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Electron spin resonance probing of E′-type defects in fumed silica nanoparticles

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Abstract

Results are presented of an electron spin resonance (ESR) characterization of E′ type defects observed in fumed ~7-nm sized silica nanoparticles. This is accomplished through K- and Q-band ESR following 10-eV irradiation used to photo-dissociate H from passivated defects. The defect analysis provides access to the structure of the nanoscale on atomic level, herewith adding an extra dimension for analysis. To assess specific physico-chemical structural aspects of the particles, the E′ centers have been monitored as a function of thermal treatment in vacuum in the range 850–1115 °C, revealing the presence of two systems of E′ centers. The first one exhibits ESR parameters very similar to those of the familiar E'_γ center encountered in bulk fused silica, while the second bath exhibits an altered zero crossing g value and line shape, attributed to variations in local structure. While the first E′ system most likely resides in the core regions of the nanoparticles, the second system may mainly be confined to the outer SiO_2 layers exposing a structurally different, possibly more strained nature than macroscopic glassy SiO_2. Probing of fundamental point defects in nanometer-sized silica particles thus reveals structural variations and non-uniformity, indicative of a structure different from bulk material.

Keywords: SiO_2; Nanoparticles; E′defect; ESR; Atomic structure

1. Introduction

The understanding of the properties of nanometer-sized particles vis-à-vis those of the bulk counterparts is a challenge that catches the interest of both the academia and industry. In particular nanometer-sized fumed silica particles promise to be useful in the future development of nanometer-sized optical and electronic devices. Consequently, they have been intensively studied theoretically as well as by a range of sensitive experimental techniques such as, positron annihilation [1] and X-ray diffraction, [2] and the key photon–solid interaction probes including optical [3] and Fourier transform infrared (FTIR) absorption [2,4,5], Raman spectroscopy [2], nuclear magnetic resonance (NMR) [6], and electron spin resonance (ESR) [1,7].

The size of the nanoparticles is well known to produce electrical and optical properties different from the bulk [2,3,5]. Nevertheless, very little is known about the exact structure of these nanoparticles; generally, however, what is known is that the nanoparticles are in the amorphous phase, interpreted as being caused by the extremely fast cooling of the pyrogene silica aggregates formed at 1400–1800 °C. Yet, previous work suggested for the nanoparticles a structure different than bulk a-SiO_2. From molecular dynamics (MD) computer simulations it was concluded that the nanoparticles would exhibit a shell-like structure [8,9]. The surface has a different density and structure as compared to the interior of the cluster, which is proposed to be structurally equivalent to bulk silica. This conclusion, however, was countered by Uchino et al., who concluded from their infrared measurements that the interior of the nanoparticles cannot be equivalent to that of macroscopic SiO_2 [2]. They suggested a more flexible network structure consisting of small-membered rings for the silica nanospheres. According to the FT-Raman spectra these small-membered rings still survive after heating up to 1100 °C, but at 1200 °C bulk-like silica is formed. The onset temperature for sintering, however, is 800 °C, as evidenced by a study of the specific surface area.

Though being the tool eponymous for point defects with atomic level physico-chemical sensitivity [see, e.g., Refs. 10–12], very little research has so far been carried out using ESR: Some ESR work has been done on fumed silica in the as-grown state [7] as well as after UV irradiation [1] with photons (~5

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eV) obtained from a low pressure Hg lamp. However, in both cases no ESR signals originating from the silica nanoparticles could be discerned, likely explaining the faded interest over the years in applying ESR to this field of research. In view of the particular preparation method 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 phenomenon is well known for Si dangling bond type defects such as the P_b ($Si_3{\equiv}Si\cdot$) [11,13,14] and E′ defects [15] in thermal Si/SiO_2. In this context, it is pertinent to note that the applied UV irradiation may energetically appear just not sufficiently efficient to reactivate defects to a detectable amount. On this matter, VUV excitation has proven to be more appropriate [16,17].

Combining such photon excitation (~10 eV) with ESR analysis, the scope of this work is to characterize E′ type defects observed in fumed silica nanoparticles. Suggestions are made about the structural nature of the nanometer-sized particles and the differences when compared to the bulk silica counterpart. To assess these structural aspects the ESR resonances are monitored as a function of post formation heating and treatment (aging, VUV excitation).

2. Experimental details

2.1. Samples

The samples studied were taken from high-purity pyrogene fumed silica powder of 7 nm average particle size and 380±40 m^2/g surface area, with a "bulk" density of 36.8 g/dm^3 and low metallic impurity content [18]. The particles are fabricated by burning silicon tetrachloride in an oxygen–hydrogen flame at ~1800 °C. During particle formation and subsequent cooling down, interparticle collisions and subsequent fusion results in the formation of chain-like aggregates from 10 to 30 units, or, put differently, from ~0.1 to 0.2 μm in length. Separate sets of samples (fresh ones for each thermal step) were subjected to postmanufacturing baking in vacuum (base pressure $\leq 4\times10^{-6}$ 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 irradiation by VUV (~10 eV) photons (flux~10^{15} cm^{-2} s^{-1}) to photodissociate H from passivated defects. Possibly, the treatment may additionally unveil strained or weak bondings (bond rupture) [16], which, however, should also add to the ultimate goal. That is, acquiring atomic scale information about the SiO_2 particles network, as these sites of defect creation, i.e., strained and/or weak bonding sites, constitute in embryo also imperfections in the a-SiO_2 matrix, although not necessarily concerning nonstoichiometry.

2.2. ESR spectroscopy

Conventional CW absorption-derivative ESR measurements were performed at K (~20.3 GHz) and Q-band (~33 GHz) in the temperature range T=4.2–300 K. The levels of the magnetic field (**B**) modulation and incident microwave power P_μ were properly watched to avoid signal distortion. More details can be found in Ref. [11]. 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. To study the characteristics of defect modification in room ambient, the ESR measurements were performed immediately upon VUV irradiation as well as after leaving the samples in room ambient for desired times (one day to weeks).

3. Results and analysis

As anticipated, no ESR signal could be observed in 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 is drastically affected by VUV irradiation. Several defects emerge, including the oxygen-associated hole centers (OHCs), the methyl radical, and, as will be the scope of research here, the familiar E′-type center. Fig. 1 shows an overall K band spectrum measured on the as-grown powder immediate upon VUV irradiation over an extended field range in the liquid helium temperature range; it exposes the totality of observed ESR signals.

After VUV irradiation, in the as received state, as displayed in Fig. 2, as well as in the samples subjected to post-manufacture annealing, a characteristic central-line two-peak powder pattern signal is observed much similar (e.g., regarding width, overall shape) to that of the common E'_γ variant [19,20] (modeled as the $O_3{\equiv}Si\bullet\ldots{}^{+}Si{\equiv}O_3$ defect) in bulk silica. For normalization (calibration) purposes we have additionally calibrated within our ESR approach based on the usage of a single high accuracy g marker, the 'standard' most widely studied E'_γ center produced in synthetic fused silica suprasil I by 1 MGy ^{60}Co γ-irradiation, as illustrated in Fig. 2(c) [21]. Detailed computer simulations of the presently observed spectra measured on the fumed silica particles, however, show slight, but clear, variations in ESR parameters depending on the

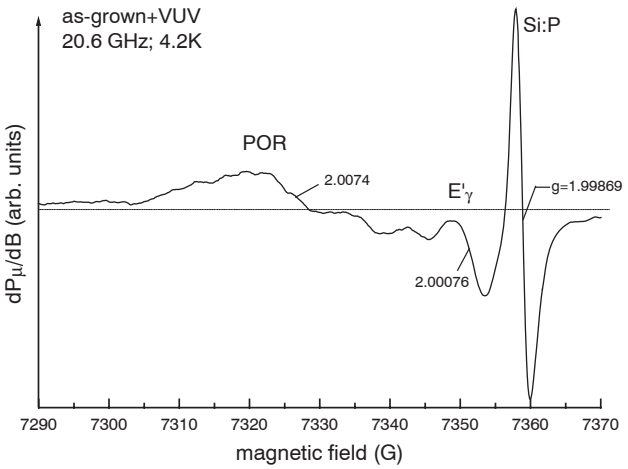

Fig. 1. Typical overall K-band (P_μ~0.2 nW; B_m~0.5 G) ESR spectrum of the defects observed in the as-grown sample after VUV irradiation. The E'_γ and peroxyradical (POR) signals are indicated.