High-energy shift of the Urbach ultraviolet absorption from attenuated dynamical disorder in fluorine modified sol-gel silica

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Fluorine modified amorphous silica has been synthetized via sol-gel route and studied through analysis of the temperature dependence of the Urbach absorption tail in the vacuum-ultraviolet region. The modified glass has a steep absorption edge above 8 eV, with the absorption coefficient $\alpha \propto \exp[E/E_U(T)]$ showing Urbach energy values $E_U(T)$ ranging between 50 and 66 meV. The comparison of $E_U(T)$ with pure silica data indicates a structural softening caused by the reduction of dynamical disorder, and suggests that the F-modified sol-gel synthesis is an appropriate route for achieving high energy shifts of the absorption edge. © *2007 American Institute of Physics.*
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Several technological areas are looking for new material compositions and synthetic routes for the production of optical materials with transmission window extending into the vacuum ultraviolet (vuv) region and with improved radiation hardness and thermal stability.[1,2] In specific applications such as photomasks for lithography at 157 nm and materials for vuv sources, silicalike structural features are unique in assuring low thermal expansion coefficient and good workability.[3] For these reasons, modifications of silica optical properties through specific synthesis or doping processes are currently being investigated to extend its operational window into the vuv. Fluorine modified silica-based materials are promising candidates for these applications, since the silica absorption edge shifts toward high energy after fluorine doping.[4–8] The structural origin of this effect was analyzed in F-modified glasses from chemical vapor deposition (CVD) methods, identifying different roles of fluorine, mainly in the modification of the mean bond energy and the structural disorder of the amorphous matrix.[5,9–11] In this scenario, fabrication of F-modified silica from sol-gel synthesis[12] should, in principle, be an interesting target because of the relatively low-cost and sustainable features of the process, and for the expected improvement in radiation hardness with respect to other types of silica.[13,14] However, only few studies on F-doped sol-gel silica have been reported regarding preforms for low-index optical fibers,[15] and no vuv data have been published on fluorinated silica from sol-gel synthesis. In fact, sol-gel silica usually contains a large number of OH groups that are responsible for a broad absorption band at 8 eV,[16] which is strongly detrimental for vuv applications. In the present work, we disclose a method for the fabrication of optical grade bulk samples of F-doped dry silica by means of a modified sol-gel method. Our results show that the achievable reduction of dynamical disorder and –OH content opens the way to the utilization of sol-gel materials in vuv applications.

Bulk samples, about 0.5 mm thick, of fluorine-modified silica were prepared by the sol-gel technique, cogelling tetraethoxysilane and trimethoxyfluorosilane, with concentration ratio 1:9. After gelation and drying, the xerogel sample was heated in oxygen (ramping at 3 °C/h, up to 1100 °C) to induce both fluorine activated drying and fluorine perturbed densification of the silica network. Optical and structural features of the final glass have been analyzed by means of refractive index measurements at 633 nm with 10^{-4} resolution, Raman scattering and infrared absorption spectroscopy, with a resolution of 0.1 cm^{-1}. vuv transmission data have been collected by means of synchrotron radiation at the SUPERLUMI experimental station of HASYLAB (DESY, Hamburg), with 0.2 nm spectral resolution. The spectral distribution of the intensity I_c, collected behind the sample along the incident beam direction has been compared with the incident intensity I_0, measured in the same configuration without the sample. The contribution I_s from scattered light has been quantified from the background signal at negligible sample transmittance. The absorption coefficient α has been obtained from $\alpha = (1/L)\ln[(I_0 - I_s)(1-R)^2/(I_c - I_s)]$, where L is the sample thickness and $(1-R)^2$ is the correction factor for the reflectivity R at normal incidence. R has been evaluated at 633 nm from the refractive index n, whereas the spectral dependence $R(\lambda)$ [inset of Fig. 1(a)] has been derived from $n(\lambda)$ calculated in F-modified silica[4] with congruent n value at 633 nm [see Fig. 1(a) where a few sets of data are compared and fitted with the Sellmeier relation].[4,17] In the Urbach region (8–8.4 eV), errors on α from the uncertainty in $(1-R)^2$ are smaller than 2%.

The Raman spectrum in Fig. 1(b) shows that the synthesis gives rise to a fully densified silicalike network. Spectral features at 440, 490, 606, 800, 1050, and 1160 cm^{-1} correspond to silica Raman modes ω_1, D_1, D_2, ω_3, ω_4(LO), and ω_4(TO), respectively.[18] The peak at 945 cm^{-1}, ascribable to Si–F stretching mode,[11] is an evidence of fluorine in $\equiv$Si–F sites. The relative intensity is consistent with a F concentration of the order of 10^4 ppm,[11] in agreement with the value estimated from the refractive index compared with data from

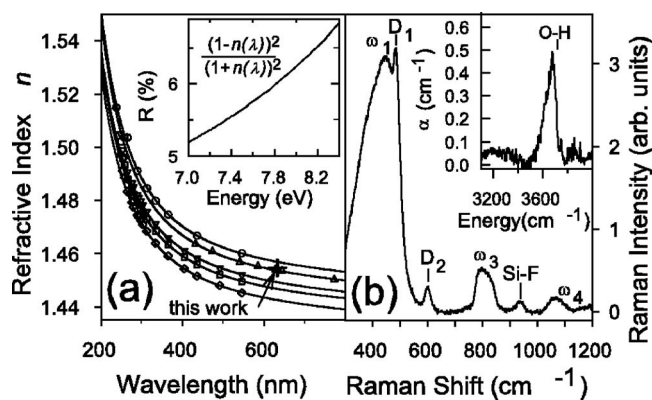[a]Electronic mail: alberto.paleari@mater.unimib.it

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FIG. 1. (a) Refractive index n at 633 nm in F-modified sol-gel silica (cross mark) compared with data by Tsukuma *et al.* (Ref. 17) on 0% (○), 2.1% (▽), 2.6% (□), and 3.7% (◇) F-doped silica, and by Smith and Moore (Ref. 4) on 0.8% F-doped silica (△); lines are calculated dispersion curves. Inset: normal incidence reflectivity in the vuv range calculated from $n(\lambda)$ of 0.8% F-doped silica. (b) Raman spectrum of F-modified sol-gel silica. Inset: infrared absorption in the range of O–H stretching mode.

FIG. 3. Temperature dependence of the Urbach energy E_U (circles) calculated from the data in Fig. 2. Fitting curves within the Einstein approximation (full line), with high-temperature E_U^{HT} and low-temperature E_U^{LT} regimes (dashed and dotted lines, respectively), are indicated.

the literature in Fig. 1(a).[4,17] This amount is about a factor 10 lower than the initial concentration of fluorinated Si molecular precursors in the sol-gel synthesis. A large fraction of fluorinated precursors are indeed released during the thermal treatment through reaction with hydroxyl groups embedded in the sol-gel network.[19] As a result, the fluorinated network is strongly dried with respect to typical sol-gel silica where the content of –OH groups is a few thousand ppm.[12] From the infrared spectrum in the inset of Fig. 1(b), the remaining –OH content is estimated[20] to be 16 ± 2 ppm, two orders of magnitude lower than in typical sol-gel silica. vuv absorption spectra in Fig. 2 indeed show a contribution at 8 eV, superimposed on the absorption edge, ascribed to electronic transitions of silanol groups,[1,8,16] and whose cross section is 5×10^{-19} cm^2. The 8 eV absorption in Fig. 2 indicates a silanol content of $10 - 20$ ppm, in agreement with the infrared analysis.

Looking at the Urbach tail in Fig. 2, three facts may be remarked: (i) the edge is steeper than in synthetic silica (dashed curve reported from the literature[5]); (ii) contributions from point defects (specifically at 7.6 eV)[8,21,22] are not detected; and (iii) the optical gap widens much more with
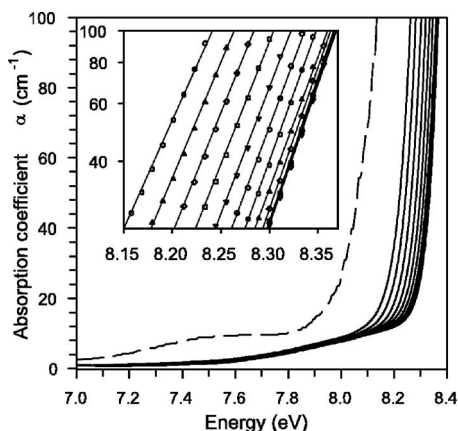

FIG. 2. vuv absorption spectra of F-modified sol-gel silica at temperatures from 300 to 25 K, in step of 25 K from left to right, compared with dry pure silica at 300 K [dashed line, from Skuja *et al.* (Ref. 8)]. Inset: exponential region of the Urbach tail with absorption coefficient on a log scale. Straight lines are linear regression of the data.
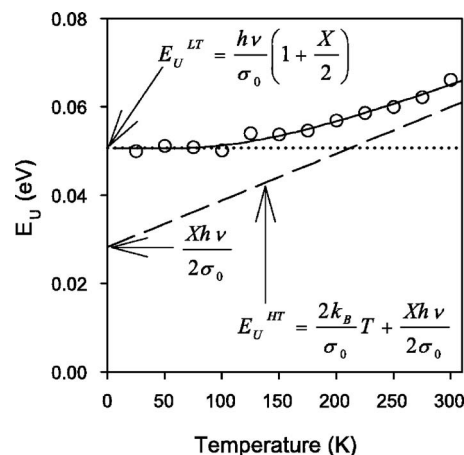
decreasing temperature than in pure silica,[22] down to temperatures less than 100 K. These features may be analyzed in detail by looking at the Urbach behavior[8,22] of the absorption coefficient $\alpha(E,T) \propto \exp[E/E_U(T)]$ as a function of the energy E, where E_U accounts for the broadness of the energy band tail caused by static and dynamical disorder on the electronic density of states.[22,23] So, the lower E_U, the sharper and steeper the edge, with a broader spectral window of transmission. In the inset of Fig. 2, we report the absorption coefficient on a semilog scale in the restricted spectral range of the Urbach tail, together with linear fits of the data. The curves shift toward higher energy with decreasing temperature, and this shift is accompanied by an increase in their slope. Indeed, within the experimental error, the curves converge at a common point at 8.75 eV, as expected with the Urbach approach.[23] Figure 3 shows the calculated $E_U(T)$ at different temperatures. The values are significantly lower than in pure silica[22] (50 meV instead of 73 meV at low temperature and 66 meV compared with 75 meV at 300 K), with a steeper increase with the temperature. Indeed, $E_U(T)$ reaches the low temperature quantum limit only below 100 K instead of 200 K in pure silica.[22] The data follow the function $E_U = [h\nu \coth(h\nu/2kT) + Xh\nu/2]/\sigma_0$ (Ref. 22) (with $h\nu = 37$ meV, $X = 2.5$, and $\sigma_0 = 1.6$), where static and dynamic contributions to the Urbach energy are explicitly accounted for. The term with X is the temperature independent contribution from static structural disorder, whereas the term with $\coth(h\nu/2kT)$ describes, within the Einstein approximation,[23] the thermal broadening of the tail caused by electron-phonon coupling. The energy $h\nu$ is the characteristic value of the Einstein approximation, corresponding to an average phonon energy that accounts for the real spectral distribution of the vibrational density of state (VDOS) in the electron-phonon coupling. The results in Fig. 3 point out a particularly low $h\nu$ value with respect to those previously reported (37 meV instead of 79 meV). This result suggests that the low-energy VDOS excess, typical of amorphous structures,[24,25] is enhanced with respect to pure silica, because of either the networking peculiarities of the sol-gel synthesis or fluorine modifications of the medium range structure. Indeed, networking and fluorine effects on the soft phonon modes were respectively observed in sol-gel silica[26] and F-doped CVD

silica.[11] By contrast, the $Xh\nu/2\sigma_0$ contribution from static disorder is 29 meV, larger than 20 meV of pure CVD silica, indicating that fluorine introduction through sol-gel synthesis does not give rise to a decreased structural disorder. Therefore, the small contribution from dynamical disorder is the main cause of the Urbach energy and high-energy shift of the absorption edge in this material. Lower $h\nu$ and larger $Xh\nu/2\sigma_0$ values indicate that the fluorine modified sol-gel synthesis gives rise to a less rigid glassy structure without ordering effects. This is consistent with the low structural stress encountered in silica from sol-gel synthesis and responsible for the higher radiation hardness of pure sol-gel silica.[14]

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