

SURFACE CHANGES INDUCED BY PLASMA TREATMENT AND HIGH TEMPERATURE ANNEALING OF SILICON DIOXIDE MICROPARTICLES

Oleg BABČENKO¹, Zdeněk REMEŠ¹, Klára BERANOVÁ¹, Kateřina KOLÁŘOVÁ¹, Jakub LÖRINC², Zdeněk PROŠEK², Pavel TESÁREK²

¹ *Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, EU, babcenko@fzu.cz*

² *Faculty of Civil Engineering, Czech Technical University in Prague, Prague, Czech Republic, EU*

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Abstract

Due to the high surface to volume ratio, the particles' surface properties modification defines its properties in general, which is crucial for their use. From this point of view, plasma processing or high temperature annealing can be considered as the universal techniques for efficient modification of materials in the form of powder. In this study, the silicon dioxide microparticles have been treated in a hydrogen, oxygen or vacuum by low temperature plasma or annealing. The change of SiO₂ microparticles properties was investigated by photoluminescence spectroscopy at room and low temperature. High temperature annealing in hydrogen induced under UV excitation photoluminescence in the near UV and visible light indicating the change of defect states on the surface of the microparticles. We believe that observed findings clearly demonstrate useful method for analysis of SiO₂ microparticles surface modification attractive also for fundamental research.

Keywords: Silicon dioxide, plasma treatment, annealing, photoluminescence, measuring setup

1. INTRODUCTION

Silicon dioxide forms 3-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to 4 oxygen atoms. SiO₂, more so than almost any material, exists in several (natural or artificial) polymorphic crystalline forms [1,2]. However, silicon dioxide can more frequently be met in an amorphous form called glass. The SiO₂ based glasses are able to retain their properties when recycled and therefore the most abundant soda-lime-silica glass is considered as one of the best recyclable materials [3,4]. On the other hand, variation in a glass waste composition, due to additives that significantly modifies the properties of different types of glass, may affect the possibility of recycling [3,4] and forces search of alternative ways for glass waste utilization. In order to reduce the environmental burden and decrease use of natural sand, crushed or milled waste glass materials are considered as a filler in cement-based composites [5,6]. Nevertheless, certain limitations for glass waste use in this case exist as well and therefore new potential applications for silicon dioxide are welcomed.

It is known that properties of crystalline and amorphous forms of SiO₂, interesting not only for industry but also for researchers, differ quite significantly. The presence of defects in the silicon dioxide matrix can dramatically change its structural and optical properties. For instance, cathodoluminescence studies revealed several kinds of bulk defects, such as nonbridging oxygen hole center or twofold coordinated silicon centers [7,8]. Photoluminescence (PL) studies of crystalline SiO₂ are difficult due to low efficiency of the PL excitation in the near UV spectral range. However, it has been suggested that an amorphous SiO₂ is present at crystalline surface [9] and PL may result from direct excitation of surface-related defects [10]. Plasma treatment or annealing in various atmospheres can effectively modify the surface [11,12]. It has been shown that weak PL of natural or artificial silicon dioxides exposed to ionizing radiation can be enhanced [13,14]. However, it can also induce new PL active defects which complicate results interpretation. Alternative option how to measure

weak PL is use of SiO₂ in micro-granular form, i.e. powder or “sand”. In the case of the existence of various forms of surface states introduced either during preparation or by surface damage, SiO₂ microparticles may have measurable PL signal in the visible optical region [9,10,13]. In these terms, the interest of building sector to luminescent cement-based composites or coatings, realized by adding of luminescent particles to composites, is especially important [15,16]. It immediately offers the potential for use of luminescent silicon dioxide in such kind of cement-based composites.

Manufacturing processes, ionizing irradiation, mechanical stress, thermal annealing, and the presence of impurities may cause the formation of defects in the silicon dioxide matrix or lead to the transformation of the existing defects to other types of defects [9-14]. Intrinsic point defects involve atoms of the host matrix only, i.e. vacancies and self-interstitials, while extrinsic point defects involve atoms chemically different from the crystal [17]. In this study the microcrystalline SiO₂ powder was modified by plasma treatment or high temperature annealing in different atmospheres. The photoluminescence properties of intrinsic and modified SiO₂ powder were analyzed using the earlier reported adaptable measurement setup [18]. The SiO₂ PL spectra measured at room and low temperature (4 K) were compared and discussed.

2. EXPERIMENT

A micro-milled silica sand, with stated SiO₂ content above 99 % (Sklopísek Střeleč, a.s.) was used in this study. The SiO₂ powder was exposed to room temperature plasma in the large area low pressure system (AK 400, Roth&Rau) or treated by annealing in the cylindric furnace with a controllable atmosphere (Clasic CZ s.r.o). The radiofrequency plasma treatment was realized for 5 min in oxygen or hydrogen at pressure 15 Pa and temperature ≤50°C, marked as room temperature (RT), and repeated for 4 times with SiO₂ powder mixing. The annealing at temperatures from 500°C to 1000°C was realized in vacuum or in oxygen or hydrogen at atmospheric pressure for the time of 12 h.

The 4 mg of the SiO₂ initial or processed powder was pressed into disk pellets with the 3 mm diameter and analyzed by means of the Fourier Transform Infrared Raman spectroscopy using the dry-air ventilated Nicolet IS50 (FTIR) spectrometer (Nicolet CZ s.r.o.). Measurements were realized in 100-3500 cm⁻¹ spectral range with 2 cm⁻¹ resolution using laser with excitation at 1064 nm and InGaAs photodiode detector.

The PL measurements were done using 5 mg powder pressed into a ø3 mm pellet and glued by double sided conductive tape on 10×10×0.3 mm Cu substrates. For PL characterization of treated powder two measuring setups were assembled. Near UV and visible spectral range PL were measured in the perpendicular geometry being excited by pulsed UV light emitting diodes equipped with band pass (BP) and long pass (LP) filters (OD6), monochromators and red-enhanced photomultipliers (PMT). Lock-in amplifiers in both setups were referenced to the frequency of UV light emitting diode (LED). Both monochromators were spectrally calibrated with ORIEL QTH #63358 halogen lamp. Prior to the phase shift measurements, the lock-in amplifier was set to zero phase at the UV LED wavelength.

The first PL setup measures in the 375-750 nm spectral range at room temperature using 20 mA UV LED (1 mW XSL-360-5E Roither Lasertechnik GmbH) directly powered by 50 MHz Keithley 3390 pulse generator, BP360 (transparent in 350-370 nm spectra range) and LP375 (fully absorbing below 370 nm and fully transparent above 375 nm) optical filters, monochromator H20VIS (F/4.2, 1200 gr/mm, linear dispersion 4 nm/mm), red-sensitive 100 MHz PMT Philips Photonics XP2203B, low noise current preamplifier Signal Recovery 5182 (1 MHz bandwidth, 10⁵ V/A transimpedance) and 100 kHz Stanford Research SR830 lock-in amplifier TTL referenced to the LED frequency.

The second PL setup measures in the visible spectral range 400-750 nm in a closed He circle Oxford Instruments Optistat Dry BLV cryostat (sample in vacuum, 3-300 K), pulsed UV LED (10 mW Thorlabs LED M365FP1, 0.7 A), optical filters BP370 (transparent in 355-385 nm spectra range) and LP400 (fully absorbing below 390 nm and fully transparent above 400 nm), double gratings monochromator SPEX1672 (F/4, 1200

gr/mm, linear dispersion 2 nm/mm), a cooled red-sensitive 500 MHz PMT Philips Photonics XP2233B, low noise current preamplifier Signal Recovery 5182 (1 MHz bandwidth, 10^5 V/A transimpedance) and a 20 kHz lock-in amplifier Signal Recovery 5105. The maximum frequency of this setup is limited to 1 kHz by the UV LED power supply Thorlabs LEDD1B T-Cube.

3. RESULTS AND DISCUSSION

Microcrystalline SiO_2 appears as a white powder due to light scattering and low optical absorption. In the earlier study we observe that according to laser diffractometry, the median particles size of used SiO_2 powder is $59,5 \pm 1,4 \mu\text{m}$, while electron microscopy showed particles with sizes from tens of nanometer to $90 \mu\text{m}$ [19]. The PL emission spectra of as-received and plasma treated SiO_2 powders measured at room temperature are shown in **Figure 1a**. The PL signal of the as-received (untreated) SiO_2 powder under UV excitation is low, but still measurable using assembled setup. In contrast to previous observation with PL emission enhancing after 0.5 Pa Ar plasma [18], in current case the PL of SiO_2 particles after low temperature ($\leq 50^\circ\text{C}$) O_2 or H_2 plasma treatment have changed not so significantly. Such weak changes Therefore, the interest was focused more on the effect of thermal annealing on SiO_2 powders PL emission.

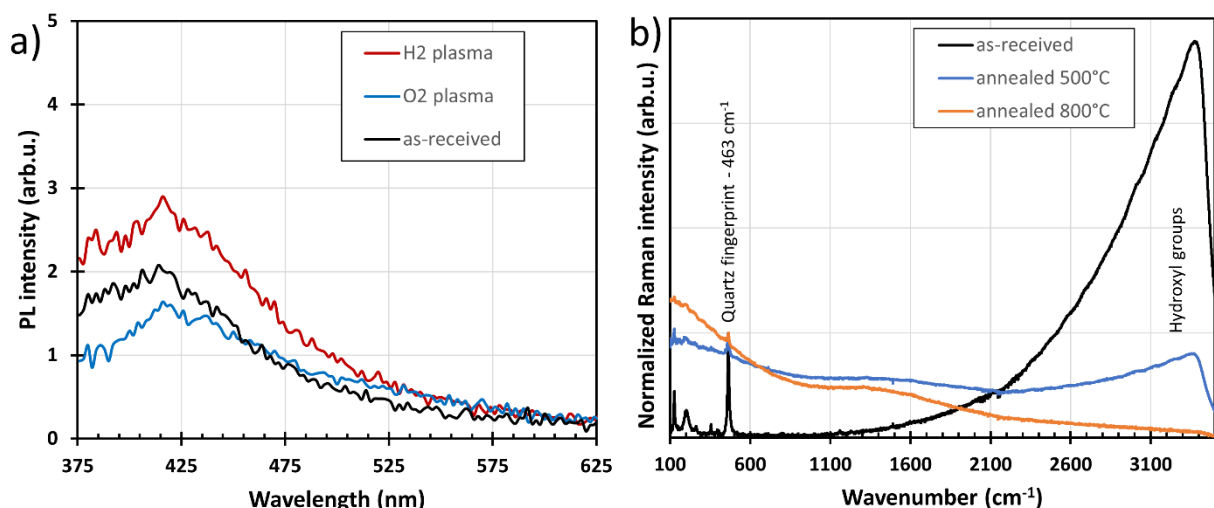


Figure 1 PL emission spectra of SiO_2 powder measured at room temperature under pulsed UV LED 360 nm excitation at 100 kHz (a) and FTIR Raman spectra of as-received and annealed in vacuum SiO_2 powder (b).

The normalized to quartz fingerprint peak (463cm^{-1}) FTIR Raman spectra of untreated (as-received) and annealed in vacuum SiO_2 powder are shown in **Figure 1b**. As can be seen, the peaks related to crystalline quartz remain detectable in the spectrum up to annealing temperature 800°C while intensity of the background vary with temperature. The background at lower wavenumbers (approximately $<1500 \text{cm}^{-1}$) increased while the broad band assigned to hydroxyl group (above 2000cm^{-1}) decreased after high temperature annealing. Indeed, on the contrast to water the hydroxyl groups on the SiO_2 surface requires quite high annealing temperatures to be vanished [20].

The PL emission spectra of annealed SiO_2 powder measured at RT are shown in **Figure 2**. We observe that the effect of high temperature annealing in the O_2 atmosphere on the PL spectra is negligible or low even for high temperatures, see **Figure 2a**. What is interesting is that intensity of band around 425 nm in PL spectra of SiO_2 powder annealed at 500°C and 800°C was slightly higher than in other cases. Annealing in vacuum (not shown) leads to similar PL spectra as annealing in O_2 atmosphere. The significant changes in PL spectra of SiO_2 powder appeared only after high temperature annealing in H_2 atmosphere **Figure 2b**. The intensity of PL emission band centered around 420 nm increase with annealing temperature. Moreover, for the SiO_2 powder

annealed at 800°C and above the multiple bands in the PL spectra were observed. The strongest observed (after annealing at 1000°C) was the band centered near 495 nm.

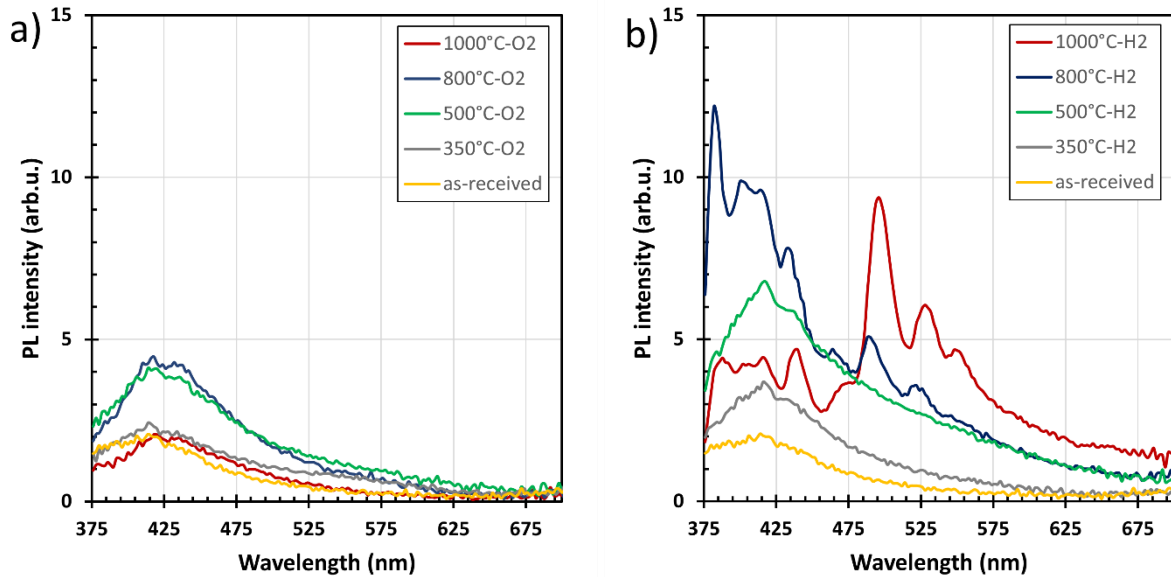


Figure 2 Comparison of PL emission spectra measured at RT under pulsed UV LED 360 nm excitation at 100 kHz for microcrystalline SiO₂ powder annealed in O₂ (a) and H₂ (b) atmospheres.

We suggest that during the high temperature annealing the stable hydroxyl groups present on the surface of SiO₂ microparticles vanish [20] which correlate with FTIR Raman (**Figure 1b**). Next, in the case of annealing in oxygen atmosphere defects after hydroxyl groups become passivated without forming PL active centers while annealing in hydrogen lead to color centers activation. Moreover, at high temperature the hydrogen may diffuse into SiO₂ microcrystals and activate color centers near the surface. Indeed, hydrogen has been proposed to passivate the silicon or oxygen dangling bonds in SiO₂ networks [21].

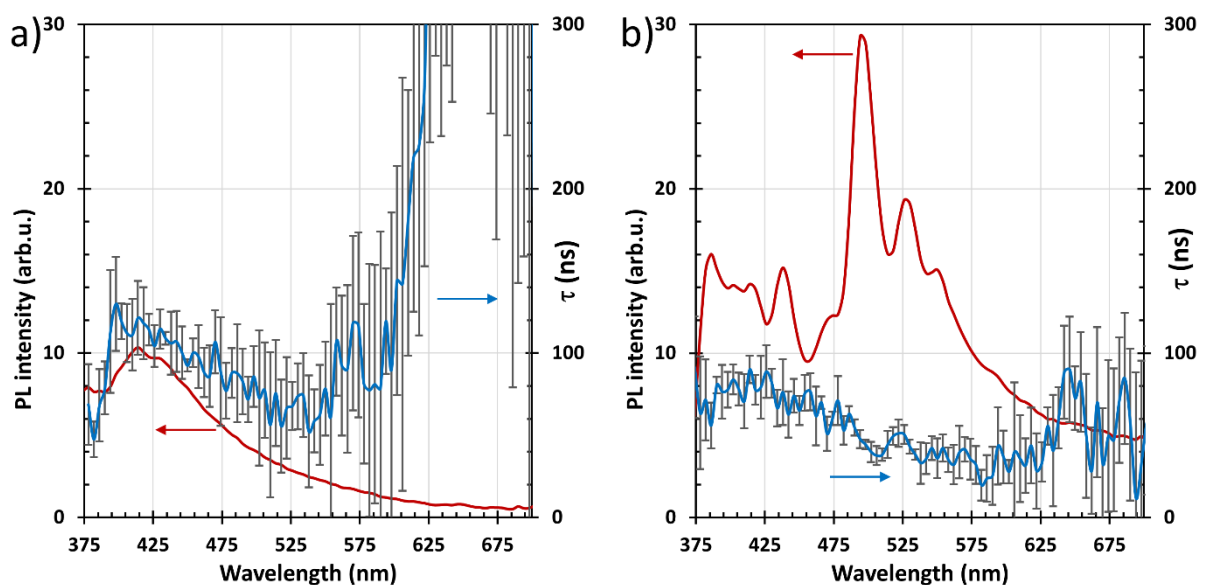


Figure 3 Comparison of the PL intensity of SiO₂ powder annealed in O₂ (a) and H₂ (b) atmosphere at 1000°C. The spectrally resolved mean time PL decay time τ was calculated from the phase shift between the sinusoidal excitation and emission. The spectral resolution was 8 nm and the lock-in time constant 3 s.

We believe that mentioned possible defects [2] are responsible for multiple band and complicated PL emission spectra seen in **Figure 3b**. In the case of vacuum annealing (not shown), the SiO₂ particles surface become free of water or hydroxyl groups but after exposing to ambient conditions the air humidity return the SiO₂ surface conditions to initial state, thus no/negligible changes in PL are observed.

Figure 3 shows the comparison of the spectrally resolved PL intensity of microcrystalline SiO₂ annealed in O₂ and H₂ atmosphere at 1000°C measured under sinusoidal UV LED 360 nm excitation at 100 kHz at room temperature and the spectrally resolved mean time PL decay calculated from the phase shift between the excitation and emission signals measured by lock-in [22]. Time resolution during measurements was about 10 ns for a 100 kHz sinusoidal excitation when the phase noise was about 0.1° [18]. Indeed, **Figure 3** suggests that the PL mean time decay is about 50 ns at 490 nm. Higher excitation frequency 5 MHz is necessary to achieve time resolution about 1 ns.

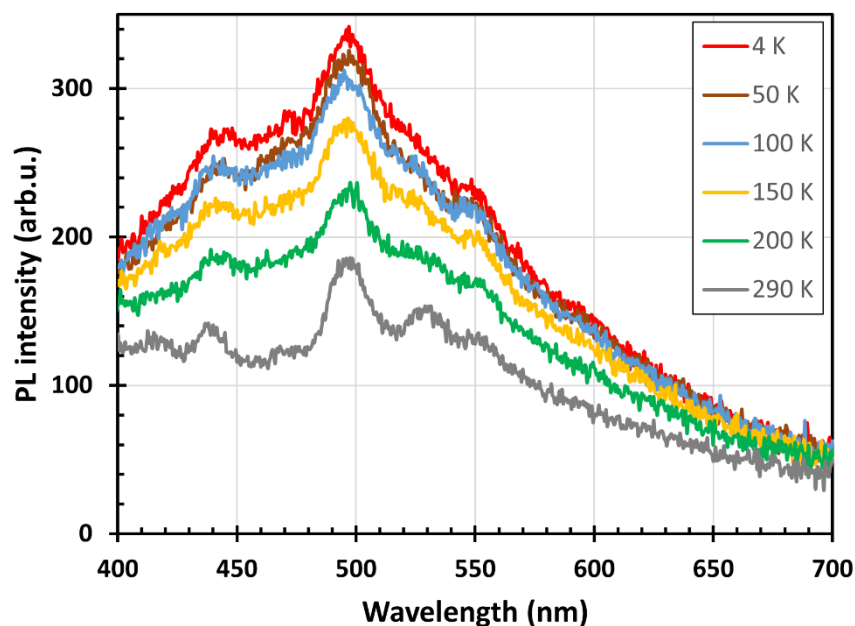


Figure 4 Comparison of the PL emission spectra of microcrystalline SiO₂ annealed in H₂ atmosphere at 1000°C and measured under UV LED 365 nm at 333 Hz at room and low temperature. The spectral resolution was 1 nm and the lock-in time constant 300 ms.

The comparison of PL spectra measured at room and low temperature (down to 4K) of microcrystalline SiO₂ annealed in H₂ atmosphere at 1000°C is shown in **Figure 4**. Unlike PL spectra shown in **Figure 2** and **Figure 3**, the spectra in **Figure 4** were measured in a closed circle He cryostat at a relatively low pulsed LED frequency 333 Hz and higher UV intensity (10 mW). The nominal low temperature was measured at the cryostat cold finger, but the intensive UV light heats the sample above the nominal temperature. **Figure 3** indicates only a moderate temperature dependence of the PL. This suggests that the PL is mainly related to the relatively fast surface states where the electron-phonon coupling is weak [8].

4. CONCLUSION

The microcrystalline SiO₂ powder was modified by low temperature low pressure plasma treatment and high temperature annealing in different atmospheres. Since defects in silica could include oxygen or silicon vacancies and their interstitials sensitive for UV excitation the change of SiO₂ microparticles properties was investigated by photoluminescence spectroscopy in two assembled setups. We have observed that the realized low temperature plasma treatment in hydrogen or oxygen atmospheres resulted to the only weak

changes in the PL emission spectra of SiO₂ powder. The most significant changes in the PL emission spectra of SiO₂ microparticles were observed for annealing in hydrogen atmosphere at temperature 800°C and above. The numerous bands in PL spectra were explained via influence of hydrogen that can diffuse into crystallites sub-surface at high temperature and form complexes with intrinsic defects or affect already existing defects. The intensity of weak blue PL increased significantly after high temperature annealing in hydrogen atmosphere indicating the changes of surface states on the surface of microcrystalline SiO₂. We believe that observed findings demonstrate the useful method SiO₂ microparticles surface modification analysis that will be attractive for fundamental research.

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REFERENCES

- [1] WIBERG, Egon, Nils WIBERG a A. F. HOLLEMAN. *Inorganic chemistry*. 1st English ed. San Diego : Berlin ; New York: Academic Press ; De Gruyter, 2001. ISBN 978-0-12-352651-9.
- [2] TRUKHIN, Anatoly, Krishjanis SMITS, Georg CHIKVAIDZE, Tatiana DYUZHEVA a Ludmila LITYAGINA. Luminescence of silicon Dioxide - silica glass, α -quartz and stishovite. *Open Physics*. [online]. 2011, vol. 9, no. 4, pp. 1106-1113. ISSN 2391-5471. Available from: <https://doi.org/10.2478/s11534-011-0016-5>.
- [3] BRISTOGIANNI, Telesilla a Faidra OIKONOMOPOULOU. Glass up-casting: a review on the current challenges in glass recycling and a novel approach for recycling "as-is" glass waste into volumetric glass components. *Glass Structures & Engineering* [online]. 2022 [vid. 2023-08-15]. ISSN 2363-5142, 2363-5150. Available from: <https://doi.org/10.1007/s40940-022-00206-9>.
- [4] BUTLER, John H. a Paul D. HOOPER. Glass Waste. In: *Waste* [online]. B.m.: Elsevier. 2019 [vid. 2023-08-18], pp. 307-322. ISBN 978-0-12-815060-3. Available from: <https://doi.org/10.1016/B978-0-12-815060-3.00015-3>
- [5] OGUNDAIRO, T. O.; D. D. ADEGOKE; I. I. AKINWUMI a O. M. OLOFINNADE. Sustainable use of recycled waste glass as an alternative material for building construction - A review. *IOP Conference Series: Materials Science and Engineering* [online]. 2019, vol. 640, no. 1, 012073. ISSN 1757-8981, 1757-899X. Available from: <https://doi.org/10.1088/1757-899X/640/1/012073>.
- [6] TAN, Kiang Hwee a Hongjian DU. Use of waste glass as sand in mortar: Part I - Fresh, mechanical and durability properties. *Cement and Concrete Composites* [online]. 2013, vol. 35, no. 1, pp. 109-117. ISSN 09589465. Available from: <https://doi.org/10.1016/j.cemconcomp.2012.08.028>
- [7] SKUJA, L. N. a W. ENTZIAN. Cathodoluminescence of Intrinsic Defects in Glassy SiO₂, Thermal SiO₂ Films, and α -Quartz. *Physica status solidi (a)* [online]. 1986, vol. 96, no. 1, pp. 191-198. ISSN 00318965, 1521396X. Available from: <https://doi.org/10.1002/pssa.2210960123>.
- [8] SKUJA, L. Time-resolved low temperature luminescence of non-bridging oxygen hole centers in silica glass. *Solid State Communications* [online]. 1992, vol. 84, no. 6, pp. 613-616. ISSN 00381098. Available from: [https://doi.org/10.1016/0038-1098\(92\)90201-J](https://doi.org/10.1016/0038-1098(92)90201-J)
- [9] SHEN, T. D.; I. SHMAGIN; C. C. KOCH; R. M. KOLBAS; Y. FAHMY; L. BERGMAN; R. J. NEMANICH; M. T. MCCLURE; Z. SITAR a M. X. QUAN. Photoluminescence from mechanically milled Si and SiO₂ powders. *Physical Review B* [online]. 1997, vol. 55, no. 12, pp. 7615-7623. ISSN 0163-1829, 1095-3795. Available from: <https://doi.org/10.1103/PhysRevB.55.7615>
- [10] SAKURAI, Yuryo; Kaya NAGASAWA; Hiroyuki NISHIKAWA a Yoshimichi OHKI. Point defects in high purity silica induced by high-dose gamma irradiation. *Journal of Applied Physics* [online]. 1994, vol. 75, no. 3, pp. 1372-1377. ISSN 0021-8979, 1089-7550. Available from: <https://doi.org/10.1063/1.356999>

- [11] DONALD, I. W. Methods for improving the mechanical properties of oxide glasses. *Journal of Materials Science* [online]. 1989, vol. 24, no. 12, pp. 4177-4208. ISSN 0022-2461, 1573-4803. Available from: <https://doi.org/10.1007/BF00544488>
- [12] LI, Da; Min XIONG; Song WANG; Xi CHEN; Shen WANG a Qiang ZENG. Effects of low-temperature plasma treatment on wettability of glass surface: Molecular dynamic simulation and experimental study. *Applied Surface Science* [online]. 2020, vol. 503, 144257. ISSN 01694332. Available from: <https://doi.org/10.1016/j.apsusc.2019.144257>
- [13] PREUSSER, Frank; Makaiko L. CHITHAMBO; Thomas GÖTTE; Marco MARTINI; Karl RAMSEYER; Emmanuel J. SENDEZERA; George J. SUSINO a Ann G. WINTLE. Quartz as a natural luminescence dosimeter. *Earth-Science Reviews* [online]. 2009, vol. 97, no. 1-4, pp. 184-214. ISSN 00128252. Available from: <https://doi.org/10.1016/j.earscirev.2009.09.006>
- [14] SKUJA, L.; B. GÜTTLER; D. SCHIEL a A. R. SILIN. Infrared photoluminescence of preexisting or irradiation-induced interstitial oxygen molecules in glassy SiO₂ and α -quartz. *Physical Review B* [online]. 1998, vol. 58, no. 21, pp. 14296-14304. ISSN 0163-1829, 1095-3795. Available from: <https://doi.org/10.1103/PhysRevB.58.14296>
- [15] LI, Peng; Tao YANG; Pengfei MA; Xiaojing FEI; Fan LI; Jiayuan YE a Peizhi ZHUANG. Luminous and bonding performance of self-luminescent cementitious coatings based on white cement and geopolymer. *Construction and Building Materials* [online]. 2023, vol. 362, 129814. ISSN 09500618. Available from: <https://doi.org/10.1016/j.conbuildmat.2022.129814>
- [16] HE, Bei; Yingli GAO; Liangchen QU; Kairui DUAN; Wenjuan ZHOU a Ganpeng PEI. Characteristics analysis of self-luminescent cement-based composite materials with self-cleaning effect. *Journal of Cleaner Production* [online]. 2019, vol. 225, pp. 1169-1183. ISSN 09596526. Available from: <https://doi.org/10.1016/j.jclepro.2019.03.291>
- [17] BASU, Sukumar, ed. *Crystalline Silicon - Properties and Uses* [online]. B.m.: InTech, 2011 [vid. 2023-10-11]. ISBN 978-953-307-587-7. Available from: <https://doi.org/10.5772/844>
- [18] REMEŠ, Zdeněk; Maksym BURYI; Jan PEJCHAL; Oleg BABČENKO; Štěpán REMEŠ; R. NOVÁK a Julia MIČOVÁ. The spectrally resolved photoluminescence decay in YAG:Er, ZnO and SiO₂ crystals. In: *32nd Joint Seminar Development of Materials Science in Research and Education: Journal of Physics: Conference Series*. 2023.
- [19] BABČENKO, Oleg; Zdeněk REMEŠ; Klára BERANOVÁ; Kateřina KOLÁŘOVÁ; Jan ČERMÁK; Alexander KROMKA; Zdeněk PROŠEK a Pavel TESÁREK. Characterization of different types of silica-based materials. In: *32nd Joint Seminar Development of Materials Science in Research and Education: Journal of Physics: Conference Series*. 2023.
- [20] GAWEŁ, Bartłomiej A.; Anna ULVENSØEN; Katarzyna ŁUKASZUK; Bjørnar ARSTAD; Astrid Marie F. MUGGERUD a Andreas ERBE. Structural evolution of water and hydroxyl groups during thermal, mechanical and chemical treatment of high purity natural quartz. *RSC Advances* [online]. 2020, vol. 10, no. 48, pp. 29018-29030. ISSN 2046-2069. Available from: <https://doi.org/10.1039/D0RA05798C>
- [21] CARTIER, E.; J. H. STATHIS a D. A. BUCHANAN. Passivation and depassivation of silicon dangling bonds at the Si/SiO₂ interface by atomic hydrogen. *Applied Physics Letters* [online]. 1993, vol. 63, no. 11, pp. 1510-1512. ISSN 0003-6951, 1077-3118. Available from: <https://doi.org/10.1063/1.110758>.
- [22] PELANT, Ivan a Jan VALENTA. *Luminescence spectroscopy of semiconductors*. Oxford: Oxford university press, 2012. ISBN 978-0-19-958833-6.