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Reactively Deposited Aluminum Oxide and Fluoropolymer Filled Aluminum Oxide Protective Coatings for Polymers

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REACTIVELY DEPOSITED ALUMINUM OXIDE AND FLUOROPOLYMER FILLED ALUMINUM OXIDE PROTECTIVE COATINGS FOR POLYMERS

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ABSTRACT

Reactive ion beam sputter deposition of aluminum simultaneous with low energy arrival of oxygen ions at the deposition surface enables the formation of highly transparent aluminum oxide films. Thick (12 200 Å), adherent, low stress, reactively deposited aluminum oxide films were found to provide some abrasion resistance to polycarbonate substrates. The reactively deposited aluminum oxide films are also slightly more hydrophobic and more transmitting in the UV than aluminum oxide deposited from an aluminum oxide target. Simultaneous reactive sputter deposition of aluminum along with polytetrafluoroethylene (PTFE Teflon) produces fluoropolymer-filled aluminum oxide films which are lower in stress, about the same in transmittance, but more wetting than reactively deposited aluminum oxide films. Deposition properties, processes and potential applications for these coatings will be discussed.

INTRODUCTION

Thin film oxide coatings have been under investigation over the last decade as a means of protecting polymeric satellite or spacecraft surfaces from the harsh environment present in low Earth orbit (LEO).^{1,2,3} In LEO, where atomic oxygen is the predominant specie⁴, these coatings have been found to act as an oxidation barrier by preventing atomic oxygen from reacting with organic substrates. These same thin film oxide coatings also have been found to have many terrestrial applications. They are currently being tested for use as gas barriers, hydrophobic water shedding coatings, and abrasion resistant surface finishes. Plastic windows in automobiles or

aircraft are examples of applications which would benefit greatly from hard, transparent, water shedding, adherent coatings.

Sputter deposited thin film coatings are typically among the most adherent coatings due to the energy of deposition and the ability to sputter clean the surface prior to deposition of the coating.² The sputter cleaning microscopically textures the surface of most materials to enable better adhesion and growth and at the same time removes contaminants which may have built up on the surface. One of the disadvantages of this coating method is that thin films typically build up intrinsic stresses which may lead to a film spalling from the substrate at film thicknesses greater than approximately 2 000 Å. For an abrasion resistant coating on a soft substrate, a thin oxide film such as this will not afford much protection because the yielding of the material underneath when a particle is rolled on or pushed into the surface will cause the film to crack. Thicker coatings can reduce the amount of coating flexure. This increases the abrasion resistance. One of the most promising low stress coatings is aluminum oxide. Aluminum oxide coatings which are the focus of this paper were investigated in order to determine if sputter deposition from an aluminum oxide target or from an aluminum target in the presence of a reactive gas (oxygen) made a difference in the stress level, water contact angle, or optical transmittance. In addition, small amounts of fluoropolymer were added to some of the coatings during deposition in order to determine the effect on these characteristics. Pure polytetrafluoroethylene was also deposited for comparison. Finally, a thicker reactively deposited aluminum oxide coating on polycarbonate was prepared to investigate the potential for abrasion resistance.

APPARATUS AND PROCEDURE

Coating Preparation

All coatings were prepared by ion beam sputter deposition onto a variety of substrates. Fused silica slides (2 cm x 2 cm) were coated for characterization of optical properties and contact angle. Intrinsic stress was measured on coated silicon wafers, and polycarbonate was used as a substrate for abrasion testing. Aluminum oxide coatings were prepared by either sputter

deposition directly from an aluminum oxide sputter target of 99.99% purity (Cerac), or by reactive sputter deposition from an aluminum target of 99.999% purity (MRC) in the presence of an air/argon plasma provided by a second ion source. The energy of the ions used for sputter deposition was maintained at 1 000 eV at a beam current of 50 mA using a 2.5 cm diameter ion source operated on argon. The second source which provided the oxidizing plasma at the samples during sputtering of the pure aluminum target was maintained at an ion energy of approximately 170 eV. This source was a 15 cm diameter source operated on a 50% mixture of air and argon. The current density varied between 20 and 40 mA due to oxidation of the anode during the process. Vacuum chamber pressure during deposition typically was 0.013 - 0.04 Pa ($1-3 \times 10^{-4}$ Torr). Addition of polytetrafluoroethylene (PTFE) was accomplished by either using a full target of PTFE for the 100% PTFE sample or placing a wedge of PTFE onto the aluminum target so that a mixture of PTFE and aluminum oxide could be attained by reactive sputter deposition. Eight percent PTFE by volume (requiring a 1.75° wedge of PTFE on the aluminum target) was chosen for this initial testing due to this level of mixture's optimum performance in a PTFE-silicon dioxide system.¹ Figure 1 contains a drawing of the apparatus used.

Coating Characterization

Coating thicknesses were determined by placing a fused silica optical flat partially covered with polyimide Kapton tape onto the sample holder. After deposition, the surface was scanned with a Dektak IIA surface profiler to measure the step change between the shielded and coated surface of the optical flat. Typical coating thicknesses ranged from 1 600 to 2 700 Å for the aluminum oxide coatings. Two samples of each type (reactively deposited and non-reactively deposited) were made in separate deposition runs and the test results within each pair were averaged for greater accuracy. The coating with the composition of approximately 8% PTFE-92% Al_2O_3 was about $3\,800 \text{ Å} \pm 260 \text{ Å}$ thick and the 100% PTFE coating was $12\,300 \text{ Å} \pm 1\,077 \text{ Å}$. Intrinsic stress was measured by placing a 111 orientation silicon wafer onto the sample holder and measuring the change in surface bow after coating using an Ionic Systems Intrinsic Stress Gauge. This technique does not take into account any extrinsic stresses produced by the substrate itself such as thermal expansion mismatch. Each sample was measured four times and the results were averaged. Water contact angle was measured on a coated fused silica surface using a Kernco

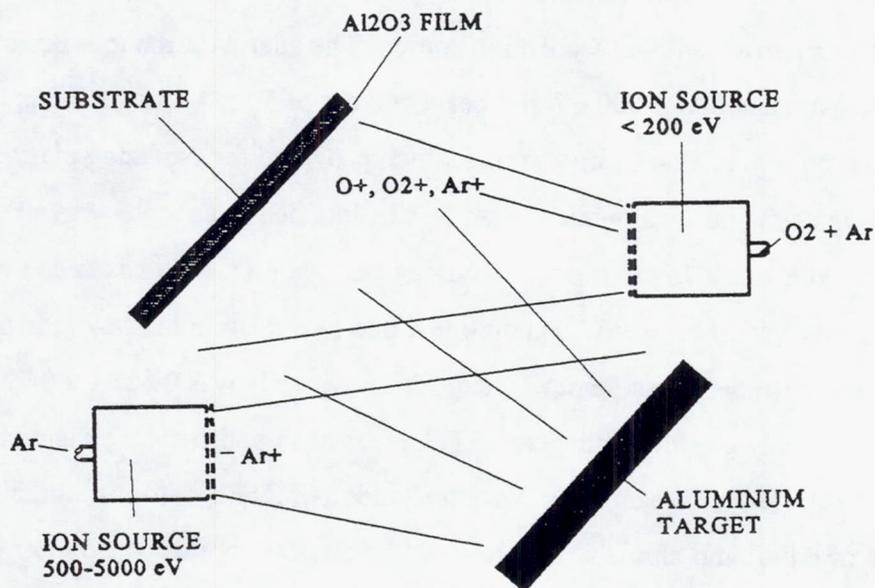


Figure 1. Ion beam sputter deposition for reactively deposited aluminum oxide. Aluminum target was replaced with an aluminum oxide target and the <math>< 200\text{ eV}</math> source turned off for sputter deposition of non-reactively deposited aluminum oxide.

Contact Angle Measurement Instrument model G1. Again four measurements were made on each coated sample and the results averaged. Coating transmittance and reflectance as a function of wavelength was measured using a Perkin Elmer Lambda-9 UV-VIS-NIR Spectrophotometer. Finally, a thicker ($12\ 200\ \text{\AA}$) coating of reactively deposited aluminum oxide was applied to polycarbonate for a rough measure of the abrasion resistance. In this case emery paper and house dust on fingers were wiped across the polycarbonate from a masked uncoated region to the coated region. Scratches were observed visually. Thick films were not generally used for the remainder of the tests due to the time involved in preparation and the difficulty in producing adherent, directly sputtered oxide films of any substantial thickness.

RESULTS AND DISCUSSION

One of the reasons for measuring thin film stress, is that the intrinsic stress is part of the force that a film puts on the underlying surface. The lower the stress, the greater the potential for applying a thick film without losing adhesion to the surface. The intrinsic stress measured for the aluminum oxide, reactively deposited aluminum oxide, reactively deposited 8% PTFE-92% aluminum oxide and pure PTFE films is shown in Figure 2. It appears that the reactively deposited aluminum oxide films are deposited with slightly lower compressive stress than those deposited from a pure aluminum oxide target. The standard error of the measurement is fairly large, as shown in Figure 2, which indicates that these films may not differ greatly in surface stress. The addition of approximately 8% fluoropolymer, however, reduces the intrinsic stress by nearly a factor of three. Pure PTFE is actually under a small amount of tensile stress when deposited. It appears that the mixing of PTFE with the aluminum oxide during deposition causes stress levels which are a hybrid of the two pure materials.

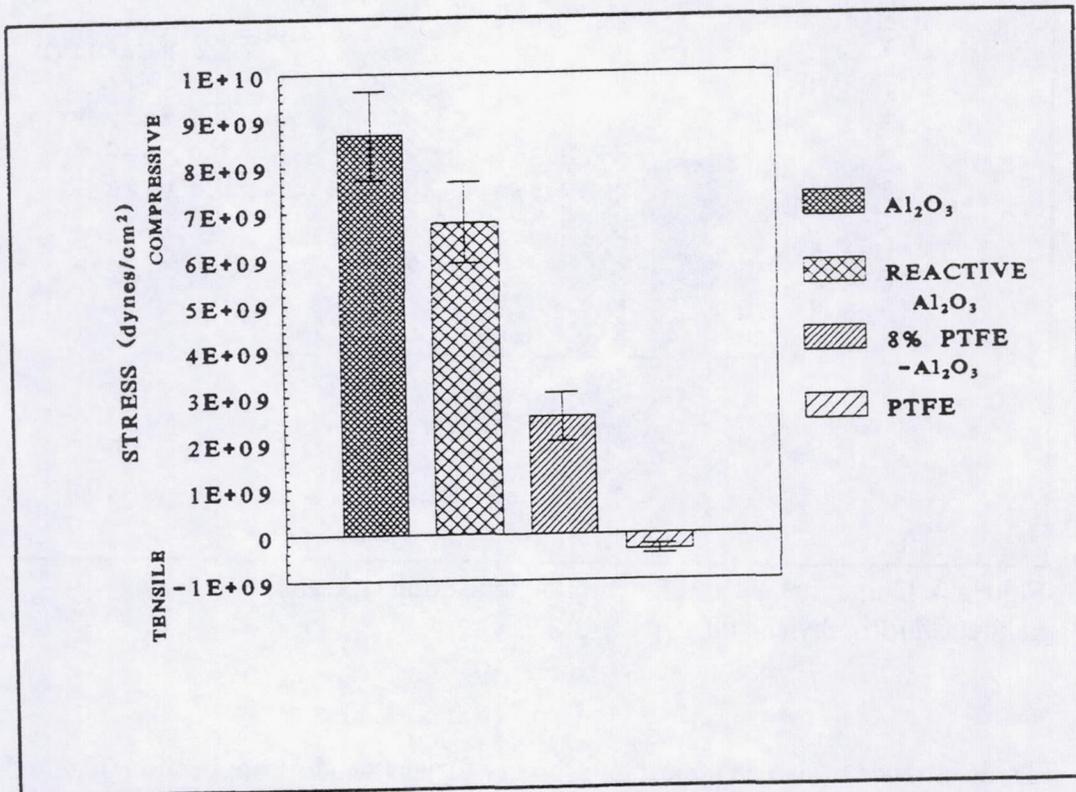


Figure 2. Intrinsic stress as a function of deposition type and polytetrafluoroethylene fill.

Hydrophobicity or the extent to which water beads up on a surface is also an important property for exterior window applications. As shown in Figure 3, the greater the contact angle measured, the greater the hydrophobicity. Aluminum oxide thin films produced by reactive sputter deposition had a slightly higher contact angle than that for films deposited directly from an aluminum oxide target. Although PTFE is a very hydrophobic material, the addition of PTFE did not produce properties in a rule of mixtures style as for the intrinsic stress. The contact angle actually decreased by a factor of over 2.5. This may be due to the formation of aluminum fluoride at the surface which is water soluble. Because the fluorine content is low, the film itself should be fairly stable once the surface aluminum fluoride is lost.

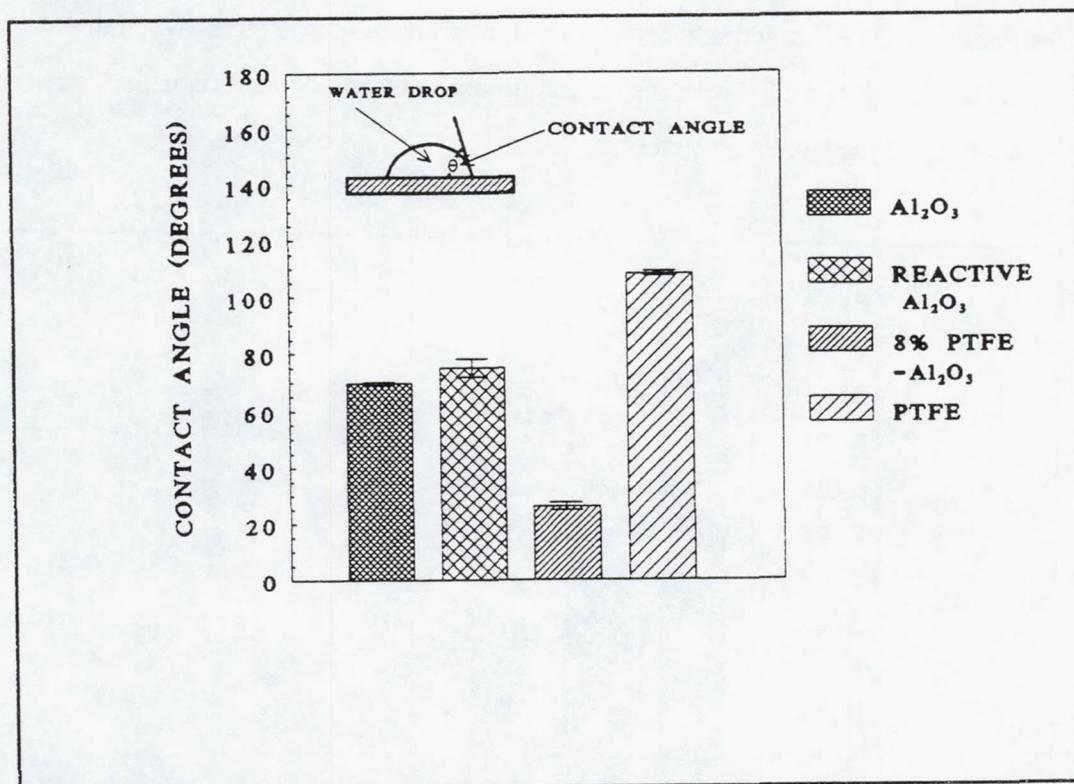


Figure 3. Contact angle as a function of deposition type and polytetrafluoroethylene fill.

Transmittance is also an important property for any window application. Figure 4 contains a plot of the transmittance as a function of wavelength for the coatings discussed on fused silica

substrates. The aluminum oxide films are typically very transparent. The aluminum oxide deposited from the aluminum oxide target, however, was slightly less transparent in the visible and very much blocking in the UV region of the spectrum. PTFE films are also slightly less transmitting in the UV but the reactively deposited aluminum oxide remains transmitting in the UV. This is not affected greatly by the addition of 8% PTFE. The differences in transmittance observed may be due to impurities in the aluminum oxide target and PTFE target. Even when the reactively deposited aluminum oxide is applied thick, the transmittance does not drop greatly as shown in Figure 5. Deposition of a 12 200 Å film of reactively deposited aluminum oxide on a polycarbonate surface resulted in only approximately a 1.8% increase in absolute absorbance as determined from the reflectance and transmittance data.

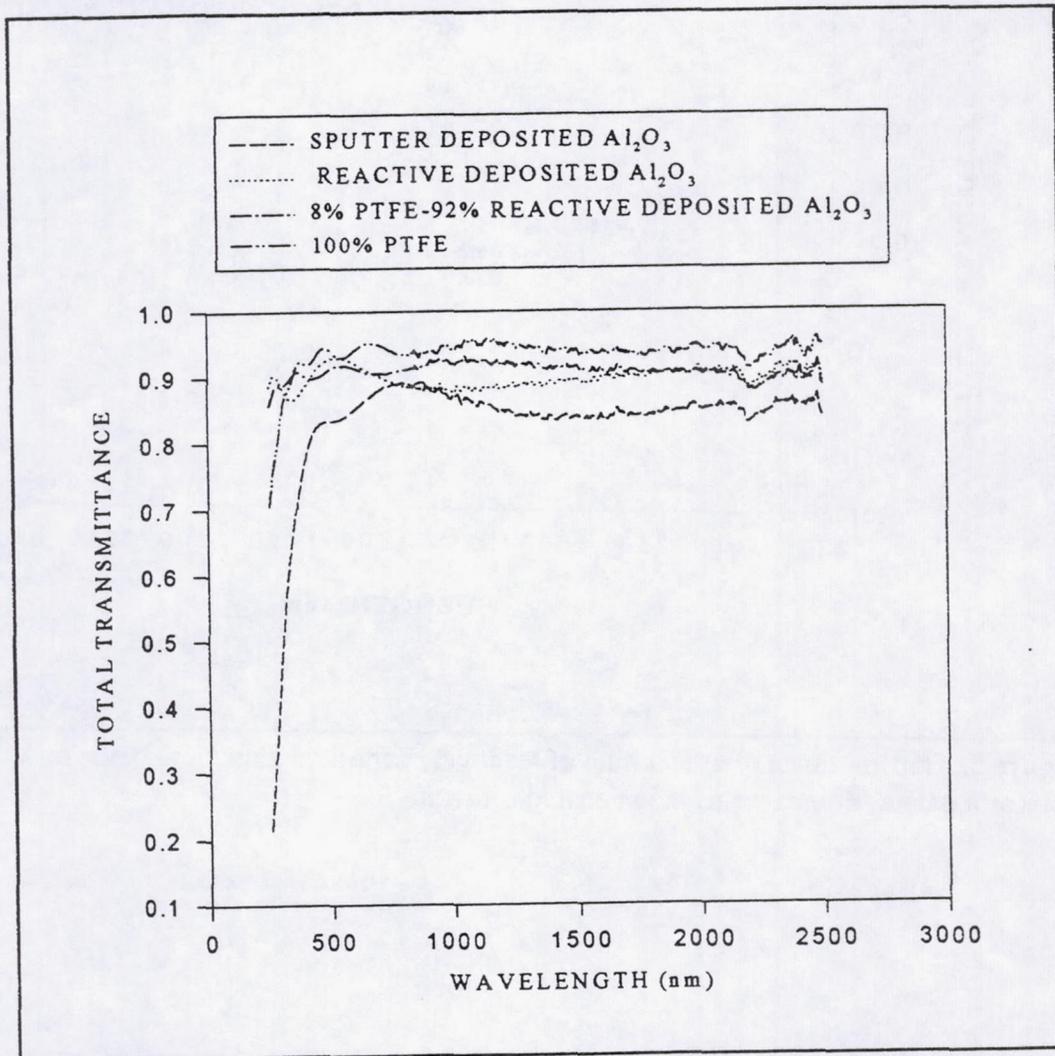


Figure 4. Transmittance comparison for aluminum oxide and PTFE filled coatings on fused silica substrates

Figure 6 contains photographs of the 12 200 Å thick film of aluminum oxide on polycarbonate that was scratched with emery paper (Figure 6a) and house dust (6b). The upper half of the photo is the coated surface and the lower half is a section of uncoated polycarbonate that was produced by masking the surface prior to coating. As can be seen, large particles are still able to get through the coating but the small particles are not able to scratch the surface. This is not a very quantitative test, but it provides some rough visual evidence that thick films of this type can provide some abrasion resistance.

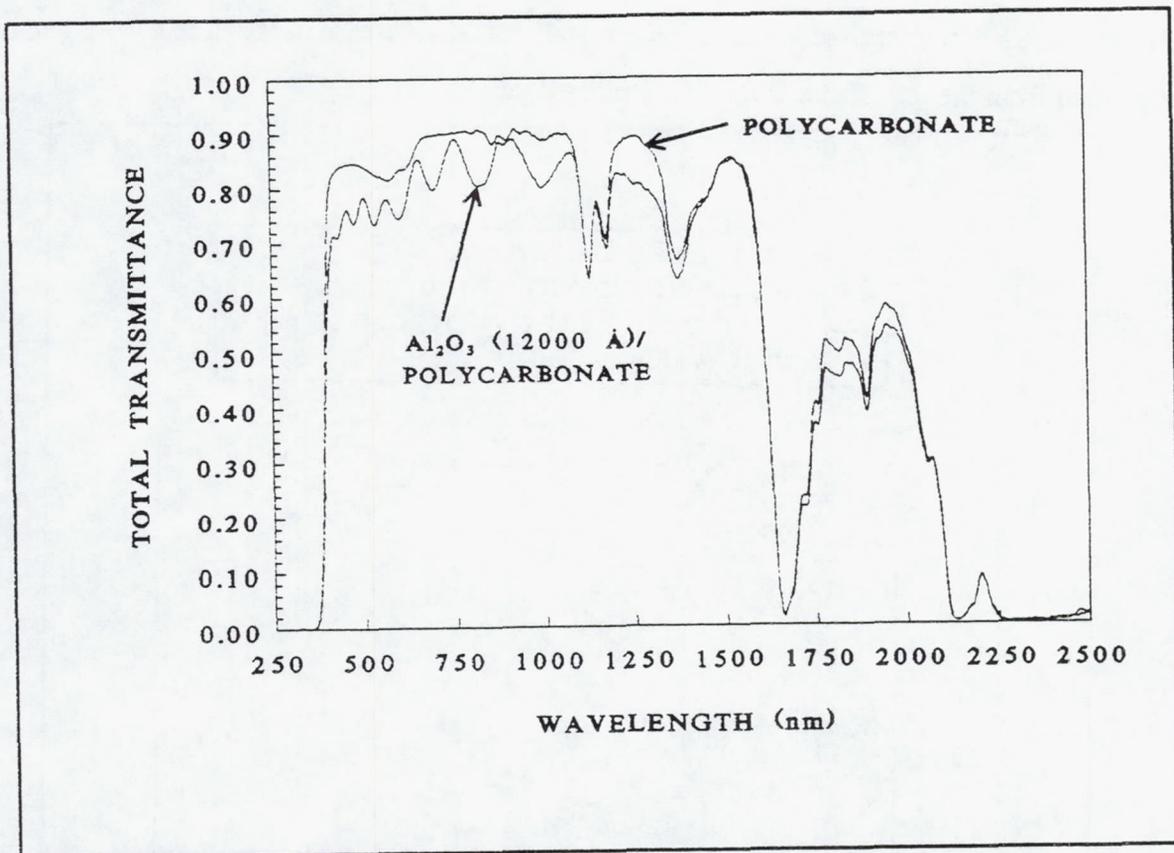


Figure 5. Transmittance of a thick film of reactively deposited aluminum oxide on polycarbonate as compared to the uncoated substrate.

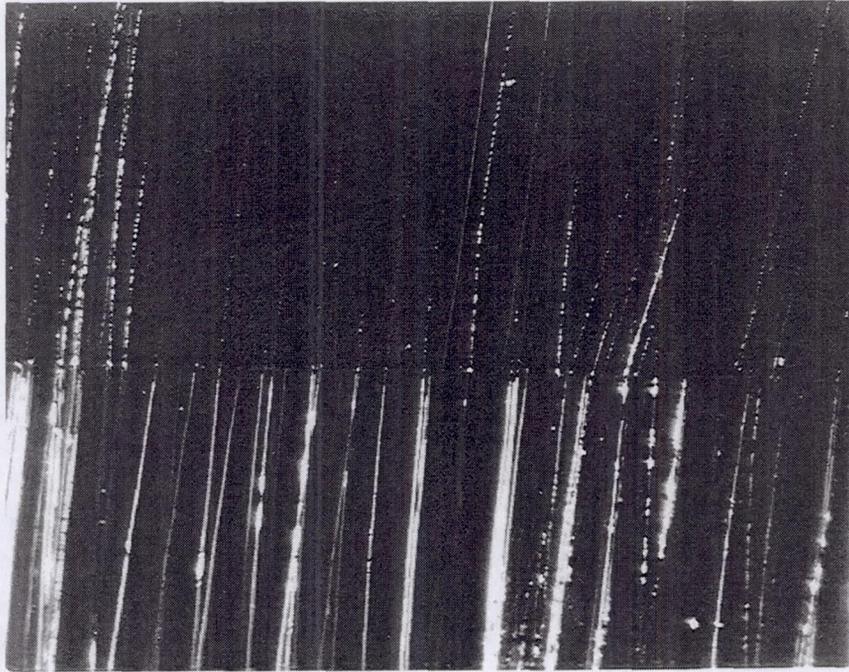


Figure 6a. Polycarbonate with top half coated with reactively deposited aluminum oxide. Surface was abraded with emery cloth.

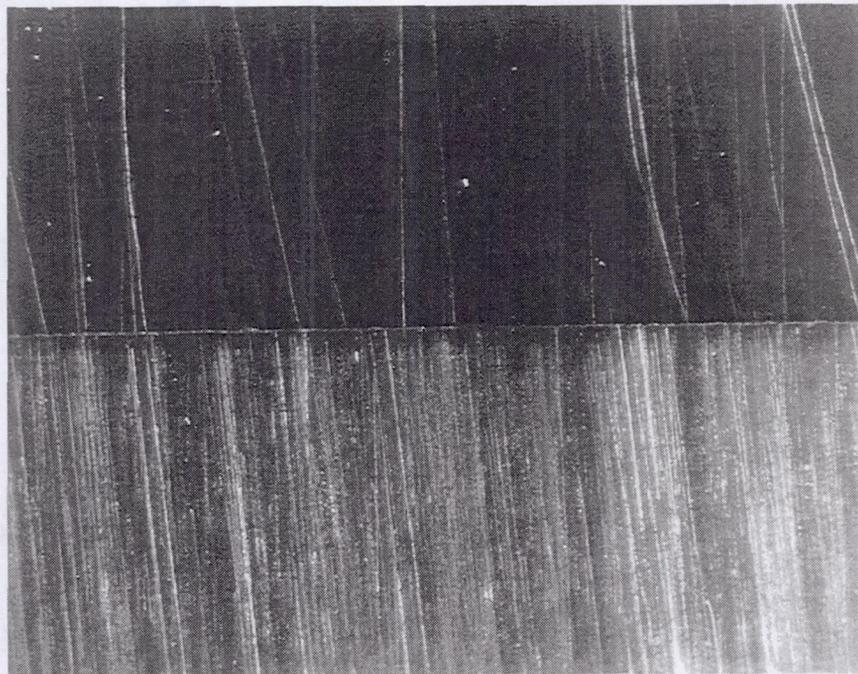


Figure 6b. Polycarbonate with top half coated with reactively deposited aluminum oxide. Surface was abraded with house dust.

CONCLUSIONS

Film stress was found to be slightly lower for films of aluminum oxide produced by reactive sputter deposition. This surface stress could be reduced further by the addition of PTFE which is itself a very low stress film. The addition of PTFE, however, did not make the surface more hydrophobic as might be expected from the contact angle measurements of pure PTFE and aluminum oxide. The contact angle was actually lowered by about a factor of 2.5. This may be due to the formation of aluminum fluoride at the surface which may be able to be dissolved off. Reactively deposited films were found to be slightly higher in contact angle than the non-reactively deposited films. They were also found to be more transmitting in the UV. This is believed to be due to fewer impurities during deposition. The addition of Teflon had a very small effect on transmittance. Thick coatings of reactively deposited aluminum oxide were found to increase the absolute absorptance of coated polycarbonate by only about 1.8%. These thick films also appear to produce abrasion resistance to small particles such as would occur when cleaning a window, optical lenses or other surfaces. Overall, aluminum oxide reactively deposited coatings show great potential as clear, abrasion resistant surfaces. It is also important to note that the properties of the surface can be tailored to suit various needs by the addition of other materials such as Teflon during the coating process.

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