Evidence of Delocalized Excitons in Amorphous Solids

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We studied the temperature dependence of the absorption coefficient of amorphous SiO_2 in the range from 8 to 17.5 eV obtained by Kramers-Kronig dispersion analysis of reflectivity spectra. We demonstrate the main excitonic resonance at 10.4 eV to feature a close Lorentzian shape redshifting with increasing temperature. This provides a strong evidence of excitons being delocalized notwithstanding the structural disorder intrinsic to amorphous SiO_2. Excitons turn out to be coupled to an average phonon mode of 83 meV energy.

Excitons are neutral quasiparticles consisting in an electron-hole pair bound via Coulomb interaction. One of the most important features of excitons is their mobility, providing a fundamental mechanism of site-to-site energy transfer in condensed matter without charge transport. While being one of the most complex manifestations of the electronic band structure of a solid, excitons play a key role in many processes occurring not only in solid state but also in nanoscale systems as well as in molecular materials. These include light emission in semiconductor devices, energy capture in photovoltaic systems [1] or generation of point defects upon exposure to high power laser light [2]. Furthermore, exciton dynamics may feature collective phenomena such as Bose-Einstein condensation which are currently the subject of intense research [3]. Exciton mobility in a crystal is influenced by their interaction with phonons, leading in some cases to the trapping of the quasiparticle. In disordered systems lacking translational order such as glasses, the very existence of excitons was disputed for some time, but it is widely accepted now. However, the properties of excitons in such systems are still debated [4], those concerning the influence of structural disorder on their mobility being poorly understood as yet. This is particularly true for wide band gap insulators, of which amorphous silicon dioxide (a-SiO_2) is an archetypal system, because their excitonic absorption is difficult to investigate experimentally, since this requires vacuum-UV ($\lambda < 200$ nm) optical technologies. a-SiO_2 is a solid of primary technologic importance in optics and microelectronics. It has lately received renewed attention aiming to further improve its optical properties in view of prospective vacuum-UV applications [5,6]. A full comprehension of exciton properties needs the thorough understanding of the fundamental band-to-band transition, which is among the basic open problems in the physics of a-SiO_2 [5,7]. This study has often been aided by the comparison with α-quartz (c-SiO_2), the most common crystalline polymorph of silicon dioxide. Several experimental results, such as the detection of photoconductivity starting from ~9 eV [8], led to estimate the latter value as the band gap

of a- and c-SiO_2 [8–11]. Some studies questioned these findings, by reporting a marked increase of photoconductivity and photoemission signals only above 11 eV, accompanied by qualitative variations of the photoelectron energy distribution [5,12]. For this reason the actual band gap of SiO_2 was proposed to lay around 11 eV [12], but this is still a matter of debate. The experimental investigation of these issues in SiO_2 requires the combined use of different techniques. Optical absorption spectroscopy can be applied from ~8 to ~9 eV, where the absorption coefficient α is smaller than 10^3–10^4 cm^{-1} and both a- and c-SiO_2 feature the exponential absorption region usually referred to as the Urbach tail [7]. Reflectance spectroscopy is necessary at higher energies, where α becomes exceedingly high for optical absorption so that absorption can be only indirectly inferred by Kramers-Kronig (KK) analysis of reflectivity data. KK analysis can be quite tricky due to the need of reliable measurements over an extended energy range. This has limited the number of KK investigations on SiO_2 to date [11,13,14] and consequently hindered the comprehensive understanding of near-edge absorption in wide band gap amorphous systems. The peak at 10.4 eV in the absorption spectra of a- and c-SiO_2 [5,9,13,14] is widely accepted to be an excitonic transition, based on its temperature dependence observed in c-SiO_2 from 300 to 600 K [9,13]. However, almost no experimental data exist on the temperature dependence of the 10.4 eV peak below 300 K, especially in a-SiO_2. Most important, the shape of this resonance is currently an open issue. Well established theoretical models describe the broadening of an exciton resonance in a crystal as resulting from exciton-phonon coupling (EPC) and the excitonic line shape as arising from the competition between mobility of excitons and thermal fluctuations of their energy [15]. Although no models exist for amorphous solids, we argue that a similar description could be used for them as well since it was suggested that the effects of a small structural disorder in crystalline systems are indistinguishable from those of thermal fluctuations [15]. In this Letter we contribute to the clarification of these topics by providing experimental data on the

temperature dependence of the reflectivity spectra of the model system a-SiO$_2$ below 300 K. Our data yield strong evidence of the existence of delocalized, closely crystal-like, excitons in an amorphous system.

We measured reflectivity $R(E)$ for 9 eV $< E <$ 21 eV (wavelength accuracy ± 0.1 nm) of commercial synthetic a-SiO$_2$ and z-cut c-SiO$_2$ samples, featuring industrial grade optical polishing. Measurements were carried out in ultrahigh vacuum in near-normal geometry under synchrotron radiation at beamline I in HASYLAB (DESY). The reflected beam was detected by a photomultiplier coated by C$_7$H$_5$NaO$_3$. Each acquired spectrum was scaled for the spectral density curve of the excitation beam. Experimental spectra were extended on the low and high energy tails using literature data down to 0 eV [13] and the ordinary analytical form in the free-electron gas approximation [16], $R(E) \propto E^{-4}$, for $E > 21$ eV. Finally, standard KK analysis was performed on $R(E)$ in order to obtain the absorption coefficient $\alpha(E)$. The influence on the 10.4 eV peak of different reasonable choices for the high energy extrapolation was verified to be very poor. Figure 1(a) shows the reflectivity spectra of a-SiO$_2$ from 10 to 300 K and that of c-SiO$_2$ at 10 K for comparison. In a-SiO$_2$ (c-SiO$_2$) spectra feature four main peaks: a first comparatively narrow and more intense peak at $\sim$10.3 eV ($\sim$10.4 eV) and three other broader peaks at $\sim$11.5 ($\sim$11.4 eV), $\sim$14.0 ($\sim$14.1 eV) and $\sim$17.3 eV ($\sim$17.3 eV), respectively. The positions of the peaks in a- and c-SiO$_2$ agree qualitatively with those reported in literature [5,11,13,14]. In a-SiO$_2$ the peaks at $\sim$10.3 and $\sim$11.5 eV change in both their positions and amplitudes as a function of temperature, whereas the peaks at $\sim$14.0 and $\sim$17.3 eV increase their intensities without noticeably changing their shapes with increasing temperature. As visible in Fig. 1(b), with increasing temperature the peak at $\sim$10.3 eV redshifts while its amplitude decreases. In Fig. 2(a) the absorption coefficient of a-SiO$_2$ is presented as calculated by KK analysis on spectra in Fig. 1. Four main peaks are present as well: at $\sim$10.4, at $\sim$11.6, at $\sim$14.1 and

FIG. 2. (a) Absorption coefficient of a-SiO$_2$ from 10 to 300 K by steps of 50 K. (b) Enlargement of the peak at $\sim$10.4 eV in a-SiO$_2$ (solid lines) and in c-SiO$_2$ (dashed line). Labels represent temperatures (K) of the closest curve.

at $\sim$17.3 eV. Figure 2(b) shows that the peak at $\sim$10.4 eV redshifts with increasing temperature while its amplitude slightly decreases, moreover it is evident that in c-SiO$_2$ the peak is narrower and more intense. Since the analysis of the peak at $\sim$10.4 eV is the main purpose of the present work, the properties of the other peaks will not be discussed in the following. The peak at $\sim$10.4 eV turns out to have a very good Lorentzian profile at all temperatures:

$$\alpha(E, T) = \alpha_0 \left[1 + \left(\frac{E - [E_0^0 + \Delta_0(T)]}{\Gamma_0(T)} \right)^2 \right]^{-1} \quad (1)$$

Figure 3 presents the normalized $\sim$10.4 eV peak of a-SiO$_2$ at 10 and 300 K and that of c-SiO$_2$ at 10 K, together with Lorentzian best fit curves: agreement with experimental data is very close even on the left band wings, as visible from the semilogarithmic plot in inset (b). We verified that introducing a baseline accounting for band-to-band absorption does not alter appreciably the Lorentzian line shape, only slightly decreasing the width. The position of the peak [inset (a)], as obtained by the Lorentzian fitting, is approximately constant around a value of $\sim$10.41 eV from 10 to 150 K, whereas it shifts to lower energies for higher temperatures. No change of the full width at half maximum (FWHM) of the peak is appreciable within the experimental error: its value is (0.85 ± 0.08) eV. In c-SiO$_2$ at 10 K the peak is at 10.5 eV and its FWHM is (0.69 ± 0.04) eV.

Although present data do not appear in contrast with previous ones [5,13,14], the accuracy of our measurements allows an unprecedented characterization of the $\sim$10.4 eV peak, leading to unanticipated insights on the physics of excitons in a-SiO$_2$. We demonstrated the excitonic peak at $\sim$10.4 eV to have a remarkably good Lorentzian line shape at all the examined temperatures. The absorption line shape of excitons in a crystal is basically governed by the competition between their mobile nature and their tendency to localization in the lattice due to EPC. The former is measured by the half-width B of the energy band of excitons, proportional to site-to-site transfer rate, while the latter is measured by the root mean square
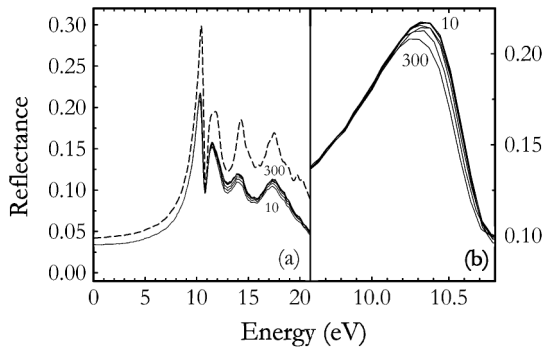

FIG. 1. (a) Reflectivity of a-SiO$_2$ from 10 to 300 K by steps of 50 K (solid lines), and reflectivity of c-SiO$_2$ at 10 K (dashed line). (b) Enlargement of the peak at $\sim$10.3 eV in a-SiO$_2$. Labels represent temperatures (K) of the closest curve.
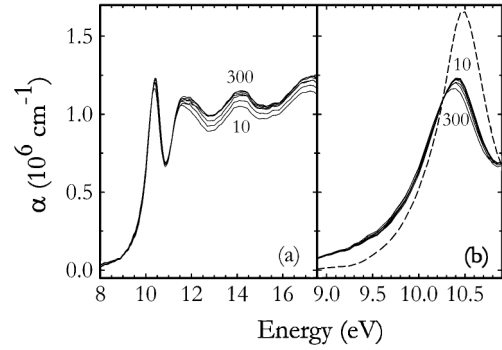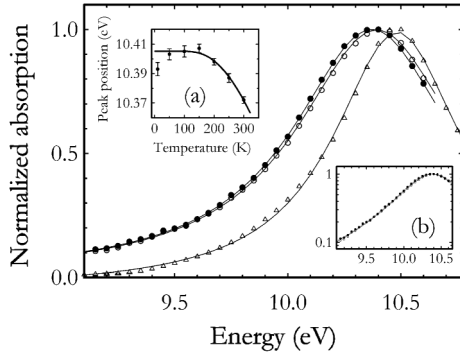
FIG. 3.   Normalized absorption at 10 K (open circles) and at
300 K in a-SiO$_2$ (filled circles), at 10 K in c-SiO$_2$ (triangles).
Continuous lines were obtained via a Lorentzian fit of each
spectrum. (a) Position of the peak in a-SiO$_2$ as a function of
temperature (b) Semilogarithmic plot of the same data on a-SiO$_2$
as in the main panel.

amplitude D of the fluctuations of exciton energy due to the
thermal activated vibrations of the lattice. Very general
theoretical arguments (Kubo oscillator) [17] strongly sug-
gest that Lorentzian absorption line shapes are expected
when mobility effects (B) prevail over energy fluctuations
(D). Indeed, the broadening of a resonance whose proper
energy undergoes random Gaussian fluctuations of ampli-
tude D can be shown to be either Lorentzian or Gaussian
when D is, respectively, much smaller or larger than $\hbar/\tau$,
where τ is the correlation time of the fluctuations. We
physically expect the mean time $\hbar/B$ between site-to-site
hops of excitons to basically represent τ (neglecting inter-
site correlations). Thus, the broadening is Lorentzian if
$D \ll B$. A detailed model of exciton-phonon interaction
in solids [15] was developed by Toyozawa, confirming the
same conclusion: if the ratio $D/B \ll 1$ and the mobile
nature of the exciton is thus prevailing (weak scattering
limit), the exciton absorption line shape is Lorentzian. This
can occur either if EPC is inefficient (small D) or if
excitons are mobile enough (large B) to compensate for
its effects. In this case, in Eq. (1) E_0^0 is the position of the
unperturbed exciton line, while $\Delta_0(T)$ and $\Gamma_0(T)$ are the
real and imaginary parts of the self-energy of the exciton in
the phonon field, giving rise to a temperature dependent
shift [$\Delta_0(T)$] and broadening [$\Gamma_0(T)$] of the exciton line.
The FWHM = $2\Gamma_0(T)$ is given by cD^2/B, where the pre-
dicted value of the constant c depends on the detailed
features of the exciton band [18]. The effect of increasing
structural disorder (e.g., dislocations, vacancies, interstitial
atoms or impurities) can be argued to be qualitatively the
same as that of increasing temperature, in that both lead to
an increase of D. For thermal or structural disorder so large
or for B so small that $D/B \gg 1$ (strong scattering limit),
the model foresees the overall exciton line shape to be
Gaussian. While Lorentzian exciton line shapes have been
reported in literature for several crystalline systems at low
temperatures [19], our analysis shows that Toyozawa's

model can be extended to an amorphous system. Present
data clearly point out that from 10 to 300 K, exciton
mobility is so large as compared to the effects of both
static disorder and EPC in a-SiO$_2$ that the exciton band
keeps its Lorentzian profile, not presenting any tendencies
towards a Gaussian one even at the highest considered
temperature (300 K). This result is remarkable because
exciton mobility is ultimately related to the translational
symmetry of the lattice. Thus, the lack of long range order
typical of an amorphous solid turns out to have a negligible
effect on the properties of excitons, meaning that the
effect of static disorder in a-SiO$_2$ is low enough to
closely preserve crystal-like delocalization of excitons.
Surprisingly enough, it appears that, at least at low tem-
perature, the difference between the excitonic properties of
a- and c-SiO$_2$ comes down to a greater width of the first
exciton absorption peak in the amorphous system, $(0.85 \pm
0.08)$ eV instead than (0.69 ± 0.04) eV, likely due to
structural disorder introducing small additional site-to-
site fluctuations of the exciton energy contributing to D.
Furthermore, present results are completely inconsistent
with the model widely accepted in SiO$_2$ literature claiming
a strong localization and consequently a low mobility of
excitons in a-SiO$_2$ [5,12]. The evidence that the peak is
accurately described by a simple Lorenztian function seri-
ously casts doubt on its previously proposed decomposi-
tion into at least four Gaussian subbands ascribed to several
types of localized excitons [5,12]. Finally we note that the
behavior of SiO$_2$ is deeply different from that of other
systems such as Si, where a dramatic change of the shape
and broadening of the absorption peak at around 3.5 eV are
observed when going from the crystal to the amorphous
solid [20].

   Toyozawa's model predicts the position of the excitonic
peak to depend on temperature according to: $E_0(T) =
E_0^0 + \Delta_0^0 \coth(\hbar\omega_0/2k_BT)$, where the parameter Δ_0^0 repre-
sents the effect of the zero-point vibrations on the shift of
the peak and $\hbar\omega_0$ is the energy of thermal vibrations
described using Einstein's model. The effect of possible
structural disorder is included in E_0^0. As evident in
Fig. 3(a), this equation well describes the observed trend
with $E_0^0 = (10.79 \pm 0.05)$ eV, $\Delta_0^0 = (-0.38 \pm 0.05)$ eV
and $\hbar\omega_0 = (0.083 \pm 0.002)$ eV, with the only possible
exception of the point at 10 K [21]. According to
Toyozawa's theory, the width should have the same
temperature dependence as the peak position, i.e., gov-
erned by $\coth(\hbar\omega_0/2k_BT)$. Under this assumption and us-
ing for $\hbar\omega_0$ the value reported above, the expected
variation of the width from 10 to 300 K is 8%, correspond-
ing to 0.07 eV, and thus not detectable within our 0.08 eV
uncertainty on the FWHM. On the other side, we believe
the observed decrease of the amplitude of the peak (Fig. 2),
measurable with a better accuracy than the width, to be an
indirect evidence of the increase of the width of the line
itself.

The fact that E_0^0 is not coincident with the converging point of the Urbach tails at different temperatures in both a- and c-SiO$_2$ ($E_U^0 \sim 8.7$ eV and ~ 9.1 eV, respectively [5]) indicates SiO$_2$ to be an indirect band gap (~ 9 eV) material, featuring a direct exciton at ~ 10.4 eV, as previously proposed by several authors [10]. Furthermore, $E_0^0 - E_U^0$ provides a rough estimation of $B \sim 2$ eV, whose value allows us to compare the above mentioned theoretical expression for the FWHM with our data and thus to estimate $D_a \sim 0.74$ eV in a-SiO$_2$ and $D_c \sim 0.66$ eV in c-SiO$_2$. Fluctuations of the exciton energy of such an order of magnitude imply a rather efficient coupling of excitons with vibrational modes, being the weak scattering condition anyway ensured by the large extension of the excitonic band, while the influence of structural disorder ($D_a \sim D_c$) is very poor, as anticipated. Thus, SiO$_2$ turns out to belong to that class of materials referred to as featuring a strong EPC but a weak scattering [15]. A similar behavior can be observed in some very wide band gap crystals such as LiF and NaF, having relatively wide (FWHM ~ 0.4 eV in LiF) yet Lorentzian exciton line shapes [19] and, as SiO$_2$, all giving rise to self-trapped exciton luminescence.

In conclusion, the observed behavior of above-edge absorption as obtained by KK dispersion analysis of the reflectance spectra of a-SiO$_2$ from 10 to 300 K demonstrates the applicability of Toyozawa's theory for excitonic line shapes to an amorphous system. The remarkably good and temperature independent Lorentzian profile of the main excitonic peak at ~ 10.4 eV proves that excitons in a-SiO$_2$ are highly mobile and retain their delocalized nature, albeit both the disorder peculiar of the amorphous structure and a strong EPC. The average vibrational energy of phonons interacting with excitons ($\hbar\omega_0 = 83$ meV) was determined.

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