Etching of Silica Glass under Electric Fields

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The etching rate of silica glass in 40% hydrofluoric acid under the influence of electric fields is studied with the help of an interferometric technique. A linear dependence of etching rate with field strength was found, with a ~2.5% etching rate change for an applied field of 20 MV/m. The experimental results are compared with those of a simple model that attributes this dependence to partial orientation of the HF molecules in the electric field. The measured dependence is sufficiently significant to account for the selective etching observed in frequency doubling glasses and fibers. [S0031-9007(97)02547-7]

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Etching of silica glass (SiO_2) in hydrofluoric acid is an important step in the processing of microelectronic components, and this motivated studies on etching mechanisms [1] and on the role played by dopants [2] in the glass matrix. Etching in the presence of an electric field has also been investigated, and contradictory results exist in the literature. While the field created by a *pn* junction was observed to be capable of stopping the etching of a film of silica [3], recent results were reported where fringing fields of intensities as high as 10 MV/m were applied to silica samples and the etching rate in a solution of HF was found to be unaffected [4]. The effect of an electric field on the etching rate of silica is of interest from a fundamental point of view and also with a view to technological applications. It has been shown that it is possible to pole by optical [5] or by electrothermal means [6] both bulk silica samples and optical fibers, creating a permanent electric field in the glass that gives rise to a strong optical nonlinearity capable of frequency doubling light. Etching is a powerful tool to study the physics behind poling, and has been used to reveal the distribution of the electric field in glass fibers [7] and in bulk glasses [8–10]. In order to extract further information from etching experiments it is necessary to learn what causes the unequal etching rates observed in poled glasses and fibers. In pure SiO_2 systems (such as found in poled bulk samples or in a frequency doubling fiber cladding) unequal etching can have two possible origins: (1) The etching rate may be influenced by embedded charges causing structural or chemical changes in the glass material and (2) a strong electric field alone could alter the etching velocity. In this paper an etching experiment of SiO_2 in HF is described where only an electric field can be responsible for an alteration of the etching rate. The

dependence of etching rate with field strength was measured. The experimental results are compared with those of a simple model that attributes the alteration to partial orientation of the HF molecules in the electric field.

An interferometric optical method was used to determine in real time the thickness of glass etched that avoided low precision mechanical measurements and the necessity to interrupt the etching process [10]. The SiO_2 samples were fixed approximately horizontally and attacked by hydrofluoric acid from below. A He-Ne laser beam illuminated the glass sample from above and was reflected at the top and bottom surfaces of the sample. The interference of these reflections was registered in real time with a photodiode and a lock-in amplifier, and the signal recorded in a computer. The measured light intensity oscillated with a frequency proportional to the etching rate. One period of oscillation corresponded to half a wavelength of the laser light in the glass material 0.217 μm (which includes a small correction caused by the angle of incidence). In order to measure the thickness of the glass plate at two adjacent positions on the sample simultaneously, the laser beam was split in two. Focusing the probe beam to a small spot on the sample ($\sim 10^{-1}$ mm diameter) ensured that the periodic signal had constant modulation depth.

Information about the dependence of the etching rate on electric fields was obtained by submitting 170 μm thick silica samples to voltages ranging from +2.7 kV to −2.7 kV. In order to prevent electrical breakdown, 1 mm thick soda-lime glass slides were attached with a very thin layer of index matching fluid or optical glue to the top of the silica samples. Since the resistivity of soda-lime glass is orders of magnitude lower than that of SiO_2, all applied voltage appeared across the silica sample, but the

thicker glass prevented the occurrence of sparks. Both a thin layer of salty water and a semitransparent film of soot deposited on the top surface of the soda-lime glass were used as electrodes, giving equal results. Both experiments were carried out with 40% hydrofluoric acid.

Figure 1 shows a typical fraction of the resulting signals. The etching rate was measured for various field strengths. This was done by determining for every voltage the average period of oscillation of the interference trace, i.e., the time taken to etch through 0.217 μm of SiO_2. A quadratic fit of the data around the extrema was used for determining with accuracy the positions of the maxima (or minima). The progressive thinning down of the sample was taken into account when relating the voltage applied to the electric field. Although a constant etching rate was expected without the application of an electric field, it was observed that in the initial stages of the experiment the etching rate $\eta = \eta(t)$ followed an exponential accommodation law of the type $\eta(t) = \eta_0(1 - 2 \times 10^{-2} \exp\{-t/\tau\})$ with a time constant $\tau \approx 380$ s. This was verified in control experiments, and could be caused by humidity on the surface of the SiO_2 sample or by a small temperature rise due to the exothermic reaction before steady state is reached. In order to eliminate this unwanted time dependence we considered only experimental data with $t > 1600$ s. Also, it has been recently shown that UV radiation or high power visible light can affect the etching rate of glass systems in HF [4]. In order to preclude such effects in the present interferometric measurements with the low power HeNe laser, the etching rate at the two spots on the sample was compared, having momentarily one of the two beams blocked. Within the experimental error no influence of the He-Ne laser light on the etching rate was found. This test was carried out with the voltages 0 and -2.4 kV applied.

Figure 2 shows the etching rate as a function of the applied electric field, obtained with a ~ 1 cm^2 soot electrode on a silica sample of 172 ± 3 μm thickness. A positive field corresponds to a positive glass and negative acid. A linear dependence is clearly visible for field strengths in the range ± 20 MV/m. In this experiment, carried out at room temperature (24 ± 3 °C), one does not expect any macroscopic charge migration in the glass. In fact, the current measured by applying 3 kV to the 170 μm thick silica glass samples at temperatures as high as 80 °C with 9 mm^2 electrodes was below 1 nA, the detection limit. The linear dependence found indicates that the influence of charge migration on the etching rate was negligible in the present experiment, since one expects that a change in etching rate caused by charge migration would have been asymmetrical with respect to the change of polarity, giving rise to different slopes in Fig. 2 for $E > 0$ and $E < 0$. Other changes, such as of chemical origin, would have led to hysteresis in the etching rate. With several changes in the sign and value of applied voltage no hysteresis effects were ever found. Consequently, the resulting dependence of the etching rate on the applied field must be due to the electric field itself.

The ratio $\rho(E_{app})$ between the etching rate under the application of a field E_{app} and that obtained for $E_{app} = 0$ is seen from Fig. 2 to be of the form $\rho(E) = 1 + \alpha E_{app}$, where

$$\alpha = (1.26 \pm 0.05) \times 10^{-9} \text{ m/V}. \tag{1}$$

It should be noted that the value of the electric field changes abruptly at the interface glass acid. The value of α here reflects the dependence of the relative etching rate ρ on the field *inside* the glass.

The above result can qualitatively be explained by a simple theoretical model that assumes partial orientation of HF molecules in the electric field. The Debye radius of the solution, as determined from conductivity measurements, is ~ 13 nm, which gives a measure of how far the electric field penetrates into the acid. Hydrofluoric acid at a concentration of 40% is almost nondissociated [1]. It is assumed that the dominant etching mechanism is the
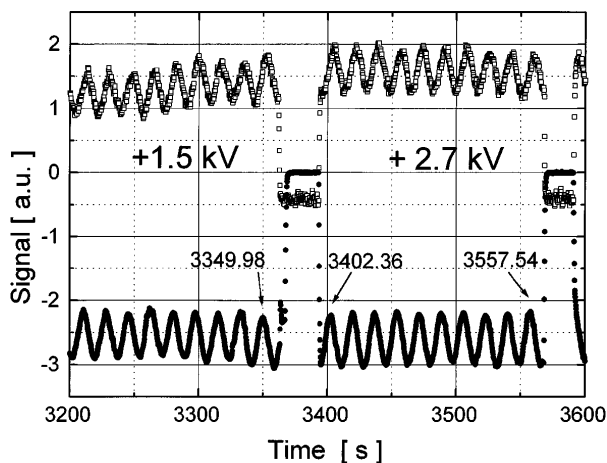

FIG. 1. Typical trace of the etching interferometer measurement. Two beams are recorded in order to measure at two positions of the sample. The number of oscillations, counting from the beginning of the experiment, determines the etched thickness for a given applied field.
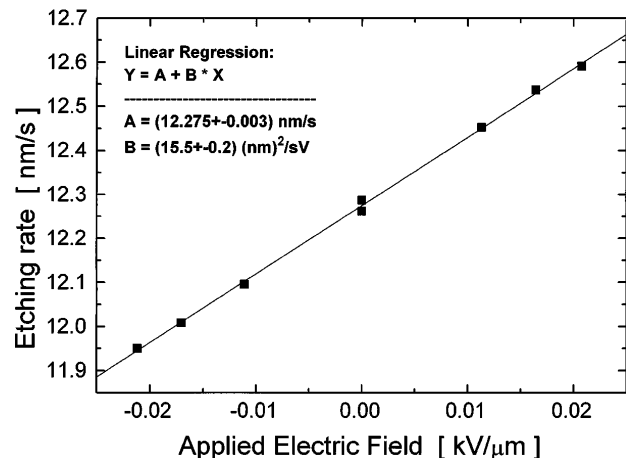

FIG. 2. Observed etching rate as a function of applied field. A linear dependence is clearly seen.

reaction of HF molecules with silicon atoms. When such a molecule approaches the glass surface its axis will in general form some angle θ with the normal of the glass surface. A chemical reaction is assumed to occur only for angles smaller than some small angle θ_0. Considering that the polar complex of moment μ has potential energy $-\mu E_L \cos(\theta)$ in a local electric field E_L, one finds from simple statistical mechanics and supposing $(1 - \cos\theta_0) \times \mu E_L/kT \ll 1$ that the relative etching rate is given by

$$\rho(E) = 2x \frac{\exp\{x\}}{\exp\{x\} - \exp\{-x\}}, \qquad (2)$$

where $x = \mu E_L/kT$. For $x \ll 1$ one may approximate expression (2) as follows:

$$\rho(E) = 1 + \frac{\mu}{kT} E_L. \qquad (3)$$

This implies that for relatively weak fields, the etching rate depends linearly on the applied electric field, as observed experimentally (c.f. Fig. 2). With the dielectric constant of silica (3.81) and of the acid (73 ± 5) one expects the local surface field inside the acid to be of the order of $E_L = 1.3 \times E_{\mathrm{app}}$. From $kT = (2.55 \pm 0.03) \times 10^{-2} \, e_0$V under the prevailing experimental conditions and from the value of the dipole moment of the HF molecule $\mu = (1.92 \pm 0.02)$ $D = (0.400 \pm 0.004) \times 10^{-10} \, e_0$m one finds the theoretical prediction $\alpha_{\mathrm{theory}} = 2.0 \times 10^{-9}$ m/V. The experimental value measured agrees within a factor of 1.6 with this figure, but confirms the model only qualitatively. In fact, the mean field type approximation that was used is known to give a poor description of a strongly polar solution which also exhibits hydrogen bridges. One may, however, use the theoretical expression (2) in order to extrapolate the experimental result to strong fields ($\approx 5 \times 10^8$ V/m). In this case, in Eq. (2) x is taken as the experimental value αE_{app} instead of $1.3 \, \mu E_{\mathrm{app}}/kT$.

Knowing how the electric field affects the etching rate of SiO$_2$, it is possible to estimate whether the selective etching of poled glasses and of frequency doubling fibers can be ascribed to this mechanism alone.

(a) Etching experiments with electrically poled silica were carried out with 1 mm thick samples biased to 3 kV at 300 °C, as described in Ref. [10]. A region depleted of Na atoms just under the anode was measured by interferometry to be 5.8 μm thick, and the etching rate was found to be relatively constant and slower there than in an unpoled region of the same sample. The ratio in etching rates measured between 2.4 and 5.5 μm was $\rho = (0.68 \pm 0.02)$ [10]. The frozen-in electric field associated with the depletion region is estimated to be $-(4 \pm 1) \times 10^8$ V/m. With the measured value of $\alpha = (1.26 \pm 0.05) \times 10^{-9}$ m/V one obtains $x = \alpha E = -(0.50 \pm 0.16)$, which gives with Eq. (2) a relative etching rate of $\rho = 0.6 \pm 0.1$, in good agreement with the rate measured in Ref. [10]. This indicates that the change in etching rate observed in those poled silica can be completely

accounted for by the effect of the electric field alone, without having to invoke any change in etching rates that would be due to the presence of imbedded charge in the material.

This important information allows interpreting the etching results of Ref. [10] in the following way: The relatively constant etching rate measured in the depletion region indicates the existence of a constant electric field along the depletion region (with a small variation in the first 2 μm). This implies that the charge that gives rise to the field is concentrated on either extreme of the depletion region. Except for a small amount of negative charge in the first 2 μm, the depletion region is free of charge. In the example of Ref. [10], the layer of negative charge is located between $\sim$5.8 and 6.0 μm into the sample, and the positive layer is located at the surface. The optical nonlinearity measured with the samples studied would then arise from the strong electric field across the depletion region that is essentially neutral.

(b) In the case of optically poled frequency doubling fibers, a periodic structure was observed by etching [7], with period corresponding to the coherence length of the frequency doubling process. There, a modulation $\leq$100 nm was observed in fibers etched from 125 μm down to 7 μm. The question addressed here is whether the field that extends outside the core of the fiber can cause such a modulation.

The radius of an optical fiber under chemical attack changes in time from its initial value r_0 as

$$r(t) = r_0 - \int_{t_0}^{t} v_0(1 + \alpha E(r(t'))) \, dt', \qquad (4)$$

where v_0 is the etching rate in the absence of the field and $E(r(t'))$ is the electric field just inside the fiber surface when its radius is $r(t')$. As α is small we may substitute $r(t')$ by $r_0 - v_0(t' - t_0)$ in the argument of E. With this first order approximation, the modulation of the fiber radius due to etching $\delta r = r(t) - [r_0 - v_0(t - t_0)]$ becomes $\delta r = -\alpha[\Phi(r) - \Phi(r_0)]$ where $\Phi(r)$ is the electric potential at radius $r(t)$ just inside the glass. Thus the etching technique provides a way to measure voltages. This dependence of etching modulation and voltages is valid as long as the charges, which produce the potential, have not been removed by the acid. In the case of a frequency doubling fiber with surface charges on the core-cladding interface the above dependence applies in the cladding. In the core, δr remains constant, its value being the one at the core radius.

The distribution of electric charges in a fiber prepared for frequency doubling may be described by a surface density on the core-cladding interface of the form

$$\sigma(z, \varphi) = \sigma_0 \cos(\varphi) \cos(kz), \qquad (5)$$

where φ and z are cylindrical coordinates and $2\pi/k$ is the coherence length.

Using this charge distribution, Coulomb's law was integrated numerically to calculate the potential as a function
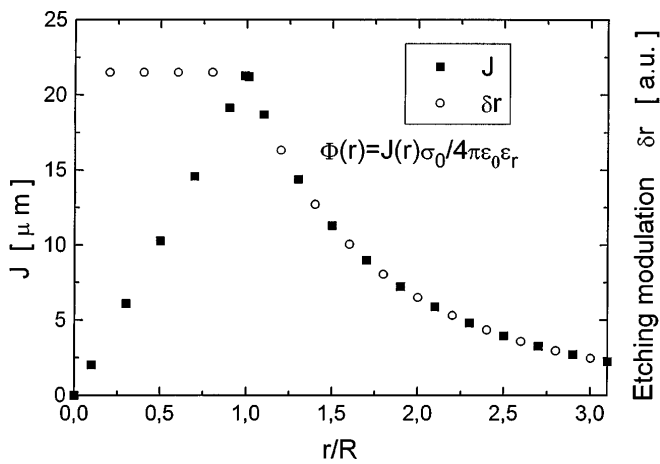
FIG. 3. Plot of the calculated electric potential divided by $\sigma_0/4\pi\varepsilon_0\varepsilon_r$ (solid square) in a frequency doubling fiber as a function of distance from the center of the core. Calculated etching modulation δr (open circles). For $r/R > 1$ the potential is proportional to δr and for $r/R < 1$ the etching modulation remains constant.

of r. The results are illustrated in Fig. 3, where the radius of $R = 4.4$ μm and $k = 2\pi/39$ μm was used, corresponding to fiber parameters of Ref. [7]. The potential at $r = R$ is given by

$$\Phi(R) = \frac{\sigma_0}{4\pi\varepsilon_0\varepsilon_G} 21.5 \ \mu\text{m} = \frac{E(0)}{4.59} 21.5 \ \mu\text{m}, \quad (6)$$

where the integration constant is chosen such that $\Phi(\infty)$ $[= \Phi(0)] = 0$. The estimated electric field in fibers optically prepared for SHG, which is of the order of 5×10^6 V/m [11,12], is used to calculate the potential $\Phi(R) = 2 \times 10^1$ V. Since $\Phi(r_0) = 0$ for the initial radius of the fiber $r_0 = 62.5$ μm $\approx \infty$, one should observe a difference of maximal and minimal etched radius equal to $r_{\text{max}} - r_{\text{min}} = 2\delta r = 6 \times 10^1$ nm which is within the order of the modulation depth observed in Ref. [7]. Furthermore, Fig. 3 indicates that the selective etching should extend even outside the core. In fact, in Ref. [7] the modulation was observed even for $r/R \approx 1.8$, where according to Fig. 3 the etching modulation is still at about 40% of its maximal value.

From the present experiments it was possible to measure with great accuracy the etching rate of silica glass in 40% concentration HF. The results clearly show that the etching rate is affected by the application of an electric field, even in the absence of frozen charge in the glass. The rate of chemical attack is linearly dependent on the field, for field strengths as high as $\pm 2 \times 10^7$ V/m. A simple model to describe the etching mechanism was developed. It was applied to extrapolate the field dependence of the etching rate into a region of higher fields. The result indicates that the electric field alone is capable of accounting for the variation of etching rate observed in poled silica samples and frequency doubling fibers. This finding provides a new insight into the charge distribution in poled silica glass. Furthermore, the knowledge of the field dependence of the HF-silica etching rate can give insight into the physics of surface phenomena and polar solutions.

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