

Ellipsometric Studies of the Diffusion of Atomic Oxygen Through Silicon Dioxide Thin Films

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Abstract

In this paper we describe the application of variable angle spectroscopic ellipsometry to the study of diffusion of atomic oxygen through SiO_2 . Data are found to be well fit to the universal growth parabola, and the diffusion coefficient is estimated to be $10^{-5} \text{cm}^2/\text{min}$.

Contents

Low Earth orbit spacecraft are exposed to atomic O, which is extremely active in degrading various materials. SiO_2 is a potentially good material for protective coating of surfaces under this oxidizing atmosphere. It is amorphous and therefore lacks any grain boundary through which atomic O might rapidly migrate. In this paper, we have investigated the diffusion of atomic O through SiO_2 using variable angle spectroscopic ellipsometry (VASE).^{1,2}

A commercially available discharge system (SPI Plasma-Prep II) was used to simulate the low Earth orbit atomic O atmosphere. From independent experiments carried out by NASA on shuttle missions, we know that the O flux was approximately 1.8×10^{17} atoms/ $\text{cm}^2\text{-min}$. SiO_2 was grown on Si(111) surfaces by introducing a high quality Si wafer into this oxidizing atmosphere for specified amounts of time. The substrate was not heated during this oxidation process. An initial thermal oxide was grown on several samples by exposing the wafer, at an elevated temperature, to steam for a certain amount of time, depending on the thickness of the initial oxide desired. Three sample groups were used: Group 1, naturally grown oxide (in atmosphere); Group 2, substrate temperature 1000°C , oxidation time 100 min.

Eight different samples were chosen out of each of these three groups and shed in atomic O for 15, 30, 60, and 90 mins and 2, 8, 24, and 48 hours. The thicknesses of the various SiO_2 layers were measured using VASE, with a typical uncertainty of less than $\pm 0.5 \text{ \AA}$. For details on VASE, see Refs. 1 and 2.

A simple model³ was used to analyze data, and we present here only the pertinent information necessary to understand the data analysis. Atomic O is carried to the oxide surface

from the gas. It then diffuses through the oxide layer and ultimately reacts with the Si surface to produce more oxide. In the steady state, these three rates are the same.

By using diffusion equations, Henry's law, and the ideal gas law, one obtains

$$F''' = N \frac{dx}{dt} = \frac{K_S}{1 + (K_S/\alpha) + (K_S x/D)} c^* \quad (1)$$

where F''' is the flux of atomic O being consumed by chemical reaction at the Si surface, N the number of O atoms bonded to silicon per unit volume of SiO_2 , x thickness of the oxide layer at time t , k_S the reaction rate constant for oxygen at the silicon surface, D a diffusion constant for oxygen through SiO_2 , c^* the concentration of oxygen in SiO_2 at the gas/oxide interface as obtained from Henry's law, assuming that oxygen has a partial pressure equal to that within the bulk of the gas and is considered to exist next to the oxide layer, and α is a proportionality constant.

The solution of Eq.(1), subject to the initial condition $x(t=0) = x_i$, is

$$x^2 + Ax = B(t + \tau) \quad (2)$$

where

$$A = \frac{2D}{(1/K_S) + (1/\alpha)}$$

$$B = \frac{2Dc^*}{N}$$

$$\tau = \frac{x_i^2 + Ax_i}{B}$$

Equation (2) can also be written in the following form:

$$\frac{x}{(A/2)} = \sqrt{1 + \frac{(t + \tau)}{(A^2/4B)}} - 1 \quad (3)$$

which is the universal growth parabola in terms of the variables x_O ($A/2$) and $(t + \tau)/(A^2/4B)$.

Short times, i.e., $(t + \tau) \ll A^2/4B$, result in the approximate solution

$$x \approx \frac{B}{A}(t + \tau) \quad (4)$$

The quantity B/A is called the linear rate constant. For long times, $t \gg A^2/4B$, $x^2 \approx Bt$, and B is the parabolic rate constant.

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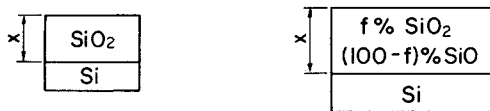


Fig. 1 Models used for the analysis of ellipsometric data: a) a SiO₂ layer of thickness x is assumed on bulk Si. b) Bruggemann mixture layer of $f\%$ SiO₂ and $(100-f)\%$ SiO having thickness x is assumed on bulk Si.

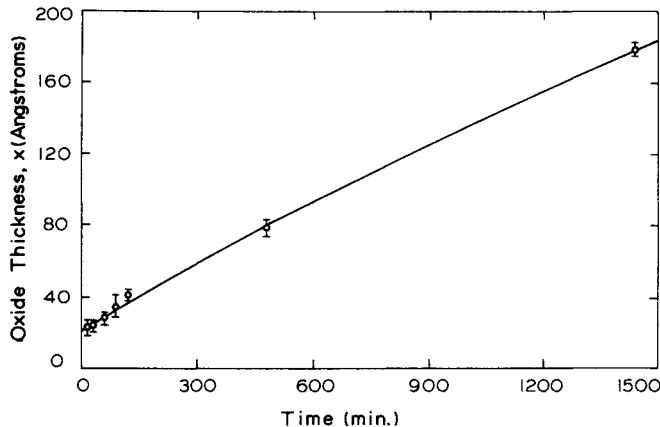


Fig. 2 Measured growth rate of oxide on group 1. The error bars are 90% confidence limits. The solid curve is the least-squares parabolic fit to the experimental data.

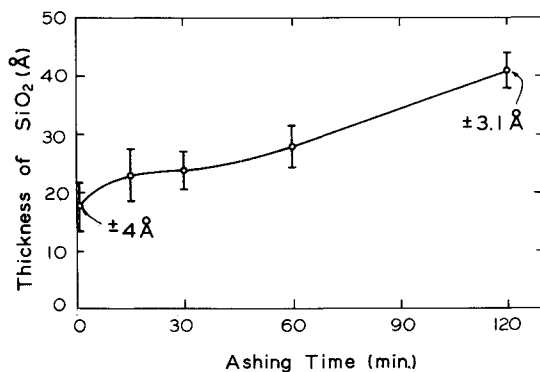


Fig. 3 Measured oxide thickness as a function of ashing time for group 1. The error bars represent 90% confidence limits.

The models used in the analysis of ellipsometric data are shown in Figs. 1a and 1b. Using the model in Fig. 1b, we found that the oxide layer was entirely made of SiO₂ (99.99...%) for all samples. The results of thickness measurements obtained for group 1 for different ashing times are shown in Fig. 2. The solid curve represents the parabolic least-squares fit to the experimental thickness data. The constants A , B , and t [in Eq. (2)] as obtained from this least-squares fit are given by $A = 769 \text{ Å}$, $B = 105 \text{ Å}^2/\text{min}$, and $t = 162 \text{ min}$. In Figs. 3 and 4 are shown the measured thickness for groups 1 and 2, respectively. Notice a striking similarity between the shoulders of these two curves near the ashing time of 15 min. We speculate that an initial (unknown) physical process for oxide growth is identical for each sample. The oxide growth on all three groups as a function of ashing time is shown in Fig. 5. It takes a long time for O to diffuse through group 3, which has an initial oxide thickness of 1100 Å.

We next estimate the diffusion constant of atomic O through the oxide layer. Taking the atomic O flux,

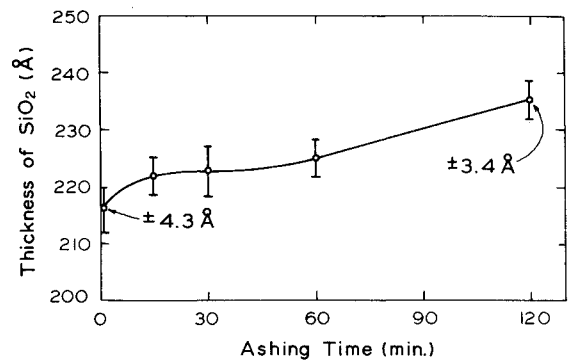


Fig. 4 Measured oxide thickness as a function of ashing time for group 2. The error bars represent 90% confidence limits. Notice the similarity of the shoulder of this curve and that in Fig. 5 at about 15 mins of ashing time.

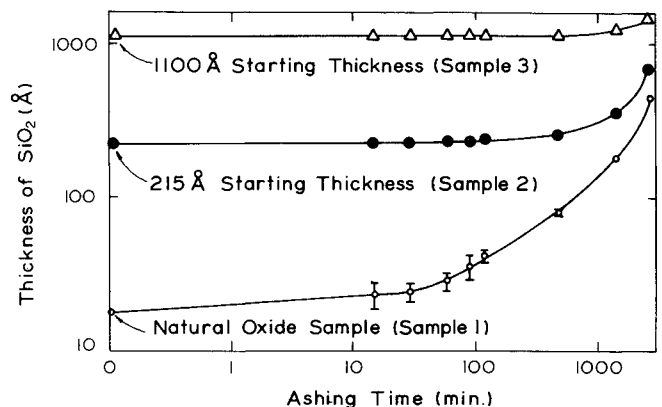


Fig. 5 Log-log plot of the thickness of oxides on three samples: group 1 (bottom curve), group 2 (middle), and group 3 (top).

$F_1 \approx 1.8 \times 10^{17} \text{ atoms} \cdot \text{cm}^{-1} \cdot \text{min}^{-1}$, and using the relationship $F_1 = F_1 c \bar{v}$ (where c = concentration and \bar{v} = average velocity), we obtain $c = 5.9 \times 10^{11} \text{ atoms/cm}^3$ for $\bar{v} = 5 \times 10^4 \text{ cm/s}$ (corresponding to an ion temperature of about 500K). Assume that this concentration is the upper limit of c_0 (the concentration of atomic O in the oxide layer at the gas-oxide interface). The exact value of N , the number of O atoms bonded to silicon per unit volume of SiO₂ in our oxide layer, was not known. Consequently, we assumed that the concentration of O atoms in fused silica ($\approx 4 \times 10^{22} \text{ cm}^{-3}$) roughly corresponds to the O-atom concentration in the oxide layer, and that $c_i \ll c_0$. Assuming steady-state conditions and $x \sim 10 \text{ Å}$ (the representative value of oxide layer thickness for Group 1), we obtain $D \sim 10^{-5} \text{ cm}^2/\text{sec}$. It is emphasized that this is just a rough estimate; D was assumed to be thickness as well as time-independent in the integration of the differential equation (1).

Acknowledgment

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