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Water diffusion coefficient measurements in deposited silica coatings by the substrate curvature method

Jeremy Thurn *

Mechanical Research and Development, Seagate Technology, Bloomington, MN 55435, United States

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ABSTRACT

The diffusion of water in silica coatings deposited by evaporation and physical vapor deposition (sputtering) is studied using the substrate curvature measurement technique. The diffusion of water into the coatings induced a swelling, which in turn caused bending (curvature) of the silicon substrate. The curvature change was measured in situ during a humidity increase from 0% to 95% at room temperature. The diffusivity of water in the sputtered silica coating was measured to be 10×10^{-12} cm^2/s and achieved equilibrium in about 10 min. The diffusion of water in the evaporated silica coating achieved equilibrium in about 2 min. Because the coatings exhibited very short equilibration times, the impact of a non-instantaneous humidity change on the calculated diffusion coefficients was also examined.

1. Introduction

Diffusion of water in bulk glass and silica coatings causes deleterious changes in properties and impacts reliability. It has been extensively studied and quantified by numerous techniques including infrared absorption [1–4] and Raman spectroscopy [5] of hydroxyl groups, water vapor transmission rate measurements [6], and secondary ion mass spectrometry of D_2O [7]. This work applies a substrate curvature method previously used to deduce the room temperature diffusivity of water in polymer coatings [8] to deposited silica coatings. This technique allows direct measurement of the room temperature swelling-induced strain in the coating in situ during humidity exposure, as well as calculation of the water diffusion coefficient, or diffusivity.

2. Theory

The concentration profile of water diffusing into a thin silica coating on an impermeable substrate is obtained from the one-dimensional concentration profile of water diffusing into a thin slab.

2.1. Instantaneous change of surface concentration

The transient concentration profile for a slab initially at a uniform concentration whose surfaces are instantaneously exposed to a new concentration is given as Eq. (4.17) in Crank [9] and reproduced here:

$$\frac{C(x,t)-C_0}{C_s-C_0} = 1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1} \times \cos\left[\frac{(2n+1)\pi x}{2L}\right]\exp\left[-\frac{D(2n+1)^2\pi^2 t}{4L^2}\right], \qquad (1)$$

where C is the concentration of water in the slab, x is the position variable, t is time, C_0 is the initial uniform concentration in the coating, C_s is the surface concentration (at $x = L$) at time $t > 0$, D is the diffusion coefficient (assumed to be independent of x and t), and L is the thickness of the coating. The interface between the substrate and coating is at $x = 0$ and the coating surface is at $x = L$.

2.2. Exponentially-changing surface concentration

The surface concentration of water (C at $x = L$) might not be instantaneously changed, but instead it may vary with time. The variation in surface concentration with time is here assumed to be exponential:

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* Tel.: +1 952 402 7384; fax: +1 952 402 8566.
E-mail addresses: jeremy.a.thurn@seagate.com, jeremy_a_thurn@yahoo.com.

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$$C(x = L, t) = C_s[-\exp(-\alpha t)], \tag{2}$$

where C_s is the surface concentration of water as time approaches infinity, α is obtained as a fitted parameter to the measured variation of humidity with time, and t is time. The concentration of water in the silica coating resultant from the time-dependent surface concentration of Eq. (2) is given as Eq. (4.29) in Crank [9] and reproduced here:

$$\frac{C(x,t)}{C_s} = 1 - \frac{\cos\left(\frac{x\alpha^{1/2}}{D^{1/2}}\right)}{\cos\left(\frac{L\alpha^{1/2}}{D^{1/2}}\right)}\exp(-\alpha t) - \frac{16\alpha L^2}{\pi}$$
$$\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)[4\alpha L^2 - D\pi^2(2n+1)^2]}\cos\left[\frac{(2n+1)\pi x}{2L}\right]$$
$$\times \exp\left[-\frac{D(2n+1)^2\pi^2 t}{4L^2}\right], \tag{3}$$

where C is the concentration of water in the silica coating, x is the position variable, D is the diffusion coefficient of water in silica, t is time, α is the fitted parameter from Eq. (2), and L is the coating thickness.

2.3. Resultant curvature change

The transient diffusion of water in a (hypothetical) detached silica coating under no external moments or forces induces elongation, bending, and internal stress [8]. At equilibrium, the detached coating swells to a strain denoted as $\varepsilon^{\mathrm{eq}}$, where the superscript 'eq' represents equilibrium. This strain is directly proportional to the equilibrium uniform concentration of water in the silica coating C_s, as given in the following equation:

$$\varepsilon_{\mathrm{eq}} = \beta C_s, \tag{4}$$

where β is the 'swelling coefficient'.

The strain of the detached coating at the midplane of the coating, $x = L/2$, is denoted as ε_D, where the subscript 'D' indicates the 'detached' nature of the coating. This strain can be calculated from the water concentration in the coating given in Eqs. (1) or (3), as shown in the following equation [8]

$$\varepsilon_D(t) = \frac{\beta}{L}\int_0^L C(x,t)\mathrm{d}x, \tag{5}$$

where β is the swelling coefficient from Eq. (4), L is the coating thickness, x is the position variation, and t is time. Additionally, the detached coating bends as a consequence of the water concentration profile through its thickness. The curvature is denoted κ_D, where the subscript 'D' again emphasizes the 'detached' nature of the coating, and is calculated as [8]

$$\kappa_D(t) = \frac{12\beta}{L^3}\int_0^L\left(x + \frac{L}{2}\right)C(x,t)\mathrm{d}x, \tag{6}$$

where L is the thickness of the coating, C is the water concentration calculated from Eqs. (1) or (3), x is the position variable, and β is the swelling coefficient.

For a composite system consisting of the silica coating perfectly adhered to a substrate under no external moments or forces, the curvature of bending is modified from that calculated in Eq. (6), due to the elastic bending resistance of the substrate. This modified composite curvature, denoted κ, can be calculated from the following equation [8]:

$$\frac{\kappa(t)}{\kappa^{\mathrm{eq}}} = \int_0^L\frac{C(x,t)}{C_s}\mathrm{d}x + \frac{12B}{L^3}\int_0^L\left(x + \frac{L}{2}\right)\frac{C(x,t)}{C_s}\mathrm{d}x, \tag{7}$$

where C is the water concentration in the coating calculated from Eqs. (1) or (3), C_s is the equilibrium uniform concentration of water in the coating, L is the coating thickness, x is the position variable, κ^{eq} is the curvature of the composite at equilibrium when the water concentration in the coating is at equilibrium and has uniform concentration C_s and B is a constant defined as

$$B = \frac{L^2\left(1 + \frac{L}{L_s}\frac{E}{E_s}\right)}{6L_s\left(1 + \frac{L}{L_s}\right)}, \tag{8}$$

where L is the coating thickness, L_s is the substrate thickness, E is the coating Young's modulus, and E_s is the substrate Young's modulus. If the composite is a circular wafer, then Young's modulus for both the coating and the substrate should be replaced by the biaxial modulus $E/(1-\nu)$, where ν is Poisson's ratio. The diffusion coefficient of the coating can be evaluated by using Eq. (7) in combination with Eqs. (1) or (3) and comparing the calculated transient curvature profile to the experimentally measured curvature profile.

3. Experimental

Silica coatings were either grown by thermal oxidation at 900 °C to a thickness of 300 nm, deposited by E-beam evaporation to a thickness of 210 nm, or deposited by non-reactive physical vapor deposition (sputtering) to a thickness of 600 nm on double-side polished single crystal silicon wafers with (100) orientation, 100 mm diameter, and 0.2 mm or 0.25 mm thickness. Some samples were cut into rectangular strips with dimensions of 10 mm × 50 mm by cleaving the wafer with the long edge perpendicular to the long flat. The biaxial modulus of the silicon wafer is 180.5 GPa and Young's modulus of the strips is 168.9 GPa [10]. Samples were stored in a desiccated 'dry box' for two weeks prior to testing.

Young's modulus of the silica coatings was measured by nanoindentation using an instrumented indenter.[1] Experiments were conducted by applying an exponentially-increasing ('constant strain rate') force to the coating surface using a 3-sided diamond pyramidal ('Berkovich') indenter tip while superimposing a sinusoidal displacement of magnitude 2 nm or less. The superimposed displacement enables measurement of elastic stiffness in situ during the indentation experiment, and the stiffness is used to calculate Young's modulus of the coating as described in Oliver and Pharr [12].[2] The Berkovich tips used for these experiments had previously been calibrated using a fused silica standard (with a two-parameter area function [11]). The in situ measured load, displacement, and stiffness data were analyzed using the Oliver–Pharr technique [12] assuming Poisson's ratio of 0.2.

Curvature measurements were made at room temperature using substrate curvature measurement tool.[3] The tool is capable of measuring curvature of wafers from 75 mm to 200 mm diameter, and was additionally modified to additionally measure 10 × 50 mm strips. Curvature was measured by scanning a laser across the wafer or strip, a procedure that takes approximately 30 s. Gaseous nitrogen containing a controlled amount of humidity was flowed over the wafer or strip at rates of 0.5–10 L/min (1–20 ft^3/h). Humidity was generated using a humidifier[4] with a DI water source (humidity must be generated ultrasonically to prevent condensation on the glass window through which the substrate curvature measurement laser passes). The relative humidity was measured using a temperature-compensated capacitive film humidity sensor. Because the sensor was too large to fit in the substrate curvature measurement chamber with the wafer or strip, it was instead placed in a small 'mixing box'

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[1] MTS NanoIndenter XP.

[2] This technique is called the 'Continuous Stiffness Option' for the MTS NanoIndenter.

[3] KLA-Tencor (now Toho Technology) Flexus FLX2320.

[4] Electro-Tec Systems (ETS) Model 5472.