

Hydrogen loading and UV-irradiation induced etch rate changes in phosphorus-doped fibers

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Abstract We show strong changes in chemical etching of phosphorus-doped fiber cores due to hydrogen loading and subsequent UV-irradiation using an atomic force microscope. The etch rate of the fiber core in a low concentration hydrofluoric acid solution (HF) is decreasing after hydrogen loading by as much as 30%. In contrast, UV-irradiation of the hydrogenated fiber increases the core etch rate to values of 27% above the etch rate of the pristine fiber. The UV-induced change in etch rate does not depend on pulse fluence, but only on total dose. We attribute the changes in etch rate to a hydrogen- and radiation-induced modification of color center population.

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1. Introduction

Atomic force microscopy (AFM) of chemically etched fiber end-faces yields topographic information on a nanometer scale due to differential chemical etching of doped and un-doped silica [1-4]. For germanium-doped fibers it has been shown that the etch profiles can be related to the core-cladding refractive index profile [1-3]. A power-law dependence of etch rate on germanium concentration was reported recently in reference [1]. On a large scale, the etch depth is independent of processing conditions, e.g. fiber drawing tension [2]. However, in a recent study on nitrogen-doped fibers, we reported on a linear correlation of etch depth with drawing tension [4]. Therefore, the exact dependence of etch rate on chemical composition (core dopants) on the one hand and drawing-induced properties of the fiber core on the other hand demands further clarification. Furthermore, the origins of etch rate changes due to UV-illumination [3-5] still require an appropriate explanation. Inniss *et al.* reported an asymmetric etch profile for hydrogen-loaded standard telecommunication fiber caused by side exposure to UV at 244 nm [3]. For hydrogenated phosphorus-doped fibers, preferential etching at the core-cladding boundary has been observed by Canning *et al.* and attributed to stress-assisted UV-initiated bond breaking at the interface [5].

Highly phosphorus-doped low-loss optical fibers are an attractive gain medium for Raman fiber amplifiers and lasers [6], where photosensitivity can be exploited by writing Bragg gratings as reflectors directly in the active fiber. Illumination of hydrogen-loaded phosphorus-doped fibers with ArF-laser irradiation at 193 nm results in an increase of the fibers refractive core index [7]. As for Ge-doped fibers, the origins of photosensitivity in phosphorus-doped fibers have not yet been completely clarified. Generally, the interaction of UV-light with glass leads to color center as well as to density changes of the matter, both modifying the refractive index of the glass. Changes in density have been verified using Raman-spectroscopy for germanium-doped fibers [8]. The change in density results in a modification of the stress distribution introduced in the fiber during its fabrication process [9]. A positive stress change, contributing negatively to the net index change via the photo-elastic effect, has been found for germanium-doped [9] as well as for phosphorus-doped fibers [10]. For phosphorus-doped fibers, it was proposed that densification is triggered by the formation of defects that involve a drastic coordination change around the phosphorus atom [11].

In this paper, we present the dependence of etch rate on dopant content for phosphorus-doped fibers as well as changes in etch rate due to hydrogen-loading and subsequent UV-irradiation. Our results suggest that the etch rate is predominately governed by the color center population in the fiber core and that changes in etch rate do not necessarily reflect index changes in this fiber.

2. Experiment and results

The fiber investigated within this work is a phosphorus-doped single-mode fiber drawn from a preform manufactured by the modified chemical vapor deposition (MCVD) method [12]. The core layers of the preform are doped with 12 mol% P_2O_5 and are surrounded by several inner cladding layers doped with 1 mol% P_2O_5 and 1 at% F. The corresponding peak core index change is $\Delta n=1 \times 10^{-2}$. The fiber was drawn with a drawing tension of 225 g. Its axial core stress is compressive with a value of -5 kg/mm^2 [10]. Before irradiation, the fiber was hydrogen loaded for about two weeks at a pressure of 110 bar at room temperature. Two pieces of hydrogenated fiber were exposed to 193 nm light from an Excimer-laser under different radiation conditions, both resulting in a total fluence of 1 kJ/cm^2 . For the first fiber, the pulse fluence was 50 mJ/cm^2 at a repetition rate of 1 Hz, resulting in an exposure time of about 330 minutes. The second fiber was illuminated with a pulse fluence of 350 mJ/cm^2 at 20 Hz repetition rate and a corresponding exposure time of 142 seconds.

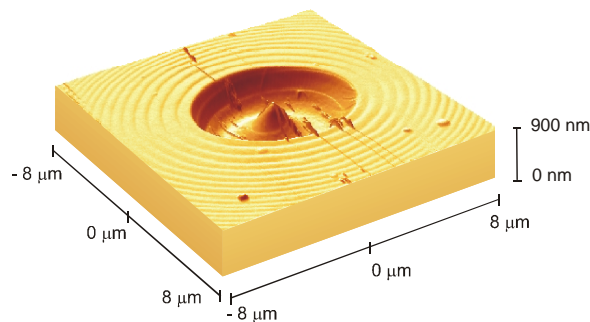


Fig. 1. AFM image of phosphorus-doped fiber after etching in hydrofluoric acid for 180 seconds. The core is observed as crater since it is etched faster than the concentric inner cladding SiO_2 layers.

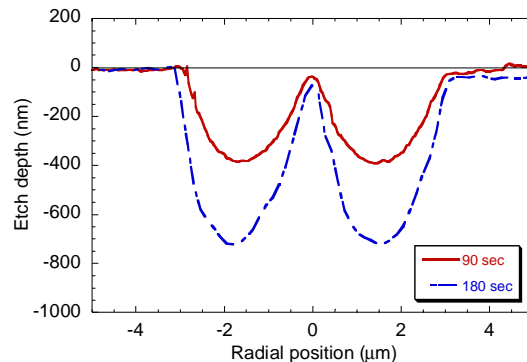


Fig. 2. Etch dynamics of the pristine phosphorus-doped fiber core for two different etch times. The difference in diameter reflects the core width error due to side etching.

For AFM-observation, the samples were cleaved and etched in a 5% HF solution for 90 and 180 seconds, respectively. Between hydrogen loading and etching, the samples were stored for about one week at room temperature to ensure that the interstitial hydrogen was out-diffused from the fiber. The AFM (TopoMetrix Explorer) was operated in contact mode in air with a standard V-shaped silicon nitride cantilever.

In Fig. 1, the topography of the pristine fiber after an etching time of 180 seconds is illustrated. The highly phosphorus-doped core layers are etched faster than the surrounding pure silica inner cladding layers. The dip in the center of the core is caused by dopant out diffusion during collapsing of the preform tube. The core is found to be elliptical; the diameters (FWHM) of the two main axes are 4.75 μm and 5.4 μm , respectively.

In Fig. 2, the etch profile of the pristine fiber is illustrated for two different etch times. The profiles have been aligned along the major axis of the elliptical core for comparison. The etch depth doubles for an increase in etch time from 90 to 180 seconds, thus confirming the linear dependence of etch depth on etch time already reported for germanium-doped fibers [2]. The increase in diameter from 5.1 μm (90 seconds) to 5.4 μm (180 seconds) between the two profiles reflects the core width error due to side etching [1].

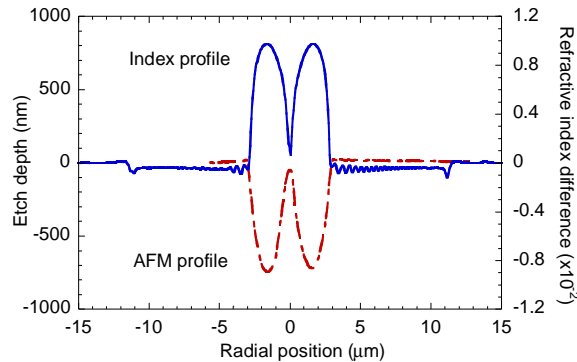


Fig. 3. Comparison of the preforms refractive index profile with the etch profile of the pristine fiber. The preform diameter has been downscaled for comparison.

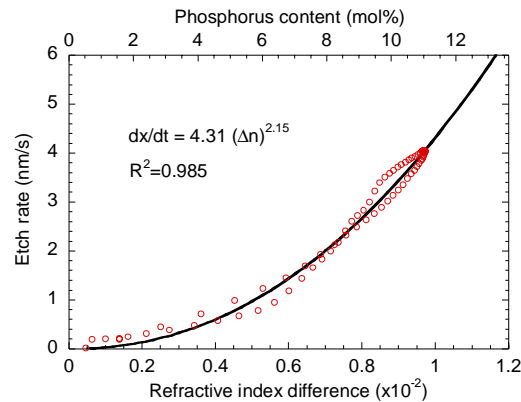


Fig. 4. Correlation of etch rate with refractive index difference and phosphorous content, respectively. As for germanium-doped fibers [1], a power-law dependence of etch rate on refractive index is found.

In Fig. 3, the etch profile of the pristine fiber etched for 180 seconds is illustrated together with the refractive index profile of the fiber preform. For comparison, the preform diameter has been downscaled to the diameter of the fiber. As the inner cladding of the fiber is co-doped with 1 at% F, the outer pure silica tubes have been chosen as reference level for the

refractive index profile. The phosphorus content in the fiber depends linearly on refractive index difference according to $[P_2O_5](\text{mol}\%) = \Delta n / (0.88 \times 10^{-3})$ [12], allowing the conversion of the refractive index profile to a dopant profile.

In [1], a power-law dependence between dopant concentration and the etch rate has been reported for germanium-doped fibers. To obtain similar information for phosphorus-doped fibers, the etch profile and the preform profile shown in Fig. 3 have been correlated within the doped core region. The etch rate was determined by dividing the absolute value of the etch depth through the corresponding etch time. The correlation curve between index/phosphorus-concentration and etch rate is shown in Fig. 4. It can be fitted to the power-law function

$$\frac{dx}{dt} = k(\Delta n)^n, \quad (1)$$

where dx/dt is the etch rate, k the reaction rate constant, Δn the refractive index and n the reaction order. The reaction constants thus obtained are $k = 4.31 \pm 0.04$ and $n = 2.15 \pm 0.06$, and the corresponding fitting curve is illustrated in Fig. 4. The reaction order of 2.15 is slightly higher than the corresponding value of about 1.7 [1] for germanium-doped silica.

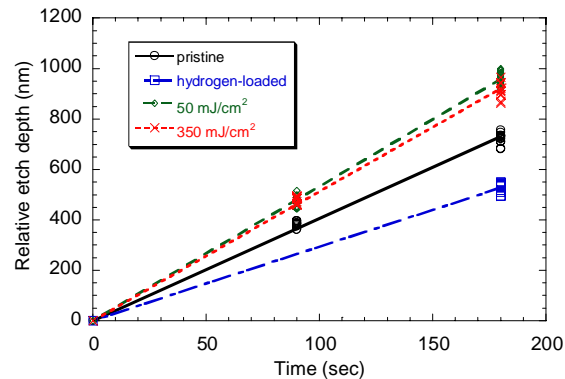


Fig. 5. Relative etch depth as function of time for the etch maxima. For all samples under investigation, the etch maxima depend linearly on time.

Moreover, the AFM-profiles obtained for hydrogenated as well as irradiated fiber have been compared with the profiles from the pristine fiber. In Fig. 5, the maximum etch depth occurring at a radial position of about $\pm 1.5 \mu\text{m}$ is plotted as a function of etch time for all samples under investigation. A linear dependence of etching depth on time is confirmed for the pristine, hydrogen-loaded, and UV-irradiated etched fiber cores. The slope of the linear fit defines the etch rate of the corresponding sample. The etch rate is about 4 nm/s for the pristine fiber and is reduced by almost 30% due to hydrogen loading. In comparison to the etch profile of the hydrogenated as well as the pristine fiber, the etch depth of the core region is increased by UV-irradiation for both pulse fluences. However, no significant dependence of etch rate on pulse fluence can be observed. The etch rate of the irradiated samples has increased by about 27% compared to the pristine sample and by about 75% compared to the hydrogenated sample.

All profiles were found to scale linearly with etch time, as has been shown for the pristine fiber in Fig. 2. Furthermore, the profile of the pristine fiber was found to scale almost linearly with the profiles obtained after hydrogenation and irradiation. Particularly, no preferential etching at the core-cladding interface can be found in contrast to already published results by Canning *et al.* [5]. As the shape of the profile does not change for all samples, only the reaction constant, not the reaction order of the process is modified by fiber treatment.

3. Discussion

The refractive index profile of optical fibers does not only depend on the dopant concentration in the core, but also on the difference in color-center concentrations [11] and stress [13] between core and cladding. Both properties are altered during the fiber drawing process as well as by UV-irradiation [14]. Also hydrogen loading was found to generate new defects in phosphorous-doped glass samples [11] and to modify residual stresses in Sn- and B- codoped germanosilicate fibers [15]. In the previous section, we assumed a linear dependence between refractive index and dopant profile of $\Delta n / [P_2O_5] = 0.88 \times 10^{-3}$, found in reference [12] for the fiber under investigation. In the same reference, several values for the ratio of refractive index and dopant concentration reported by different groups have been compared. The results were found to vary considerably within 0.83 to 1.3×10^{-3} , depending on the sample processing conditions. The scattering of data even for equally doped samples has been explained primarily by the occurrence of stress, modifying the index through the photo-elastic effect. As the variance in etch rates found within this study is comparable to the variance in molar refractivity reported in [12], the difference in etch rate might also be caused by stress or defects introduced into the fiber core during fabrication. In the following discussion, we correlate our etch rate results with reported changes in refractive index, stress and color center concentration introduced by hydrogen-loading and subsequent UV-irradiation. In this way, we are able to isolate the parameter determining the differences in etch rate.

For the fiber under investigation, the total index change between core and inner cladding is $\Delta n = 1 \times 10^{-2}$. For phosphorus-doped glass samples, the reported changes in UV absorption due to hydrogen loading are small [11]. The corresponding index changes, estimated using the Kramers-Kronig relationship, are on the order of some ppm. Mean Bragg-grating index changes on the order of several 10^{-4} have been found after irradiating the fiber with a total fluence of 1 kJ/cm^2 [10]. If the reaction rate was linearly related to refractive index, the increase in reaction rate after UV-irradiation should almost be one order of magnitude smaller than the 27% reported in the previous section. Furthermore, the reduction of reaction rate after hydrogen loading should be negligible. We thus conclude that the reaction rate does not only depend on refractive index, as reported for Ge-doped fibers in [1], but that the proportionality factor between reaction rate and index depends on processing like hydrogen loading or UV irradiation.

Can the increase in etch rate be explained by stress changes? In [4], we reported an increase in etch rate with fiber drawing tension for nitrogen-doped fibers drawn from the same preform. This result indicates an increase in etch rate with compressive core stress, as the fibers core stress was found to decrease linearly with drawing tension [4]. An increase of etch rate with compressive stress has also been reported by Agarwal and Tomozawa [16] for quenched bulk silica glass samples. However, for phosphorus-doped fibers, stress changes due to hydrogen loading were found to be smaller than $\pm 1 \text{ kg/mm}^2$ (error in stress measurements), and an increase in core stress was found after subsequent UV-irradiation [10]. If stress was the parameter dominating the reaction rate, we would thus expect no change in etch rate with hydrogen loading and a decreasing etch rate after UV-illumination. This is in contradiction with our experiments, so we conclude that stress does not influence the etch rate in our case.

Hydrogen loading as well as UV-irradiation alters the defect population of the glass. For phosphorous-doped glass samples, an increase in UV-absorption after hydrogen loading has been found for photon energies $>5.5 \text{ eV}$ [11,17]. Furthermore, an increase in absorption due to POH formation after hydrogen loading has been reported for phosphorus-doped fibers at room temperature [18]. Hosono *et al.* explained the electron spin resonance (ESR) spectra of hydrogen loaded glass samples after irradiation with 6.4 eV photons by a superposition of the two spectra from paramagnetic PO_2 and PHO_2 centers [11]. The defects are created from hydrogen-induced precursors causing the absorption band for photon energies $>5.5 \text{ eV}$. The PO_2 and PHO_2 centers involve a drastic coordination change around phosphorus, resulting in a densification of the glass [11].

We suggest that the reaction rate changes reported in this paper are governed by color center concentrations and their modification due to hydrogen loading and subsequent UV-illumination. The rate-limiting reaction for the dissolution of silica by hydrofluoric acid is the substitution of a surface SiOH group, which is bonded to three neighboring oxygen atoms, by a SiF group [19]. The same should hold true for dopants introduced in a silica glass matrix. A color center is a defect where at least one of the four bonds to neighboring oxygen atoms has been replaced by non-bridging oxygen, paired- or unpaired electrons, hydride-, or hydroxyl groups. It is directly evident that the exact nature of the defect can hamper or facilitate its substitution by fluorine considerably. Following this picture, hydrogen loading of the fiber results in a passivation of drawing induced defects, which hampers their substitution by fluorine. In contrast, the irradiation of the hydrogen loaded core glass results in the formation of PO₂ and PHO₂ centers [11], which are only linked to two bridging oxygen atoms. The drastic change in coordination number, accompanied by the formation of unpaired electrons, facilitates the adsorption of fluorine on the phosphorous atom, thus enhancing the etch rate.

The stress change of the core glass has not been found to depend significantly on pulse fluence, whereas the induced refractive index change more than doubles for a pulse fluence of 50 mJ/cm² as compared to a pulse fluence of 350 mJ/cm² [10]. It was concluded that the densification process does not explain the difference in refractive index for the two fluences. In this study, however, we could not either find a significant dependence of etch rate on pulse fluences. A possible explanation for the index difference might be the creation of an additional color center for low fluences, which neither contributes to densification, nor affects the core etch rate.

In contrast to the results reported by Canning *et al.* [5], we did not observe any preferential etching at the core/cladding interface after UV-irradiation. The fiber used within this study has about the same phosphorus concentration as the fiber investigated in [5], but no details about irradiation conditions were given in the publication. The effect reported in [5] might thus only occur for a limited range of irradiation parameters.

4. Conclusion

The dependence of etch rate on dopant concentration for phosphorus-doped fibers has been derived. Changes in etch rate due to hydrogen loading and subsequent UV-irradiation have been studied. The etch rate decreases by about 30 % after hydrogen loading and increases by about 30 % after UV-irradiation with respect to the pristine fiber. No etch rate dependence on pulse fluence is observed. We conclude that the reaction rate of the etching depends on processing like hydrogen loading and UV irradiation. AFM-measurements thus yield geometric information about the fiber index profile, but do not provide absolute information about the refractive index even for a single dopant. Changes in defect population are suggested to be the reason for the observed etching behavior. Etching of optical fibers can thus be used to get additional insight in the color center concentration and changes of the glass network.