Durable Super-Hydrophobic Nano-Composite Films

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ABSTRACT

A durable super-hydrophobic nano-particle based coating based on an ALD/CVD deposition process of alumina has been characterized. This new conformal coating is ideal for protecting printed circuit boards from water damage. Products coated with this composite film exhibit excellent resilience when exposed to aqueous solutions. The mechanical durability of this film was improved by using silane surface reactions which improved inter-particle and surface adhesions. Under water erosion tests, an improvement of >400x over non-reinforced films has been obtained. The shear failure of the film is tuned to allow electrical connections to be made through the coating. This allows many existing products, such as printed circuit boards, to be protected with a non-wetting surface coating without product redesign.

Keywords: super-hydrophobic, super-oleophobic, nano-composite, conformal coatings, water-safe electronics.

1 INTRODUCTION

For decades naturally occurring non-wetting and super-hydrophobic surfaces such as lotus leaves have captivated the imagination of engineers in their efforts to overcome failures and problems arising from water damage in unwanted places. With the recent development of a durable super-hydrophobic coating, protection methods against water damage are shifting from traditional physical barriers by encapsulation, or from costly packaging techniques with rubberized seals around ingress openings. Currently, printed circuit boards are covered with a protective film or "conformal coating" consisting of an organic material such as silicone, epoxy or urethane. The added thickness of these conformal coatings becomes problematic and must be accounted for in product packaging, because of the compact and sleek design requirements of popular portable consumer products. In addition, the added film causes contact resistance and inter-connectivity problems between electronic assemblies. Thus, the critical connectors are not coated and are often the failure points from shorts and electrical leakages caused by accidental exposures to liquids.

The mechanical structures required to create the properties of a super-hydrophobic coating are on the scale of nano-meters (10^{-9} meters) and thus require careful engineering [1,2]. As a result of the required ultra-fine structure, these nano-structured protective films are often fragile and have limited durability. In the past, the various techniques used to create the nano-structures depended on the targeted material and their application over large areas and complex 3D shapes tended to limit their applicability, which also was costly.

In this paper, a non-wetting, super-hydrophobic coating which can be economically applied to large surfaces is briefly described. The mechanical durability developed to provide a commercially acceptable coating for protecting electronics is shown in Fig. 1. The ability of these types of durable coatings is not limited to PCB's and could be applied to other applications which will be discussed in the future.

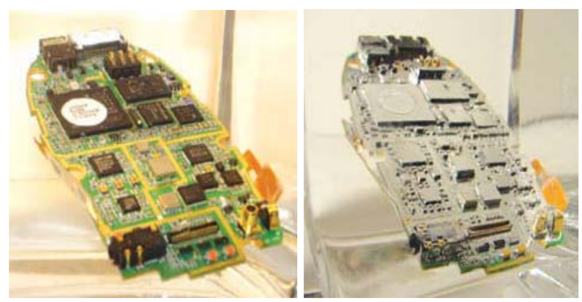

Fig 1: LEFT: A cell phone PCB immersed in water. The entire boards gets wet. RIGHT: Also immersed in water, a cell phone PCB that has been coated with a super-hydrophobic film. This coating, normally invisble, acts as a virtual force field that pushes water away from the surface, yielding a silvery appearance under water that protects the board from water damage.

2 EXPERIMENTAL AND APPARATUS

The coating technology developed is called "Vapor Particle Deposition" (VPD) for creating nano-particle composite films. The VPD method uses a sub-atmospheric gas-phase flow-through reactor which is suitable for large batch processing. The nano-composite structure is created using a hybrid atomic layer deposition (ALD) / chemical vapor deposition (CVD) process in which super-saturated vapor conditions are created [3]. During the process (patent pending), a metal organic precursor is oxidized in such a way that the proper film roughness and film coverage over the substrate are achieved. Subsequently, these nano-particles are encapsulated into a glass-like matrix to improve the film's durability. The final step includes a surface modification treatment to create a low surface energy state.

Nano-scale roughness of alumina were formed by the following oxidation reactions:

$$2Al(CH_3)_3 + 3H_2O \longrightarrow Al_2O_3 + 6CH_4 \quad \text{or by}$$

$$2AlOH^* + 2Al(CH_3)_3 \longrightarrow 2[Al\text{-}O\text{-}Al(CH_3)_2]^* + 2CH_4$$

$$2[Al\text{-}O\text{-}Al(CH_3)_2]^* + 3H_2O \longrightarrow Al_2O_3 + 2AlOH^* + 4CH_4$$

where * are surface bound species.

Alkyl bridge silanes are used to create silsesquioxane structures to strengthen the composite film and improve the mechanical durability of the film [4,5]. These were formed by the oxidation of silanes as described by the reactions of:

$$SiCl_4 + 2H_2O \longrightarrow SiO_2^* + 4HCl$$

$$C_2H_4Cl_6Si_2 + 6H_2O \longrightarrow SiO_x\text{-}(CH_2)_2\text{-}SiO_x^* + 6HCl + 3H_2O$$

$$C_6H_{12}Cl_6Si_2 + 6H_2O \longrightarrow SiO_x\text{-}(CH_2)_2\text{-}SiO_x^* + 6HCl + 3H_2O$$

The critical process parameters of the VPD process include the chemical doses and timing between the metal organic and oxidation precursors in the ALD/CVD reaction, which affect the surface diffusion and the chemical reaction. If the chemical injections are spatially partitioned to prevent gas phase interactions, an ALD type surface reaction occurs with insufficient roughness and structure formation. Conversely, a simultaneous injection of precursors results in a gas-phase CVD reaction in which "nano-dust" is formed with very poor surface coverage. The key process challenge was to allow sufficient and controlled intermixing so that the super-saturated condition was precisely tailored to create nano-particles uniformly through-out the reactor volume, leading to sufficient surface coverage of particles over the parts to be coated.

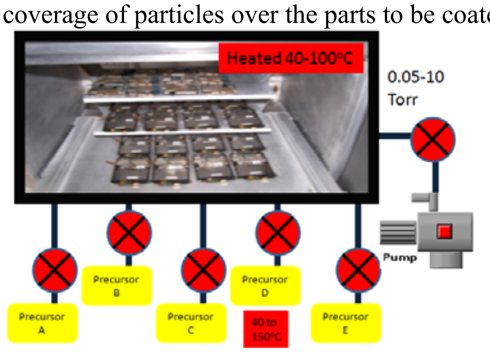

Fig 2: Schematic of the VPD coating chamber. Precursor vapors are introduced sequentially or concurrently to create composite layered films. A multi-shelf chamber configuration is available for large batch processing.

The coating equipment used was the RPX-540 manufactured by Integrated Surface Technologies (IST) (www.insurftech.com). The RPX-540 can deliver up to 5 different chemical precursors to create a custom nano-composite film. The entire coating system is precisely temperature controlled to ensure vapor delivery to the process chamber without condensation. Precursor chemistries can be heated from 40-150°C and the process chamber to 100°C. The process timing control is based on National Instruments' LABVIEW®. The process chamber can be configured to accommodate a variety of media, including printed circuit boards, small objects like hearing aids, or glass and plastic substrates. Batches of materials up to 2000-in^2 of flat board material can be processed in a single batch in about 30 minutes. The super-hydrophobic coating described for printed circuit board water protection is currently sold as "Repellix™". Low surface energy monolayers can be also processed, typically used as MEMS anti-stiction or imprint release layers or for a variety of adhesion promoters or bio-compatible anti-fouling coatings.

3 RESULTS AND DISCUSSIONS

Super-hydrophobic composite films were prepared under a variety of process conditions with varying roughness, thickness, and linking (glue) schemes. Since these films consist of "glued reinforced" particles or roughness, it was observed that film roughness alone (rms) was inadequate for predicting the performance of these films. An improved classification method which includes aerial surface density (or coverage) was determined a key part of film quality. Coverage between 25-60% was required. Future publications on this metrology characterization are forthcoming.

3.1 Film Characterization

Films were routinely characterized utilizing AFM, SEM, and Contact Goniometry. Additional metrology included TEM, FTIR, XPS, mechanical scanning wear by Hysitron, water erosion, optical transmission and TGA-MS. IST also perfomed biocompatibility tests based on ISO-10993 FDA guidelines and the material was deemed to be biocapatible. Film roughness ranged from 30-700nm rms (Fig. 3). The as-deposited composite is normally super-hydrophilic (water contact angle (CA) <10°)). After surface modification with a perfluoronated silane, the films exhibited super-hydrophobic (CA: >160°) and super-oleophobic (olive oil >160°) properties (Fig. 4). No change on contact angle was observed even under immersion conditions for >9 months. The surface energy of perfluoronated silicon was ~20 dyne-cm and the rough composite film was <5 dyne-cm. Typical film thicknesses ranged from 50-200nm.

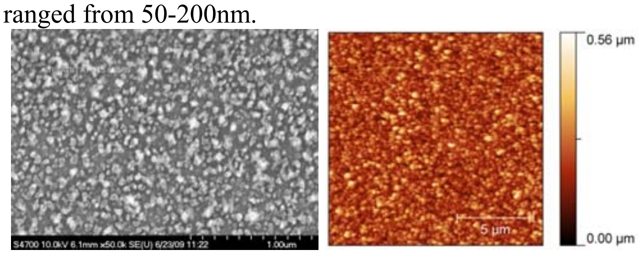

Fig 3: SEM and AFM of the super-hydrophobic nano-composite film. The rms roughness was ~164nm, average particle size ~30-35nm with an aerial surface coverage of ~42%.

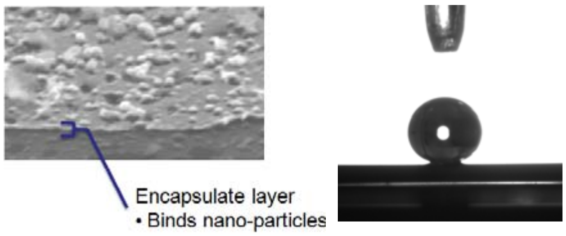

Fig 4: LEFT: An electron micrograph showing the glueing encapsulant for improved interparticle and particle-to-surface adhesion. RIGHT: After surface modification, the water contact angle is greater than 160^o.

3.2 Electrical Performance

This unique material is a non-wetting film that can be deposited over large areas or over entire assemblies, even over sensitive electrical connection points, creating a boundary layer of air. This feature provides protection so that manufacturers do not have to re-engineer the packaging enclosures of their products to accommodate for any thickness and stiffness. It is essential that the film permits electrical contact when mating with electrical connectors. To test contact resistance, a classic 4-point probe technique was employed. Molex brand flex ribbon connectors with 10 pins and 0.5mm pitch were coated with a super-hydrophobic film. The connectors were unmated during coating, and mated once for initial testing. A challenge current of 1mA was used and the voltage across each contact point was measured. The measured values differed only slightly from the nominal (manufacturer supplied value).

Various surface mount 40 pin socket connectors shown in Fig. 5 were also tested before and after the non-wetting Repellix coating was deposited. The chart in Fig. 6 shows the typical contact resistance of uncoated and coated connectors. No statistical significance was observed.

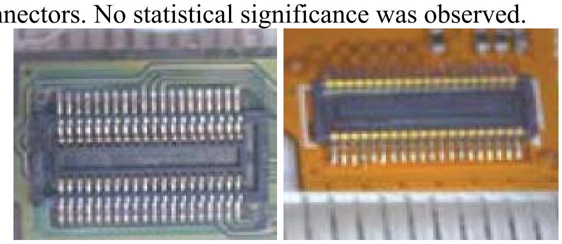

Fig 5: Typical multi-pin surface mounted connectors that are used in many consumer electronic products.

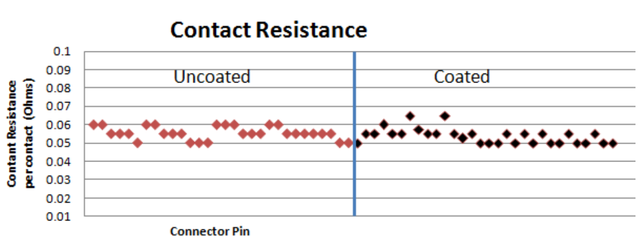

Fig 6: A representative chart of measured contact resistance of an array of connectors compare before and after coating results.

The durability of the nano-composite film is tuned by the inclusion of various levels of silane oxides which serve as inter-particle and surface adhesion "glues". This accounts for the cohesion of the film and the durability to accommodate light handling during the assembly process. During the connector insertion, the composite film is mechanically abraded, allowing physical contact to be made (Fig. 7). While a very small area of the sliding connector surface is exposed, surface tensions of aqueous liquids will not wet the contacting surfaces. If the glue oxide is made too thick, the mechanical force of the connector could be insufficient to reliably penetrate the composite film. In Fig. 8, the thick composite film shows areas in which good and poor contacting surfaces are achieved.

Fig 7: Optical micrograhs of the super-hydrophobic film which has been scraped away by the contacting barbs of the connector. The surface tension keeps the connecting pads from being wetted by liquids.

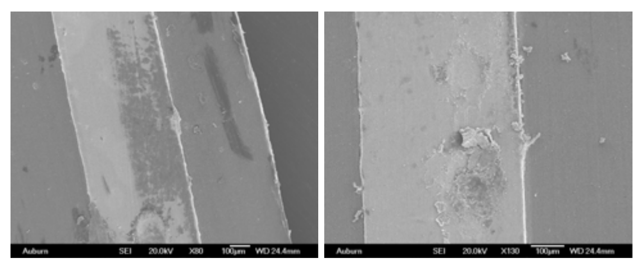

Fig 8: Durability of the connecting surface is controlled by the glueing agent process and the thickness of the film. Left: the non-wetting nano-composite film which is displaced by the mating connector revealing the base metal for good electrical connection. Right: A more durable coating which is not removed by the mating connector, leading to high resistivity and therefore electrical connection problems.

3.3 Durability Characterization

The mechanical durability of the nano-composites was tested using a Hysitron TI-950 Triboindenter. Wear patterns are created by raster scanning the nano-composite film with a given force predefined by the user. The scan can consist of a single pass or multiple passes over the same area within one test. By applying a known force and selecting the number of passes over which this force is applied, the amount of material that is removed during a scan can be measured post-testing, using the probe in an AFM contact mode as shown in Fig. 9.

Another technique used was a water droplet erosion test in which a stream of water droplets was used to erode a

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fixed area. The impact and shear force on the film can be calculated from the incident angle, impact height, rate, drop volume and time [6]. Shown in Fig. 10, an improvement of >400x can be obtained with increased inter-particle silanation.

The nano-composite films were also subjected to environmental stress testing and neutral pH salt fog. The particle film itself was resilient to these stresses and its super-hydrophobicity remained unchanged.

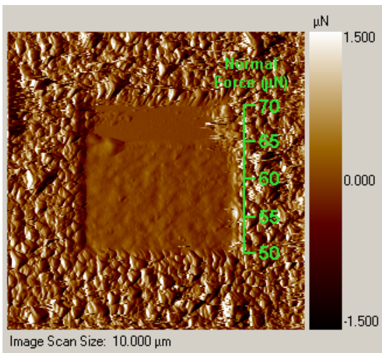

Fig 9: A 10x10µm topographical SPM image showing the 5x5µm worn area and surrounding surface. In this case, the film failed at a normal force of roughly 62µN.

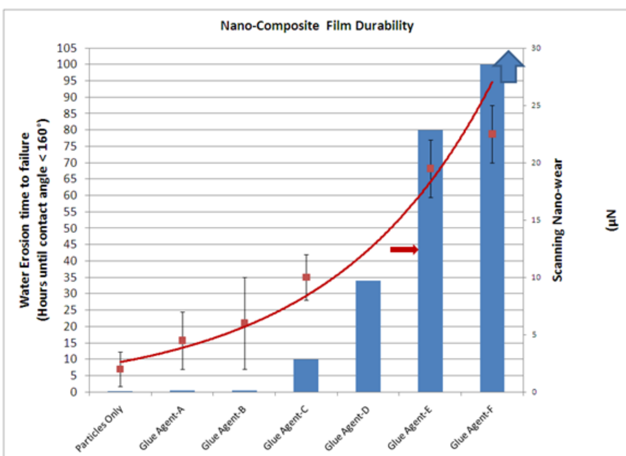

Fig 10: Chart showing the film failure time from water erosion tests overlaid with the failure loads from the TriboIndenter ScanningWear Tests. A film with a Scanning Wear failure of 25µN failed at 100 hours under water erosion.

3.4 Water Resistance Performance

The water resistance performance was tested by exposing a number of products to a variety of harsh liquid exposures. In Fig. 11, comparisons of several cell phones were tested in a rain-simulation spray chamber. Additional tests were performed by immersing them into Gatorade. The Gatorade electrolyte solution consisting of potassium phosphate / citric acid instantaneously shorted any uncoated products, while Repellix coated devices were resistant up to 30 minutes.

Depending on the Repellix film thickness, the particular device packaging and ingress points, coated PCB's can still be subjected to electro-chemical induced corrosion around high voltage field points such as power-supply lines. However, overall, the coated devices significantly out performed the uncoated devices.

Phone Vendor	Brand A	Brand B	Brand C
Style	Candy Stick	Slider	Flip
Control	1 minute	2-3 minutes	1 minutes
Repellix	20 minutes	20-30 minutes	2 minutes
Sample Size	20	5	1
Phones Passed	19	5	1

Fig 11: Table shows performance of three (3) brands of cell phones which were exposed in a "rain chamber". In all observed cases, the Repellix coated electronics outperformed all uncoated products.

4 CONCLUSIONS

An improved durable particle based nano-composite film in which bridge oxides are used to improve the mechanical durability has been characterized. This water resistant conformal coating is ideally suited for electronic applications to protect printed circuit boards used in cell phones and other portable devices from water damage. Further improvements are expected and the application to other devices and surfaces is expected.

5 ACKNOWLEDGEMENTS

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[6] Water Drop Height: 0.20 meters, Volume 0.046cc, Velocity: 1.979 m/sec, Rate: 2.3 Drops/sec, Incident Angle: 45^{o}, (Estimated Impact Force: 901µN)