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Bruce A. Banks, Sharon K. Rutledge, and Joyce A. Dever
Lewis Research Center
Cleveland, Ohio

Paul D. Hambourger, Patricia Walters, and Eric J. Bruckner
Cleveland State University
Cleveland, Ohio

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**MIXED COMPOSITION MATERIALS SUITABLE FOR
VACUUM WEB SPUTTER COATING**

BY

BRUCE A. BANKS, SHARON K. RUTLEDGE, JOYCE A. DEVER

**NASA LEWIS RESEARCH CENTER
21000 BROOKPARK ROAD, M/S 309-2
CLEVELAND, OH 44135
U.S.A.**

PAUL D. HAMBOURGER, PATRICIA WALTERS, ERIC J. BRUCKNER

**CLEVELAND STATE UNIVERSITY
1983 E. 24TH STREET
CLEVELAND, OH 44115
U.S.A.**

ABSTRACT

Ion beam sputter deposition techniques were used to investigate simultaneous sputter etching of two component targets so as to produce mixed composition films. Although sputter deposition has been largely confined to metals and metal oxides, at least one polymeric material, polytetrafluorethylene, has been demonstrated to produce sputtered fragments which re-polymerize upon deposition to produce a highly cross-linked fluoropolymer resembling that of the parent target. Fluoropolymer-filled silicon dioxide and fluoropolymer-filled aluminum oxide coatings have been deposited by means of ion beam sputter coat deposition resulting in films having material properties suitable for aerospace and commercial applications. The addition of fluoropolymer to silicon dioxide films was found to increase the hydrophobicity of the resulting mixed films; however, adding fluoropolymer to aluminum oxide films resulted in a reduction in hydrophobicity, thought to be caused by aluminum fluoride formation.

Co-deposited films of indium tin oxide and magnesium fluoride were found to produce highly transparent films whose sheet resistivity increases as the volume fraction of magnesium fluoride is increased. The films of approximately 83% indium tin oxide and 17% magnesium fluoride were found to produce a mixture having low but adequate sheet resistivity (10^6 - 10^7 Ω/\square) suitable for draining charge from spacecraft surfaces.

INTRODUCTION

Co-deposition From Mixed Material Sputter Targets

Although most sputter deposition processes involve sputter deposition of a single material, sputter deposition from targets composed of two or more materials has been considered and holds potential for deposition of mixed property films [1, 2]. If ion beams or RF magnetron sputter deposition processes are used, then mixed composition sputter targets can be used which are composed of conducting as well as insulating component parts. Most co-deposited coatings have been achieved using combinations of various metals and/or ceramics. However, polymers such as PTFE Teflon and FEP Teflon have been demonstrated to cause the deposition of clear, lubricious, hydrophobic films which are very similar to the parent fluoropolymers with the exception of being harder as a result of being more cross-linked [3].

The sputter etching of PTFE Teflon appears to be dependent upon the power density of the arriving ions

raised to the 1.4 power, and the sputter ejected polymer scission fragments appear to be dominated by C_2F_6 groups [3]. Co-sputter deposition by means of sputter targets consisting of PTFE Teflon and other materials have been used to deposit molecular mixtures of fluoropolymer with other materials including copper, SiO_x (where $1.9 < x < 2.0$), gold, and diamond-like carbon. Water contact angles of co-deposited films from PTFE Teflon and SiO_2 targets smoothly transition from that which is produced by PTFE Teflon to that of pure SiO_2 , depending on the compositional mix. Fluoropolymer-filled SiO_x coatings deposited by ion beam sputter deposition have demonstrated the ability to increase the strained failure in comparison to pure SiO_x coatings [4]. The fluoropolymer-filled SiO_x coatings have been effectively used for atomic oxygen protection of spacecraft polymers where high strain environments may exist which would crack conventional thin film glass coatings [5].

Although fluoropolymers are the only polymers that have been able to be deposited by sputtering processes, very few mixed films containing composition fluoropolymers have been explored.

Spacecraft surfaces in orbits ranging from low Earth orbital, highly inclined orbits to geosynchronous orbits can be confronted with differential charging leading to electrical breakdowns which can potentially compromise spacecraft electronic devices. Remediation of this problem is possible if the spacecraft has a slightly conductive surface in which the surface resistivity is of the order of 10^8 ohms per square [6]. Indium tin oxide is a potential candidate for a conductive surface on spacecraft solar arrays. However, its high conductivity may cause parasitic electrical losses in the solar array. The addition of co-deposited magnesium fluoride with indium tin oxide presented in this paper was intended to reduce the electrical conductivity to acceptable levels while maintaining acceptable transparency, atomic oxygen durability and vacuum ultraviolet radiation durability.

Reactive Sputter Deposition

Sputter deposition of compounds can be achieved by sputter etching compound targets or by reactive deposition using an elemental target in a background gas or plasma which reacts with the depositing element. The reactive deposition of aluminum oxide from aluminum sputter targets is preferred over deposition from aluminum oxide targets because higher purity aluminum is available than aluminum oxide. In addition, aluminum readily oxidizes in oxygen and

oxygen plasma environments. Highly transparent adherent aluminum oxide films can be deposited by reactive sputter deposition processes for providing low-stress, thick, abrasion-resistant coatings on polycarbonate [7]. When sputter depositing by one or more targets in a reactive gas environment, a variety of potential compounds can be deposited in addition to those of the parent sputter targets. Two such reactively deposited films discussed in this paper include fluoropolymer-filled aluminum oxide films and indium tin oxide with magnesium fluoride mixed films.

APPARATUS AND PROCEDURE

Co-Deposition From Mixed Material Sputter Targets

Ion beam sputter deposition processes were used for the deposition of films discussed in this paper. These deposition techniques are well-suited for research purposes, and production techniques suitable for web coatings are very adaptable from the concepts presented herein. The films presented in this paper were deposited using an IonTech 2.5 cm diameter beam electron bombardment argon ion source in a vacuum facility which allowed a second 15 cm diameter beam of oxygen or argon to impinge upon the sputter depositing films. The volumetric mix of the sputter depositing materials was computed based on measurements from individual 12.7 cm diameter targets of each of the materials making up the mixed material target. Because the argon ion beam current density is a Gaussian distribution, approximately centered on the middle of the target, appropriate included angle pie-shaped wedges of each of the target materials was used to produce a desired volumetric mix based on the sputter deposition rates from the individual targets [7]. Figure 1 shows the ion beam sputter deposition configuration including the mixed target for co-deposition. This configuration was also used to deposit fluoropolymer-filled reactively deposited aluminum oxide films as well as indium tin oxide (91% In_2O_3 , 9% SnO_2) mixed with magnesium fluoride films.

Reactive Deposition

Reactively deposited aluminum oxide and fluoropolymer filled aluminum oxide films were accomplished using the ion beam sputtering system shown schematically in Figure 1. During reactive deposition, the 15 cm diameter ion source operating on air was used to oxidize aluminum as it was being deposited on the deposition substrate. The 15 cm diameter ion source could be operated at low energy or simply with a

plasma discharge.

RESULTS AND DISCUSSION

Indium Tin Oxide and Magnesium Fluoride Mixed Films

Indium tin oxide and magnesium fluoride mixed films were ion beam sputter co-deposited with varying compositions ranging from pure indium tin oxide to 17% (by volume) magnesium fluoride. Figure 2 shows the solar transmittance as a function of volume fraction of magnesium fluoride for such films. There is a slight gain in transmittance for the higher magnesium fluoride compositions compared to pure indium tin oxide.

Figure 3 shows the sheet resistivity as a function of volume content of magnesium fluoride in indium tin oxide for these same mixed composition deposits. Small additions of magnesium fluoride increase the sheet resistivity by many orders of magnitude. As can be seen in Figure 3, the coatings with approximately 17% by volume magnesium fluoride have sheet resistivity within one or more orders of magnitude of the desired 1×10^8 ohms per square. Sputter etching of indium tin oxide simultaneous with magnesium fluoride can also produce compounds such as indium fluoride, tin fluoride, magnesium oxide and magnesium nitride. For these mixed material coatings to be useful, it is important that they are reasonably durable in material processing environments such as immersion in water. However, SnF_2 , SnF_4 , Mg_3Sn_2 , MgO , and Mg_3N_2 either dissolve or decompose in water. Profilometry measurements of the thickness of indium tin oxide and magnesium fluoride mixed films did not show a statistically significant change with exposure to water for durations up to 100 hours. However, the sheet resistivity tended to increase by up to a factor of two over a duration of 24 to 36 hours and then decrease slightly thereafter.

Mixed indium tin oxide and magnesium fluoride coatings used in low Earth orbit must be durable to vacuum ultraviolet radiation as well as atomic oxygen. The exposure of such mixed coatings to 300 equivalent sun hours of vacuum ultraviolet radiation from deuterium lamps indicates a negligible loss in transmittance. Exposure of such mixed coatings to atomic oxygen inside a Faraday cage designed to allow atomic oxygen from a plasma asher to impinge upon the sample but prevent direct line-of-sight vacuum ultraviolet radiation exposure of the sample, resulted in a very slight decrease in sheet resistivity as a function of effective atomic oxygen fluence as shown

in Figure 4. Thus, co-deposited indium tin oxide and magnesium fluoride coatings appear to have the desired characteristics of weak electrical conductivity, reasonable immunity to processing in water, as well as durability to vacuum ultraviolet radiation and atomic oxygen, whereas coatings of pure indium tin oxide darken in exposure to atomic oxygen and VUV exposure from the atomic oxygen plasma [8].

Fluoropolymer-Filled Al_2O_3 Films

Fluoropolymer-filled reactively-deposited aluminum oxide films were found to display many of the merits of reactive deposition as well as co-deposition with only slight problems associated with using these processes. As in the case for indium tin oxide and magnesium fluoride mixed films, compounds can be formed from the elements of the constituent PTFE Teflon and aluminum targets which result in slight property variations not necessarily desired. This was manifested in water contact angle measurements in which an 8% fluoropolymer-filled reactively deposited aluminum oxide film had a water contact angle of approximately 20° which was much lower than reactively deposited aluminum oxide with no fluoropolymer and pure fluoropolymer deposit films which had water contact angles of 75° and 105° respectively. This was thought to be due to the formation of a small population of aluminum fluoride molecules from a small amount of atomic sputtering of the PTFE Teflon target resulting in the fluorine reacting with the depositing aluminum instead of oxygen reacting with the aluminum. The spectral transmittance of 8% fluoropolymer-filled reactively deposited aluminum oxide films ranged from 88% to 91% over the visible spectrum for thicknesses ranging from 1600 to 2700 Å. These spectral transmittance characteristics are very similar to that of pure fluoropolymer-filled films as well as unfilled reactively deposited aluminum oxide films. However, aluminum oxide films deposited from aluminum oxide sputter targets resulted in films having spectral transmittances in the visible which were 5%-10% lower than the reactively deposited films.

The addition of fluoropolymers to aluminum oxide films greatly reduces the intrinsic stress of the films, as can be seen in Figure 5. As is shown, a mere 8% fluoropolymer fill reduces the intrinsic stress in the reactively deposited aluminum oxide films by over 60%. It is not clear why the reactively deposited pure aluminum oxide films show slightly lower stress than aluminum oxide films deposited from an aluminum oxide target.

Web coating of fluoropolymer filled reactively deposited aluminum oxide films could be achieved by DC sputter etching of aluminum cathodes in a plasma environment containing oxygen and tetrafluoroethylene gas to allow both reactive deposition of aluminum oxide simultaneous with the arrival of polymerizing CF_2 radicals. Such films may be suitable where barrier properties as well as flexibility are required.

SUMMARY

Indium tin oxide and magnesium fluoride mixed films produced by co-sputter deposition result in high transmittance films which are much less conducting than pure indium tin oxide films. Such films demonstrate durability to immersion in water, vacuum ultraviolet radiation and atomic oxygen. These films hold potential for applications on spacecraft solar array surfaces to eliminate differential charging.

Fluoropolymer-filled reactively deposited aluminum oxide films exhibit high transmittance of visible light and are of significantly lower stress than pure aluminum oxide films. The films have a lower water contact angle than either aluminum oxide or Teflon as a probable consequence of some degree of aluminum fluoride formation. These films hold potential for barrier coating applications where transparency and flexibility are required.

REFERENCES

1. Hudson, W. R., Robson, R.R., and Sovey, J. S., "Ion-Beam Technology and Applications," NASA TM X-3517, May, 1977.
2. Dwight, D.W., "Ion Beam Surface Modification: Characterization by ESCA and SEM," NASA Grant Report, NSG-3204, June, 1979.
3. Banks, B.A., Sovey, J.S., Miller, T.B., and Crandall, K.S., "Ion Beam Sputter Etching and Deposition of Fluoropolymers," NASA TM 78888, presented at the 8th International Conference on Electron and Ion Beam Science and Technology, sponsored by the Electro-chemical Society, Inc., Seattle, WA, May 21-26, 1978.
4. Banks, B.A., Mirtich, M.J., Sovey, J.S., Naha, H., and Rutledge, S.K., "Flexible Fluoropolymer-Filled SiO_2 Protective Coatings," NASA CP 3109, Vol. 2, pp.

179-184, presented at the Technology 2000 Conference, sponsored by NASA Headquarters Code CU, Washington, DC, Nov. 27-28, 1990.

5. Banks, B.A., Rutledge, S.K., and Cales, M.R., "Performance Characterization of EURECA Retroreflectors with Fluoropolymer-Filled SiOx Protective Coatings," Proceedings of the LDEF-69 Months in Space, Third Post-Retrieval Symposium held in Williamsburg, VA, NASA Conference Publication 3275, Nov. 8-12, 1993.

6. Banks, B.A., and LaMoreaux, C., "Performance and Properties of Atomic Oxygen Protective Coatings for Polymeric Materials," Proceedings of the 24th International SAMPE Technical Conference, Toronto, Canada, October 20-22, 1992.

7. Rutledge, S.K., Banks, B.A., and Hunt, J., "Reactively Deposited Aluminum Oxide and Fluoropolymer-Filled Aluminum Oxide Protective Coatings for Polymers," NASA TM 106966, paper presented at the 1995 Spring Meeting, sponsored by the Materials Research Society, San Francisco, CA, April 17-21, 1995.

8. Banks, B.A., Rutledge, S.K., de Groh, K.K., LaMoreaux, C., and Olle, R., "Fluoropolymer-Filled SiO2 Coatings: Properties and Potential Applications," paper presented at the Society of Vacuum Coaters 35th Annual Technical Conference, Baltimore, MD, March 22-27, 1992.

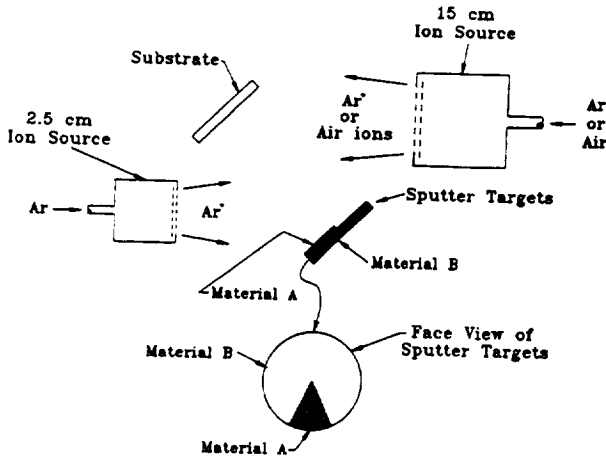


Figure 1. Configuration of ion sources, sputter targets and deposition substrate.

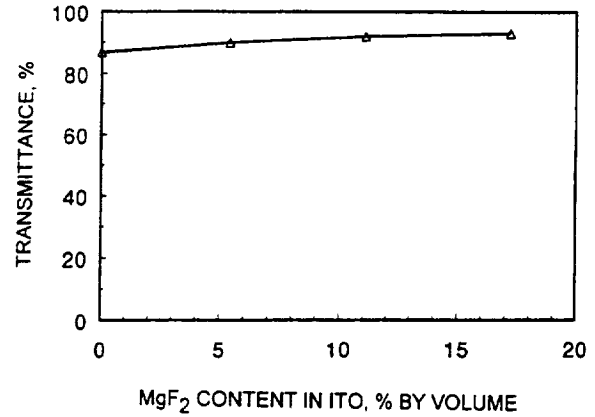


Figure 2. Transmittance of indium tin oxide and magnesium fluoride mixed coatings.

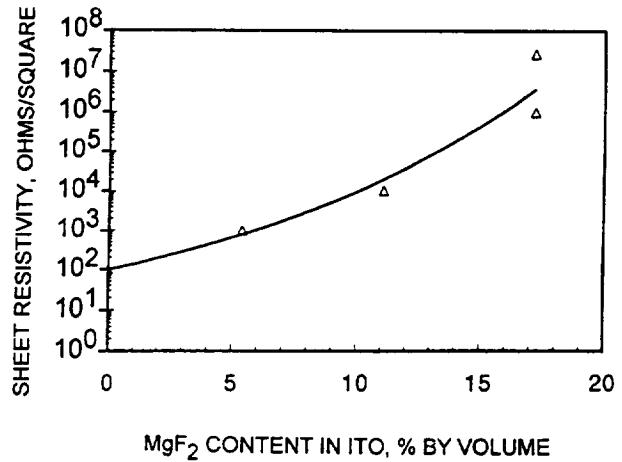


Figure 3. Sheet resistivity of indium tin oxide and magnesium fluoride mixed coatings.

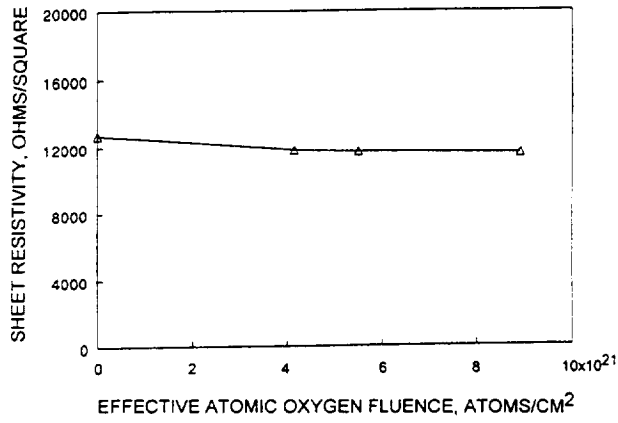


Figure 4. Effect of atomic oxygen exposure on sheet resistivity of mixed indium tin oxide/magnesium fluoride coatings.

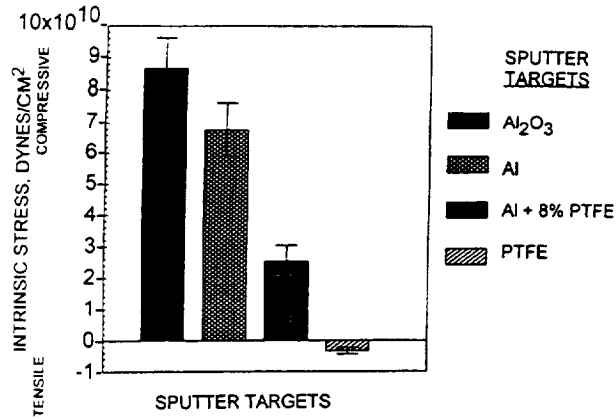


Figure 5. Intrinsic stress for various types of sputter deposited films.

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