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14. ABSTRACT

This report results from a contract tasking Bar Ilan University as follows: The contractor shall develop organic monolayers with which to modify alumina surfaces on both flat coupons and woven fiber cloths. These monolayers would present a uniform array of phosphonate, sulfonate, and/or carboxylate functional groups on the exposed surface of suitably modified material. These organic monolayers will provide a suitable interface for the attachment of subsequent layers of adherent rhabdophane coatings. The contractor shall develop both the surface priming and the necessary liquid phase deposition chemistry to deposit titania on the surface of Kapton in order to improve its resistance to atomic oxygen and UV radiation.

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EOARD Grant # 043063

Contract Title: "Interfacial Control of the Formation and Adhesion of Oxide Films"

Final Report

Project Period September 2004 - September 2005

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General Project Goals and Achievements

This project had two independent goals: a) deposition of oxide coatings on Kapton films in an effort to improve its thermo-oxidative stability and b) to use monolayer coatings to control the chemical and physical properties of an alumina surface and its interface with a ceramic overlayer. We have demonstrated that ceramic films of TiO₂ or ZrO₂ could be effectively deposited from aqueous solution onto coupons of Kapton. We also demonstrated crack free films of limited thickness can be created and that the degree of cracking in films with thicknesses ranging from 300-1000 nm could be dramatically reduced (though not completely eliminated) by using drying procedures which involved exchange of the solvents and controlled humidity. We have also used similar aqueous deposition procedures to create ceramic coatings on the surface of alumina coupons and alumina fibers.

Workplan

The main focus of the work accomplished on this project was the deposition of titania on Kapton. The principle effort was expended in optimizing titania adhesion to the Kapton and in developing techniques that allow for the deposition of ceramic oxide layers of controlled thickness and crystallinity with a minimum of cracks and/or pores.

Results

We investigated the processing of TiO₂ films with an eye towards controlling the thickness, rate of growth, and crystallinity of TiO₂ films grown by the liquid phase deposition method (LPD). We found that TiO₂ films are readily deposited using either the method of Deki (0.3 M H₃BO₃ and 0.1 M (NH₄)₂TiF₆, initial pH of 3.88, ambient temperature – method #1) or the method of Koumoto (0.15 M H₃BO₃ and 0.05 M (NH₄)₂TiF₆, initial pH of 2.88, 50 °C – method #2). Films produced by both Methods #1 and #2 adhere well to Kapton samples

after UVOCS or plasma activation. They do not adhere well to unactivated Kapton. Films produced by method #1 were amorphous, while those made by method #2 were comprised of oriented crystals of anatase.

We focussed more attention on method #1 since their amorphous nature made them a more likely choice as a barrier material. We found that the TiO₂ adhered well only to Kapton coupons that had been both cleaned with solvents and activated by UVOCS or plasma treatment. External reflection FTIR microscopy studies compared the IR spectrum of uncoated Kapton to that of material that was coated with each of these oxides and showed a shift in the imide absorption from 1713 cm⁻¹ to 1705 cm⁻¹ after TiO₂ coating. This difference was not due to the activation procedure and led to the suspicion that some surface hydrolysis of the Kapton occurs during TiO₂ deposition. XPS measurements were consistent with limited imide bond cleavage leading to formation of surface amide and carboxyl acid groups.

Using Back-Scattering SEM measurements and cross-section analysis, the thickness of the TiO₂ films could be directly measured. SEM of these films showed evidence of cracking, despite the fact that they were stable to both sonication and to tape tests. We explored various ways to create TiO₂ films without cracks. We evaluated the effect of post-deposition rinsing procedures with various solvents, as well as the use of controlled humidity drying. The optimized processing conditions for all deposition methods involved removing the samples from the LPD solution, rinsing with water followed by rinsing with methanol, followed by drying in a climatic chamber at a constant temperature of 70 °C while reducing the relative humidity. This was either done in steps of 1 day each from 80% to 60% to 40% to 20% RH. We were able to clearly demonstrate that the combination of the exchange of solvents and drying at higher temperatures by varying the humidity is an excellent way to improve film quality and prevent film cracking. Even this method, however, was limited and only films up to 190 nm thickness could be made completely crack free film (no cracks of even 3 nm width). In the case of the thicker amorphous film (250-300 nm) the size of the cracks could be reduced to 20-50 nm, but no further.

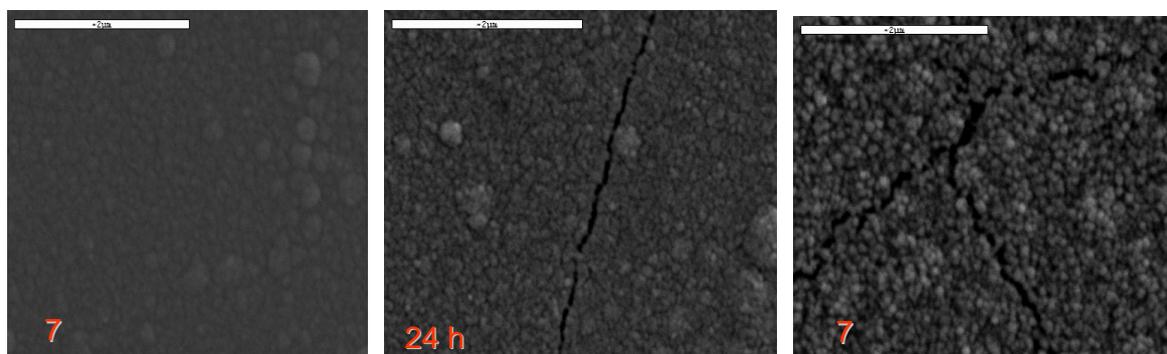
We also began an assessment of the stability of LPD TiO₂ to thermal cycling. This was done for Kapton samples that had originally been activated either by UVOCS or by plasma. These experiments involved depositing a TiO₂ layer and exposing the coated substrate to a cycle of thermal changes. A 150 nm thick TiO₂ layer was put into a 25 °C oven, heating it gradually (over 60 minutes) to 300 °C, holding at 300 °C for 3 hours, cooling back to 30 °C over 60 minutes, holding at 30 °C for 1 hour and then repeating the cycle. After 10

cycles there was no delamination evident and no cracks could be seen in the optical microscope. Careful investigation by SEM revealed a very small amount of film cracking after the thermal cycling, but further work is needed to better define the effects of the thermal challenge on the oxide coated Kapton films.

Efforts to create films of ZrO_2 without cracks failed. Independent of film thickness, cracks of ~80-130 nm could be seen even after we applied the solvent exchange and controlled humidity methods described above for titania. While the ability to create relatively continuous conformal zirconia films was in itself an achievement, reducing the cracks in these films will require further work.

The work on alumina surfaces was pursued in a different fashion. Using flat alumina coupons, we first established the conditions for successful modification of the alumina surfaces with functionalized self-assembled monolayers bearing either amine or sulfonic acid groups. We then applied these same methods to the modification of alumina fibers. We found that the ZrO_2 adhered well to SAM-modified surfaces. EDAX analysis showed substantial attachment of ZrO_2 to the surface of such fibers. Further work is needed on this system, but, the concept of SAM enhanced ceramic adhesion to alumina surfaces has been demonstrated.

As samples of the kinds of data obtained in this project, we include below micrographs of both method #1 (Deki) and method #2 (Komouto films) on Kapton. The pictures on the left and in the center show examples of a crack-free method #1 film and of the kinds of cracks that develop in this film when it is grown to thicknesses of over 250 nm. The micrograph on the right illustrates the different texture of films grown by method #2 and shows yet another example of the cracks that we cannot yet prevent in films >250 nm in thickness.



Supplement to Final Report

Project Period September 2004 - September 2005

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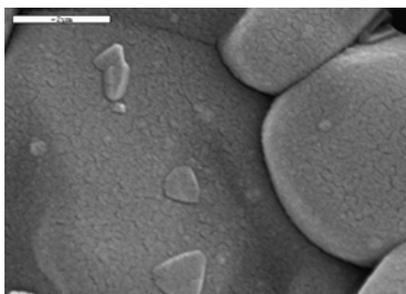
The following information is provided in response to the request for additional information on our EOARD sub-project involving using monolayer coatings to control the chemical and physical properties of an alumina surface and its interface with a ceramic overlayer. This project centered on using aqueous deposition procedures to create ceramic coatings on the surface of monolayer modified alumina coupons and alumina fibers.

Using flat alumina coupons, we first established that the alumina surfaces could be activated using either UVOCS or an air plasma. We proceeded to work primarily on air-plasma activated surfaces since the UVOCS activated surfaces showed small changes in their IR spectra and some evidence of discoloration.

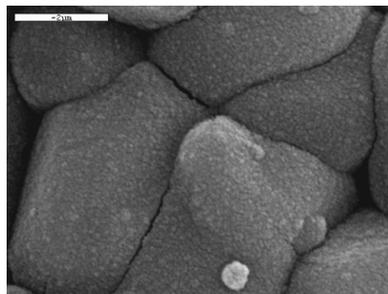
We explored the application of silane, phosphonate, and carboxylate anchored monolayer films onto the alumina surfaces. Silane deposition used trimethoxysilanes and an acetic acid catalyst. Depositions were done for 24 hours from DCH solution. Phosphonate anchored monolayers were deposited from boiling THF for 24 hours and carboxylate monolayers were deposited from either ethanol or iso-octane for 48 hours at room temperature. The siloxane and phosphonate anchored alkyl monolayers achieved in this way were well packed and showed contact angles of 122 and 103 degrees respectively. The carboxylic acid monolayer was very poorly adherent and gave water contact angles of only 56 degrees. The superiority of the siloxane-anchored film (suggested by the above contact angle data) was also seen in its external reflection FTIR spectrum where the C-H stretching peaks were both narrower and at lower wavenumber (both consistent with better packed monolayer films).

Thioacetate functionalized siloxane anchored films were deposited on the alumina surfaces and they were successfully oxidized to give uniformly sulfonated surfaces. Similarly, bromide-bearing surfaces were created and transformed into amine-bearing surfaces. Surfaces bearing simple alkyl groups, thioacetate and/or sulfonic acid groups, and amine groups were all used as templates for the deposition of both crystalline (anatase) and amorphous titania onto

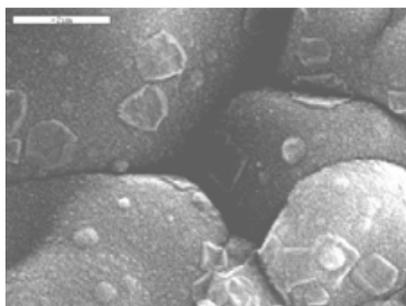
clean alumina and onto these modified alumina surfaces. All surfaces showed formation of adherent films. Scanning electron micrographs of each of these films are shown below.



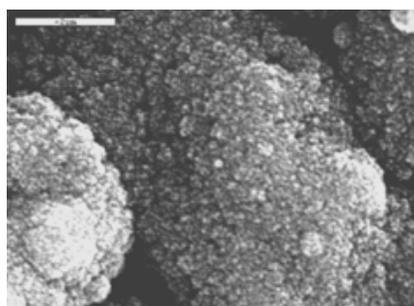
amorphous titania on alumina



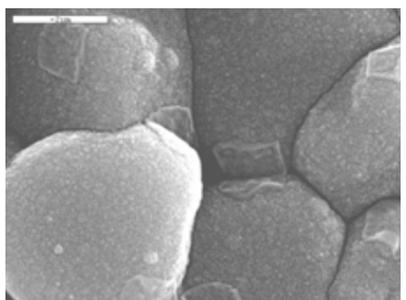
anatase on alumina



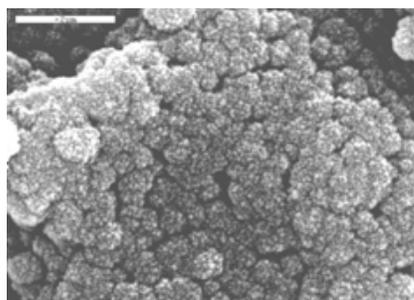
amorphous titania on amine
functionalized alumina



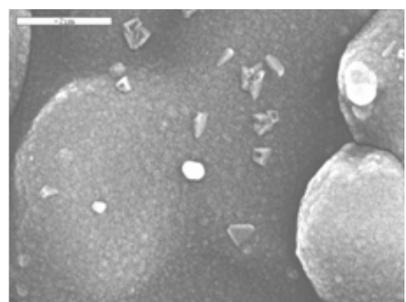
anatase on amine
functionalized alumina



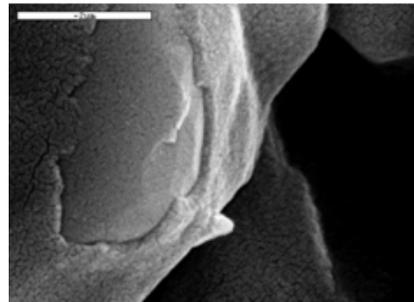
amorphous titania on thioacetate
functionalized alumina



anatase on thioacetate
functionalized alumina



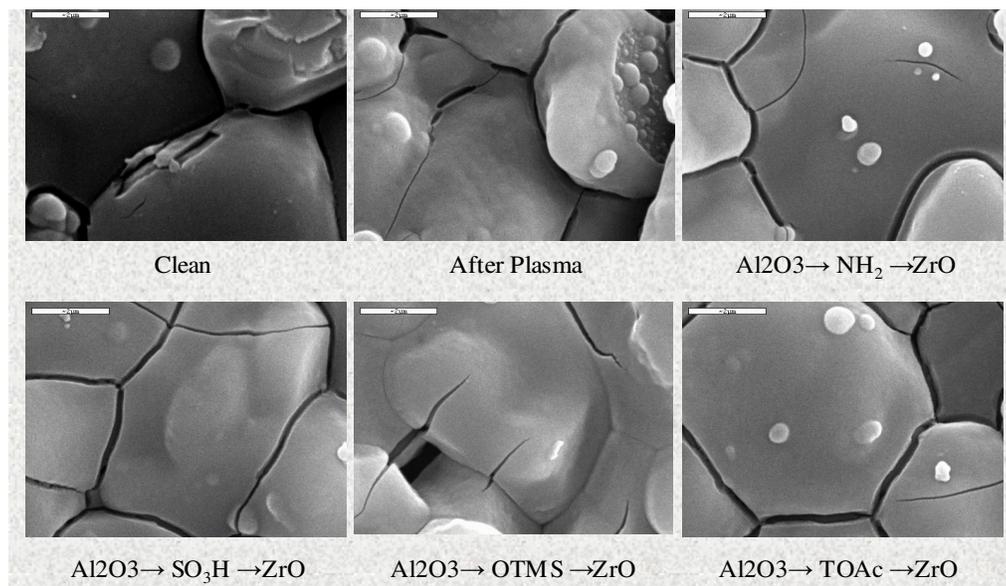
amorphous titania on sulfonate
functionalized alumina



anatase on sulfonate
functionalized alumina

The different textures of the amorphous and anatase films are clear. There is also an indication that the films formed on the monolayer modified surfaces, particularly on the sulfonate-bearing surface, provide more complete and continuous surface coverage.

A similar array of functionalized surfaces was used to promote the deposition of zirconia onto modified alumina surfaces. The array of results achieved (all formed continuous zirconia films) on unprimed alumina, on air plasma primed alumina, on amine-bearing alumina, on sulfonated alumina, on hydrocarbon-bearing alumina and on thioacetate bearing alumina are all shown below. All four of the monolayer coated samples showed more continuous zirconia films than the alumina without the monolayers.



We then applied these same methods to the modification of alumina fibers. We found that the ZrO₂ adhered well to SAM-modified surfaces. EDAX analysis showed substantial attachment of ZrO₂ to the surface of such fibers. Further work is needed on this system, but, the concept of SAM enhanced ceramic adhesion to alumina surfaces has been demonstrated.