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SUMMARY

Diffusion of oxygen in thin films of silicon dioxide has been studied using oxygen isotopically enriched in oxygen of atomic mass 18 (^{18}O). This subject is of interest because thin films of dielectrics such as SiO_2 are proposed for use as protective coatings for solar mirrors in low Earth orbit, which is a strongly oxidizing environment. Films of this material were prepared with a dc magnetron using reactive sputtering techniques. To produce ^{18}O-enriched SiO_2, a standard 3.5-in.-diameter silicon wafer was reactively sputtered using ^{18}O-enriched (95 percent) oxygen as the plasma feed gas. The films were characterized using RBS and SIMS to establish stoichiometry and purity. Subsequently, the films were exposed to an air-derived oxygen plasma in a standard laboratory plasma reactor for durations of up to 10 hr. The concentration ratio of ^{16}O as a function of depth was determined using SIMS profiling and compared to a baseline, nonplasma exposed sample. A value for the diffusivity of oxygen near the surface of these films was obtained and found to be about 10^{-15} cm^2/sec.

INTRODUCTION

Electrical power generation for the inital configuration of Space Station Freedom will be accomplished by traditional photovoltaic panels providing a total of 75 kW. At a later date, two 25 kW solar dynamic power system modules will be added. Solar dynamic systems generate electricity by directing sunlight into the receiver of a thermal-to-electric power conversion unit, such as a Rankine or Brayton cycle heat engine. Collection and focusing of sunlight will be accomplished by a parabolic concentrator composed of 456 triangular (1 m) facets arranged into 19 hexagonal petals of 24 facets each (fig. 1). Details of the concentrator module design and construction are provided elsewhere (ref. 1 and 2).

Protection of the concentrator reflective medium (either silver or aluminum) from the low Earth orbit (LEO) atomic oxygen environment will be

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accomplished by overcoating the metal layer with one or more thin layers of
transparent dielectric, such as aluminum oxide or silicon dioxide. While much
previous work has demonstrated the resistance to oxidation by these metal/oxide
systems, there has remained the question of the likelihood of long-term
diffusion of atomic oxygen through these films to the dielectric/metal
interface. This may cause oxidative degradation of the metal, and possibly the
substrate, as well. The purpose of the present study was to measure the rate
and extent, if any, of oxygen atom penetration through an oxide coating. This
was accomplished by preparing a thin film of silixon dioxide by reactive
sputtering of a silicon wafer target where the reactive gas was oxygen of
atomic mass 18. Subsequent exposure to an ^{16}O plasma and comparison with an
unexposed sample provided a means of measuring any oxygen diffision.

APPARATUS AND PROCEDURE

Preparation of the ^{18}O-enriched silica was accomplished using a dc
magneton with a boron-doped, (111) silicon wafer target mounted on a 10.16 cm
(4 in.) diameter by 0.635 cm (0.25 in.) thick aluminum wafer occupying the
normal target position. The arrangement is depicted schematically in
figure 2. Electrical contact between the silicon and the aluminum was suf-
ficient for proper operation of the unit. The belljar was first pumped down
to a pressure 1 mtorr. Argon was then bled into the chamber at a rate of 852
SCCM, which raised the pressure to 5 mtorr. The magnetron was then started
and set to ramp to 0.3 kW in 10 min. ^{18}O (Scott Specialty Gases) flow was
started 9 min into the ramp cycle in order to conserve ^{18}O. Typical sput-
tering times were 2 min at 0.3 kW, giving films about 1000 to 1100Å thick.

Films of $Si^{18}O_2$ were deposited on <100> silicon wafer substrates and
analyzed by Rutherford backscattering spectrometry (RBS) for stoichiometry and
purity. Separate samples were exposed to an air-derived oxygen plasma in a
standard labroatory plamsa asher (thus ^{16}O was the diffusing species of
interest) to simulate the oxidizing environment of LEO for varying lengths of
time. The asher generates an oxygen plasma by RF excitation of air at
13.56 MHz, providing a variety of oxygen species at thermal energies. The
utility of oxygen plasma ashers for LEO atomic oxygen simulation is discussed
elsewhere (refs. 3 to 5). Any diffusion oxygen through the silica layer was
then measured by depth profiling with secondary ion mass spectroscopy (SIMS)
to look for changes in the $^{16}O/^{18}O$ ratio. These concentration profiles
were used to calculate the diffusivity of oxygen through silica. Table I pre-
sents data on the deposition parameters for the films prepared in this study.
The subsequent analysis performed is also listed.

RESULTS

Chemical Analysis

RBS analysis of the first four samples permitted determination of the
stoichiometry of the SIO_x films (table II). Flow rates above 10 SCCM were
sufficient to obtain approximately stoichiometric SiO_2. Even at ^{16}O flow
rates of zero, significant amounts of oxygen were present in what were pre-
sumed would be pure Si films. The source of this oxygen is probably

residual moisture in the chamber. Its presence did not hinder the course of these experiments, however, since ^{18}O enrichment was successfully obtained in films prepared with ^{18}O replacing ^{16}O as the reactive feed gas. Figure 3 shows raw SIMS data for sample 7A, which was prepared with ^{18}O. The level of ^{18}O was increased considerably versus the normally expected natural abundance of ^{18}O (0.204 percent). Figure 4 shows raw SIMS data for sample 1A, which was an attempt to prepare a pure SI film (but did in fact incorporate oxygen impurity) and was the only nonenriched sample for which a SIMS profile was obtained. The expected natural abundance of ^{18}O was in fact observed. Thus it was possible to detect an increase in ^{16}O concentration levels in samples prepared identically to 7A after exposure to the ^{16}O plasma.

Figure 5 depicts ^{16}O concentration profiles as a function of depth for samples 7A (nonashed), 8B (1 hr ashed, 1.17×10^{19} atoms/cm^2 equivalent fluence of O atoms), and 8C (10 hr ashed, 1.17×10^{20} atoms/cm^2 equivalent fluence). Because the concentration of ^{16}O in the bulk of these films should be the same (since they were prepared during the same deposition run), and because the accuracy of the concentration measurements is good only to a factor of two with this technique, the concentration profiles were normalized to the bulk values. The concentration profile of the nonashed sample was then subtracted out and the data replotted as bulk-normalized concentration difference versus depth (fig. 6)

It should be noted that the concentration profiles reached their peaks at a depth of about 100Å, rather than at the surface, as would be expected. This is most likely due to out-diffusion of near-surface oxygen during the time (about 2 weeks) between oxygen plasma exposure and subsequent SIMS analysis. Therefore, in figure 6, the profiles begin at about 100Å depth.

Diffusion Model

Analysis of the concentration profiles was accomplished by modeling the system as a one-dimensional, nonsteady-state diffusion into a semi-infinite slab according to the technique described by Dosdale and Morris (ref. 6). Such diffusion is described by Fick's second law (ref. 7).

$$\frac{\partial Ca}{\partial t} = \frac{\partial}{\partial x}\left[D(Ca)\frac{\partial Ca}{\partial x}\right] \qquad (1)$$

where C_a is the concentration of the diffusing species, x is distance (in this case, depth), t is time, and $D(C_a)$ is the diffusivity which in general is a function of concentration. If it is assumed that D is independent of concentration, equation (1) reduces to

$$\frac{\partial Ca}{\partial t} = D\frac{\partial^2 Ca}{\partial x^2} \qquad (2)$$

Assuming the boundary condition that the surface concentration is constant at C_{ao} and the inital condition that $C_a = 0$ for all $x > 0$ at $t = 0$, then by the following substitutions

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$$\eta = \frac{x}{2\sqrt{t}} \tag{3}$$

$$C = \frac{C_a}{C_{ao}} \tag{4}$$

equation (2) may be written as

$$-2\eta \frac{dc}{d\eta} = D \frac{d^2 C}{d\eta^2} \tag{5}$$

The solution to equation (5) is the complementary error function of $(\eta/\sqrt{D})$, or

$$C = \text{erfc}\left(\frac{\eta}{\sqrt{D}}\right) \tag{6}$$

If the inverse of equation (6) is taken,

$$\text{erfc}^{-1} C = \frac{\eta}{\sqrt{D}} \tag{7}$$

and if z ia defined as

$$z = \text{erfc}^{-1} C \tag{8}$$

then we have the simple equation

$$z = \frac{\eta}{\sqrt{D}} \tag{9}$$

Thus a plot of z versus η should be linear with slope equal to $1/\sqrt{D}$. In practice, its is necessary to transform the original data by equations (3) and (8).

Performing the above analysis on the concentration profiles for the 1 and 10 hr exposures yielded η versus z curves such as shown in figure 7 for the 1 hr sample. Based on the slopes of a least-square fit to these lines, values of D were calculated and are shown in table III.

These values are in reasonable agreement and are between the ranges of values typically seen for gas-solid and solid-solid diffusion (table IV). Given the larger size of the oxygen atom relative to the helium atom, as well as uncertainties inherent in measurements such as this, the values obtained here appear reasonable.

From the values, calculations were made of time required for concentration at the interface (assumed to be at depth of 1000Å) to reach various fractions of the maximum concentration. These values are presented in table IV.

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DISCUSSION

As described elsewhere, (refs. 2, 3, 9, and 10) much work has been done to evaluate the durability oxidative attack of silver/dielectric systems exposed to an oxygen plasma. In those studies, any effect of oxygen was measured as a loss in refectance. A thin film of silver with no protective coating loses reflectance very rapidly (2 to 3 hr exposure results in a loss of about 30 percent) in the plasma asher environment (ref. 9). Exposure times have ranged to many hundreds of hours (far more than predicted in table V) with little or no oxidative degradation evident, as determined by reflectance measurements. The results obtained here would not predict this. It is not clear what concentration level of atomic oxygen at the SiO_2/Ag interface is necessary before macroscopic effects, such as reflectance loss, become observable. It is intuitively reasonable, however, that 10 or 20 percent or more of the plasma concentration should be suffficient. Clearly then, atomic oxygen is not reacting at the rates which might be predicted from these concentration profiles.

There are at least two possible explanations for the observed lack of oxidation: (1) oxygen is actually arriving at the interface, but is somehow prevented from reacting with the silver, or (2) oxygen is not arriving at the interface. Based on the assumptions made in using the semi-infinite slab approximation, the second explanation is the more likely. The semi-infinite slab model works best for short times and short distances. It is probable that, as the level of oxygen in the film increases, the diffusion rate of later arriving oxygen is retarded or even stopped altogether as the driving force (concentration difference) for that diffusion is lessened.

It is interesting to note that the extent of diffusion was approximately the same (about 300Å) in both the 1 and 10 hr cases. It would be instructive to repeat these experiments for longer exposure times (up to 100 hr) and then profile with SIMS to determine if diffusion extends beyond this depth. The structure of these amorphous silica films may be such that a certain degree of porosity exists near the surface which permits a small degree of diffusion to occur there. This would be consistent with earlier findings that SiO_2 films, among many others, are successful in protecting silver from atomic oxygen attack. The results obtained here would be useful in predicting the rate of oxygen diffusion in thinner films (<300Å).

CONCLUSIONS

Thin films of SiO_2, isotopically enriched in ^{18}O, were successfully prepared, and diffusion of [16]O from an air-derived oxygen plasma through these films were detected. Calculation of a diffusivity for [18]O in these SiO_2 films yielded values which would predict a relatively rapid build-up of oxygen atoms at an SiO_2/Ag interface. The lack of experimental evidence for this, as measured macroscopically by reflectance loss, suggests that oxygen atoms are not actually reaching the interface, but may in fact diffuse only into the topmost 200 to 300Å.

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TABLE I. - SAMPLE PREPARATION PARAMETERS AND ANALYSES PERFORMED

Sample	Gas flow, SCCM			Film thickness, Å	^{16}O plasma exposure, hr	Subsequent analysis
	Ar	^{16}O	^{18}O			
1A	852	--	--	1040	--	RBS, SIMS
2A	852	10	--	1070	--	RBS
3A	852	25	--	1100	--	RBS
4A	852	40	--	1100	--	RBS
7A	568	--	40	580	0	SIMS
8B	568	--	40	580	1	SIMS
8C	568	--	40	580	10	SIMS

TABLE II. OXYGEN FLOW RATES AND
RESULTING STOICHIOMETRY

Sample	16O flow rate, SCCM	Si/O ratio
1A	0	1.1
2A	10	.59
3A	25	.52
4A	40	.52

TABLE III. - CALCULATED DIFFUSIVITIES

Exposure time, hr	D, cm2/sec
1	1.30×10^{-16}
10	2.16×10^{-17}

TABLE IV. - TYPICAL GAS-SOLID
DIFFUSIVITIES

$[cm^2/sec, 20°C; ref. 8.]$

He in SiO_2	2.4×1^{-10}
He in pyrex	4.5×10^{-11}
He in SiO_2	2.1×10^{-8}
Bi in Pb	1.1×10^{-16}
Sb in Ag	3.5×10^{21}
Al in Cu	1.3×10^{30}

TABLE V. - TIME REQUIRED TO
REACH THE GIVEN FRACTION OF
C_{ao} AT THE DEPTH OF 1000Å[a]

C $(=C_a/C_{ao})$	Time, hr
0.1	41
.2	66
.3	100
.4	153
.5	241

[a]The D calculated from
the 1 hr exposure data
was used.
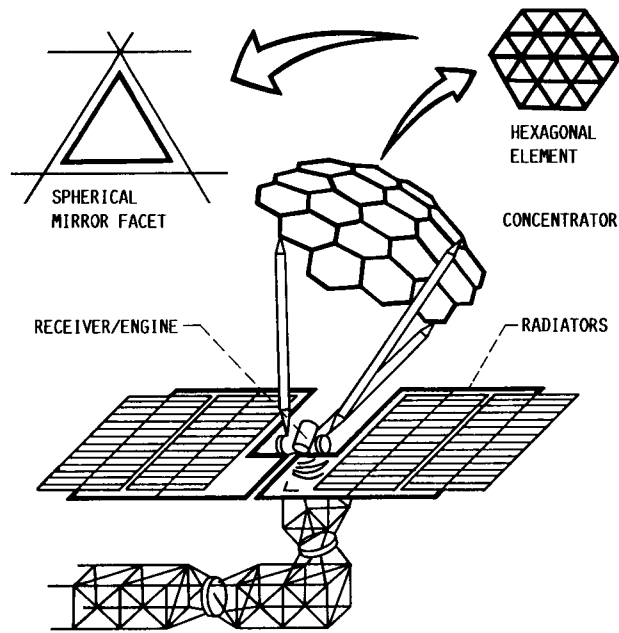
FIGURE 1. - SCHEMATIC DIAGRAM OF A SOLAR DYNAMIC POWER MODULE,
WHICH INCLUDES A CONCENTRATOR MADE UP OF HEXAGONAL ELEMENTS,
EACH OF WHICH IS COMPRISED OF SPHERICALLY CONTOURED TRIANGU-
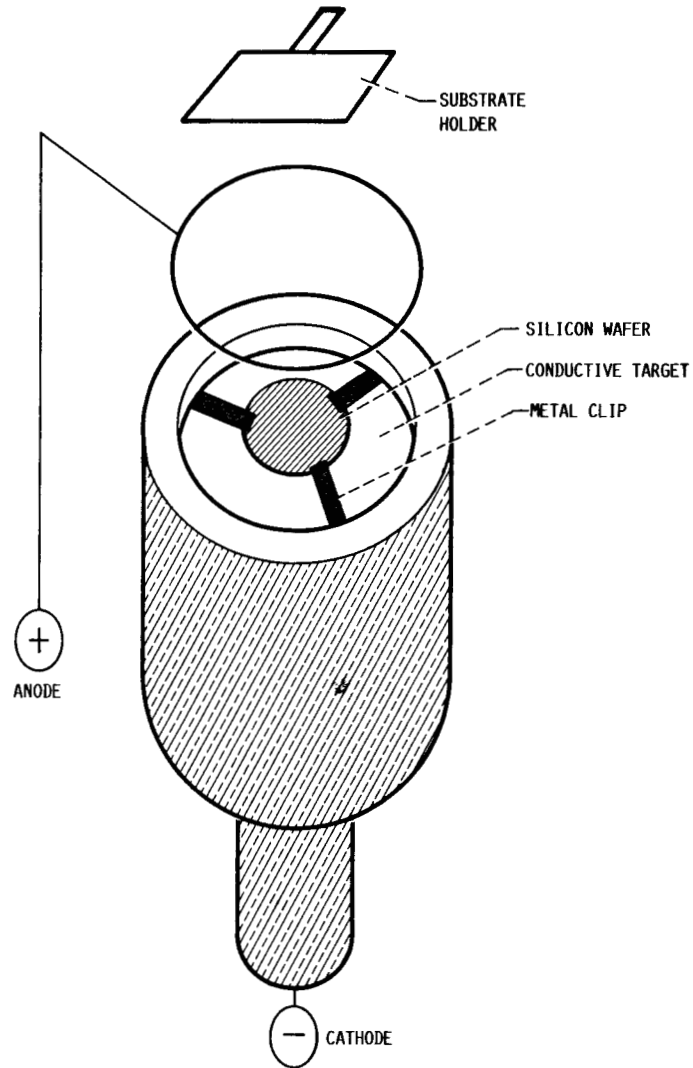LAR FACETS. ALSO SHOWN ARE THE RECEIVER/HEAT ENGINE AND RA-
DIATOR.

FIGURE 2. - SCHEMATIC DIAGRAM OF THE DC MAGNETRON SPUTTERING SYSTEM.
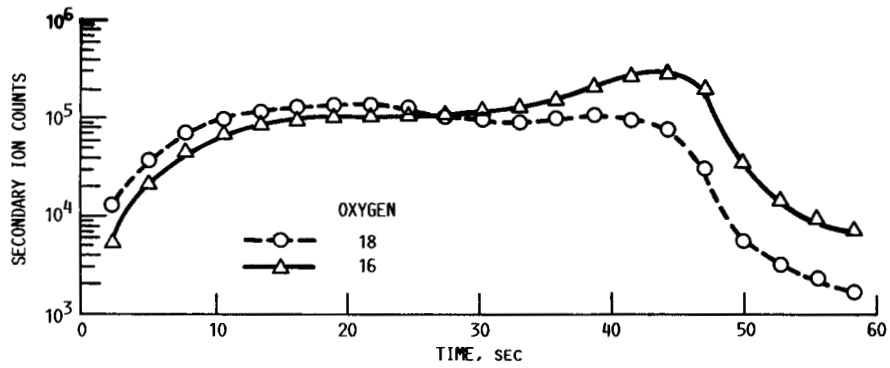
FIGURE 3. - SIMS PROFILE FOR ^{16}O AND ^{18}O FOR SAMPLE 7A, WHICH WAS PREPARED USING ^{18}O-ENRICHED OXYGEN. THE CONCENTRATION OF ^{18}O IS GREATLY INCREASED OVER THE EX-PECTED NATURAL ABUNDANCE (0.204 PERCENT).
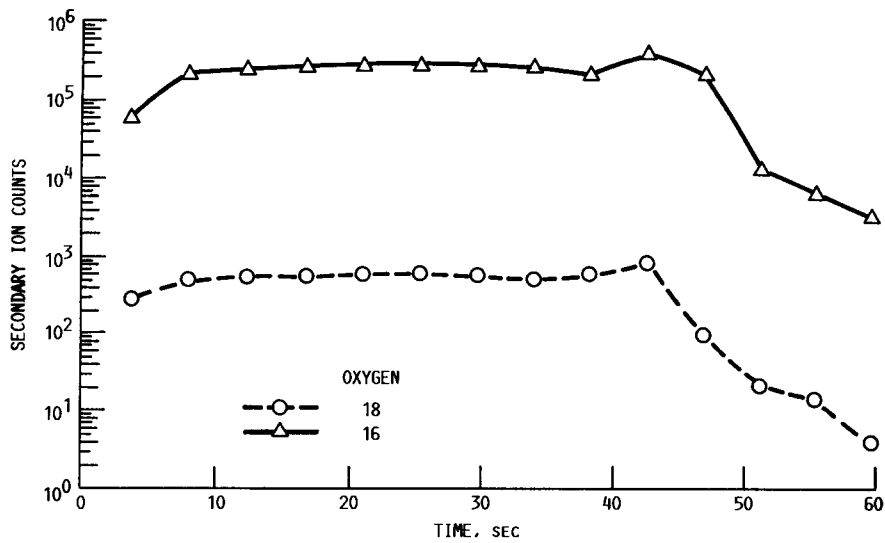
FIGURE 4. - SIMS PROFILE OF ^{16}O AND ^{18}O FOR SAMPLE 8A, WHICH WAS PREPARED ONLY WITH ARGON SPUTTERING GAS (NO OXYGEN GAS PRESENT AT ALL). THE TOTAL AMOUNT OF OXYGEN IN THE FILM WAS QUITE HIGH, INDICATING RESIDUAL OXYGEN IN THE CHAMBER. THIS FIGURE DEMONSTRATES THE NATURAL ABUNDANCE OF ^{18}O VERSUS ^{16}O.
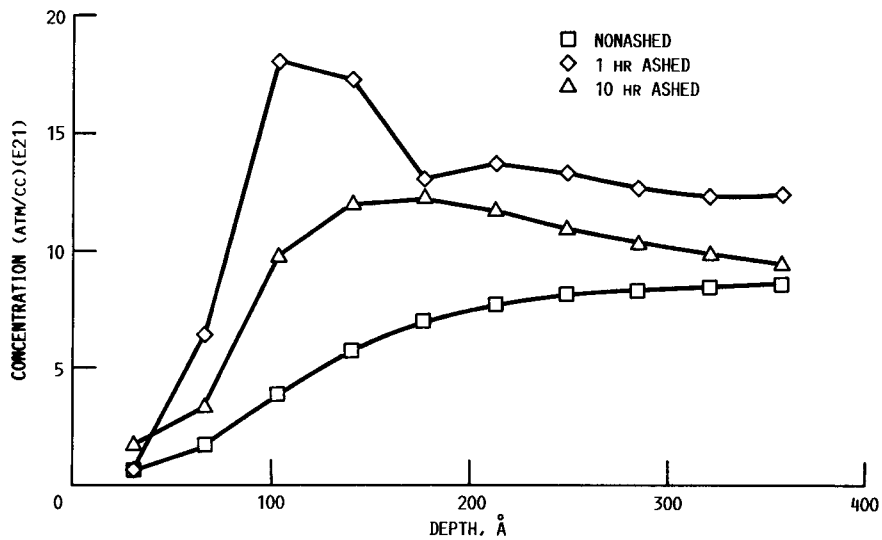

FIGURE 5. - ^{16}O CONCENTRATION PROFILES FOR ^{18}O-ENRICHED SiO_2 FILMS EXPOSED TO AN AIR-DERIVED ^{16}O PLASMA FOR VARYING LENGTHS OF TIME. ^{16}O-ENRICHMENT IS CLEARLY EVIDENT.
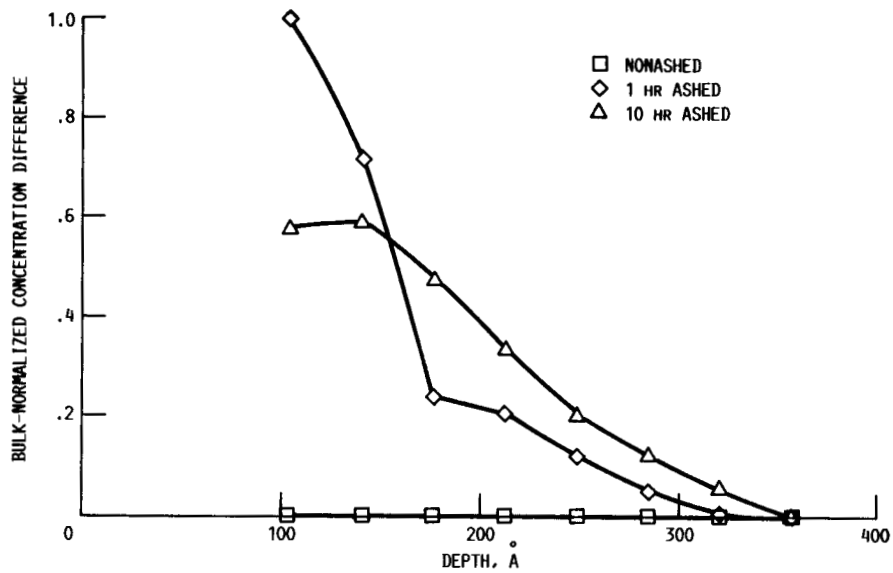
10

FIGURE 6. - BULK-NORMALIZED ^{16}O CONCENTRATION PROFILES USED TO CALCULATE THE DIFFUSI-VITY OF OXYGEN ATOMS IN THESE SiO_2 FILMS.
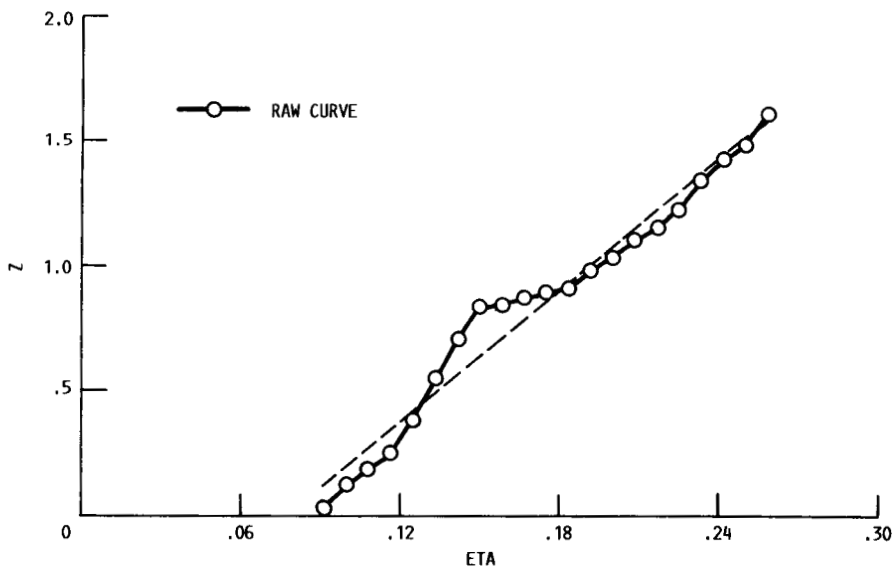

FIGURE 7. - PLOT OF η VERSUS Z FOR THE ONE HOUR EXPOSURE SAMPLE.

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16. Abstract

Diffusion of oxygen in thin films of silicon dioxide has been studied using oxygen isotopically enriched in oxygen of atomic mass 18 (^{18}O). This subject is of interest because thin films of dielectrics such as SiO_2 are proposed for use as protective coatings for solar mirrors in low Earth orbit, which is a strongly oxidizing environment. Films of this material were prepared with a DC magnetron using reactive sputtering techniques. To produce ^{18}O-enriched SiO_2, a standard 3.5-in.-diameter silicon wafer was reactively sputtered using ^{18}O-enriched (95 percent) oxygen as the plasma feed gas. The films were characterized using RBS and SIMS to establish stoichiometry and purity. Subsequently, the films were exposed to an air-derived oxygen plasma in a standard laboratory plasma reactor for durations of up to 10 hr. The concentration ratio of ^{16}O as a function of depth was determined using SIMS profiling and compared to a baseline, nonplasma exposed sample. A value for the diffusivity of oxygen near the surface of these films was obtained and found to be about 10^{-15} cm^2/sec.

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