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LETTER TO THE EDITOR

Are intrinsic point defects inadequate as the origin of optical band gap narrowing in fumed silica nanoparticles?

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Abstract

Point defects in fumed ∼7 nm sized silica nanoparticles have been studied by means of K- and Q-band electron spin resonance following photodissociation of H from passivated defects. Generally, the spectra are dominated by the presence of intrinsic oxygen-associated hole centres (OHCs), probably of two types, one of which could be identified as the peroxy radical ($O_3{\equiv}Si{-}O{-}O\bullet$). Determination of the upper limit of the density of all defects observed suggests that, in conflict with previous inference, OHCs cannot account for the observed optical band gap narrowing. Probably that effect is related instead to nm size induced structural alterations in the SiO_2 network.

The study of fumed silica keeps attracting a lot of attention, since nanoparticles promise to be very useful in the future development of nm sized optical and electronic devices [1, 2]. In order to assess the nanoparticles' unique properties a range of sensitive experimental techniques have been applied including the key photon–solid interaction techniques [3–12] such as the IR [3, 5, 12] and light absorption [9], Raman spectroscopy [5], nuclear magnetic resonance (NMR) [12] and electron spin resonance (ESR) [4, 11] approaches.

A recent letter reports on white light emission from transparent SiO_2 glass prepared from fumed silica, a property that could be of importance in the field of display and lighting technologies [13]. The exact origin of the white photoluminescence (PL) is as yet unknown. It was, however, demonstrated that the white PL emission cannot arise from the same defects as those at the origin of the previously observed red and green PL bands originating from silica nanoparticles.

Glinka *et al* [6, 8] ascribed these two PL bands to non-bridging oxygen-associated hole centres (NBOHCs) and hydrogen-related species (≡Si–H) on the surface of the silica nanoparticles, respectively. This picture was partially retained when Altman *et al* [9] attributed the non-exponential absorption of light observed by them in fumed silica nanoparticles to a drastic change in band structure ensuing from a high concentration of NBOHCs. It thus seems that the occurrence of (inherent) point defects has a great impact on the nanoparticles' optical

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properties. Characterization and identification of the defects occurring is therefore without doubt one of the key goals for future research.

Though ESR is the tool eponymous for point defects with atomic level physico-chemical sensitivity (see, e.g., [14–16]), very little research has so far been carried out using it. Some ESR work has been performed on fumed silica in the as-grown state [11] as well as after UV irradiation [4] with photons (∼5 eV) obtained from a low pressure Hg lamp. However, in both cases no ESR signals originating from the silica nanoparticles could be discerned, probably explaining the fading of interest over the years in applying ESR in this field of research. In view of the particular method of preparation of fumed silica particles (oxy-hydrogen flame), this ESR failure is possibly due to the fact that occurring (inherent) point defects may be left passivated by bonding to hydrogen (H) in the as-prepared state, thus rendering them ESR inactive. Such a phenomenon is well known for Si dangling bond-type defects such as the P_b ($Si_3{\equiv}Si$) [15, 17, 18] and E′ defects [19] in thermal Si/SiO_2. In this context, it is pertinent to note that the applied UV irradiation may appear energetically just not sufficiently efficient to reactivate defects to a detectable extent. In this regard, VUV excitation has proven to be much more appropriate [20, 21].

By combining such photon excitation (∼10 eV) with ESR analysis, several (inherent) point defects are newly revealed. In the current letter we focus on the ESR observation and identification of the OHCs in fumed silica nanoparticles. An upper limit is estimated for the density of OHC-type defects occurring. The results are compared with those obtained from previous PL and light absorbance measurements [6–9].

Samples were obtained from high purity pyrogene fumed silica powder of 7 nm average particle size and 380 ± 40 $m^2\ g^{-1}$ surface area, with a bulk density of 36.8 $g\ dm^{-3}$ and low metallic impurity content[1]. These were fabricated by burning silicon tetrachloride in an oxygen–hydrogen flame at ∼1800 °C. Separate sets of samples (fresh ones for each thermal step) were subjected to post-manufacturing heating in vacuum (base pressure: $<4\times10^{-6}$ Torr) for ∼1 h at desired temperatures (T_{an}) in the range 850–1115 °C. After initial ESR tests, to maximally reveal defects, samples (both in the as-grown state and after additional heat treatment) were subjected at room temperature (RT) to prolonged VUV irradiation (∼10 eV) photons (flux: $\sim10^{15}\ cm^{-2}\ s^{-1}$) to photodissociate H from passivated defects. Possibly the treatment may additionally unveil strained or weak bondings (bond rupture) [20]. As checked by intermittent ESR observations, the VUV irradiation dose was driven to the level of exhaustive ESR defect activation.

Conventional cw absorption derivative (dP_μ/dB) K − (∼20.3 GHz) and Q-band (∼33 GHz) ESR measurements were performed in the range 4.2–300 K, along the lines described elsewhere [15]. A co-mounted calibrated Si:P marker sample (spin $s = 1/2$; $g(4.2\ K) = 1.998\,69$) was used for g factor and defect (spin) density calibration. Typically, an ESR sample comprised ∼3–4 mg of fumed powder, with physically the same samples being used for both K- and Q-band ESR observations.

As anticipated, no ESR signal could be observed for the as-fabricated silica particles. This is ascribed, at least in part, to defect inactivation by hydrogen due to the abundance of H_2 during the flame growth. But that situation changes drastically upon VUV irradiation. Several defects emerge, including the familiar E′-type centre, the methyl radical and, as will be focused on here, oxygen-associated hole centres. Figure 1 shows an overall K-band spectrum measured for the as-grown sample immediately upon VUV irradiation over an extended field range in the liquid nitrogen temperature range. It corresponds to the totality of observed ESR signals. The most eye-catching part in this ESR spectrum, without doubt, concerns the left part

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[1] Sigma-Aldrich Inc., Missouri, USA

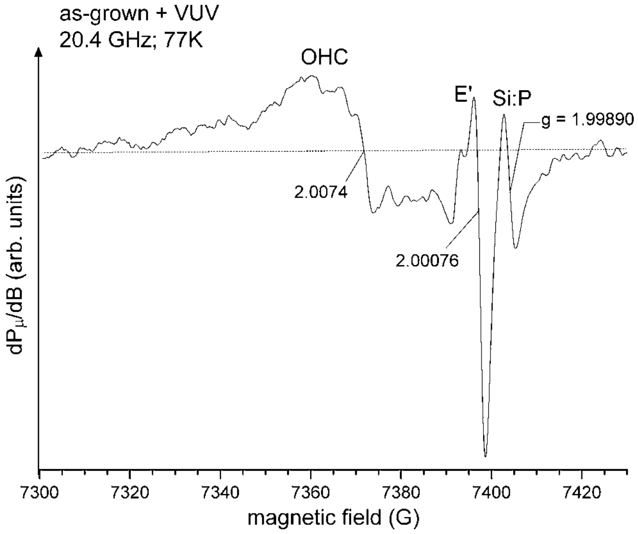

Figure 1. Overall K-band ($P_\mu \sim 8\ \mu$W; $B_m \sim 0.6$ G) ESR spectrum observed for the as-grown sample after VUV irradiation. The oxygen-associated hole centres clearly dominate the spectrum.

of the spectrum, exhibiting broad resonance features. The position and shape of these broad ESR signal(s) points to OHCs [22]. The ESR signal was investigated with great care in order to assess more detailed information. The ESR resonances were monitored as a function of observational temperature, revealing some striking variations. It became clear that the broad ESR feature centred at zero crossing g value $g_c \sim 2.0074$ is the resultant of at least two resonant responses.

One of them, centred at $g_c = 2.0074 \pm 0.0005$, exhibits powder pattern properties, and could be quite well simulated (symbols in figure 2) in the temperature range ~77–100 K—consistently for K- and Q-band observations—using a simple spin Hamiltonian of effective spin $= 1/2$, with one set of g matrix principal values given as $g_1 = 2.0020$, $g_2 = 2.0078$, $g_3 = 2.0670$. The latter g_3 is taken from [23], and in fact is almost immaterial here, as the corresponding resonance peak in the powder pattern could not be resolved, despite intensive efforts, which is ascribed to the expected low signal intensity and line broadening. Interestingly, these ESR parameters are very similar to those pertaining to the well-known peroxy radical (POR) ($O_3\equiv$Si–O–O•) [23]. Inferred defect densities were up to $(3.1 \pm 0.3) \times 10^{15}$ g^{-1} or about 1×10^{-3} defects/nanoparticle. This would indicate that fumed silica is somewhat *oxygen rich*.

The other part of the broad resonance line could not be assigned conclusively. There is a possibility that this line also concerns some (other) types of OHC, possibly the NBOHC $O_3\equiv$Si–O• (characterized by [23] $g_1 = 1.9999$, $g_2 = 2.0095$, $g_3 = 2.0078$). But this is more of a suggestion.

However, even with a lack of full identification, we can still provide, as a useful number, an upper limit on the density of all OHCs possibly present from the added intensities of all pertinent signals. The density was determined for different VUV irradiation times in order to ensure that most, if not all, centres present are indeed ESR activated (attaining the density saturation level). The modulation amplitude B_m of the applied magnetic field **B** and the incident microwave power P_μ were restricted to levels not causing any (noticeable) signal distortion; this, however, does not appear very demanding for the OHCs. This leads to a maximum

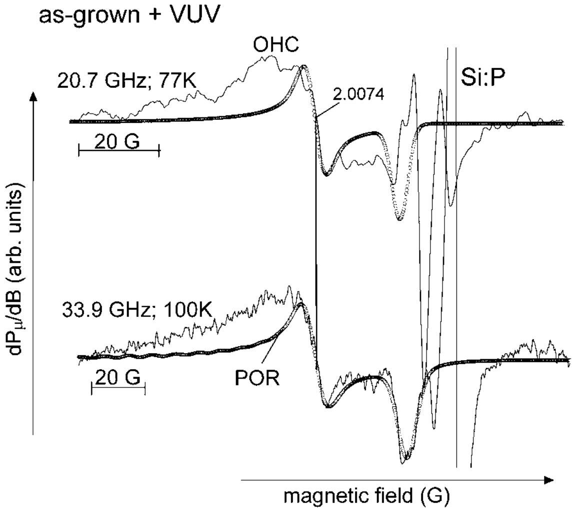

Figure 2. K-band ($P_\mu \sim 8\ \mu$W; $B_m \sim 0.6$ G) and Q-band ($P_\mu \sim 0.17$ mW; $B_m = 1$ G) powder pattern ESR spectra of the peroxy radicals in the as-grown sample after VUV irradiation. Extreme ESR measurement parameters are used to enhance the signals in the g range 2.02–2.0015 and to simultaneously (partially) saturate the other signals (E′-like centre, methyl radical) present. The symbols represent POR spectra simulations, using the same principal g values $g_1 = 2.0020$, $g_2 = 2.0078$ and $g_3 = 2.0670$ for the simulations at both frequencies.

number of OHC defects possibly present of (0.07 ± 0.01) defects/particle, which means that only one in about every 14 particles may contain such a defect. Even if one takes *all* ESR active defects observed in the as-grown sample immediately upon VUV activation (the OHC-type centres, the E′-type centre and the methyl radicals) into account, still no more than one in about every 14 particles may house an ESR active defect. The broad resonance line which can possibly be assigned to the NBOHCs is indeed by far the most intense of the observed resonances. Another observation is that the broad resonance lines, and therefore the OHCs, decrease drastically on subjecting samples to additional heat treatment.

These observations contrast with the conclusions arrived at by Altman *et al*, who studied the light absorption of silica nanoparticles [9]. Their experiments revealed a non-exponential behaviour of light absorption in the visible region, which they attributed to the presence of a large concentration of NBOHCs. They also suggested that the concentration of these defects amounts to such levels that they may cause narrowing of the optical energy gap through strong Coulomb disorder. The current observations, however, disfavour this suggestion, at least in a statistically uniform picture, since for these defects to cause changes in the band gap there should be at least more than one defect present in each nanoparticle. Of course, defect bunching cannot be excluded, i.e., a small minority of particles could contain several to many OHCs per particle, the remainder and major portion of the SiO_2 particles then being OHC free. We would have two particle subsystems in terms of OHC content. However, this may appear unfeasible. So, without contesting any of the valuable sets of data presented in [6–9], the current results would suggest that the underlying physical basis for interpretation of some results needs adaptation. Probably the explanation for the observed narrowing in optical band gap should be searched for in systematic structural differences in the a-SiO_2 network of the nanoparticles as compared to bulk SiO_2, for which there is recent experimental evidence [5].

The presence of such large concentrations of NBOHCs in fumed silica was also suggested by Glinka *et al* [6–8], who studied 7 and 15 nm size nanoparticles—quite like the ones studied here. They compared the PL properties of bulk fused silica with those of fumed silica [7], and attributed a main difference in PL properties to a large concentration of surface NBOHCs in the nanoparticles. They suggest that during particle formation a large concentration of surface structural defects, i.e., E′ (≡Si•) and OHC (≡Si–O•), result from ≡Si–O–Si≡ bond splitting [6, 8]. E′-type centres (and OHC-type centres) are indeed observed in the as-grown sample upon VUV activation, albeit at rather small densities, the upper limit being determined as $(2.4 \pm 0.1) \times 10^{15}\ \mathrm{g}^{-1}$. This corresponds to about 1×10^{-3} defects/nanoparticle.

Another assumption made by Glinka *et al* is that upon post-manufacture heating in air at temperatures ⩾600 °C, NBOHCs are formed in the fumed silica nanoparticles by the process [6]

$$2(\equiv\mathrm{Si{-}OH}) \xrightarrow{T_{\mathrm{an}} \geqslant 600\,^{\circ}\mathrm{C}} (\equiv\mathrm{Si{-}O}\bullet) + (\equiv\mathrm{Si}\bullet) + \mathrm{H_2O}\uparrow. \quad (1)$$

The concentration of the NBOHCs should thus increase with increasing annealing temperature and accordingly [6] dominate the PL spectrum of the sample annealed at $T_{\mathrm{an}} = 900\,^{\circ}\mathrm{C}$. This conclusion is not supported by the current results: the broad ESR resonance line, possibly due to some type of OHC, decreases drastically upon additional heat treatment. According to equation (1) not only the concentration of NBOHCs but also the concentration of E′-type centres should increase since they are formed in pairs. However, no such increase in E′ concentration could be observed either. These two observations make it quite unlikely for the reaction described by equation (1) to play a dominant role. In fairness, though, it should be mentioned that the post-manufacture heat treatments applied by Glinka *et al* (2 h in air) differ from those applied in this research (∼1 h in vacuum), which, given the nanodimensions of the particles, may be linked to the difference in the results attained. This would require further investigation.

In conclusion, the present ESR results on fumed silica nanoparticles show strong evidence for the presence of the peroxy radical in the as-grown sample upon VUV irradiation. Possibly some other kinds of OHC-type centres are also present. Determination of the upper limit of the occurring density of all of these OHC defect types (0.07 defects/particle), revealed a discrepancy between our results and previous conclusions drawn from PL and light absorbance measurements [6–9]. (i) The NBOHCs are not present in ‘large’ concentrations in the as-grown samples upon VUV irradiation, since no more than one in every fourteen particles may contain such a defect. Thus, none of the ESR active defects observed in the nanoparticles is present in such numbers that they may cause any significant changes in the optical band gap. (ii) It seems very unlikely that NBOHCs are formed upon post-manufacture heating in air at temperatures $T_{\mathrm{an}} \geqslant 600\,^{\circ}\mathrm{C}$, since, in ESR terms, the density of the OHC-type defects is found to decrease drastically after post-manufacture heating in vacuum, rather than increasing.

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