

Photoadsorption processes on the surface of silicon dioxide

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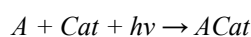
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The photoadsorption of O₂ on SiO₂ was investigated as a function of pre-treatment temperature varying from 200 to 1000 °C. The maximum photoadsorption activity was observed at a pre-treatment temperature of 800 °C. Photosorption activity is dependent on both intensity and wavelength of the incident light. The relationship between photoadsorption rate and wavelength follows a logarithmic trend. Dehydroxylation and dehydration of the silicon dioxide samples were studied using IR spectroscopy. It was found that UV irradiation leads to a decrease in the intensity of OH-group signals, while oxygen photoadsorption results in a partial restoration of surface hydroxyl groups.

Keywords: Photosorption, dehydroxylation, silicon dioxide, light intensity, IR spectra, pre-treatment temperature

INTRODUCTION

Photosorption is defined as: adsorption, typically chemisorption (a stoichiometric reaction of adsorbate molecules with a solid surface), initiated by light absorbed by either the adsorbate or the adsorbent [1]. This can be represented by the following equation [2]:



where A denotes adsorbate molecules, ACat represents photosorbed species.

Photoadsorption processes have been studied extensively over a long period (the earliest investigations into photosorption and photodesorption date back to the 1930s). However, a comprehensive understanding of all aspects in this field is still missing. Photosorption phenomena can serve as model systems for photocatalytic reactions, aiding in the study of more complex photocatalysis scenarios. Of particular interest, crucial for catalysis and related fields, are the mechanisms of catalytically active light energy absorption and energy transfer between the catalyst and adsorbed molecules.

Equally important is the physics of photoadsorption processes themselves, as the results obtained can be useful for understanding the mechanisms of phenomena occurring on the surface of semiconductors and dielectrics. For example, such phenomena include the photoconductivity of thin films (widely used in the electronics industry), spectral sensitization of the internal photoeffect in semiconductors, and so on [3-6].

Photoexcitation of wide band gap solids ($E_g > 3\text{eV}$) is inherently complex. In heterogeneous gas/solid systems, these processes often cannot be simplified to elementary interactions.

It is conventional to distinguish between photoelectrically active and photoelectrically inactive light absorption, depending on the generation of free charge carriers in the solid upon illumination (see, for example, [6]). Light quantum absorption can be associated with regular crystalline regions (fundamental or intrinsic absorption), as well as with crystal lattice imperfections, i.e., intrinsic and extrinsic lattice defects (see, for example, [5]).

Intrinsic defects include vacancies, interstitial atoms, and their aggregates (point or zero-dimensional defects).

Amorphous silicon dioxide (silica) is a crucial technological material widely employed in numerous applications [7-10]. Silica is predominantly associated with optoelectronic applications, such as optical fibers (OFs), and as a gate insulator in metal-oxide-semiconductor field-effect transistors (MOSFETs) [8]. In optical fibers, silica provides high transparency across a broad wavelength range, enabling light transmission over long distances with exceptional speed, stability, and, importantly, reliability. Silicon-based semiconductor technology has long relied on silica due to its large band gap [11, 12].

A review of the literature reveals widespread interest in photosorption phenomena, and research in this area remains highly relevant [16-20].

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RESULTS AND DISCUSSION

The sample was pre-treated as follows: initial annealing in air for 72 h with intermittent evacuation, followed by heating in oxygen at 400°C. Subsequently, prior to each experiment, the sample underwent heating in oxygen for one h at 400 °C and evacuation under vacuum for 30 min at a defined temperature. This pre-treatment protocol effectively removes traces of organic contaminants from the surface.

The pre-treatment temperature of SiO₂ varied from 200 to 1000°C. Before each experiment, the purity of the sample was checked using the method described above.

Our selection of pre-treatment temperatures was based on the following considerations: at 200°C, physically adsorbed water (hydrogen-bonded water) is removed from the SiO₂ surface, while at 400°C, coordination water is also eliminated. At 600-1000°C, the surface exhibits varying hydroxyl group densities. At 600 °C, hydrogen-bonded OH-groups are still present, whereas at higher temperatures only isolated OH-groups remain. Furthermore, at temperatures exceeding 600 °C, the effect of SiO₂ sintering becomes relevant, potentially reducing the specific surface area of the sample.

The experimental results of O₂ photoadsorption on SiO₂ are presented in Figures 1-6.

Oxygen photoadsorption on silicon dioxide occurs at all pre-treatment temperatures considered [13]. The initial photoadsorption rates, depending on the calcination temperature, can differ by 2-3 orders of magnitude (Fig. 1). Increasing the calcination temperature to 1000°C causes a sharp decrease (5-6 times) in the photo-adsorption rate compared to the previous temperature. Presumably, at this temperature and above, surface sintering becomes significant, possibly leading to a decrease in the specific surface area of SiO₂.

The observation of O₂ photoadsorption beyond the long-wavelength edge of the intrinsic absorption band suggests the presence of photosorption sites on silicon dioxide, activated by impurity absorption. The 'pre-irradiation memory effect' (Solonitsyn effect), characterized by gas adsorption upon admission to a pre-irradiated sample, was not observed on SiO₂. However, post-adsorption, a type of 'memory effect', is evident on SiO₂. Even after the illumination is turned off, adsorption continues briefly, indicating that the adsorbent 'remembers' the irradiation. In our experiments, this post-adsorption effect was observed only at $T_{pre} \geq 700^\circ\text{C}$. At this treatment temperature, the after-effect duration (τ) is

approximately 5 sec. Our findings indicate that τ increases proportionally to the pre-treatment temperature, is independent of the irradiation duration, and weakly dependent on the amount of pre-adsorbed oxygen. At $T_{pre} = 900^\circ\text{C}$, τ ranges from 1 to 1.5 min.

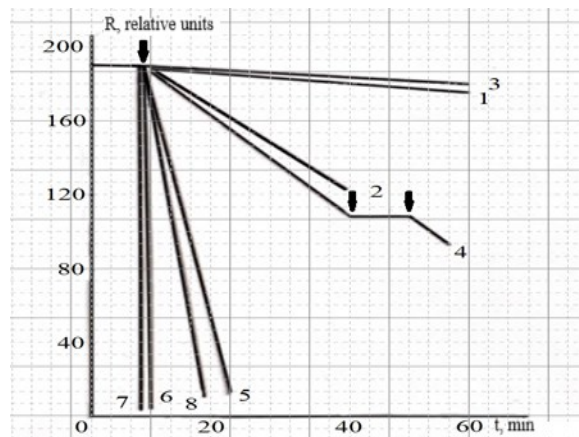


Figure 1. Kinetics of O₂ photoadsorption on SiO₂ at 1 – 400 °C, 2 – «dirty» sample, 3 – 500 °C, 4 – 600 °C, 5 – 700 °C, 6 – 800 °C, 7 – 900 °C, 8 – 1000 °C. The arrows indicate the moments of radiation exposure.

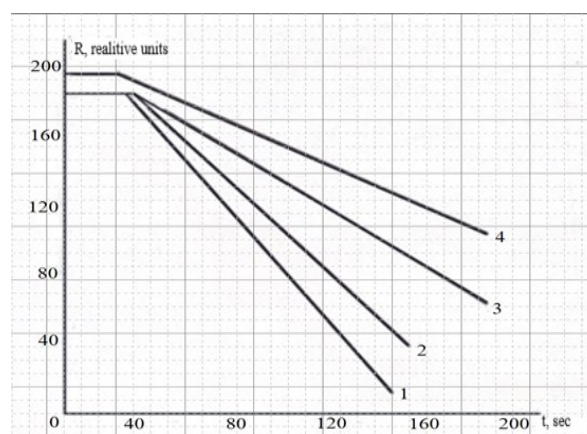


Figure 2. Kinetics of oxygen photoadsorption on SiO₂ at different UV radiation intensities. 1 - $I=I_0$, 2 - $I=0.89I_0$, 3 - $I=0.69I_0$, 4 - $I=0.39I_0$.

Figure 2 shows the kinetic curves (photobarograms) of O₂ photo-adsorption on SiO₂ ($T_{pre} = 900^\circ\text{C}$) at different intensities of light incident on the sample. Light intensity was varied by adjusting the distance between the light source and the sample. In the figure, the intensities are in the ratios of 1:0.78:0.63:0.35, while the photoadsorption rates are in the ratios of 1:0.83:0.56:0.36. As can be easily noticed, the photoadsorption rate has a linear dependence on the intensity of the incident light, indicating a single-photon nature of the photosorption process, at least in the initial section of the kinetics.

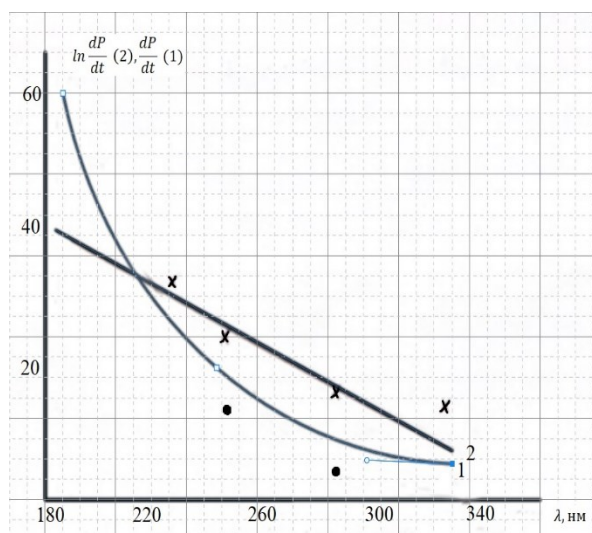


Figure 3. Spectral characteristics of O₂ photoadsorption on SiO₂ (T_{pre} = 1000 °C)

As seen in Figure 3, as λ decreases from 340 to 200 nm and below, the rate of photoadsorption increases by 2–3 orders of magnitude. The dependence of the initial rate on λ follows a pattern of the $\ln \frac{dP}{dt} \sim \frac{1}{\lambda}$ type (Figure 3, curve 2), meaning that as it approaches the intrinsic absorption region (bandgap width of SiO₂, E_g = 10 eV), the rate increases.

In the subsequent experiments, where adsorption processes in the SiO₂ – O₂ system under irradiation were investigated, manometric and spectrometric (IR and mass spectrometry) methods were employed. Photoadsorption processes in these systems were examined in relation to the pre-treatment of the adsorbents [14].

Figure 4 presents the IR spectrum of silica gel synthesized in the laboratory after thermal vacuum treatment for 6 h at different temperatures (25-800 °C). A distinctive spectral feature is a narrow, intense absorption band at 3750 cm⁻¹, superimposed by broader bands at 3665, 3580, and 3400 - 3300 cm⁻¹ on the lower frequency side. The intensity of these broader bands is strongly dependent on the degree of hydroxylation of the samples (103, 105, 107). The 3750 cm⁻¹ band is attributed to isolated, non-interacting OH - groups. Its intensity decreases more gradually with increasing sample pre-treatment temperature in vacuum (T = 300 °C). In the region of Si-OH deformation vibrations, a broad band appears at 790-870 cm⁻¹, narrowing with increasing treatment temperature. The intensity of the 3665 cm⁻¹ band significantly weakens with increasing temperature from 300-400 °C and completely disappears at 520-620 °C. This band is generally

assigned to hydrogen-bonded OH-groups [8]. An absorption band at 3580 cm⁻¹ is also observed in the IR spectra, with its intensity starting to diminish noticeably after sample evacuation at 300-350 °C. Complete disappearance occurs at 400-450 °C. Several interpretations exist for this band's assignment. However, its appearance is observed subsequent to the emergence of the 3665 cm⁻¹ absorption band associated with hydrogen-bonded OH-groups. Therefore, it can be inferred that the 3580 cm⁻¹ absorption band is due to water molecules adsorbed on surface hydrogen-bonded OH-groups.

In the frequency range of 3400–3300 cm⁻¹, a broad band is observed, attributed to the physical adsorption of water [7, 8].

Its intensity decreases upon evacuation even at room temperature, and it completely vanishes after heating with simultaneous evacuation at 150-200 °C.

The intensity of the band at 1627 cm⁻¹ decreases considerably upon evacuation up to 200 °C (Figure 4).

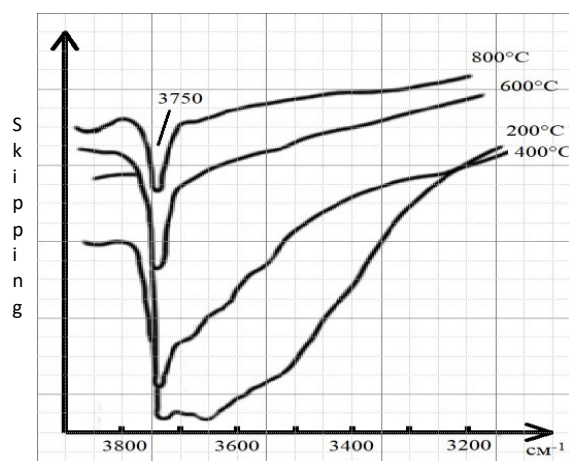


Figure 4. IR spectra of SiO₂. 1- T_{pre} = 200 °C, 2 - 400 °C, 3 - 600 °C, 4 - 800 °C

The effect of UV irradiation on SiO₂ is characterized by the appearance of new absorption bands, and a complex evolution of the hydroxyl coverage of silica gel.

The silica gel samples under investigation were subjected to thermal vacuum treatment at 200, 400, 600, and 800 °C for 6 h. Absorption spectra were recorded in the frequency range of 800-3800 cm⁻¹ after 1, 4, and 5 h of irradiation. Concurrently, the kinetics of oxygen photoadsorption on silicon dioxide was also monitored.

Selecting multiple pre-treatment temperatures anticipates that the photoadsorption process will occur on surfaces with varying degrees of dehydration across this broad temperature range. Samples treated at 600 and 800 °C contain only isolated hydroxyl groups on their surface (absorption band at 3750 cm⁻¹

¹) (Figures 5 and 6). Treatment at 400°C does not completely remove hydrogen-bonded OH-groups, hence absorption is still present in the 3300-3600 cm^{-1} region. The sample evacuated at 200 °C contains water in addition to these, and the concentration of isolated OH-groups is low due to screening by physically adsorbed water.

Introducing oxygen to a partial pressure of 7×10^{-2} mm Hg into the chamber containing the sample pre-treated at 200°C does not alter the spectral profile. After one h of UV irradiation, absorption bands at 1470 and 1520 cm^{-1} appear, along with a slight decrease in the intensity of the isolated OH-group absorption band. In the water deformation vibration region, a band at 1627 cm^{-1} emerges. With further irradiation for 4 h, the 3750 cm^{-1} absorption band continues to decrease, while a band at 3665 cm^{-1} appears on the lower frequency side, indicative of hydrogen-bonded OH-group formation. Bands at 1470, 1520, and 1700 cm^{-1} remain unchanged.

The absorption spectra of the SiO₂ sample pre-treated at 400 °C reveal a complex nature of the photosorption process. In addition to absorption bands at 1470, 1520, and 1700 cm^{-1} , bands appear in the 3600-3700 cm^{-1} range, and a weak peak emerges at 1720 cm^{-1} in the water deformation vibration region. Initially, irradiation leads to an increase in the 3750 cm^{-1} band, followed by a decrease upon prolonged irradiation.

A similar pattern is observed when investigating photosorption on samples treated at 600 °C. This variation in OH-group concentration suggests the possibility of not only a radical adsorption mechanism for oxygen, involving photosorption of hydroxyl groups and formation of free radicals as adsorption sites for oxygen, but also an alternative process. This alternative could be the oxidation of residual organic contaminants, accompanied by water formation and subsequent dissociation. Likely, the simultaneous occurrence of these two processes with different kinetics leads to the observed trend in the OH-group concentration curve.

On the sample treated at 800 °C, the OH-group intensity also exhibits a change following a curve with a maximum. Even upon oxygen introduction, weak peaks at 1470, 1520, 1627, and 1700 cm^{-1} are observed. After one hour of irradiation, the intensity of the 1470 and 1520 cm^{-1} peaks increases, a weak peak at 1720 cm^{-1} appears, and the intensity of the OH-group absorption band diminishes. A band at 3680 cm^{-1} emerges on the shorter wavelength side (hydrogen-bonded OH-groups). The intensity of absorption bands at 1700, 1720, 1450, and 1520 cm^{-1} increases. Following another hour of irradiation, the OH-group intensity further increases, water

becomes more pronounced (1627 cm^{-1}), and an absorption band at 3580 cm^{-1} appears in the stretching vibration region. Subsequent two-hour irradiation results in a decrease in OH-group intensity.

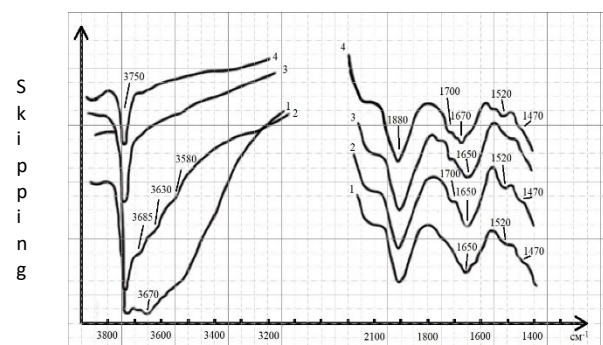


Figure 5. IR spectra of SiO₂ containing photosorbed oxygen. 1- $T_{\text{pre}} = 200$ °C, 2 - 400 °C, 3 - 600 °C, 4 - 800 °C

To further elucidate the role of residual organic impurities in oxygen photosorption, the silica gel sample was subjected to a specific cleaning procedure. This involved sequential annealing at 600 °C in oxygen followed by evacuation at the same temperature for 30-40 min. This cycle was repeated 5-6 times, followed by a three-hour evacuation, and then the sample spectrum was recorded. Unfortunately, this rigorous treatment did not resolve the issue, as absorption bands at 1470, 1520, and 1700 cm^{-1} were already present in the initial spectrum of the treated sample. These bands are typically observed in simply vacuum-treated samples only after oxygen admission and subsequent irradiation. The oxygen adsorption rate on the sample treated at 600 °C in oxygen was lower compared to the sample subjected to simple vacuum pre-treatment. This suggests that the sample is likely saturated with oxygen during the treatment process itself. Hydroxyl groups also exhibit different behavior. First, the 3750 cm^{-1} absorption band displays a shoulder on the lower wavelength side. Second, the intensity of this band remains nearly constant for up to nine h of irradiation. After 9 h of UV exposure, the intensity of the 3750 cm^{-1} band decreases by approximately 30%.

With UV irradiation of SiO₂ in the presence of oxygen, our experiments demonstrated intense oxygen adsorption, which is irreversible at room temperature. The photosorption rate, the maximum amount of photosorbed oxygen, and the reverse desorption effect are dependent on the sample pre-treatment temperature, light intensity, experimental temperature, surface cleaning conditions, and other factors that are not always controlled.

wavelength edge of intrinsic absorption. Our data on the action spectrum of oxygen photosorption on SiO₂ demonstrate that photosorption is possible at certain pre-treatment temperatures (above 873 K) and beyond the intrinsic absorption region. This implies that impurity absorption or absorption by crystal lattice defects is also active.

CONCLUSION

The photoadsorption of oxygen on silicon dioxide is dependent on the pre-treatment temperature, reaching a maximum at 800°C.

The spectral dependence of O₂ photoadsorption on SiO₂ follows a logarithmic function. The photoadsorption rate exhibits an inverse relationship with light intensity.

Strained siloxane bridges and impurity atoms can act as photosorption centers. Photooxidation processes may also occur.

The binding energy of adsorbed molecules is influenced by the adsorbent pre-treatment temperature. Higher pre-treatment temperatures result in higher thermal stability of adsorbed molecules. For samples treated at 1173 K, adsorbed oxygen molecules remain stable up to 773 K and above. In contrast, for pre-treatment temperatures of 673–873 K, the surface is typically completely desorbed at significantly lower temperatures (473–673 K).

Regarding the 'memory effect' on SiO₂, our experiments only revealed the post-irradiation effect, which was also dependent on the pre-treatment temperature (increasing with temperature).

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