3-R MCT detector.

All techniques and instruments to characterized film of Titania are illustrated and described in previous publications [2, 6].

2.2. Samples

Kapton® grades 500HN (or VN) with thickness 125 mm were received from DuPont TM Company.

2.3. Surface activation

To activate the surface, samples were treated for 20 minutes in a UVOCS cleaner or for 20 min in air-plasma to both sides and used immediately upon removal (Fig. 1). Samples treated in this way were substantially more hydrophilic than untreated polymer (contact angle of samples was exchanged from 64° to 0°).

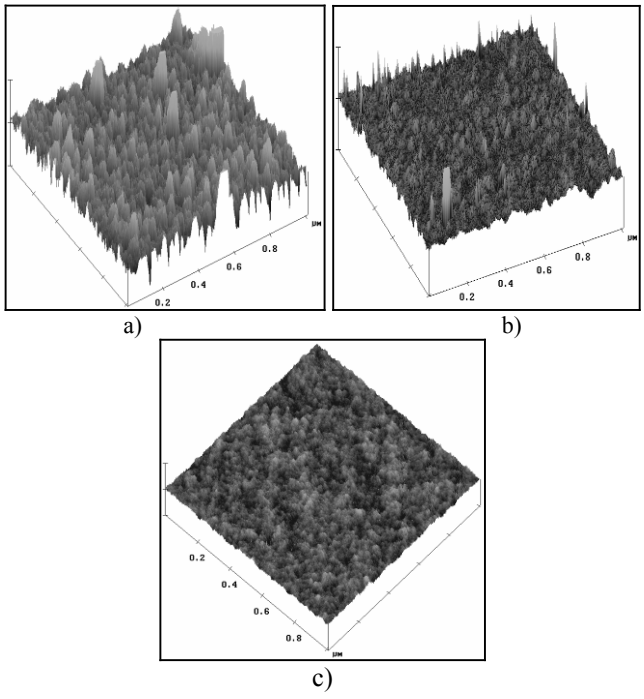


Fig. 1. AFM of Kapton surface: a) After 20 min UVOCS; b) After 20 min air-plasma; c) Clean Kapton

2.4. LPD of titania

LPD of Titania was made by three different methods.

LPD using TiF_4 (Method #1) [4]: The procedure involves immersing a sample (vertically) into 0.3 M H_3BO_3 and 0.1 M $(NH_4)_2TiF_6$ solution kept at room temperature. Substrates were left in the solution for 4 to 48 h, after which they were washed with water and dried using one of the procedures detailed below.

LPD using TiF_4 with added HCl [2] (Method #2): The procedure involves immersing (vertically) a sample (either a silicon wafer or polymer into a 0.15 M H_3BO_3 and 0.05 M $(NH_4)_2TiF_6$ solution. HCl was added to adjust the pH to 2.88 and the solution was kept at 50 °C. Substrates were left in the solution for 2-22 h and then washed with water and dried using one of the procedures detailed below.

Method Nr.3: solution of [CH3CH(O)-CO2NH4]2-Ti(OH)2, pH = 1.76, 70 °C.

2.5. Drying of TiO_2 films

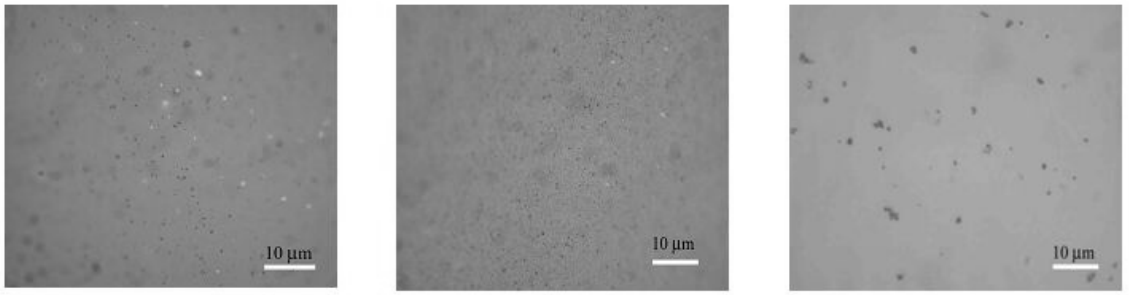
Drying samples by changing the humidity (while maintaining a constant temperature) was done in 3 methods. They involve: a) relative humidity was controlled by equilibration over various salt solutions, where temperature was kept at 25 °C; b) dried by slowly reducing the humidity in steps from 70/80 % to 60 % to 40 % to 20 %, when the drying was done at 70 °C, c) humidity was reduced in a steady ramp down from 70 % to 20 %, when the drying was done at 70 °C [6]. Fig. 3 summarizes the 90 hr step and ramp drying procedures.

Treatment of the Kapton® by UVOCS gave badly incomplete films of Titania after 2 h by method #2 Fig. 5, unlike method #1 Fig. 4. However, it yielded full-coverage films in 7 h in both methods. The Fig. 8 indicates the differences in growth rates attained by the method #2 dependence of activate surface of substrate. In addition, significantly, Titania film on the Kapton® after 24 h is smoother.

Observations by optical microscopy revealed that the film cracked on the surface of the Kapton® during the drying stage when DI water was used. When methanol instead of water was used as the drying solvent, the extent of cracking was significantly reduced as shown by SEM in Fig.4. This situation was right only in compose with humidity step program of the drying process.

LPD methods were applied to deposit TiO_2 on surface-activated Kapton® samples. All of the TiO_2 on-Kapton® coatings reported herein were found to be stable to sonication in water and were sufficiently adherent so that they could not be removed by a standard tape test.

Cleaning and activation of the surface of the Kapton® coupons were done by first rinsing in ethanol and then exposing the Kapton® surface by two methods: UVOCS activation for 20 min and air-plasma activation for 20 min on the both sides. The survey by XPS measurement showed that the plasma (or UVOCS) treatment led to changes in elemental composition for the surface of the Kapton film. The comparison of the O/C and N/C atomic ratio for the Kapton films treated by two methods for 20 min were following. The O/C and N/C atomic ratios determined by XPS for the untreated Kapton film are 0.197 and 0.056, respectively, that are slightly lower than those calculated from the repeating unit structure, $C_{22}H_{10}N_2O_3$, O/C = 0.227 and N/C = 0.091. This difference, similarly reported by Pertsin and Pashunin [3], may be due to carbonaceous contamination or heterogeneous structure of the outermost layer.



a) b) c)

Fig. 2. Optical microscope measurements. The best results showed films created by Method # 1(a) and Method # 2(b). Method # 3(c) doesn't give any film of Titania

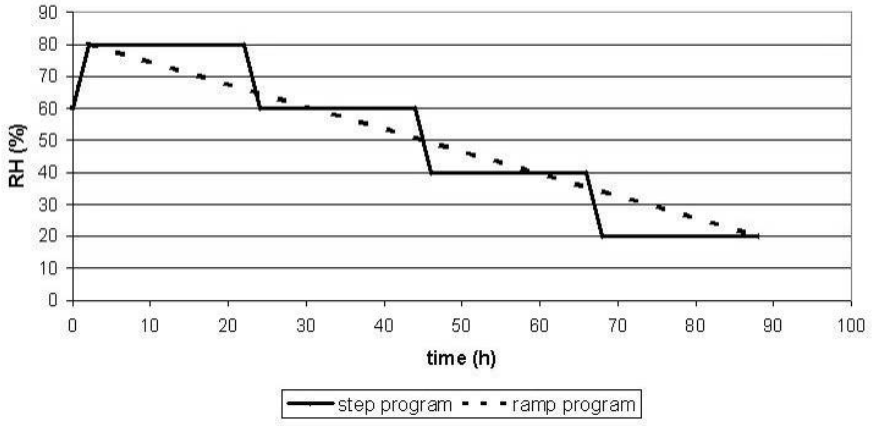
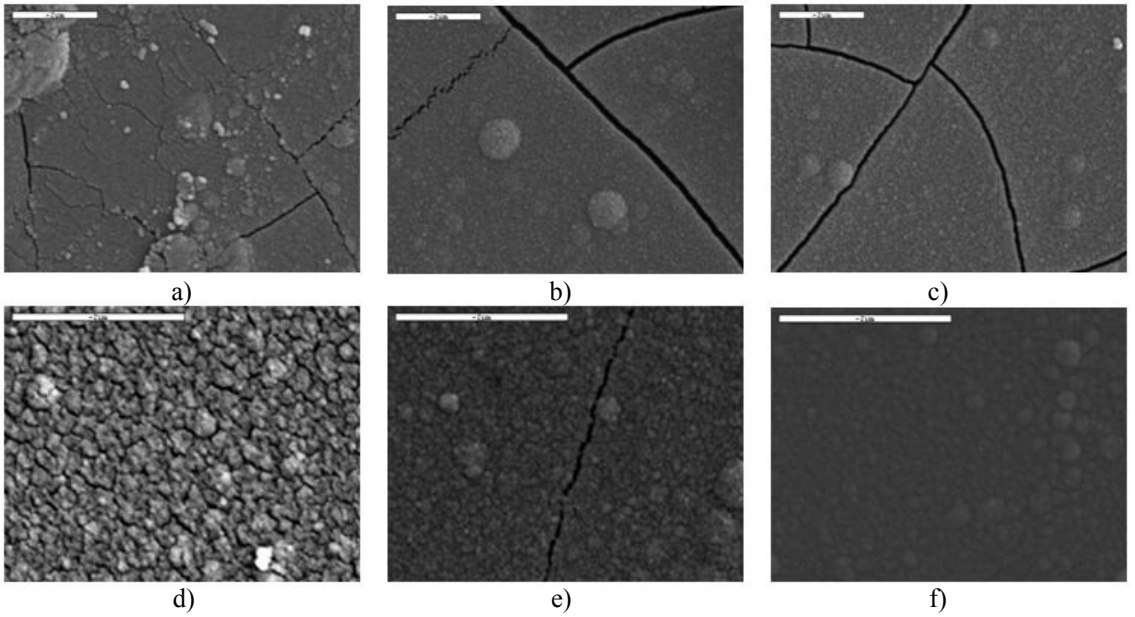


Fig. 3. Schematic of the 90 hour step and ramp drying programs



a) b) c)

d) e) f)

Fig. 4. SEM micrographs of method #1, pH = 3.88, rt, films deposited, washed by water: a) 48 h, b) 24 h, c) 7h, washed by methanol: d) 48 h, e) 24 h, f) 7 h (bar - 2µm)

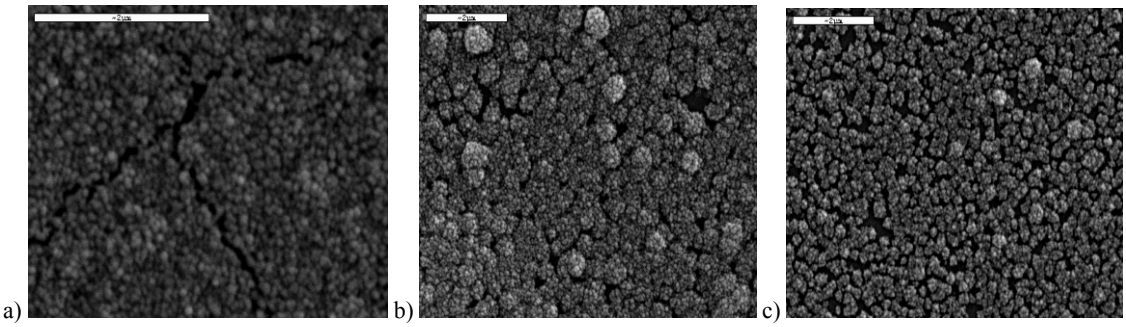


Fig. 5. SEM micrographs of method #2, pH = 2.88, films deposited: a) 2 h, b) 3 h, c) 7 h. (bar 2µm)

XRD analysis of the specimen of TiO_2-coated Kapton shown in Figure 6. The reference spectrum for anatase (JCPDS 84-1286) is indicated at the bottom of the figure.

The thickness of the titania coating was determinated by cross-sectional SEM. Fig. 7 shows samples ranging in thicknesses from 200–500 nm. EDAX verified the identity of the Titania layer and its thicknesses could be directly determined from the SEM images.

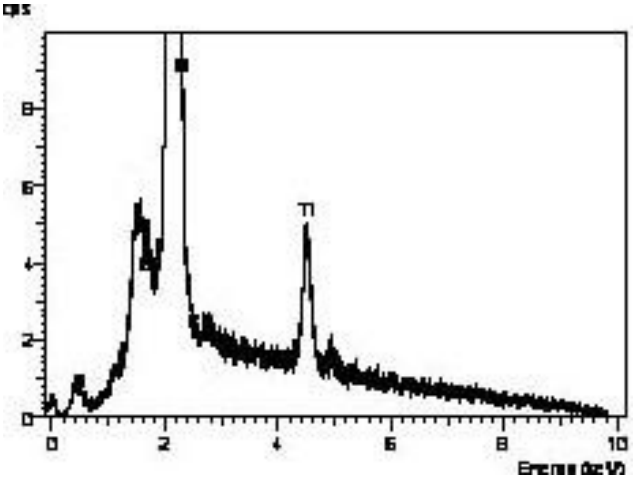


Fig. 6. XRD analysis of the specimen of TiO2-coated Kapton

3. Discussion and conclusions

3.1. Titania deposition and characterization

Given their relatively low acidity and low temperature, LPD methods are ideally suited to polymer substrates. The Method #1 (pH = 3.8; room temperature) was applied to unactivated Kapton. SEM analysis showed that the deposited Titania was 200 nm thick after 24 h and a 400 nm film was deposited in 48 h.

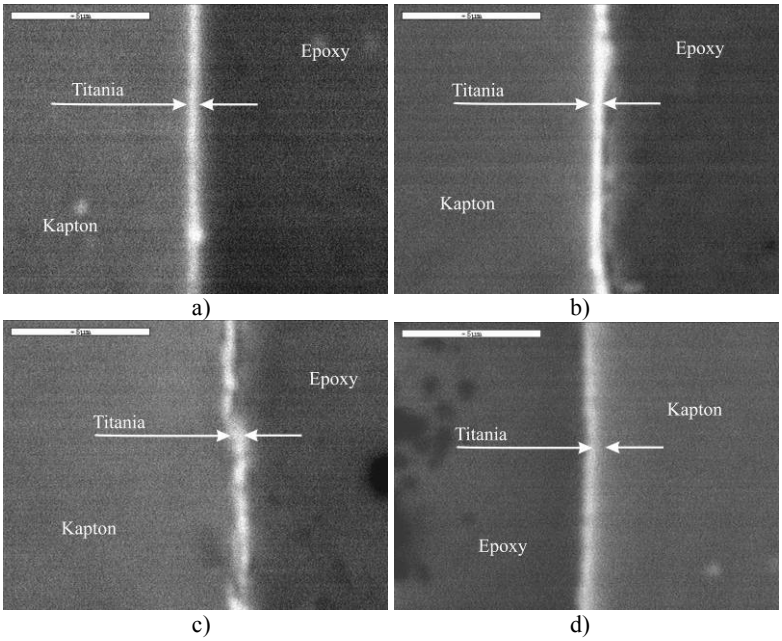


Fig. 7. Cross-sectional SEM images of Kapton coated with TiO2 a) method #1, 24 hours coating time (thickness ~ 200 nm); b) method #1, 48 hours coating time (thickness ~ 400 nm); c) method #2, 3 hours coating time (310 nm); d) method #2, 7 hours coating time (thickness ~ 16 nm)

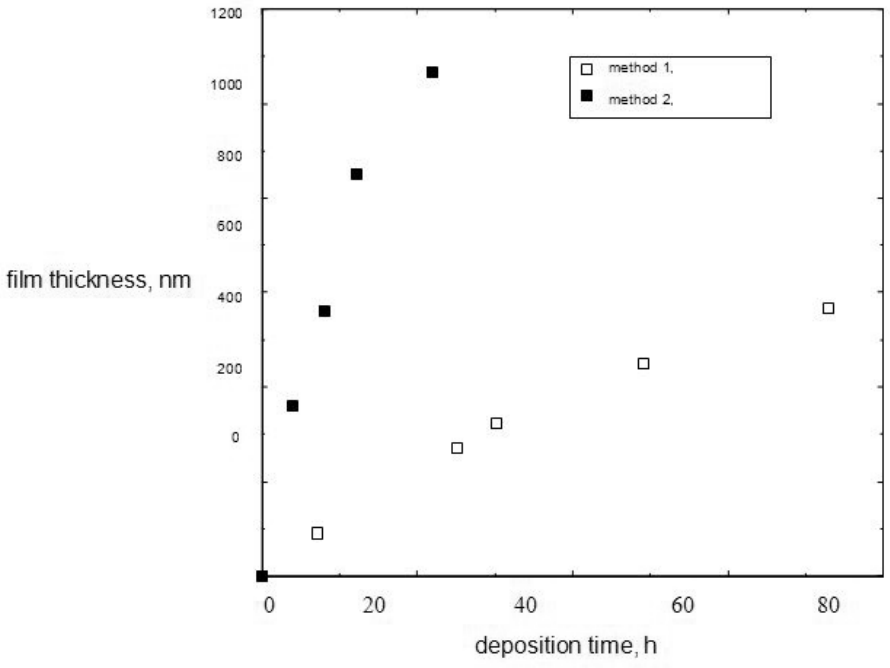


Fig. 8. Deposition growth rate of Titania thin films

Method #2 (pH 2.8, 50 °C) was used to deposit (7 h) TiO2 on Kapton. It yielded a film that was 400 nm thick in SEM (Fig. 7).

Depending of deposition time thickness of Titania coatings on Kapton is 100–400 nm (Fig. 8).

Exchanging of the solvent to the solvent with less surface tension in the cleaning step and drying in a controlled fashion does contribute to the minimizing of cracks in the films and (likely) to the effectiveness of its barrier properties.

Films with thickness less 250 nm are uniform and without cracks. Thicker films are with small amount of cracks (width of cracks is ≈ 50 nm).

Each potential application must be examined in terms of the effect of the deposition chemistry on the mechanical and thermal properties of the polymer substrate, the requisite thickness of the ceramic layer, and optimization of post-processing steps.

The low-cost and convenience of LPD coatings and their lack of line-of-site limitations strongly recommend their being considered as a general strategy. Moreover, the relatively mild conditions for ceramic film formation using LPD methodology makes them prime candidates for application on polymer substrates.

It is interesting that variations in the LPD recipe that give rise to very different rates of ceramic film formation (Method #2 > Method #1) and that can be controlled to provide either crystalline (Method 2) or amorphous (Method 1) titania are both equally effective in producing adherent conformal thin film coatings on Kapton® [5].

Finally, the severity of cracking was reduced when the wash solvent was changed from water to methanol.

As methanol has a lower surface tension, this indicated that the film cracking was due to the capillary stresses exerted by meniscus of the drying solvent on the walls of nanosized pores as it moved through the film. Independent of technique and substrate, film thicker than a few hundred nm exhibited cracks, attributed to stresses that result during drying of the film.

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