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Generation of defects in amorphous SiO_2 assisted by two-step absorption on impurity sites

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Abstract

Generation of the Si dangling bond defect in amorphous SiO_2 (E' centre) induced by tunable pulsed UV laser radiation was investigated by *in situ* optical absorption measurements. The defect generation efficiency peaks when the photon energy equals ~5.1 eV, it depends quadratically on laser intensity and is correlated with the native linear absorption due to Ge impurities. We propose a model in which the generation of E' is assisted by a two-step absorption process occurring on Ge impurity sites.

1. Introduction

The interaction between solid insulators and photons of energy smaller than the electronic bandgap, mainly driven by multi-photon processes, is a fundamental scientific issue encompassing solid state physics, material sciences and photonics, and is a particularly active subject of investigation for materials having a strong technological impact, such as amorphous SiO_2 (silica glass, bandgap ~ 9 eV). Silica is a key material widely employed in current optical and electronic technologies including optical lenses, fibres and insulating layers in ubiquitous Si-based microelectronic devices. Exposure to high-power light sources in several applications such as photolithography with ultraviolet (UV) excimer lasers, KrF (5.0 eV), ArF (6.4 eV) and F_2 (7.9 eV), requires a high radiation toughness to inhibit the generation of point defects detrimental for the performance of the material [1, 2]. The most common defect, observed in all irradiated SiO_2, is the Si dangling bond, also known as the E' centre, consisting of an unpaired electron localized on a threefold coordinated Si atom, $\equiv Si^{\bullet}$. The practical relevance of E' is due to its absorption band at 5.8 eV, which dominates the UV absorption profile of irradiated SiO_2, and to the role of E' as a charge trap in electronic devices [1–5]. The generation of the E' centre triggered by sub-bandgap laser light has been widely investigated, and represents an interesting model system for understanding multi-photon processes leading to permanent damage in solids [2, 6–19]. The most fundamental defect generation mechanism in silica, also common in ionic crystalline insulators [20], is the non-radiative decay of self-trapped excitons generated by two-photon absorption (TPA) of laser light by the SiO_2 matrix [8, 9, 18, 21]. However, this process, which produces defects out of a defect-free SiO_2 structure, is generally believed to be dominant only in high-purity silica exposed to very intense radiation, particularly that emitted by femtosecond lasers [18, 19]. In contrast, the strong observed dependence of the generation efficiency of the E' centre on the manufacturing procedure of the material has suggested that in most cases the defects are usually formed by transformation of pre-existing centres (precursors) [1, 2, 7, 10–12, 17]. The precursors of the E' centre are expected to belong to a few possible types, i.e. oxygen vacancies, Si–H or Si–Cl groups, or 'strained' Si–O–Si bonds. Their conversion into the defect can occur either by direct absorption of laser photons or by interaction with excitons (or free charges) made available in the first place by TPA on the SiO_2 matrix [7, 10, 11]. While the precursor can sometimes be identified by correlating the induced E' centres with the variation of a pre-existing spectroscopic signal, it is usually very difficult to go over this general scheme and precisely specify the nature of the laser–solid interaction which produces the defects. This issue remains elusive, primarily because current knowledge on the subject is founded on irradiation experiments performed using only excimer lasers with fixed photon energies [2, 6–19]. In contrast, the use of an appropriate laser source permitting accurate measurements of

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a genuine excitation spectrum of the defect generation process is mandatory to achieve a thorough understanding. To this end, in this paper we studied *in situ* the generation of E' centres under tunable UV laser radiation. Such an experiment allowed us to identify a midgap electronic level, associated with Ge impurities, that assists the process of generating the E' centre. Specifically, we put forward a model in which Ge impurities enhance the defect generation efficiency by allowing the generation of electron–hole pairs via a two-step absorption process.

2. Materials and methods

We irradiated bulk silica samples at $T = 300$ K with light pulses of duration $\tau = 5$ ns emitted by a Vibrant Opotek tunable laser system. This is an optical parametric oscillator (OPO) pumped by the third harmonic (355 nm) of a Nd:YAG laser. The OPO output beam is frequency-doubled within a BBO nonlinear crystal so as to emit UV radiation tunable in the 210–420 nm range with 1–2 mJ maximum pulse energy. The laser beam, weakly focused with a lens, had a cross section of $\sim$1 mm^2 in the position where it entered the sample. We used several standard commercial silica specimens supplied by Heraeus Quarzglas GmbH and Quartz and Silice, and belonging to two classes: (a) Fused silica (commercial names Infrasil301, Herasil1, Herasil3, Q912, Vitreosil), manufactured by fusion and quenching of natural quartz, with variable OH content (8 < [OH] < 150 ppm), and typical[1] concentration of impurities of $\sim$20 ppm in weight. In particular, Ge is present in typical concentrations of $\sim$1 ppm as estimated by neutron activation measurements [22]. (b) Synthetic silica (commercial names Suprasil1 and Suprasil300), virtually impurity-free (<1 ppm) and 1 ppm < [OH] < 1000 ppm. The E' centres were absent in the as-grown samples, as checked by electron spin resonance measurements. We detected *in situ* the optical absorption (OA) spectra of the samples being irradiated by an Avantes optical fibre (OF) spectrophotometer, equipped by a D_2 lamp source and a detector sensitive in the 200–400 nm range. The probe beam is carried from the lamp to the sample by an OF and traverses the sample perpendicularly to the laser beam. The transmitted beam is collected by another OF and carried to the detector. The instrument allows one to measure the OA spectrum of the sample after each laser pulse. We also performed photoluminescence measurements on the samples excited by laser radiation. Light emitted by the samples was dispersed by a spectrograph (SpectraPro 2300i, PI Acton) with 150 lines mm^{-1} and detected by an air-cooled intensified charge-coupled device (CCD; PIMAX, PI Acton).

3. Results and discussion

In figure 1 the typical absorption spectrum of as-grown fused silica and synthetic silica are reported. All fused silica materials feature a measurable absorption in the 4.0–6.0 eV region due to the presence of trace impurities. The main signal

[1] Heraeus Quarzglas, Hanau, Germany, Base Materials Catalogue; Quartz and Silice, Nemours, France, Catalogue.

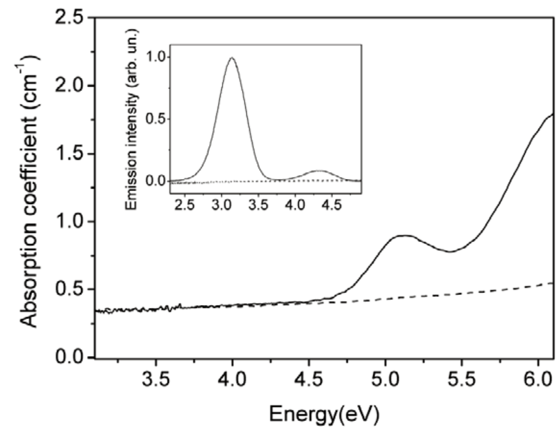

Figure 1. Typical absorption spectrum of an as-grown fused silica (continuous line) and an as-grown synthetic silica (dashed line) sample. Inset: typical luminescence emission observed in the two types of sample under excitation with 5.1 eV laser light.

is an OA band peaked at 5.1 eV ($B_{2\beta}$ band), the amplitude of which varies from sample to sample between 0.05 and 0.50 cm^{-1}. Previous studies on fused silica conclusively attributed this OA band to twofold coordinated Ge (=$Ge^{\bullet\bullet}$) centres (see [1, 23] and references therein). This defect is the prevalent arrangement of Ge impurities in as-grown fused silica [22, 24]. Since it is known that other defects may contribute to absorption in this spectral region, we unambiguously attributed the signal in figure 1 to Ge impurities by experimentally observing (see inset) under 5.1 eV laser excitation the typical 3.1 and 4.3 eV photoluminescence (PL) bands that are a well-known fingerprint of (=$Ge^{\bullet\bullet}$) defects [1, 23–26]. We also verified that, consistent with previous works [25], these two PL signals are observed in all fused silica samples used here, and their intensity is correlated with the $B_{2\beta}$ band. It is worth noting that PL measurements, in particular, allow us to rule out the presence of the twofold coordinated Si (=$Si^{\bullet\bullet}$) defect [1, 23] in all the investigated samples: this centre, usually present only in oxygen-deficient silica specimens, is absent here within 10^{14} cm^{-3} as inferred by the lack of its 4.4 and 2.7 eV emissions under 5.0 eV laser excitation [23]. Even a possible minor contribution of the Si-related 4.4 eV band to the signal in figure 1 can be ruled out based on the luminescence decay properties. Indeed, we verified that the PL signal at 4.3 eV in figure 1 decays exponentially at $T = 8$ K with a radiative lifetime of (8.0 ± 0.5) ns, consistent with previous studies on twofold coordinated Ge defects [25], while being markedly different from the 4 ns lifetime associated with the Si-related 4.4 eV band [23].

As expected, figure 1 also shows that the $B_{2\beta}$ band is absent in virtually impurity-free synthetic silica samples. The weak absorption signal measured in such materials is mostly due to surface reflection, the actual absorption coefficient $\alpha(E)$ being lower than 10^{-2} cm^{-1} for any $E < 6$ eV. No luminescence signal is observed in the investigated synthetic samples under excitation for any $E < 6$ eV.

We performed several irradiation sessions on fused silica specimens using different laser photon energies E_L. Since no

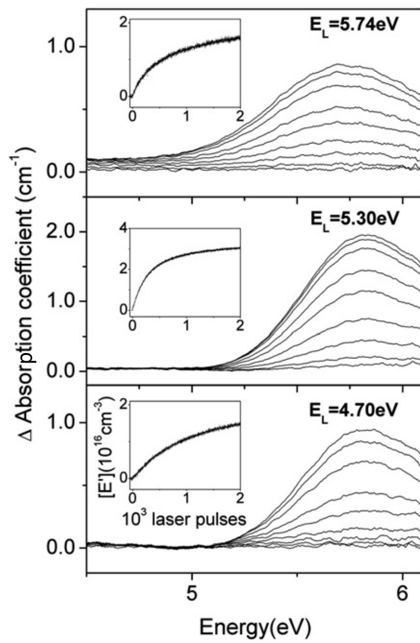

Figure 2. Evolution of the difference OA spectrum measured *in situ* during the irradiation of 'Infrasil301' fused silica performed using three different laser photon energies E_L. Insets: kinetics of the concentration of the E' centres.

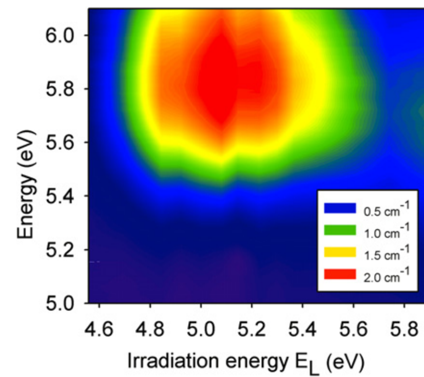

Figure 3. Contour plot of the absorption profile measured in the UV range after irradiation of fused silica with 2000 laser pulses of photon energy E_L.

(This figure is in colour only in the electronic version)

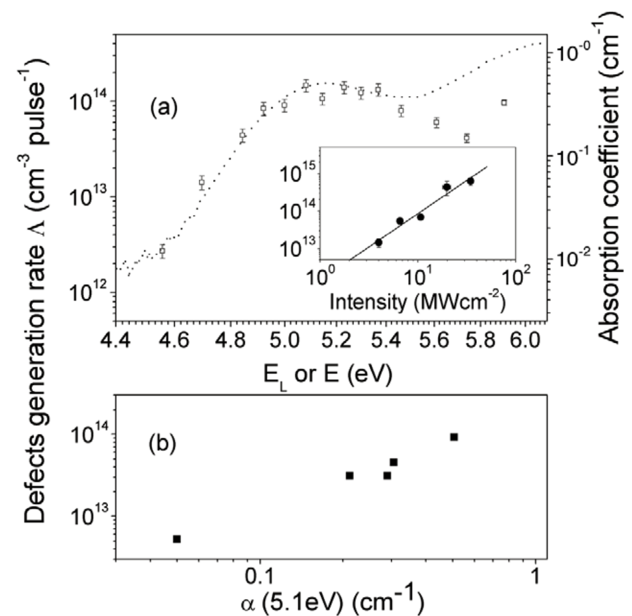

Figure 4. (a) Generation efficiency Λ (open symbols) of E' centres for irradiation of fused silica with different photon energies E_L and intensity $I = 10$ mW cm^{-2}. Absorption spectrum $\alpha(E)$ of the as-grown material (dotted line). Inset: $\Lambda(E_L = 5.1$ eV) measured at different laser intensities. By least-square fitting with the equation $y = ax^b$ we obtain $b = 1.8 \pm 0.3$. (b) $\Lambda(E_L = 5.1$ eV) measured in several commercial silica samples, plotted against their native absorption coefficient $\alpha(5.1$ eV).

induced OA (within 0.01 cm^{-1}) was detected for $E_L < 4.5$ eV, we report the results obtained for 4.5 eV $< E_L <$ 5.9 eV. In each experiment, an as-grown specimen was irradiated with 2000 pulses of peak intensity $I = 10$ MW cm^{-2} with a 1 Hz repetition rate. In figure 2 we report the kinetics of the induced OA as measured during the irradiation sessions of 'Infrasil301' fused silica with three different values of E_L. The main signal growing during irradiation is the 5.8 eV band associated with the E' centres [1, 2, 27], whose kinetics and spectral characteristics depend on E_L. For $E_L < 5.3$ eV, the band peaks at 5.83 eV with 0.71 eV FWHM, while for $E_L > 5.3$ eV the peak progressively shifts down to 5.73 eV while the FWHM increases to 0.91 eV, both measured at the end of the experiment at $E_L = 5.9$ eV. From the band area and the known oscillator strength [1, 2, 27], we estimate the concentration $[E']$ of the defects, which is plotted in the insets against the number of pulses N.

Figure 3 summarizes the induced OA profile between 5 and 6 eV measured at the end of all the irradiation sessions. The induced absorption initially grows with increasing E_L above 4.5 eV, while keeping the shape of a single band peaked at ~5.8 eV. The intensity of the band reaches a maximum for E_L~5.1 eV, after which it decreases. The growth rate of $[E']$ at the beginning of irradiation, $\Lambda = \mathrm{d}[E']/\mathrm{d}N$ $(N = 0)$, measures the efficiency of the defect generation process. Λ is estimated by a linear fit on the first ~50 pulses of the kinetics (insets of figure 2) and plotted as a function of E_L in figure 4(a). $\Lambda(E_L)$ is a bell-shaped curve peaking at 5.1 eV. By measuring Λ under irradiation with different laser intensities at $E_L = 5.1$ eV (inset of figure 4(a)), we found a quadratic dependence.

The dependence on laser photon energy of the generation efficiency of the E' centres in fused silica suggests a resonance activated by laser light to underlie the defect generation process. The quadratic dependence of Λ on laser intensity indicates that the absorption of two photons is involved in the generation of the defect. In previous works we demonstrated that the E' centres generated in fused silica by a Nd:YAG laser ($E_L = 4.7$ eV) mainly arise from breaking of Si–H precursors [27, 28]. The role of Si–H as an important precursor of E' centres had already been put forward after experiments on irradiated bulk silica [1, 7, 10, 29–32], or

Si/SiO_2 interfaces [33]. Specifically, it was proposed that the E' centre is formed by hole trapping on Si–H causing the rupture of the silicon–hydrogen bond [33]. However, existing data do not rule out the possibility of Si–H breaking by non-radiative decay of excitons [29, 30, 33] or by direct photon absorption on the precursor site [10, 34]. Now, the variations at $E_L > 5.3$ eV of the spectral features of the 5.8 eV band (figure 2) suggest either a second parallel generation process of the E' centre under laser irradiation or inhomogeneity effects affecting the OA band. However, this issue will not be discussed further here. The following arguments, mostly independent of the precursor from which E' centres are supposed to arise, allow us to clarify the nature of the defect generation process by discussing its efficiency and spectral dependence.

The nonlinear dependence of the generation efficiency on laser intensity may actually correspond to a variety of different processes. On the one hand, aside from a 'proper' two-photon absorption process that takes place via a virtual intermediate electronic level, the quadratic dependence may also arise from a *two-step* absorption process (TSA), namely the consecutive absorption of two photons via a real intermediate excited energy level with a lifetime of a few nanoseconds. On the other hand, we should distinguish between the generation of E' centres by a *direct* interaction process between laser photons and the precursor and an *indirect* process, in which the defect is formed by trapping on precursor sites of free charges of excitons generated by the interaction of laser photons with another site of the matrix.

In this context, since the photon energy giving maximum generation efficiency (5.1 eV) resembles half of the first excitonic peak in SiO_2 (10.4 eV) [1, 35], it may be tempting to interpret the generation of E' as due to non-radiative decay on Si–H precursors of excitons made available by TPA on the silica matrix. However, we can rule out this model on the basis of efficiency considerations. In fact, the exciton concentration produced by a single laser pulse of intensity $I = 10$ MW cm^{-2} is given at most by $\Lambda_0 = \tau\beta I^2(h\nu)^{-1}$, where β is the TPA coefficient, reported[2] to be $\beta(4.7\ \mathrm{eV}) = (1.9 \pm 0.3) \times 10^{-11}$ cm W^{-1} [36], and $\beta(5.0\ \mathrm{eV}) = 8 \times 10^{-11}$ cm W^{-1} [37]. So we get $\Lambda_0(4.7\ \mathrm{eV}) = 1.4 \times 10^{13}$ cm^{-3} and $\Lambda_0(5.0\ \mathrm{eV}) = 5.9 \times 10^{13}$ cm^{-3}. These values are smaller than the corresponding generation efficiencies in figure 4(a), thus leading to a very unlikely picture in which each TPA event on the SiO_2 matrix eventually leads to the generation of an E' centre from a precursor with an efficiency of $\sim$1. We can also exclude the simplest possibility of TPA occurring directly on any precursor site of concentration $[P]$, leading to a hypothetical unstable excited state (10.4 eV higher than ground state) from which P is converted into an E' centre. In fact, in this case we should have $\Lambda(5.1\ \mathrm{eV}) = [P]I^2\sigma_{(2)}\tau(h\nu)^{-2}$, where $\sigma_{(2)}$ is the cross section of the TPA process. Using the typical order of magnitude of $\sigma_{(2)}$ (10^{-49}–10^{-50} cm^4 s) [38], we can invert the last equation and estimate $[P] \sim 10^{21}$ cm^{-3}. This estimate is orders of magnitude larger than the concentrations of all known precursors of the E' centre in silica [1, 2].

Such an unexpectedly large defect generation rate can be accounted for only by supposing that the nonlinear process ultimately leading to defect generation is two-step absorption. In fact TSA, which requires significant linear absorption at the laser energy, is typically much more efficient than TPA in which the intermediate level is virtual [38]. In principle, TSA could be conceived as occurring directly on a suitable precursor of E' centres featuring an excited electronic level near 5 eV, thus explaining the resonance in figures 3 and 4. Nevertheless, the Si–H group in SiO_2 is well known to have no significant absorption below the bandgap, its first excited level being above $\sim$8 eV as obtained by theoretical calculations [2, 10]. Even if we temporarily put aside the idea of E' being generated from Si–H precursors, we observe that the only other proposed precursor of E' absorbing at $\sim$5 eV is the twofold coordinated Si ($=$Si$^{\bullet\bullet}$) [2]. However, as discussed above, this defect is absent in all the investigated samples within 10^{14} cm^{-3}, at least two orders of magnitude lower than the concentration of induced E'. As a consequence, it can be ruled out as a possible precursor of E' centres in the present experiment.

On the other hand, we know from figure 1 that fused SiO_2 features impurity-related absorption in the 4.5–6.0 eV region. This OA corresponds to electronic transitions occurring on impurity sites and induced by single-photon absorption at these energies. We report again as a dotted line in figure 4 the native OA profile $\alpha(E)$ of fused silica from figure 1 after correction for surface reflection. We can see that $\alpha(E)$ is quite similar to the $\Lambda(E_L)$ curve, at least for energies $<$5.3 eV. Since the main 5.1 eV peak is due to the $B_{2\beta}$ band of the twofold coordinated Ge impurity, which accounts almost completely for the absorption coefficient of fused silica at 5.1 eV, this similarity strongly suggests ($=$Ge$^{\bullet\bullet}$) sites to be indirectly involved in the generation of E'. Namely, data strongly indicate that twofold coordinated Ge must be the defect that provides the intermediate electronic level on which TSA occurs. In order to provide an independent experimental test of this statement, we repeated the measurement of $\Lambda(5.1\ \mathrm{eV})$ on several types of commercial fused silica materials. We found that Λ is clearly correlated with $\alpha(5.1\ \mathrm{eV})$ (figure 4(b)), i.e. the defects are generated more efficiently where Ge-related native linear absorption is higher. Finally, at any $E_L < 6.0$ eV we did not detect appreciable ($\Lambda < 10^{12}$ cm^{-3}) concentrations of E' centres in virtually Ge-free synthetic samples, where $\alpha(5.1\ \mathrm{eV}) < 10^{-2}$ cm^{-1}.

Hence, we propose the following model: TSA processes mediated by the 5.1 eV excited electronic state of ($=$Ge$^{\bullet\bullet}$) impurities, allow the efficient generation in fused silica of e^-–h^+ pairs under laser. Then, as the elementary excitations migrate from the initial generation site, a portion of them ultimately lead to the formation of E' centres by interaction with precursors. In particular, since Si–H is the main precursor of E' in fused silica [27, 28], consistent with previous works we suppose here the E' to be ultimately generated by h^+-trapping on Si–H sites [33]. It is worth noting that the excited level at 5.1 eV of ($=$Ge$^{\bullet\bullet}$) features a lifetime of a few nanoseconds [1, 26], suitable for an efficient TSA process.

[2] These β were estimated by measuring the intensity-dependent transmittance of ultrashort laser pulses on several standard commercial silica types [36, 37].

As synthetic silica lacks the impurities required to assist TSA processes, the impurity-assisted generation model proposed here predicts that in this case the formation of E' centres under sub-bandgap light should be driven by TPA processes only. Consistently, typical concentrations of E' reported on high-purity SiO_2 exposed to KrF ($E_L = 5.0$ eV) laser are 20–100 times smaller than measured here at comparable laser intensity (see, for example, [7, 17]). Further experiments on oxygen-deficient silica samples, usually containing twofold coordinated Si defects ($=Si^{\bullet\bullet}$), may allow us to find out if these centres, also absorbing near 5 eV [23], may act as mediators of TSA processes as ($=Ge^{\bullet\bullet}$) centres do.

While the present data strongly suggest TSA on Ge sites to drive the generation of E' centres, they do not allow to conclusively describe the specific mechanism by which absorption of two photons by twofold coordinated Ge can produce an e^-–h^+ pair. It is known that the level scheme of ($=Ge^{\bullet\bullet}$) features two excited singlet levels, S_1 and S_2, 5.1 and 7.4 eV higher than ground state respectively, and that excitation to either the S_1 or the S_2 state does not lead to any ionization of the defect, which reversibly returns to the ground state by radiative or non-radiative de-excitation. [26] Since 2×5.1 eV is larger than the bandgap, the consecutive absorption of two 5.1 eV photons is very likely to ionize the centre from the ground state via the S_1 state. Hence, TSA on ($=Ge^{\bullet\bullet}$) is expected to produce a free e^- in conduction band, while leaving behind a $(=Ge^{\bullet})^+$ defect. This ionized version of the twofold coordinated Ge is known from studies on Ge-doped silica and designated by some authors as the Ge(2) centre [39]. The interpretation proposed up to this point is consistent with the actual observation by ESR spectroscopy of small concentrations of Ge(2) centres in fused SiO_2 after Nd:YAG laser irradiation [40]. However, we still need to explain the origin of the positive charge, i.e. the hole supposedly responsible for the generation of E' by trapping on Si–H. In regard to this point, we can only tentatively propose h^+ to be formed by trapping of valence band electrons by the positively-charged Ge(2) centre. This could occur spontaneously at room temperature if the ground level of Ge(2) is sufficiently close to the top of valence band. In this way, the overall effect induced by TSA would be the production of an e^-–h^+ pair, with Ge(2) returning to the initial ($=Ge^{\bullet\bullet}$) state. Further studies are needed to confirm this hypothesis.

4. Conclusions

In summary, we studied the generation of the silicon dangling bond defect in amorphous SiO_2 under UV laser light of tunable photon energy $E_L < 6.0$ eV. The generation efficiency of the defect peaks at $E_L \sim 5.1$ eV and depends quadratically on laser intensity. Also, the process is correlated with the native linear absorption at $E = E_L$ due to Ge impurities. Our findings point to a new model for defect generation in silica containing Ge impurities. Twofold coordinated Ge impurities at a low concentration strongly enhance the generation of e^-–h^+ pairs under laser light by allowing a two-step absorption process resonant with their excited electronic state at 5.1 eV. The excitations so produced migrate and ultimately generate defects by interaction with precursors. This model clarifies the long-standing issue of explaining the role of impurities in reducing the radiation resistance of silica. Similar mechanisms may be active in other insulators as well, enhancing laser-induced damage in the presence of impurities.

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