High-Temperature Oxidation Resistance of SiO_2-Coated Polyimide Composite

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Silicon dioxide films (500–5,000 Å-thick) were deposited on silicon wafers and polyimide composite surfaces by plasma-enhanced chemical vapor deposition. The chemical reaction takes place on the surface and depends on substrate conditions and process parameters. In the present study, SiO_2 films were deposited from tetraethylorthosilicate (TEOS) in the 275–400°C temperature range under the influence of a radio frequency discharge (13.56 MHz). The properties of the deposited films, such as refractive index, density, stoichiometry, and adhesion, were obtained. The deposition characteristics of the films were studied as a function of process parameters including temperature, pressure, and RF power level. Finally these TEOS-SiO_2 films were found to be effective in the protection of polyimide-based composites for higher-temperature (350–400°C) applications.

Introduction

Polyimides are an important class of materials which can be used as the matrix material in carbon-fiber-reinforced composites. Polyimide-based composites have already found extensive application in space exploration, and the most well known polyimide, Dupont Kapton, will be used as the solar cell mount for the Space Station Freedom solar array. The maximum service temperature of conventional polyimides is about 370°C. At higher temperatures (to 450°C) in an ambient air environment, conventional polyimides undergo oxidative degradation, rendering them useless as structural materials at these temperatures. The focus of the present study is to explore new ways to improve the oxidation resistance of polyimide-based composites in higher temperature applications, and the approach is to use thin-film coatings to prevent oxygen contact with the polyimide surface.

The chemical vapor deposition (CVD) technique has been chosen as the method for deposition of the protective thin film onto the composite surface. Although various CVD techniques have been extensively studied and applied to thin-film deposition in the field of microelectronics, its use in applications such as the deposition of protective coatings onto structural materials is yet to be fully explored. The primary advantages of the CVD technique are its ability to prepare a large variety (metals and ceramics) of coatings and to provide, in some cases, conformal coverage over an irregularly shaped or rough surface, such as might be encountered at the surface of a composite material.

Oxidation protection of a material by the application of a protective coating requires that the coating itself be immune to oxidation. In general, ceramic materials, such as silicon dioxide, silicon carbide, and silicon nitride, are highly oxidation resistant, even to temperatures as high as 1,300°C (Maeda et al., 1988a,b). Ceramics have been successfully applied as oxidation resistant coatings to metals, other ceramics, and carbon-carbon composites. Amorphous silica has been deposited by the plasma-enhanced chemical vapor deposition (PECVD) process onto nickel-based superalloys and has been shown to significantly reduce the degree of oxidation of these materials at temperatures above 1,000°C (Bennet et al., 1989).

A significant amount of work has been done in the area of oxidation-resistant coatings for space applications. For example, the prevention of atomic oxygen attack on space borne solar mirrors and photovoltaic array blankets has been accomplished by the application, by a variety of different techniques, of coating materials such as silicon dioxide and aluminum oxide (Gulino et al., 1987; Gulino, 1988; Banks et al., 1985).

In the present study, a near-stoichiometric SiO_2 film was deposited onto a composite surface from an organosilicon precursor (tetraethylorthosilicate) by the plasma-enhanced chemical vapor deposition technique (Adams, 1986; Chin and Van de Ven, 1988; Hess, 1984; Hey et al., 1990; Nguyen and

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Murarka, 1990; Selamoglu et al., 1989). Tetraethylorthosilicate (TEOS) was chosen as the source material because of its nontoxic and nonhazardous nature and its ease of handling vs. other common silicon sources such as silane. Also, TEOS contains sufficient oxygen to allow the formation of stoichiometric silicon dioxide by pyrolytic and plasma-induced decomposition without the need to supply additional oxygen.

Through the use of the PECVD technique, the activation energy required for the chemical reaction is overcome by dissociation of the gaseous reactants in the plasma due to collision with the high-energy electrons. This enables film deposition to take place at temperatures considerably lower than that required for conventional (thermal) CVD. This is particularly important when working with polyimide composites, which cannot be subjected to temperatures much higher than about 370°C.

When a solid surface is exposed to a radio frequency (RF) glow discharge (plasma), a variety of phenomena occur on the material surface which can affect film deposition. Bombardment of the surface with energetic particles generated by the plasma (ions, neutrals, electrons, and photons) affects the surface chemistry, bonding structure and properties of the deposited films on the substrate (Hess, 1990). The pyrolytic, plasma-induced decomposition of tetraethylorthosilicate occurs through a heterogeneous reaction which takes place at the composite surface. The reaction can be represented in an overall stoichiometric equation as (Rojas et al., 1989):

$$Si(OC_2H_5)_4 = SiO_2 + 4C_2H_5 + 2H_2O$$

The overall process can be considered as a sequence of the following physico/chemical steps: 1) forced flow of the reactant in vapor form with the carrier gas (argon) into the reaction chamber; 2) transport of TEOS fragments toward the composite surface; 3) adsorption and decomposition of the reactant species at the surface to form the product; and 4) desorption and diffusion of the product gases from the surface to the bulk gas.

Experimental Procedure

The deposition of SiO_2 films onto polyimide composite surfaces was performed in a PECVD reactor (Figure 1) which consisted of a process chamber with a capacitively-coupled radio frequency generator (13.56 MHz). The area of the electrodes was 400 cm^2. In addition to RF power, an electrically powered substrate heater was also provided. The process chamber was 20 cm in length and 10 cm in diameter, and was constructed of glass and copper and was evacuated by means of a mechanical pump (base pressure ≈0.01 Torr). Copper coils were brazed to the outside of the portion of the process chamber surrounding the substrate heater to provide water cooling of the chamber walls.

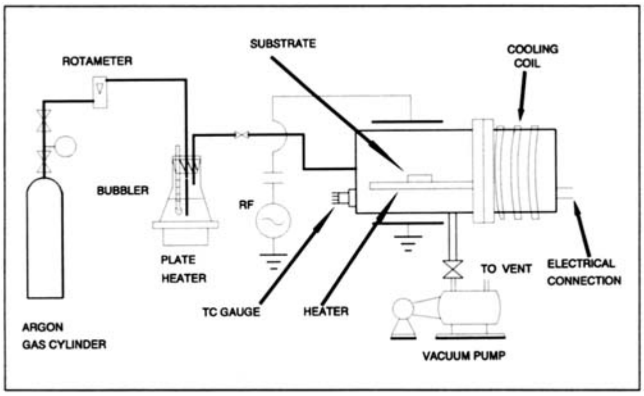

Figure 1. PECVD system.

Table 1. SiO_2 Deposition Parameters

System Pressure:	300-1,000 mtorr
Substrate temperature:	265-425°C
Gas composition:	TEOS + Argon
RF frequency:	13.56 mHz
RF power:	0.22-0.40 W/cm^2
Carrier gas flow rate:	180-250 sccm

The substrate heater was positioned in the center of the deposition chamber and electrically grounded. Silicon wafer pieces and polyimide composite samples (2 cm^2) were placed horizontally on the heater. The silicon wafers served as witness coupons for characterization of process parameters.

Tetraethylorthosilicate (Aldrich, 99.999%) was placed in a glass bubbler and heated to 60°C to enhance vaporization of the liquid (boiling point of 168°C). As the carrier gas, argon was introduced into the bubbler, and the entrained vapor was carried to the reaction chamber through 0.25-in-dia. (6.4-mm-dia.) stainless steel tubing which was wrapped with heating tape to maintain 60°C throughout to prevent condensation of TEOS vapor inside the tubing. The Ar flow rate was monitored and controlled by passing the gas through a rotameter installed in the line. The pressure was controlled by a throttle valve and was measured by a thermocouple gauge located downstream from the chamber.

Film stoichiometry was measured by Rutherford Backscattering Spectroscopy (RBS). Fourier Transform Infrared Spectra of the deposited films were obtained on a Perkin-Elmer Model 1600 FTIR Spectrophotometer. Film thicknesses were measured on a Sloan Dektak IIA surface profilometer, and refractive indices were measured by ellipsometry (J. A. Woollam Co.).

Results and Discussion

Deposition parameters for the PECVD process are listed in Table 1. Film thicknesses (and hence deposition rates) were measured by placing a witness sample consisting of a silicon wafer fragment in the chamber adjacent to the substrate of interest. A portion of this witness sample was masked with a second piece of silicon during deposition. Afterward, the mask was removed and the resulting step profiled with the profilometer. Direct measurement on film thickness on those composite samples subsequently studied by RBS confirmed the values obtained from this witness technique. The stoichiometry of the films was analyzed by RBS, and the Si:O ratio was found to be 1:2 (to within 10%). The hydrogen content itself in the films was analyzed using proton recoil detection (PRD). The PRD spectrum showed less than 3% hydrogen, and this was the only measurable impurity for all films deposited under the process conditions listed in Table 2. Both the experimental RBS spectrum and the simulated (theoretical) result for a typical film are shown in Figure 2.

Table 2. Process Conditions for TEOS-SiO_2 Film Deposition by PECVD

Substrate Temp. (°C)	Pressure (mtorr)	Carrier Gas (Ar) Flow Rate (std. cm^3)	Deposition Rate (Å/min)	Uniformity Variation (%)
265	1,000	200	215	8.2
300	1,000	200	165	24.5
300	800	220	150	6.7
300	600	250	135	11.6
300	400	200	140	13.4
300	300	180	131	15.6
320	800	250	167	4.8
340	800	200	175	2.6
390	1,000	220	123	11.4
425	1,000	250	80	22.4

The highest rate of deposition achieved was 215 Å/min, and the range of film thicknesses obtained was 500 to 5,000 Å. Film thickness uniformity was calculated from five separate measurements in different locations on the silicon wafer witness samples. The film thickness variation across the wafer was calculated as follows:

$$\text{Variation}\ (\pm\%) = 100(D_{\max} - D_{\min})/(D_{\max} + D_{\mathrm{mm}})$$

where $D_{\max}$ and $D_{\min}$ are the maximum and minimum thicknesses, respectively.

Fourier transform infrared spectroscopy (FTIR) over the spectral range 400–4,000 cm^{-1} was used to reveal the bonding structure in the deposited films. Figure 3 shows a typical transmittance spectrum. The strong absorption band at 1,070 cm^{-1} (Si-O stretching) is similar in location to that of thermally grown SiO_2, which has been reported at 1,080 cm^{-1} (Pliskin, 1977). The band at 800 cm^{-1} (Si-O bending) is also indicative of SiO_2 (Pliskin, 1977).

To test the adhesion strength of the films, peel adhesion ("Scotch tape") tests were performed (ASTM, 1984a,b). This technique measures the threshold value of the film-substrate bond strength, above which the film is peeled away. After performing the peel adhesion test on a number of samples, it was found that thinner films (less than 1,000-Å-thick) were more adherent (as judged by the approximate percentage of the film surface under the tape which remained on the substrate) to the composite surface than were the thicker films (generally greater than 2,000-Å-thick), which appeared to lose adhesion to the substrate. This behavior is most likely due to increased tensile stress in the thicker films.

The refractive indices (n) of the films match closely to that of thermally grown SiO_2 (1.46). Although only a few samples were analyzed, covering the deposition temperature range of 268°C to 390°C (measured as the temperature of the heater surface; the temperature of the substrate surface itself averaged approximately 10°C less than the heater surface), behavior similar to that seen previously (Rojas, 1989) was observed. This behavior is an increase in the refractive index with increasing temperature to a point (in the present case, 300°C), followed by a decrease at still higher temperatures.

From the refractive index, the film densities (Table 3) were calculated using the Clausius-Mossotti (CM) relationship (Rojas et al., 1989):

$$\rho = \frac{k(n^2-1)}{n^2+2}$$

where ρ is the density and k is a constant equal to 8.1148. The value for the constant is obtained empirically from the data obtained on thermally grown (920°C) SiO_2.

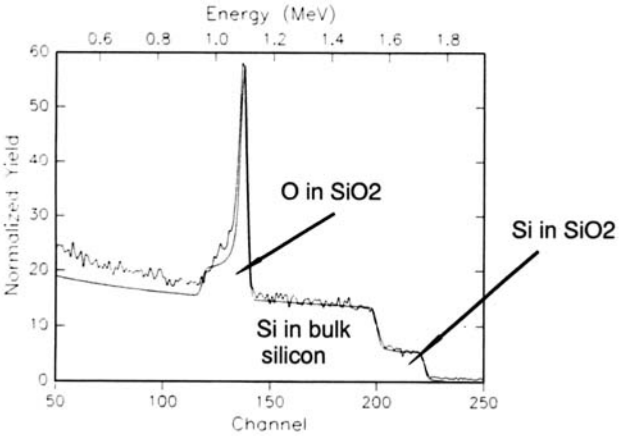

Figure 2. Rutherford backscattering spectrum of a typical SiO_2 film.

Both the silicon and the oxygen in the film are observed. The peak is due to an oxygen resonance.

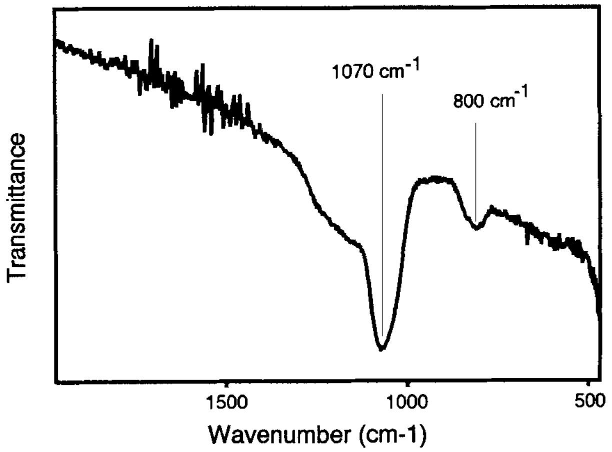

Figure 3. FTIR spectrum of a typical SiO_2 film.

The peaks identified are indicative of the presence of Si-O bonds, with the peak 1,070 cm^{-1} due to Si-O stretching and that at 800 cm^{-1} due to Si-O bending.

Table 3. Calculated Densities of Several SiO_2 Films

n (600 nm)	Dep. Temp. (°C)	ρ (gm/cm^3)
1.4611	268	2.227
1.4672	300	2.252
1.4615	390	2.229

A wet etch test was also performed on the SiO_2 films. Upon exposure to a 100:1 H_2O:HF solution, the etch rate was observed to vary between 145 Å and 225 Å per minute. This compares favorably with other reported etch studies (Huo et al., 1991) and indicates a reasonably dense film with little or no pinholes or other bulk defects.

The deposition rate was found to decrease when the substrate temperature was increased. The trend is similar to that reported by Chin and Van de Ven (1988), Kulisch et al. (1989), and Chang et al. (1990). This behavior may indicate an adsorption-controlled reaction. As the substrate temperature rises, the active species gain kinetic energy; consequently, the probability of adsorption is reduced and that of desorption is increased. Increasing temperature may also promote surface recombination of the adsorbed precursors, thus causing the negative dependence of the deposition rate with temperature. The apparent heat of adsorption, which is the thermodynamic correspondent for the activation energy of TEOS-SiO_2 film deposition, was calculated from an Arrhenius plot (Figure 4) and found to be 4.1 kcal/mol (17 kJ/mol). This compares very well with an activation energy of 4.7 kcal/mol (19 kJ/mol) reported by Chin and Van de Ven (1988) and in qualitative agreement with a value of 2.6 kcal/mol (11 kJ/mol) reported by Webb et al. (1989). In both of these experiments, the investigators used a mixture of TEOS and oxygen as the reactant precursors.

The deposition rate was found to increase with an increase in RF power (Figure 5). With such an increase in power, the plasma density increases with a corresponding increase in the concentration of ions and free radicals formed as a result of TEOS dissociation. This is expected to enhance decomposition of the gaseous TEOS species and lead to a higher deposition rate.

The process total pressure was varied from 300–800 mtorr (constant residence time), and the deposition rate was found to be affected slightly. This is shown in Figure 6. Two opposing forces interplay as the pressure is increased. As the TEOS partial pressure is increased, the deposition rate is also increased. Consequently, a reduction in the effective diffusivity of the species is likely to change the reaction from the surface-controlled regime to the diffusion-controlled one, and thus dampen the deposition rate.

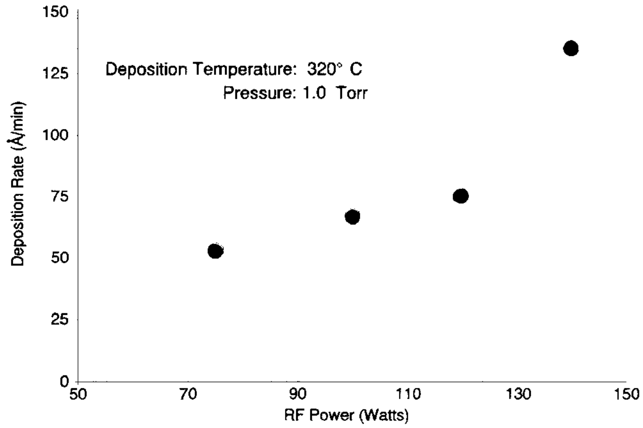

Figure 5. Deposition rate vs. RF power.

Several coated samples were tested for their ability to resist oxidation by exposing them to high temperature in an ambient environment for increasing lengths of time. Uncoated samples were also tested for comparison. The masses of samples were monitored at regular intervals for up to 300 h at several temperatures in the range 380–400°C. The results indicated that the coatings were effective in preventing thermo-oxidative mass loss under these atmosphere and temperature conditions. The weight losses after exposure of the coated samples were all significantly lower than that of the uncoated one (Figure 7).

Figure 8 shows the observed percent mass loss after 300 hours as a function of SiO_2 film thickness. There is a minimum in this curve in the 800–1,000 Å range, suggesting that thinner films gave poor coverage, perhaps at the edges and corners. Thicker films were observed to spall (as a result of tensile stress, as discussed above), which would likely result in defects permitting oxidation of the substrate surface.

The best results were obtained with twice-coated samples (Figure 9). In these cases, one film of 1,250–1,500 Å was ap-

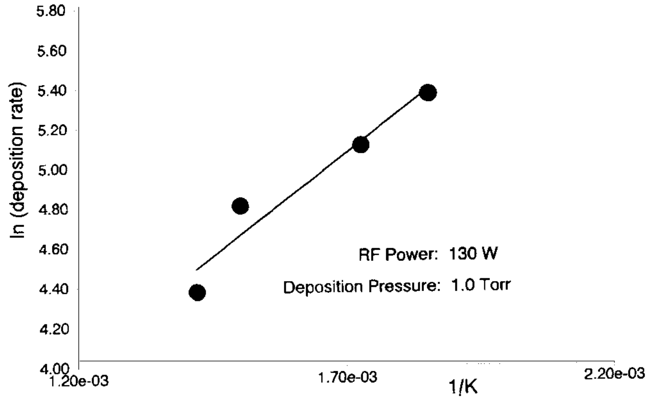

Figure 4. Arrhenius plot for SiO_2 deposition from TEOS.

The slope of the least-squares fit yielded a calculated activation energy of 4.1 kcal/mol (17 kJ/mol).

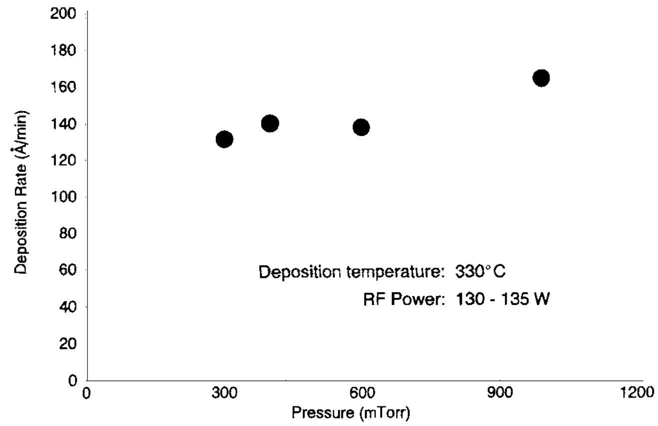

Figure 6. Deposition rate vs. pressure.

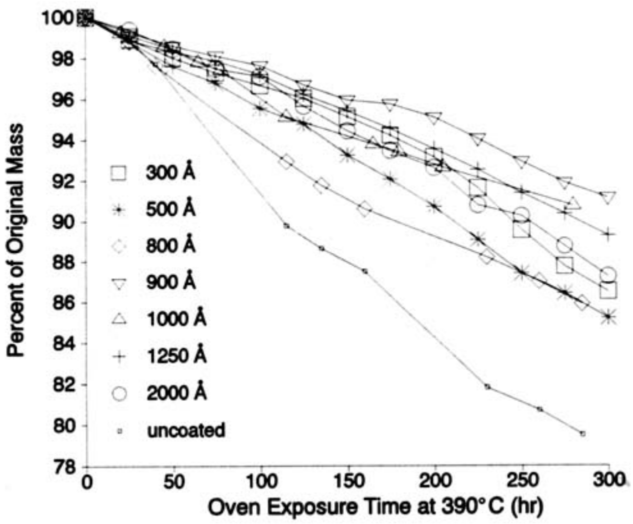

Figure 7. Effect of exposure to ambient atmosphere at elevated temperature on the mass of SiO_2-coated samples of PMR-15 polyimide composite.

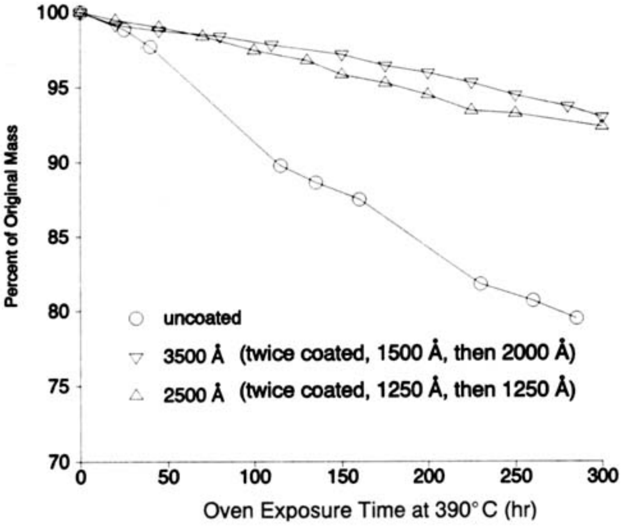

Figure 9. Effect of exposure to ambient atmosphere at elevated temperature on the mass of PMR-15 polyimide samples "twice-coated" with SiO_2.

plied, the chamber brought to atmosphere, and then the deposition process repeated to apply a second coating directly over the first. A possible explanation for this behavior may be elucidated from studies done by Crowell et al. (1990, 1991). They investigated the fundamental mechanism of SiO_2 film growth from TEOS onto SiO_2 surfaces and found that partial dissociation of the TEOS molecule occurs upon adsorption to the SiO_2 surface, leaving two-to-three ethoxy ligands per reaction site. This adsorbed species then decomposes to form SiO_2 by beta-hydride elimination. They also point out the involvement of hydroxyl groups in the initial reaction of TEOS with the SiO_2 surface. Thus, consumption of hydroxyl groups to produce adsorbed siloxane on SiO_2 surface is a possible mechanism and is likely to produce more uniform coverage for the second film.

As a check, polyimide composite samples were heated to 390°C in a nitrogen-only atmosphere at a pressure of 0.01 torr. A small amount of mass loss (less than 1%) was observed after 200 hours. This is likely due to the loss of volatile impurities, but overall indicates that the composite is not subject to pyrolytic decomposition at this temperature.

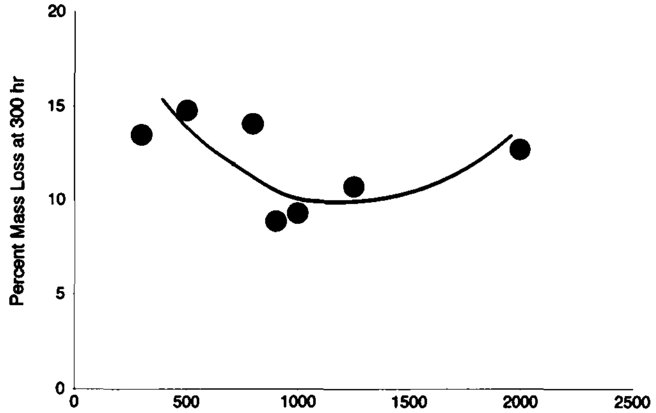

Figure 8. Percent mass loss at 300 hrs exposure to ambient atmosphere at 390°C as a function of SiO_2 film thickness.

It is important to note that oxidation of the coated samples was not altogether eliminated, and this is likely due to oxidation at the edges or corners of the samples. Current efforts are directed to further improve the coating of the deposited sample so that better oxidation resistance is achieved.

Conclusions

Near stoichiometric silicon dioxide films were deposited from tetraethylorthosilicate by PECVD onto silicon wafer and polyimide composite substrates. The growth rate of the films was correlated with process parameters and was found to proceed by an adsorption-controlled reaction mechanism, which is substantiated by the observation that the deposition rate decreased as the substrate temperature was increased. At thicknesses ranging from 2,500 to 3,500 Å, the films provided significant thermo-oxidative protection to polyimide composite at temperatures of 390–400°C.

Acknowledgment

The authors gratefully acknowledge partial support by NASA under grant NCC3-194. We also wish to thank Dr. John Woollam and his group at the University of Nebraska for performing the ellipsometry measurements, and Dr. David Ingram of the OU Department of Physics for performing the RBS studies. S. N. acknowledges partial support through a CMSS Research Assistantship.

Notation

D_{max} = maximum film thickness, Å
D_{min} = minimum film thickness, Å
k = constant
n = refractive index
ρ = density, g/cm^3

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Manuscript received Feb. 3, 1992, and revision received May 4, 1992.