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FLEXIBLE FLUOROPOLYMER FILLED PROTECTIVE COATINGS

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ABSTRACT

Metal oxide films such as SiO_2 are known to provide an effective barrier to the transport of moisture as well as gaseous species through polymeric films. Such thin film coatings have a tendency to crack upon flexure of the polymeric substrate. Sputter co-deposition of SiO^2 with 4%-15% fluoropolymers has been demonstrated to produce thin films with glass-like barrier properties that have significant increases in strain-to-failure over pure glass films, thus improving their tolerance to flexure on polymeric substrates. Deposition techniques capable of producing these films on polymeric substrates are suitable for durable food packaging and oxidation/corrosion protection applications.

Introduction

Polymeric materials used on spacecraft in the low-earth-orbital environment have been shown to degrade through oxidation because of reaction with the environmental atomic oxygen (ref. 1). Atomic oxygen in the low-earth-orbital environment is formed by photodissociation of the diatomic oxygen by solar photons whose wave length is less than 2430Å. Atomic oxygen is a predominant species between the altitudes of 180 and 650 km (ref. 2). Polymers have not yet been developed which are durable to atomic oxygen interaction. As a result, current approaches to prevent atomic oxygen degradation have utilized protective coatings over the oxidizable substrates. These coatings have consisted of metal oxides such as SiO_2 and Al_2O_3, as well as mixed metal oxide/fluoropolymer films (refs. 1,3 and 4). Because metal oxides are typically in their highest oxidation state, they act as ideal atomic oxygen protective barriers to prevent oxidation of the underlying polymeric materials. However, pure metal oxide films such as SiO_2 have a very limited strain-to-failure, thus decreasing their utility on substrates which are subjected to flexure. The addition of a small fluoropolymer content to the predominantly SiO_2 films greatly increases the strain-to-failure of the films while still maintaining their protective properties. Numerous aerospace spinoff applications exist such as: hermetic coatings, protective transparent coatings, and non-stick coatings. this paper will present deposition techniques for the application of flexible thin film fluoropolymer filled SiO_2 protective coatings, as well as discuss film properties and potential applications.

Deposition Technique

Molecularly mixed metal oxide/fluoropolymer films can be produced by simultaneous sputter etching of sputter targets consisting of silicon dioxide and polytetrafluoroethylene (PTFE-Teflon) (Ref. 3). Figure 1 shows the ion beam sputter deposition configuration for co-deposition of SiO_2 or Al_2O_3 with a fluoropolymer. this apparatus consists of an electron bombardment ion source operating on 500-1000 eV argon ions to sputter-etch targets of metal oxide simultaneous with the polytetrafluoroethylene (PTFE-Teflon). As a result of the simultaneous bombardment of both types of materials, a molecular mixture of metal oxide and fluoropolymer scission fragment species deposits on surfaces exposed to the sputter ejecta from these targets. Because the ion beam current density distribution is typically normally distributed, the ratio of deposition species can be readily controlled by utilizing a pie-shaped polytetrafluoroethylene target segment on top of a circular SiO_2 sputter target (ref. 5). Figure 2 shows a typical plot of the volume fraction of fluoropolymer in the deposited SiO_2/fluoropolymer-mixed film as a function of the polytetrafluoroethylene target angle. The deposition can be performed by either ion beam or RF magnetron deposition with the substrate at room temperature. The deposition rates produced by ion beam sputter-deposited films are typically lower than those which may be produced by RF magnetron deposition processes.

Thin Film Properties

Although silicon dioxide and aluminum oxide are known to be durable to atomic oxygen attack, pure fluoropolymer deposited films are oxidizable by atomic oxygen attack. However, small quantities of fluoropolymers can be molecularly mixed with metal oxide films and still provide atomic oxygen protection if the thin film thickness is slightly increased over that of the pure metal oxide film. Figure 3 shows the minimum thickness fluoropolymer-filled SiO_2 film necessary for permanent atomic oxygen protection as a function of fluoropolymer content fraction in the SiO_2 film (ref. 3). Thinner protective coatings do not provide durable protection thus allowing atomic oxygen reaction with the underlying polymer. For atomic oxygen protective coatings in space, the film thicknesses typically between 650-1500Å are used.

Fluoropolymer filled SiO_2 protective coatings appear colorless and quite transparent on polymeric substrates. Figure 4 illustrates the differences in reflectance, absorptance, and transmittance of SiO_2 films containing up to 4% fluoropolymer sputter deposited on 127μm thick polyimide Kapton.

The value of adding the small addition of fluoropolymer to the metal oxide films is to increase the strain to which the silicon dioxide can be subjected without brittle fractures developing. Figure 5 illustrates the increase of strain-to-failure by small additions of fluoropolymer to the film as well as the minimum radius curvature which film can survive when deposited on a 127μm thick polyimide Kapton substrate without brittle fracture. As can be seen from Figure 5, a fluoropolymer fill fraction of 15% will increase the strain-to-failure by a factor of three. In addition, thin polymeric materials with a 15% fluoropolymer fill fraction can be bent around a radius of curvature of approximately 1mm without brittle fracture. However as can be seen from Figure 3, such films must be at least 600Å to provide atomic oxygen oxidation protection. Oxygen diffusion through thin films appears to be limited to not more than 300Å based on isotope labeled diffusion studies conducted in reference 6. However, it appears that 15% fluoropolymer-filled SiO_2 films whose thicknesses exceed 600Å are quite flexible and atomic oxygen durable. Sputter deposition of these co-deposited films has been shown to produce an intrinsic stress which can tend to deform the substrate polymers. Figure 7 is a plot of the intrinsic stress of co-deposited thin films on silicon substrates for various composition films and film thicknesses (ref. 7).

Atomic oxygen durability of pure SiO_2 and 4% fluoropolymer-filled SiO_2 films were evaluated in space and found to reduce oxidation by a factor of 3,7500 over that of unprotected polyimide Kapton (ref. 7).

Potential Application

One of the primary space applications considered for such films is for the protection of flexible polyimide Kapton solar array blankets that would be used in low earth orbit. the fluoropolymer content of such films may enable inflatable structures to be protected from oxidation as well. Polymeric materials which must be subjected to flexure or small radius of curvature would be ideally suitable for use with fluoropolymer filled films because of their tolerance to high strain in comparison to that of pure metal oxide films.

Because the fluoropolymer-filled SiO_2 films are clear, flexible, corrosion-resistant, chemically inactive, and an effective moisture barrier, there may be numerous non-aerospace applications. One of the most obvious applications is the packaging of food products where it is desirable to prevent diffusion of water vapor through the thin film polymeric container. Generally acceptable long-term hermetic protection is achieved by metallization of plastic film packages. However, such containers do not allow visual inspection of the content of the containers. The flexible fluoropolymer-filled SiO_2 films would be both visibly transparent and offer a hermetic protection in excess of that of uncoated polymeric packaging. The fluoropolymer content of the film may be useful in cases where a slight reduction in coefficient of friction is also important. There may be obvious non-stick applications where the durability of the SiO_2 component can be utilized in concert with the non-stick fluoropolymer component for such applications as cookware.

The chemical properties of the fluoropolymer ion beam sputter-deposited component of the films is thought to be similar to that of polytetrafluoroethylene based on the deposition of pure fluoropolymer films from polytetrafluoroethylene targets (ref. 8). The sputter-deposited fluoropolymer films are very similar to that of the bulk polytetrafluoroethylene except the sputter-deposited fluoropolymer is slightly more cross-lined, which produces a higher thermal decomposition temperature (ref. 8). Applications where abrasion-resistance, oxidation protectiveness, and transparency are requirements include durable acrylic coatings for surface protection of floor coverings, sky light transparency protective coatings, and protection of polycarbonate face shields. These oxidation protective coatings, their deposition process, and associated apparatus have been patented by NASA under U.S. Patent Numbers 4,664,980,4, 560,577and 4,604,181 respectively.

SUMMARY

Molecularly mixed fluoropolymer-silicon dioxide films cannot be fabricated by conventional bulk melting or mixing processes. However, these mixed films can be deposited by ion sputter co-deposition, as well as magnetron sputter deposition processes. Fluoropolymer contents up to 15% by volume enable a factor of three (3) gain in strain-to-failure of the silicon dioxide films, thus allowing a much greater flexibility in the films to be applied on thin polymeric substrates. The co-deposited films are clear, atomic oxygen durable, and pose potential for hermetic coatings for applications ranging from food stuff packaging to face shields. The fluoropolymer content in these coatings may be advantageous to non-stick applications as well.

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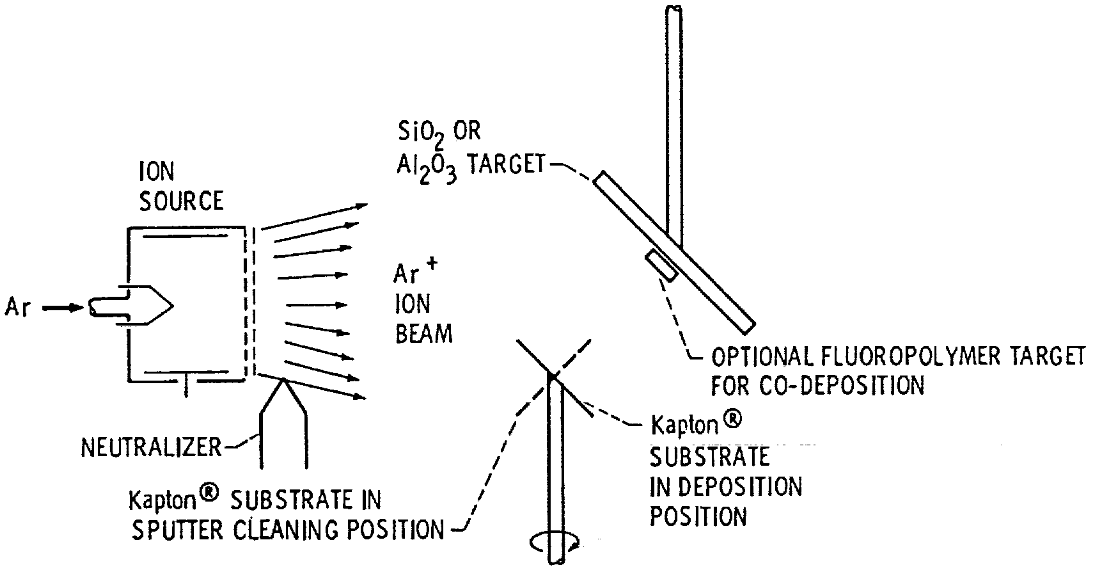


Figure 1. Ion beam sputter deposition system for molecularly mixed metal oxide fluoropolymer thin films.

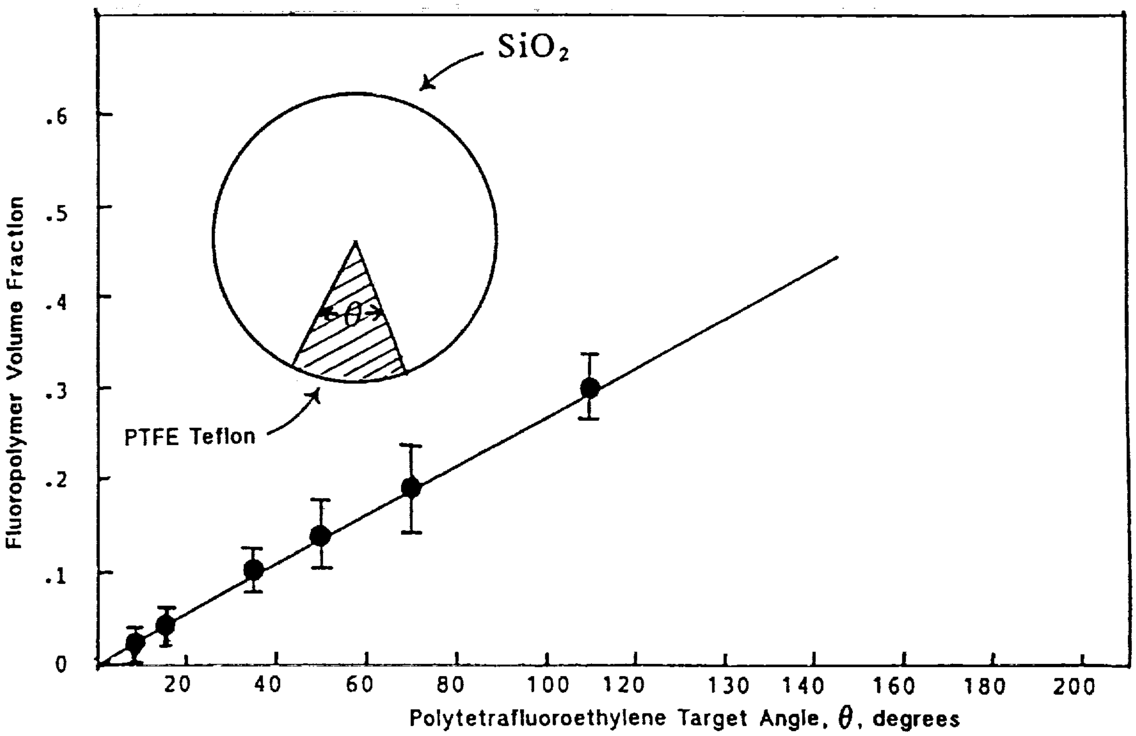


Figure 2. Fluoropolymer volume fraction of fluoropolymer filled SiO_2 sputter deposited films.

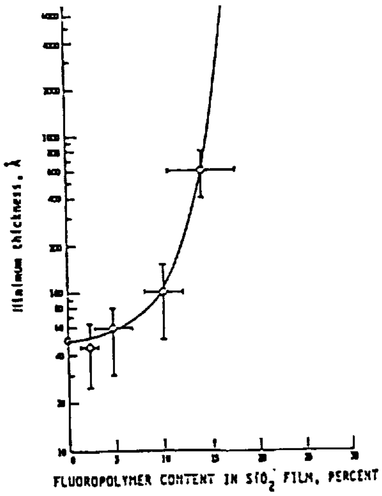


Figure 3. Minimum film thickness for atomic oxygen protection as a function of fluoropolymer content in fluoropolymer film SiO_2 sputter deposited films.

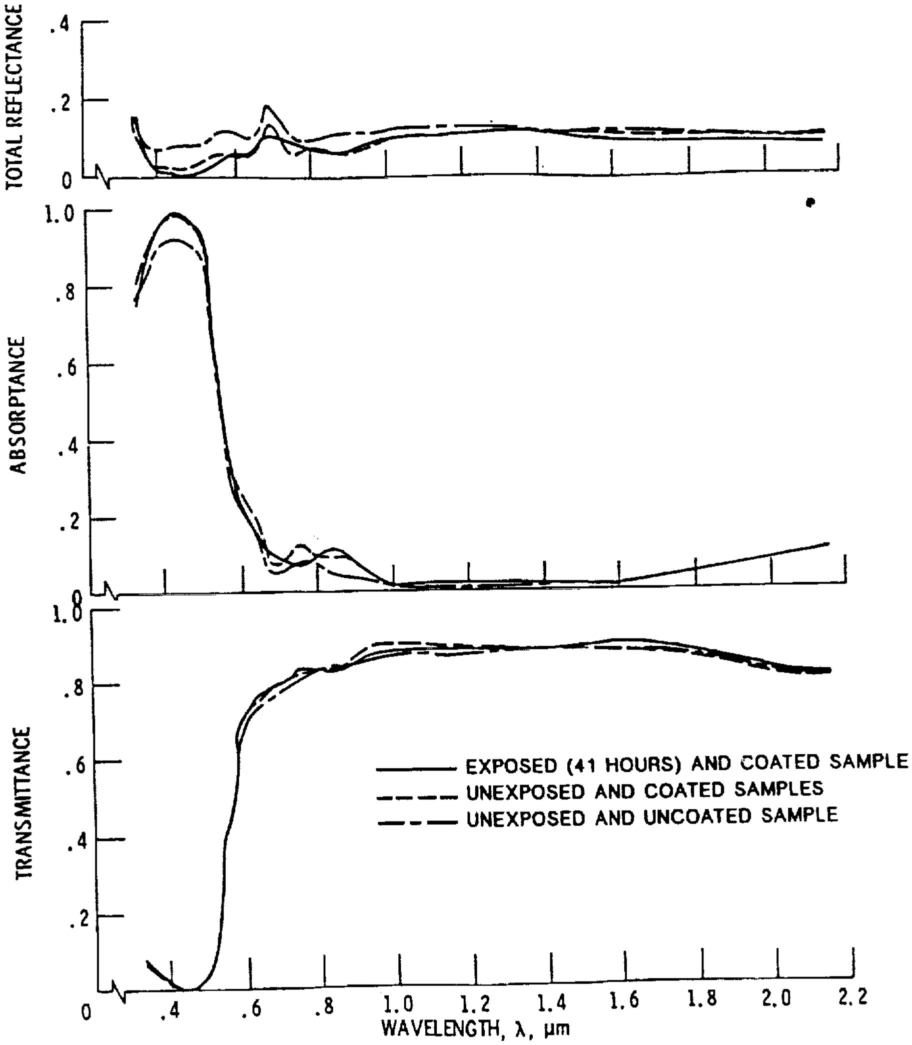
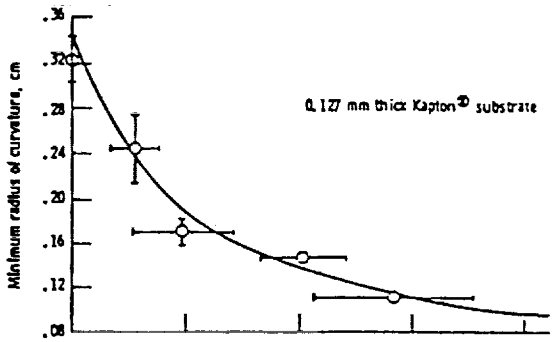
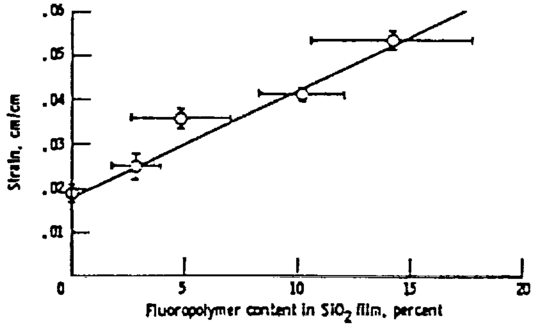


Figure 4. Optical properties of ≥ 96% SiO_2 ≤ 4% PTFE coated Kapton samples unexposed and exposed to low-earth-orbital environment compared with uncoated and unexposed Kapton.



(a) Minimum radius of curvature.



(b) Maximum strain without brittle fracture.

Figure 5. Minimum radius of curvature and maximum strain that a co-deposited SiO_2-fluoropolymer film (1000Å) can survive without brittle failure.

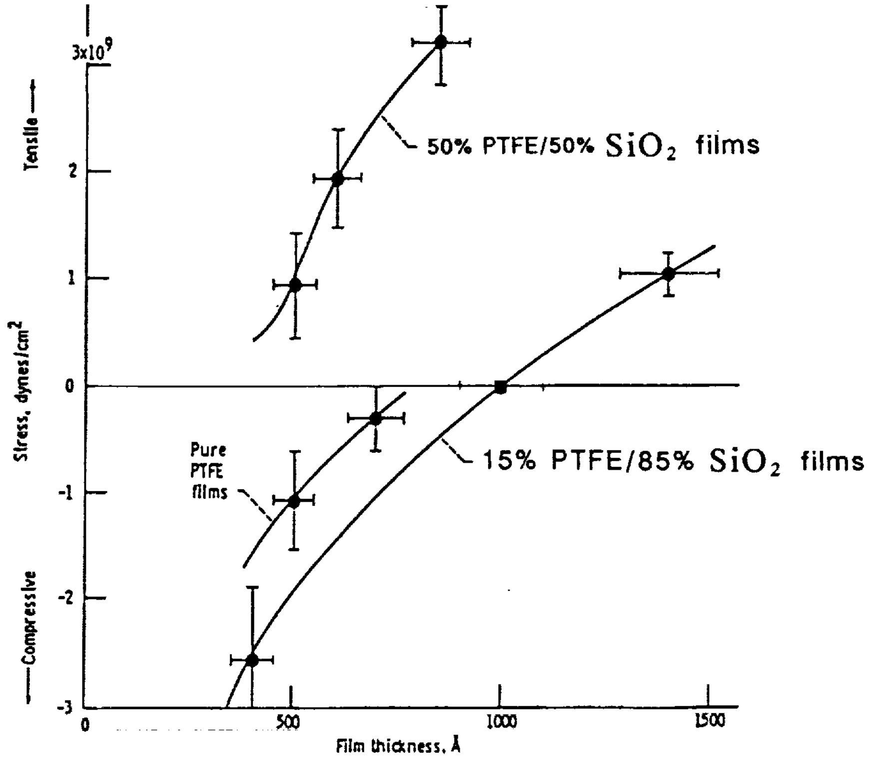


Figure 6. Intrinsic stress of co-deposited thin films on silicon substrates.