

Super-Hydrophobic Nano-Composite Films

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ABSTRACT

A super-hydrophobic nano-particle coating has been characterized that protects cell phones and other portable electronic products from water damage. Aluminum oxide nano-composite coatings are deposited onto printed circuit boards prior to insertion into their cases, to protect the electrical circuits from water damage.

A material with nano-scale roughness is deposited in a vapor phase environment that is subsequently treated with a low surface energy type of material. This coating encapsulates the printed circuit boards including the connectors and thereby protects the electrical circuits on the boards from water damage, while maintaining perfect contact at the connectors. The typical thickness of these films is between 100 and 500 nm. Water contact angles of 165 degrees are achieved on polished silicon, when measured with a Goniometer. Water simply bounces off the coated surfaces. Batches of printed circuit boards can be coated in a 30 to 40 minute process cycle. Current applications include cell phone printed circuit boards, hearing aids and other consumer electronics products.

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

1 INTRODUCTION

Cell phones and other portable electronic devices have become necessities in our daily lives. We rely on them for personal communications with family and friends. We use them for emergencies, as well as for business. Recent advancements in smart phones make them even more valuable because of all the new and ever expanding applications that are available and we cannot afford to lose them or have them inoperable for very long. Accidental exposure to water or spilled liquids cause most of the units to quit functioning because liquids enter through the connectors or other open areas and short out the electrical circuits on the printed circuit boards inside the phones. The battery is also a critical portion of the problem, because it supplies the current that causes the printed circuit boards to corrode fairly quickly. Manufacturers of cell phones actually have a sensor built in that turns color when it senses water and thereby voids the warranty. There are waterproof phones available using gaskets and rubber seals, but they are expensive and generally bulky. On the technology front, we have been successful with the recent development of the low cost, easily applied super-hydrophobic coating to provide the preferred protection

method against water damage. Now, the industry can shift away from traditional physical barriers by encapsulation, or from costly packaging techniques with rubberized seals around ingress openings. Printed circuit boards today are covered with a protective film or “conformal coating” consisting of an organic material such as silicone, epoxy or urethane that is 25 to 200 microns thick. The added thickness of these conformal coatings must be accounted for in product packaging and the added film causes contact resistance and inter-connectivity problems between electronic assemblies. Thus, with these processes the critical connectors are masked and therefore not coated and they become the failure points causing shorts and electrical leakages, when accidental exposure to liquids occurs.

In the past, various techniques were used to create nano-structures that depended on the material and its application over large areas. Complex 3D shapes made it difficult and costly to apply them. 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 protection these coatings give is not limited to PCB's but they can be applied to hearing aids and other products as well.

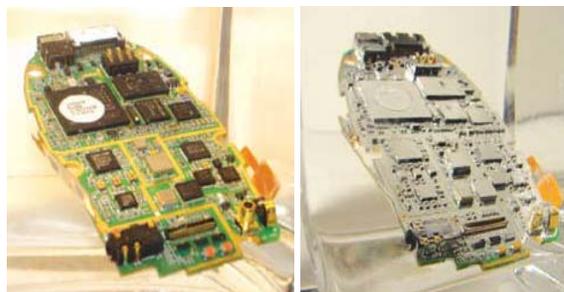


Fig 1: LEFT: An uncoated cell phone PCB immersed in water. The entire boards gets wet. RIGHT: Also immersed in water, a cell phone PCB that has been coated with a super-hydrophobic film. This coating, normally invisible, acts as a virtual force field that pushes water away from the surface, yielding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

2 PROCESS AND HARDWARE

The coating technology developed is called “Vapor Particle Deposition” (VPD). It creates nano-particle composite films and uses a sub-atmospheric gas-phase

flow-through reactor that is suitable for large batch processing. The nano-composite structure is created by using a hybrid atomic layer deposition (ALD) & chemical vapor deposition (CVD) process in which super-saturated vapor conditions are created [3]. During the patent pending process, a metal organic precursor is oxidized to create the proper film roughness and film coverage over the entire board. The following step in the process encapsulates these nano-particles into a glass-like matrix. That improves the film's durability. The final step creates a low surface energy state over the entire film.

The critical parameters in the ALD/CVD reaction are controlled and monitored by a Labview Controller. The proper chemical doses and the timing between the metal organic and the oxidation precursors affect the surface diffusion and the chemical reaction. If the timing of the chemical injections is not correct, and prevents gas phase interactions, an ALD type surface reaction occurs with insufficient roughness and structure formation, which causes lower hydrophobicity. Whereas, simultaneous injection of precursors results in a gas-phase CVD reaction that creates "nano-dust" that has very poor surface coverage. The key process that has been developed allows controlled intermixing of the chemicals so that super-saturated conditions occur, where nano-particles are uniformly created on surfaces through-out the entire reactor.



Fig 2: View of the VPD coating system. The process chamber is behind the upper door. Precursor vapors are introduced into the process chamber to create composite layered films. The VPD coating system can deliver 5 different gases sequentially or in parallel to create the required composite structures.

The coating equipment used was the RPX-540 manufactured by Integrated Surface Technologies (IST) (www.insurftech.com). The RPX-540 stores up to 5 different chemical precursors in cartridges and delivers them vaporized to the process chamber to create a custom nano-composite film. The entire coating system is carefully temperature controlled to deliver the vapors into the process chamber without causing any condensation. Precursor chemistries are heated until they vaporize and then

delivered into the process chamber, which is also heated. The process timing control is based on National Instruments' LabVIEW[®]. The process chamber can be configured with trays or special fixtures to accommodate various products. Printed circuit boards can be coated on one side only or on all sides. The coating deposits over all the components mounted on them, including the connectors. Both male and female connectors are coated and when they are mated, they maintain perfect electrical contact with each other, because the coating is pierced only at the contact area, therefore the connectors are fully protected. The super-hydrophobic coating discussed is named "Repellix[™]". Other products such as hearing aids, or glass slides and plastic substrates can also be coated.

Various flex circuits are coated and shown in Fig. 3. Note, that all surfaces of these modules are coated during the deposition process. Special fixtures are available for volume production.



Fig 3: A large batch of flex circuit boards are coated in the RPX chamber.

The system is very versatile. Depending on the chemistry used, low surface energy monolayers can also be produced. They are used in MEMS as anti-stiction coatings or useable as imprint release layers. Other coatings such as adhesion promoters or bio-compatible anti-fouling coatings can be deposited as well.

3 RESULTS AND DISCUSSIONS

Film Characterization

Super-hydrophobic films are characterized with AFM, SEM, Goniometer, TEM, FTIR, XPS, and TGA-MS metrology. Also performed were water erosion and optical transmission tests. Integrated Surface Technologies also had biocompatibility tests based on ISO-10993 FDA guidelines performed. The coatings were found to be biocompatible. Film roughness was measured and ranged from 30-700nm rms (Fig. 4). The super-hydrophobic coatings are routinely checked. The water contact angle on a polished Silicon wafer is $>160^\circ$. The super-oleophobic coating, using olive oil is $>160^\circ$ (Fig. 5). The contact angle remained unchanged after the samples were immersed for >18 months. The surface energy of the perfluorinated silicon was ~ 20 dyne-cm and the rough composite film was <5 dyne-cm. Typical film thickness is 100-500 nm.

Mechanical scanning wear tests by Hysitron measured up to 65uN.

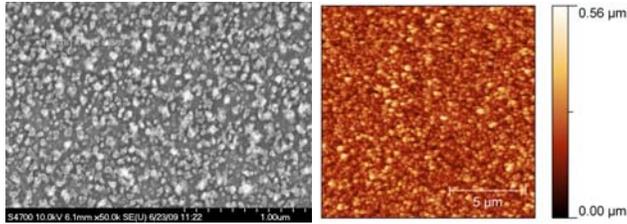


Fig 4: SEM and AFM of the super-hydrophobic nano-composite film. The rms roughness was ~164nm, average particle size ~30-35nm with an aerial surface coverage of ~42%.

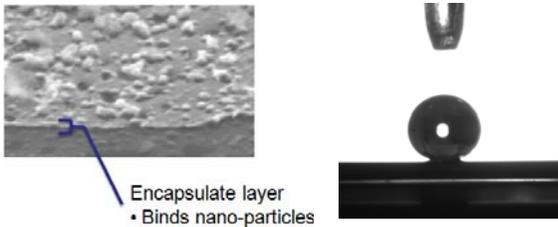


Fig 5: LEFT: An electron micrograph shows the glueing encapsulant for improved interparticle and particle-to-surface adhesion. RIGHT: After super-hydrophobic coating, a Goniometer measures the water contact angle at greater than 160° (measured on a polished silicon wafer).

Electrical Performance

Super-hydrophobic coating is a non-wetting film that can be deposited over large areas or over entire assemblies. Electrical connectors or other connecting points are also coated. The film is permeated by the barbs in the connectors for perfect electrical contact with the mating connectors. The contact resistance was measured with a standard 4-point probe. Molex brand flex ribbon connectors with 10 pins and 0.5mm pitch were coated with a super-hydrophobic film. The connectors were apart during the coating, and afterwards mated once for the test. A current of 1mA was used and the voltage across each contact point was measured. The measured values differed only by <0.01 Ohm from the nominal manufacturer supplied value. The chart in Fig. 6 shows the typical contact resistance of uncoated and coated connectors. No statistical significance was observed.

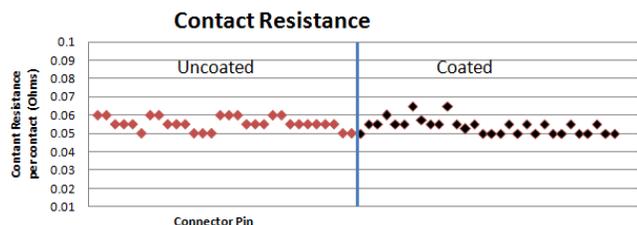


Fig 6: A representative chart of measured contact resistance of an array of connectors is shown before and after coating them.

The super-hydrophobic film is tuned by adding a glue layer. Various levels of metal-oxides become inter-particle and surface adhesion “glues”. Therefore coated PC boards can be handled by operators during insertion of the coated

boards into the cases. During the connector mating, the composite film is mechanically abraded, which gives physical contact at the connecting surfaces (Fig. 7). Since only a very small area of the sliding connector surfaces are exposed, where contact is made, the surface tensions of any liquids near the connectors will not wet the connecting surfaces. If the glue layer is made too thick during the deposition, as discussed earlier, the mechanical force of the connector may not be sufficient to reliably penetrate the composite film. In Fig. 8, the thick composite film shows areas in which good and poor contacting surfaces are shown.



Fig 7: Optical micrographs of the super-hydrophobic film have been scraped away by the contacting barbs of the connector. The surface tension of any liquids approaching the connectors keep the connecting points dry.

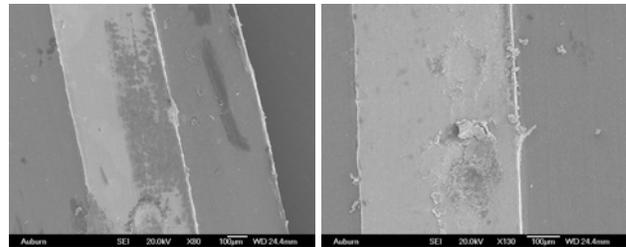


Fig 8: Durability of the connecting surface is controlled by the glueing agent process and the thickness of the film. Left: the super-hydrophobic nano-composite film is removed by the mating connector. It shows the base metal and that the connector made good electrical contact. Right: A thicker, more durable coating is not removed by the mating connector, leading to high resistivity and therefore electrical connection problems.

Water Resistance Performance

The water resistance performance was tested by exposing printed circuit boards to several harsh liquids. Fig. 9, shows a comparisons of several cell phones that were tested in a rain-simulation spray chamber. Additional tests were performed by immersing the boards into Gatorade. The Gatorade electrolyte solution is a potassium phosphate / citric acid solution, which instantly shorted the uncoated products, while the Repellix coated devices resisted this corrosive solution >30 minutes.

Depending on the Repellix film thickness, the device packaging and the size of the ingress points, super-hydrophobic coated PCB's can still be subjected to electro-chemical induced corrosion around the battery contact

points and power supply lines. However, overall, the coated devices significantly outperformed 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 9: 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 CONCLUSION

An improved, durable particle based super-hydrophobic nano-composite film deposited in a vacuum chamber under controlled conditions has been characterized. This water resistant conformal coating is ideally suited for electronic applications to protect printed circuit boards used in cell phones and in other portable devices from water damage. Further improvements are expected and the application to other devices is forthcoming.

5 ACKNOWLEDGEMENTS

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