Thin Solid Films 646 (2018) 53–60

Contents lists available at ScienceDirect

Thin Solid Films

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

Failure mode analysis on thermally aged hydrophobic coatings applied to electro wetting

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ARTICLE INFO

Keywords:
Adhesion
Electrowetting
Interface
Ageing
Surface

ABSTRACT

The aim of this study is to investigate the degradation of hydrophobic coatings at the origin of reliability failure. Various properties such as adhesion and wetting after thermal ageing have been investigated. The layers studied, parylene C, Cytop and Fluoropel deposited on silicon wafers are widely used in electrowetting, MEMS and Lab-on-chip devices. A detailed failure mode analysis is presented, involving chemical surface modification through secondary ion mass spectroscopy by time of flight, X-ray photoelectron spectroscopy, surface energy and tensile strength measurements. We've been able to identify and quantify the origin of failure for each type of coating and the method we applied can be extrapolated to other hydrophobic coating as a benchmark for reliability improvement.

1. Introduction

Adhesion and durability of coatings on substrates is a major issue in many fields such as painting, adhesive, or wear protection. Understanding the way coatings bond with surfaces remains the more straightforward manner to study rupture mechanisms and long term reliability. For this reason durability of polymer adhesive on different substrates such as ceramic or metals has been studied [1–4]. Improvement from adhesive bonding combined with proper characterization methods prove to be the way to increase durability of adhesive bond, between polymer and metals for example [1]. More specifically, Comrie et al. demonstrated the impact of moisture associated with heat treatment on adhesive joint and the evolution of reliability [2] using a non-destructive method to study and characterize the evolution of joint in a very humid environment. Other improvement on adhesion of paint on plastics involve the composition [5], or the adhesion enhancement (plasma, flame treatment or coupling agents) [6–8]. Garbassi et al. for example, shows the impact of flame treatment on the top surface chemistry and the depth of oxidation for polypropylene pieces. The treated surface is then studied by XPS, TOF-SIMS and contact angle. After several flame treatment, adhesion is promoted thanks to the creation of hydroxyl group on polypropylene pieces surface; and oxidation is shown by apparition of carboxyl group [8].

Electrowetting on dielectric [9] actuation is now widely used for lab-on-chip [10–12], display [9,13], or liquid lenses [14,15] and is based on modulation of wetting properties of electrolyte droplets on surfaces thanks to an electric polarization. It results from the equilibrium of two forces: electrostatic force, which tend to spread electrolyte droplet and surface tension force which tends to limit the expansion of the liquid interface. Even though electrowetting actuation is now available in actual products, many parts of the phenomena remain unknown and need further research since any non-controlled properties modification could lead to device breakdown or dysfunction.

Ageing/breakdown of layers used in electrowetting for instance has been mostly studied when voltage is applied (DC or AC) [15]. Dhindsa et al., studied the self-healing properties of an oxide layer to prevent and repair breakdown [16]. Gupta et al. showed the performance loss of layers by pinning the triple contact line [17]. Optimal thickness used in electrowetting on dielectric (EWOD) correlated with hysteresis is investigated by Chae et al. [18]. In addition to operating conditions, product lifetime is also critical for market acceptance and it is important to evaluate thermal ageing while not in use. Indeed, it is very important to get devices lasting for a very longtime both in use and idle.

In this paper, layers commonly used in electrowetting such as Parylene C, Fluoropel and Cytop are thermally aged in water for seven days at 85 °C, to simulate accelerated ageing while stocking. Strong modifications from such treatment are described through surface modification including chemical modification and de-cohesion of layer

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https://doi.org/10.1016/j.tsf.2017.11.034
Received 2 August 2017; Received in revised form 16 October 2017; Accepted 26 November 2017
Available online 28 November 2017

Table 1
Thickness and capacitance of layers studied in electrowetting.

	Insulating layer		Hydrophobic coating		Capacitance
	d (nm)	ε	d (nm)	ε	Cs (F/m^2)
Parylene C	5600	3.1	–	–	4.9E − 06
Fluoropel covered parylene C	5600	3.1	50	2.1	4.8E − 06
Cytop covered parylene C	5600	3.1	50	2.1	4.8E − 06

to identify failure mode for these coatings and improvement strategies.

2. Experimental details

2.1. Sample preparation

Parylene C coatings have been prepared on silica substrate by CVD using a Kisco system. The Dichloro-di-para-xylylene cyclic dimer precursor has been provided by Kisco as diX C. Cytop® CTX 809 has been supplied by AGC Chemicals. Hydrophobic coatings based on fluorinated polymers have been obtained by spin coating of a solution of Cytop® directly spun on the latter dielectric coatings of Parylene C at 4000 rpm for 90 s, Fluoropel® 1601 V has been supplied by Cytonix Co. The as-received product has been spun at 6000 rpm on dielectric coatings of Parylene C. Samples are then annealed at 90 °C for > 15 h on a hot plate. Three types of samples are studied: pristine Parylene C substrate, a Fluoropel covered Parylene C and Cytop covered Parylene C. Parylene C coating is 5.6 μm thick and additional layer of Cytop and Fluoropel are about 50 nm thick (see Table 1).

2.2. Ageing procedure

A hermetic sample holder, with a capacity of 12 cells, permits to age any surfaces in any liquid. In our case, we used de-ionized water as we previously established (internal work within Varioptic) that it was critical for both hydrophobic properties and adhesion of the layer studied. In order to have a reproducible ageing procedure, we also used a standardized treatment [19], storing samples for one week at 85 °C in 10% of relative humidity in a controlled conditions Binder oven. This ageing procedure is described in IEC 60068-2-2 norm.

2.3. Surface energy

The theory behind these methods (one liquid OWKR and two liquids) are used as described by Maillard et al. [20]. Contact angles have been measured on a Kruss easydrop® goniometer associated to the software Drop Shape Analysis using water [21], decane [22], octane [22], diodomethane [23], ethylene glycol [24,25], and bromonaphtalene [24] as reference liquids. Different coatings have been used such as Parylene C coatings [19] covered or not with fluorinated coatings of Cytop and Fluoropel. Each surface is tested with at least three different liquids for reproducibility. For each tested liquid, three drops of 3 μL are deposited onto the surface, measuring the advancing contact angle in an ambient medium (air or electrolyte). Since substrates are made of ⟨100⟩ silicon wafer, surface roughness is extremely low (ra < 1 nm) and deposition method for Parylene C and top-coats does not significantly increase roughness [26,27].

2.4. Adhesion

A modified tension-compression machine has been used to test adhesion of samples. Customized pulling test pieces have been made: the section for testing is of about 2.2cm^2. Then, the different parts of the system are glued with epoxy-amine (Araldite 90s) on the coating side and cyanoacrylate glue (Loctite Superglue 3) on the substrate. Each side of the samples are spread with the corresponding glue, hold for 30 s and finally let to dry overnight. The testing area is delimited by cutting the coating around the pulling test-piece in order to control the de-adhesion surface. Thanks to a software coupled to the machine, the strength leading to the surface break is given and adhesion can be appreciated with the equation: C = F/S with C the constraint in Pascal, F the force in Newton and S the surface in square meters.

Each coating has been tested at least 5 times to be representative and reproducible.

Afterwards, the rupture zone is observed with Scanning Electron Microscopy (SEM) and analyzed by energy-dispersive X-ray spectroscopy (EDS) in order to characterize species remaining on the samples and establish failure mode.

2.5. Scanning electron microscopy (SEM)

The SEM used is the FEI Quanta 250 FEG allowing us to take pictures between 1 and 10 kV at around 400 × magnitude under high vacuum. Each sample were fixed using carbon scotch on sample holder. Parylene C coatings have been metalized with platinum on a Balzers MED 010. Fluoropel and Cytop coatings were not metalized because of their low thickness (≤ 25 nm), in order to avoid roughness and surface aspect artifacts.

2.6. XPS and TOF-SIMS

Measurements were done using a PHI Quantera SXM instrument (Physical Electronics, Chanhassen, USA) equipped with a 180 hemispherical electron energy analyzer and a monochromatized Al K$_\alpha$ (1486.6 eV) source operated at 15 kV and 4 mA. The analysis spot had a diameter of 200 μm and the detection angle relative to the substrate surface was 45°. Standard deviations were calculated from measurements performed on two different areas. Data were analyzed using the Multipak software. The depth probed of XPS analysis is between 5 and 10 nm. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurements were carried out on a TRIFT III ToF-SIMS instrument from Physical Electronics operated with a pulsed 22 keV Au + ion gun (ion current of 2 nA) rastered over a 300 μm × 300 μm area. An electron gun was operated in pulsed mode at low electron energy for charge compensation. Ion dose was kept below the static conditions limit. Data were analyzed using the WinCadence software. Mass calibration was performed on hydrocarbon and fluorocarbon secondary ions. The coatings were analyzed on < 3 nm of depth and under ultra-vacuum.

3. Results and discussion

3.1. Failure test: EWOD

A simple way to see whether or not a layer is aged, is to perform an electrowetting test. Electrowetting corresponds to the modification of wetting properties, from an electrolyte fluid standing on an electrically polarized dielectric coating and it results from the equilibrium of interfacial energy between the spreading electrolyte on a surface and electrostatic energy condensing ions from electrolyte solution near the contact line. Phenomenon occurs whether medium surround electrolyte is air or any non-conducting fluid such as oil and is well described by Young-Lippmann Eq. (1):

$$\cos\theta(V) = \cos\theta_0 - \frac{1}{2}\frac{\varepsilon\varepsilon_0}{e\gamma_{LG}}V2$$

where θ is the contact angle from the non-conductive medium at a given voltage, θ_0 the natural contact angle, ε the permittivity of the material and ε_0 the vacuum permittivity, e is the dielectric thickness, V is the applied voltage and γ_{LG} is the interfacial tension between the drop and the medium (usually around 15 mJ/m^2 with the liquids used).