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Chemical Modification of a Porous Silicon Surface Induced by Nitrogen Dioxide Adsorption

Constantine S. Sharov,* Elizaveta A. Konstantinova, Lyubov A. Osminkina,
Victor Yu. Timoshenko, and Pavel K. Kashkarov

M. V. Lomonosov Moscow State University, Physics Faculty, Leninskie Gory, Moscow, 119992 Russia

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The effect of gaseous and liquid nitrogen dioxide on the composition and electronic properties of porous silicon (PS) is investigated by means of optical spectroscopy and electron paramagnetic resonance. It is detected that the interaction process is weak and strong forms of chemisorption on the PS surface, and the process may be regarded as an actual chemical reaction between PS and NO₂. It is found that NO₂ adsorption consists in forming different surface nitrogen-containing molecular groups and dangling bonds of Si atoms (P_b-centers) as well as in oxidizing and hydrating the PS surface. Also observed are the formation of ionic complexes of P_b-centers with NO₂ molecules and the generation of free charge carriers (holes) in the volume of silicon nanocrystals forming PS.

1. Introduction

Porous silicon (PS) consisting of silicon nanocrystals is a very fascinating and a good prospect for investigation. It was initially obtained in 1956 but still remains under researchers' close attention.^{1,2} The rapid development of the hi-tech industry during the past decade caused some novel requirements for semiconductor chips, the main one being to decrease the structure size down to hundreds, even dozens, of nanometers. PS does possess excellent properties to meet these requirements.³ The principal ability for PS to be used for microelectronic devices has been repeatedly outlined.^{2–5} But the low stability of PS in the air and the consequent rapid degradation of its physicochemical properties prevent it from being used as a construction material for optoelectronic devices.

Another useful feature of PS lies in the fact that it is a unique porous adsorbent due to its huge and nonhomogeneous surface equal to $\sim 1000 \text{ m}^2/\text{g}$.⁶ Equilibrium charge carriers in great amounts (10^{17} – 10^{19} cm^{-3}) were recently found in PS. Their concentration is sensitive to surface coverage of PS and molecular ambience of silicon nanocrystals.² This property arises from the fact that a large part of silicon atoms in a silicon nanocrystal (up to a third) is situated on its surface.² Therefore PS can serve as a material for a wide spectrum of sensors including ecological ones and model devices for investigating fundamental properties of adsorption processes.⁷

The enormous PS surface area results in a very large affinity for a great number of comparatively active substances and, in turn, opens up wide prospects for constructing sensitive and selective sensors of a new generation for those substances. There are compounds whose adsorption on PS from the gaseous phase is actively investigated, for example, oxygen, water, ethanol, tetracyanoethylene,⁸ methanol,⁹ ammonia,¹⁰ and O,N-containing amino acid derivatives.¹¹ Surely, nitrogen dioxide is much less studied,¹² for the most part thanks to the complexity of processes in silicon nanocrystals occurring on its adsorption. If one suggests a sensor for a definite compound, close attention should be paid to the development of a surface coating for PS stable both in air and in the atmosphere of the compound in question.

So far as nitrogen dioxide is concerned, in addition to a fundamental interest, there is an applied one which is of great practical importance. As a matter of fact, NO₂ is a very poisonous substance that is always present in the environment of large cities, in industry districts, and near car highways and railways because of plant furnace emissions and motor gases. So, the invention of a sensor for NO₂ would be an excellent challenge to the unique PS properties, taking into account the urgency of the problem.

In our work, we touched upon the essence of the modification of the chemical structure of the PS surface caused by NO₂ adsorption, a problem which unfortunately has not attracted scientists' attention thus far. It was a complex of FTIR, EPR, and UV–vis techniques that provided us an opportunity to clarify the processes occurring in silicon nanocrystals volume and on their surface under NO₂ adsorption.

2. Experimental Details

The standard means that most investigators usually follow was used to obtain PS samples, that is, the electrochemical anodic etching of crystal silicon wafers in hydrofluoric acid (HF) ethanolic solution (see, for instance, ref 13 and references therein). Initial crystal silicon substrates of p^+ -type (doped with boron) with surface orientation (1 0 0), doping level $p = 5 \times 10^{18} \text{ cm}^{-3}$, and electrical resistivity $\rho = 15 \text{ m}\Omega \text{ cm}$ commonly employed for fabricating mesoporous silicon consisting of silicon nanocrystals of up to 50 nm in dimension¹⁴ were used. The electrolyte content was HF (48 vol %)/C₂H₅OH (96 vol %) = 1:1. Current density was maintained at 50 and 100 mA cm^{-2} and etching time was 20 min, with the experimental conditions resulting in obtaining silicon nanocrystals of 7–9 (for 50 mA cm^{-2}), and 3–5 nm (for 100 mA cm^{-2}) in dimension.^{15,16} The former is denoted by PS-1, and the latter is represented by PS-2. Free-standing PS films were lifted from the crystal silicon substrate by a short (1–3 s) current pulse of 800 mA cm^{-2} . We avoided rinsing the samples in water after the synthesis lest they should be drastically hydrated and oxidized and hence should complicate treating the spectra obtained. Porosity of free-standing films measured gravimetrically was approximately 50 and 72%, thickness determined by

* Corresponding author. Phone/fax: +7 (095) 304-2522. E-mail: const@proxima.idb.ac.ru.

As far as N_2O_4 is concerned, we see not only the band described above (Figure 1a, curve 2), but also another N–O stretching mode exhibiting its characteristic maximum near 1270 cm^{-1} . Although wavenumbers of the modes in N_2O_4 involved are a little bit different from those supposed typical for N–O vibration in the nitrogen dioxide dimer, namely 1748 and 1262 cm^{-1} ,^{17,18} it could be explained by adsorption surface effects already known for a long time^{19,20} that may shift bands by up to several decades of reverse centimeters.

PS-2 samples also adsorb nitrogen dioxide in the form of N_2O_4 that is pointed out by apparent slopes at $1750\text{--}1770\text{ cm}^{-1}$. Still, the concentration of N_2O_4 is much lower than that of other nitrogen-containing compounds on the PS surface, even if we ignore the spectral sensitivity to the compounds. Also N_2O_4 is completely desorbed on pumping and in the atmosphere in about 1 day after NO_2 adsorption, so it does not play a substantial long-range role in the processes that take place in silicon nanocrystal ensembles. In summary, we should emphasize that monomeric NO_2 is not adsorbed on the PS surface. Therefore, one should conclude that the heat of either N_2O_4 or NO_2 adsorption on PS does not exceed the energy of a N–N bond in a dimeric N_2O_4 molecule equaling $57.43 \pm 0.04\text{ kJ mol}^{-1}$ ^{21,22} and believed low as compared to a many other gaseous substances (commonly hundreds and thousands of the units concerned). We can scarcely accept quite dissimilar values of adsorption enthalpy suggested by other authors²³ only on the basis of theoretical calculations performed within the limits of cluster analysis. Thus, the heat of nitrogen dioxide adsorption on PS in either form is relatively low, and this fact will prevent it from physisorbing on PS in large amounts and will aid it in causing different surface transformations which are of chemical origin.

Finally, unlike PS-1 samples, those of PS-2 demonstrate the presence of two other surface substances. First, one can see a wide band at 1418 cm^{-1} and another detected not so well at 1340 cm^{-1} on the slope of silicon nitrate peak which are characteristic for N–O stretching modes in covalent *cis*-nitroso silicon. Most of the nitroso compounds tend to dimerize extensively, especially when solidified,¹⁸ and PS is not an exception. The bands ascribed precisely to *cis*-forms of nitroso dimers are not accompanied by any spectral lines related to *trans*-forms, so it is a characteristic feature of PS as a substrate. Second, for a longer time of the NO_2 exposition, a narrow maximum appears at 1255 cm^{-1} assigned to silicon N-oxide.¹⁷ On the whole, this compound is similar to the nitroso dimer in structure but contains only one N–O bond, while the other is reduced.

In addition to forming nitrogen-containing surface compounds, nitrogen dioxide is shown to oxidize PS heavily and that is indicated by a strongly dominating wide band at $1050\text{--}1160\text{ cm}^{-1}$ coming into being owing to different SiO_x stretching modes (Figure 1a,b) and by shifting Si-H_x stretching vibration bands from $2090\text{--}2140\text{ cm}^{-1}$ to $2130\text{--}2260\text{ cm}^{-1}$ resulting from oxidizing back-bonds in Si-H_x groups (Figure 1). Silicon oxide is hydrophilic, consequently a noticeable amount of water is being gradually adsorbed on the PS surface during NO_2 adsorption confirmed by an incredible growth of O–H stretching modes bands both in a H_2O molecule and in a Si-OH group within the range $3215\text{--}3700\text{ cm}^{-1}$. Thus, high values of wavenumbers may be referred to the effect of the hydrogen bonds²¹ terminating the PS surface.

The overall quantity of the oxide and water increases with an increase in NO_2 pressure and in the time of adsorption. Nitrogen dioxide interacted with PS, and it becomes PS surface

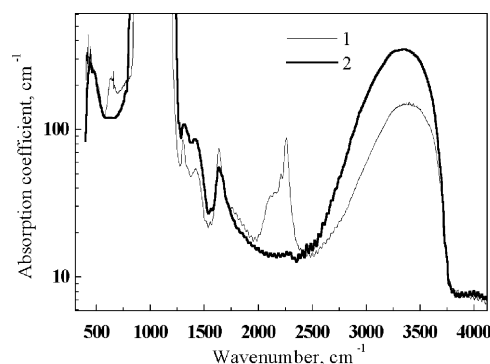
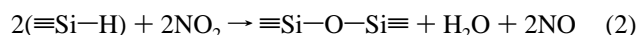


Figure 2. Typical IR absorption spectra of PS-2 samples subjected to gaseous (1) and liquid (2) nitrogen dioxide adsorption. The time of exposure 100 min.

oxidized and hydrated, as the spectra show. The degrees of PS oxidation and hydration under interaction with NO_2 in the air exceed that in a vacuum by several times. As for oxidation, it should be accounted for by the combined action of NO_2 and atmospheric oxygen, the latter aiding in oxidizing the surface to a great extent. Nitrogen dioxide destroys many Si–Si bonds and creates the doubled number of surface defects, which is to be described in detail a bit later. Those defects are formed and oxygen immediately reacts with them, resulting in the formation of silicon oxide. Regarding water, there should be different mechanisms of its adsorption in a vacuum and in the atmosphere. Discussing experiments in a vacuum on PS-1 samples, as NO_2 is dried over phosphoric anhydride it does not contain water vapor, so what is the source of water? The answer will be the following reaction affirmed by the change in area of Si–H_x and H_2O bands:



This is an oversimplified version of the actual process, because the real equation would include the formation of nonstoichiometric substances on the PS surface. The amount of atmospheric water vapor which hydrates silicon oxide formed on the surface is obviously much more than that if water is a product of hydrogenated covering oxidation according to eq 2. The increase in the O–H absorption band at $3400\text{--}3800\text{ cm}^{-1}$ was also observed in the adsorption experiments with the evacuated samples.

3.2. Interaction between PS and Liquid Nitrogen Dioxide.

Figure 2 demonstrates the resemblance and the difference between the influence of gaseous and liquid NO_2 upon the PS surface.

We see that liquid nitrogen dioxide adsorption involves a few effects other than those arising from gaseous substance adsorption. The most important of them is the absolute absence of hydrogen-containing groups on the surface of silicon nanocrystals despite the fact that they are present in the initial PS-2 sample. The explanation consists of kinetic and thermodynamic reasons. The first is that the concentration of NO_2 in the liquid phase is beyond the comparison with that in gaseous phase; consequently, the process described by eq 2 proceeds with much higher rates. The second is that liquid NO_2 possesses a very high affinity for water, thanks to indefinite water solubility in liquid NO_2 ¹⁸ which leads to instantaneous and complete removal of water from the scope of the reaction (eq 2). As a result of this, the reaction equilibrium constant is raised according to Le Chatelier's principle.

The amount of oxide and water adsorbed on it is approximately 3 times more in the samples subjected to liquid

TABLE 1: Nitrogen Containing Compounds Appearing on Nitrogen Dioxide Adsorption Upon PS Surface

Compound	Molecular structure	Structure symmetry	Type of N-O stretching vibration	Wavenumber, cm ⁻¹		Presence in	
				in the present paper	in literature ^{17,18}	PS-1	PS-2
Covalent Si <i>cis</i> -nitrite		C _s	A'	1620-1630	1610-1621	+	+
Covalent Si <i>trans</i> -nitrite			A''	1680-1685	1650-1680	+	+
Covalent Si nitrate		C _s	A'	1288, 1302	1250-1290	+	+
			A''	1631-1638	1610-1650		
Si <i>cis</i> -nitroso dimer		C _{2v}	A'	1340	1370-1410	-	+
			A''	1418	1405-1435		
Nitrogen dioxide dimer		D _{2h}	B _{2u}	1730, 1750-1770	1748	+	+
			B _{3u}	1270	1262		
Si N-oxide		C _s	A'	1255	1230-1320	-	+

NO₂ adsorption than that in the samples exposed to gaseous substance. The sets of nitrogen-containing molecular groups arising from liquid and gaseous NO₂ adsorption are for the most part alike. To mention but one exception, nitrogen dioxide in the gaseous phase does not always give rise to N-oxide appearance, though it is the case rather often; however, if it is present in liquid phase, NO₂ does not lead to synthesizing N-oxide ever.

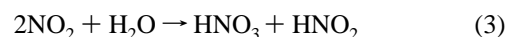
3.3. Generalization of the Interaction Processes. In summary, on the whole, liquid NO₂ adsorption on PS does not result in any principally different mechanisms of PS surface modification dissimilar with the gas adsorption. Even nitrogen dioxide dimer N₂O₄ is not adsorbed on the surface from the liquid phase in larger amounts than from the gaseous phase, although the liquid particularly consists of the dimer (99.95 mol % of N₂O₄ at 0 °C^{21,22}). We suggest that this fact should be accounted for by the disregarding affinity of the PS surface for liquid nitrogen dioxide. PS is relatively unpolar, with dielectric constant ϵ assumed to equal that of monocrystalline silicon, namely, 11.9.²⁴ Therefore, very polar liquid NO₂ with $\epsilon > 300$ ¹⁷ does not tend toward adsorption on the unpolar surface.

If we summarize all pieces of information in Table 1, we will be in a position to consider the point on the whole.

To comment on the processes taking place in PS upon NO₂ adsorption, let us divide the discussion into several subchapters in accordance with the types of the compounds synthesized.

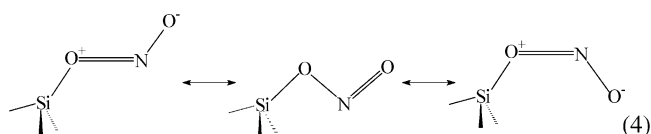
3.3.1. What Substance Oxidizes a PS Surface? The question arises: if adsorbed water is present on the surface in large

amounts, may it be possible that NO₂ reacts with it, giving nitric acid as a result of the reaction



and, in turn, that nitric acid oxidizes silicon atoms as an actual oxidizing agent? PS samples were treated by a mixture of NO₂ and water vapor in stoichiometric amounts as shown in eq 3, and we found that the oxidation degree does not depend on water content in the adsorbate. It is the direct oxidation of PS by NO₂ rather than by HNO₃ that occurs on the surface, because the degrees of oxidation by the mixture involved and by pure NO₂ are equal.

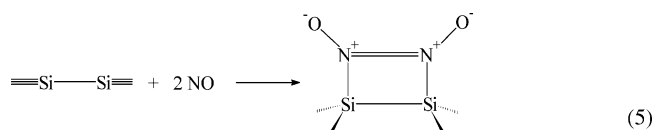
3.3.2. Silicon Nitrite. It seems strange from the first glance that covalent nitrites are present in PS principally in *trans*-forms. Whatever substrate R in R-ONO compound to which nitrite group is bonded may be chosen, this is generally not the case and the quantities of the isomers are comparable. It is probable that the reason for this lies in the following. Although nitrites are represented in Table as though they contained charged oxygen atoms, one is to comprehend that there is a resonance equilibrium:



One quasioptical isomer containing $\text{N}=\text{O}^+$ group undergoes the transformation into the other within a femtosecond scale,¹⁷ hence the equilibric concentrations of the isomers are equal if no factors shifting the equilibrium are present. Regarding PS, there is a tendency to *trans*-isomer in eq 4 since silicon dangling bonds repel O^- ion from the surface by local Coulomb fields.

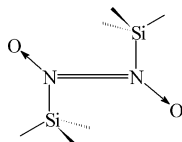
3.3.3. Silicon Nitrate. Silicon nitrate is present in either type PS samples in large amounts. Nitrogen atom is oxidized to oxidation number +5. It is a consideration to admit the possibility for NO_2 to be oxidized near the surface with the help of the catalytic activity of PS. The reaction of direct NO_2 oxidation by oxygen is prohibited thermodynamically.²⁵ Even though it were enabled, it would never lead to covalent silicon nitrate but only to nitrate ion, so the question is: what is the source of oxygen atom taking an electron from NO_2 and making the oxidation state of nitrogen equal to +5? The answer will be evident from the mechanism of the interacting NO_2 with PS about to be discussed.

3.3.4. Nitroso Silicon. Nitroso silicon is dimerized with the simultaneous transformation of the double $\text{N}=\text{O}$ bonds to donor–acceptor N^+-O^- bonds when it reacts with Si–Si surface bonds:



We may expect that the formation of such a substance proceeds in a few stages and the reaction shown in eq 5 follows the interaction of PS with nitrogen dioxide. Otherwise we have a process of the third order which is almost impossible. As contrasted to silicon nitrate, discussed in the previous subsection in which the nitrogen atom is oxidized, in nitroso silicon the nitrogen is reduced to oxidation number +2. Thus, the fact that contraveral processes take place on the PS surface can be stated even not considering the details.

Trans-isomers of nitroso silicon dimers are absent on the surface, and it is not unexplainable. NO_2 molecules attack surface silicon atoms situated on one side of a pore. The morphology of pores is not suitable for *trans*-modifications



synthesized on pore borders, wherever the attack may take place, perhaps with only one exception—the pore bottom. But even if they were formed there, the overall amount of *trans*-dimers can be ignored.

3.3.5. Silicon N-Oxide. In this compound, the oxidation state of the nitrogen atom is +1, and N-oxide is shown to represent an extreme degree of reducing nitrogen in nitrogen-containing molecular groups found on the PS surface. Here we should search for a reducing agent removing one oxygen atom from the nitroso silicon dimer.

Nitroso silicon is synthesized only on the PS-2 surface, so is N-oxide. The presence of Si–Si bonds on the surface in PS-2 and its absence in PS-1 play the crucial role in it.

3.3.6. Free Charge Carriers. One observes not only spectral absorption maxima in Figures 1 and 2, but also a strong increase in absorbance with a decrease in wavenumbers. It is attributed to absorption of IR radiation by free charge carriers, theorizing

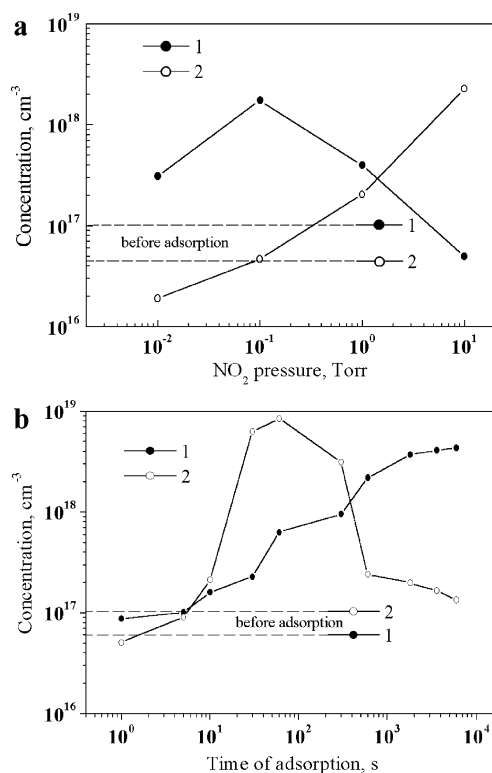


Figure 3. (a) The dependences of hole (1) and P_b -center (2) concentrations in PS-1 upon NO_2 pressure. Adsorption effected in a vacuum. (b) The dependences of hole (1) and P_b -center (2) concentrations in PS-1 upon the time of NO_2 adsorption. Adsorption effected in the air.

about PS-1 and PS-2 holes (Drude absorption). It is enhanced on NO_2 adsorption. Undeniable arguments in favor of existing pronounced Drude absorption in PS are described in ref 26. Once NO_2 is adsorbed from vacuum, hole concentration is dependent upon NO_2 pressure nonmonotonically with a maximum at 0.1 Torr²⁷ which is shown in Figure 3a. But if it is adsorbed from the air, hole concentration growth does possess monotonic character vs the time of adsorption (Figure 3b). The dependences are somewhat contrary concerning NO_2 pressure and time of exposure. The decrease in hole concentration toward high NO_2 pressures demands that surface defects should be taken into consideration.

3.3.7. Paramagnetic Defects in PS. There is a large amount of paramagnetic defects of crystal lattice in PS resulting from uncompensated bonds of silicon atoms which are generally referred to as P_b -centers. Different types of P_b -centers are described in detail in refs 28–32, and they are dissimilar primarily in the number of back-bonded oxygen atoms, symmetry, and charge. As for our research, the main components values of the g -tensor (orthorhombically symmetric $g_1 = 2.0098 \pm 0.0005$, $g_2 = 2.0061 \pm 0.0005$, and $g_3 = 2.0018 \pm 0.0005$) in EPR spectra lead these defects to be regarded as dangling bonds of silicon atoms situated at silicon/silicon oxide interfaces, or P_b -centers.^{30,31} EPR spectra of PS-2 samples subjected to different times of NO_2 adsorption are presented in Figure 4.

The concentration of P_b -centers can be calculated by double integrating the spectra and comparing the result with the etalon. The dependence of P_b -center concentration on the time of NO_2 adsorption is demonstrated in Figure 3.

We have noticed²⁷ that the P_b -center concentration is enhanced with an increase in NO_2 pressure monotonically as contrasted to nonmonotonic dependence of hole concentration and suggested that it should be accounted for by capturing holes

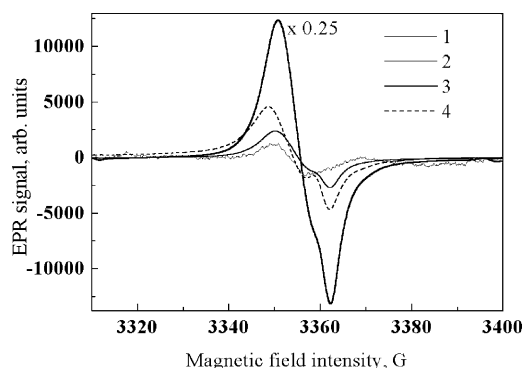


Figure 4. EPR spectra of PS-2. An as-prepared sample (1), samples subjected to NO₂ adsorption with the time of adsorption 10 s (2), 1 min (3), and 10 min (4).

to P_b-centers, passivating P_b-centers by NO₂, and consequent releasing holes by such passivation. In the presence of atmospheric oxygen, this is not the case and another oxidation mechanism is present. A decrease of P_b-center concentration is detected at short times of PS exposure in NO₂, small as it is. It is trapping electrons from P_b-centers by NO₂ molecules rather than forming new P_b-centers that prevails at this stage.

With an increase in adsorption time up to 1 min, trapping electrons and synthesizing new P_b-centers by NO₂ takes place which result in an increase both in hole and in P_b-center concentrations. Then the interaction of atmospheric oxygen with P_b-centers that gives rise to silicon oxide commences to dominate over the second process concerned, and the amount of P_b-centers reduces. Oxygen is less active than nitrogen dioxide, and the oxidation of surface defects does not start at once but only after a stage of induction.

Hole concentration in PS on NO₂ adsorption does not exceed that in the initial crystal silicon. Thus, there is a good reason to believe that in as-prepared PS most holes are captured by P_b-centers. Only when NO₂ interacts with P_b-centers do these centers finish trapping holes and instead release them.

3.3.8. On the Question of Other Compounds Which Are Expected to Be Present on the PS Surface. Let us consider the supposed possibility of some other compounds present on the PS surface. First of all, it is difficult to understand a reason why NO₂⁻ anions bands are not distinctly seen in IR spectra, and this obstacle has already attracted investigators' attention.²⁶ The response of silicon nanocrystals electronic properties (Figure 3) is essential, and nitrite anions are unlikely to be present on the surface, and even if present, they are present in such small amounts that apparently they cannot be detected by the rather sensitive technique of IR spectroscopy. We can attribute this fact to the effect of suppressing molecular vibrations by strong Coulomb fields.^{19,20} When near the surface, an NO₂ molecule undergoes weakening oscillators' strength and the bands in IR spectra become less pronounced.

Further, it may be quite unclear why we do not observe any amount of nitro groups on PS surface. The NO₂ molecule is a free radical containing an unpaired electron at the 1b_{1u} molecular orbital that becomes clear from Figure 5. From the beginning, it seems probable that direct combination of the two electrons involved should take place. The first reason underlying the fact that it does not take place is the very large affinity of NO₂ for an electron. Quantum mechanical calculations show that for the NO₂ molecule to seize an electron is more preferable than to form a covalent bond with such a rather nonelectronegative atom such as silicon.³³ The second consists of the low binding energy of the nitro group when bonded to a σ -orbital substrate such as

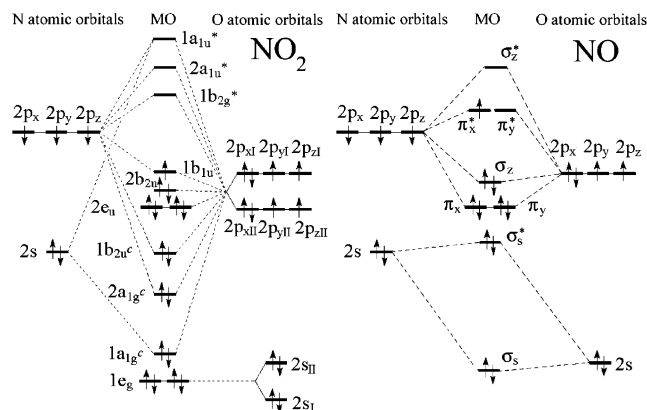


Figure 5. The diagram of NO₂ and NO molecular orbitals. Loosening orbitals are denoted by an asterisk. In triple centered NO₂ orbital system, connecting orbitals are designated by letter c, in double centered NO orbital system all nonloosening orbitals are connecting ones.

an sp^3 -hybridized P_b-center.¹⁷ If NO₂ were bound with a π -orbital one, for example benzene, the binding energy would be much greater thanks to a stabilizing -NO₂ group with π -bond structure by π -conjugation. Finally, the third consideration involves the free rotation of a nitro group around an R-N bond, where R is a substrate. The nitro group exhibiting C_{2v} symmetry generally possesses a very high rate of changing its conformations.³⁴ PS is characterized by considerable lack of surface uniformity and hence low symmetry of its fragments, and this free rotation is prevented or even prohibited by different sources of nonuniformity such as P_b-centers, silicon atoms terminated by hydrogen or hydroxyl radicals, oxygen atoms in $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ molecular groups, adsorbed water molecules, etc. All these reasons combined make the formation of a nitro group on the PS surface not very possible.

It is the oxidation number of the nitrogen atom +1 that is stated to represent the extreme degree of nitrogen reduction in nitrogen-containing molecular groups on the PS surface. Still, there is a slight possibility for the group with 0-oxidized nitrogen present to be present on the surface, namely, $\equiv\text{Si}-\text{N}=\text{N}-\text{Si}\equiv$. But even if it were present, this group could scarcely be detected by FTIR spectroscopy in PS as -N=N- stretching modes are within far IR range; to be more precise, their wavenumbers are less than 250 cm⁻¹,¹⁷ and in the presence of very strong Drude absorption in this range they cannot be observed distinctly.

3.4. Mechanism of the Interaction. It is desirable that the discussion of interacting NO₂ with PS should be divided into several parts, according to the nature of bonds formed between the substances in question.

3.4.1. van der Waals Interaction. For every substance in question approaching the PS surface, this type of binding always makes a definite contribution to adsorption, but this nonspecific interaction is the most essential for the N₂O₄ dimer adsorbed on the surface. As we have supposed above, the heat of N₂O₄ adsorption on PS is low and not enough for an N-N bond to be broken. There is an undisputable explanation for it. With N₂O₄ being on the whole not a dipole molecule (both of the $\cdot\text{NO}_2$ dipoles compensate each other), its dipole interaction with the surface (regarding half a molecule $\cdot\text{NO}_2$ bonded to silicon nanocrystals) is very weak. van der Waals interaction is one of the main factors resulting in physisorbing N₂O₄ on PS, while the hydrogen-bond effect is not realized for N₂O₄ nonexcited molecules.

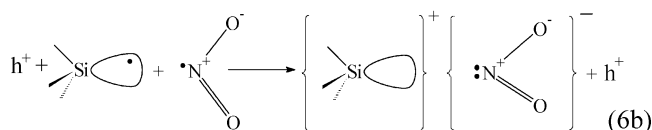
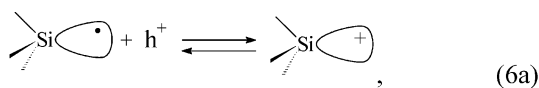
3.4.2. Hydrogen Bond Interaction. For example, water is adsorbed on silicon oxide primarily by strong hydrogen bonds

formed between an oxygen atom either in a $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ or in a $\equiv\text{Si}-\text{OH}$ group and protons in water molecules. The energy of such a hydrogen bond existing at a nanocrystal/gas interface is believed to be extremely strong and to equal about $100\text{--}150\text{ kJ mol}^{-1}$, while the energy of van der Waals binding water with a solid substrate commonly do not exceed 15 kJ mol^{-1} .^{33,34} Also, hydrogen-bond formation can be confirmed experimentally by shifting bands of vibrations taking part in it toward lower wavenumbers. It arises from diminishing energy constants of bonds. As to most of the substances considered, their bonding to the surface by a hydrogen bond is physisorption, but concerning water it is weak chemisorption taking into account high values of binding energy.

3.4.3. Ionic Interaction. Both ionic and covalent NO_2 interacting with PS are preceded by breaking the N–N bond in a N_2O_4 molecule which leads to two NO_2 molecules being virtually free radicals. In general, any exothermic physicochemical process giving an energetical profit which exceeds the N–N binding energy in the nitrogen dioxide dimer may occur.

Nitrogen dioxide contains one unpaired electron at the odd $1b_{1u}$ triple centered orbital (Figure 5) which is neither a connecting nor a loosening one. In other words, the energy of this orbital is halfway between that of beneficial low states and that of disadvantageous high ones. On the one hand, this orbital is not loosening and it gives rise to capturing another electron from a P_b -center and coupling it with its own electron, or ionic interaction. On the other hand, this orbital is not connecting, and it results in high chemical activity of NO_2 , or covalent interaction.

Considering the former case, there is an electron transfer e^- (sp^3 in Si) $\rightarrow 1b_{1u}$ in NO_2 . The mechanism of the process involved consists of several steps:



Equation 6a describes the stage occurring before NO_2 adsorption, namely, the capture of a hole at the P_b -center, which is equivalent to injecting an electron into silicon nanocrystals. Still, this step is not indispensable, and there is a certain amount of noncharged P_b -centers in as-prepared PS. Their presence justifies the slight decrease in P_b -center concentration at low NO_2 pressures as well as at short time spans of adsorption (see section 3.3.7). When NO_2 approaches a P_b -center, the reverse process in eq 6a, namely, releasing a hole from a P_b -center, commences to prevail. The liberation of a hole will occur as a result of acceptor properties of NO_2 at the adsorption on a semiconductor surface and inductive effect of shifting electron density (see eq 6b).³³ The shift concerned is caused by NO_2 attracting electron density to the P_b -center through back-bonds of a silicon atom. The second step, summed up by eq 6b, is the virtual interaction of NO_2 with a P_b -center, enabled by partial overlap of molecular orbitals of a silicon atom and a NO_2 molecule. It is to emphasize that as a result of the three processes discussed, a free hole is immersed into silicon nanocrystals volume. This process is not direct, owing to the seizing of an electron from a P_b -center by NO_2 in an indirect way (by passivating a P_b -center by NO_2). If carrying a positive charge,

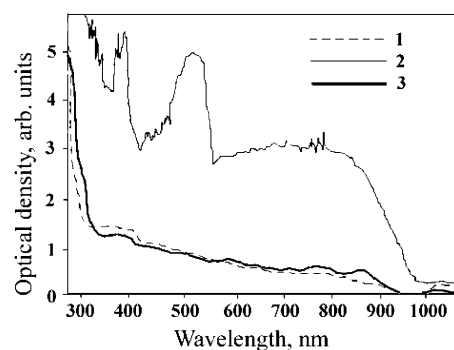


Figure 6. UV-vis spectra of diphenylamine solution without impurities (1), diphenylamine solution on adding $1.250 \times 10^{-8}\text{ M NaNO}_2$ (2), and the dispersion of 4.3 mg of PS in 4 mL of diphenylamine solution (3). Solvent: concentrated sulfuric acid. Diphenylamine concentration $5.882 \times 10^{-2}\text{ M}$. The detection limit of the procedure employed is approximately $2.5 \times 10^{-9}\text{ M}$, or $1.5 \times 10^{12}\text{ ions mL}^{-1}$.

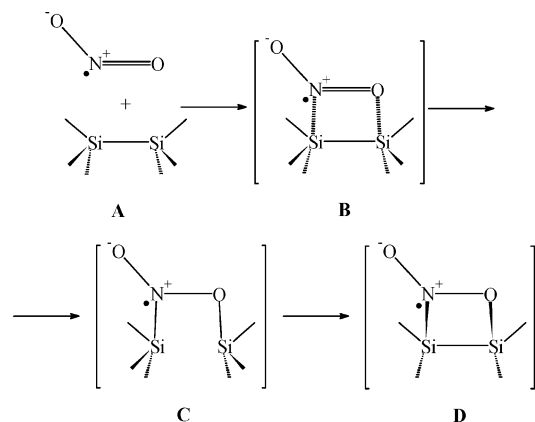
P_b -centers cease capturing holes and the hole concentration that is fixed experimentally grows.

The transfer of an electron is complete and the complex formed is exactly of ionic nature and exists only because of Coulomb attraction force. There may not be any other type bond between a P_b -center and an NO_2^- anion because (1) the P_b -center has an empty sp^3 -hybridized orbital and no electrons which may be liberated without breaking back-bonds with Si (O) atoms, and (2) the nitrite ion possesses no vacant non-loosening orbital.

It is essential that the values of ionic binding energy are between those of hydrogen-bond energy and the covalent bond energy, approximately within the interval $50\text{--}200\text{ kJ mol}^{-1}$.^{22,33} Ionic interaction does possess properties of chemisorption, that is, withstanding strong chemical attacks. If subjected to the action of strong concentrated nonoxidative acids, namely, sulfuric, phosphoric, perchloric, and hydrobromic acids, an ionic bond between PS and a nitrite anion is not broken and nitrite anions remain chemically nonactive. Figure 6 demonstrates a piece of experimental evidence for this statement by showing UV-vis spectra of the dispersion of PS with adsorbed NO_2 molecules in sulfuric acid with the addition of diphenylamine and etalon diphenylamine solutions. Colorless diphenylamine dissolved in concentrated sulfuric acid is oxidized by free nitrite anions to benzidinic violet dye whose even dilute solution possesses high values of optical density, thanks to the tremendous molar absorption coefficient of the dye $\alpha > 4 \times 10^8\text{ M}^{-1}\text{ cm}^{-1}$.²¹ In Figure 6, one can see that the spectrum of PS dispersion is similar to that of pure diphenylamine and differs drastically from that of benzidinic violet. Consequently, the amount of free nitrite anions in the dispersion is lower than the detection limit. They are firmly bonded to P_b -centers and not removed by sulfuric acid, and this is also the case for phosphoric, perchloric, and hydrobromic concentrated acids. This fact states that ionic interaction of PS with NO_2 is a form of chemisorption.

When PS samples are placed in a vacuum, nitrite anions return captured electrons to silicon nanocrystals and desorb from the surface on transforming back to NO_2 and, in turn, to N_2O_4 molecules, which is affirmed by a partial decrease in hole concentration. Pumping ensures an energetical benefit for NO_2^- to liberate an electron, and the process of desorption in the noncharged form (that was earlier forbidden) becomes possible. Thus, ionic interaction between NO_2 and PS should be considered as a form of weak chemisorption.

3.4.4. Covalent Interaction. This type of interaction of PS with NO_2 commences with the formation of an intermediate

SCHEME 1: Formation of the Intermediate Complex

state. Generally speaking, all nonprimitive chemical processes consisting of several stages pass through an intermediate state. This state is desynthesized almost instantaneously after coming into being; to be more exact, from atto- up to picoseconds, depending on the type of a process.³³ There is no reason to believe that the interaction between PS and NO_2 has another character. If we made the thorough analysis of all possible intermediate states, the four-centered N,O,Si,Si -containing intermediate complex (IC) would uncontroversially be the most justifiable. The double silicon fragment $\equiv\text{Si}-\text{Si}\equiv$ (DSF) is crucial for the interaction process to commence because hydrogen-terminated silicon atoms are comparatively inert for direct attacks. Scheme 1 aims at clarifying the formation of the intermediate state discussed.

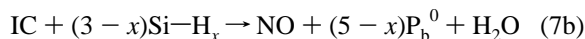
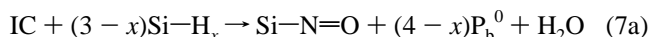
Step A is the approach of an NO_2 molecule to DSF, step B is the coordination of a NO_2 molecule by DSF, step C is the formation of a covalent bond between N, O, and the two silicon atoms in DSF, and step D is the closing of the four-centered cycle. The final step occurs for silicon atoms in DSF to have nearly tetrahedral surround. Complex C does not exist because of a structure that is too strained, resulting from unnatural valent angles for the silicon atom.³³

Two silicon atoms near DSF bonded to it before adsorption by broken bonds transform to P_b -centers. Complex D gives rise to the different number of P_b -centers which is dependent on final products. These P_b -centers may react with oxygen to become silicon oxide, or with water to transform to silicon hydroxide, or remain as P_b -centers. Further destiny of IC prodigious in reactivity depends on a substance interacting with it which becomes evident from Scheme 2.

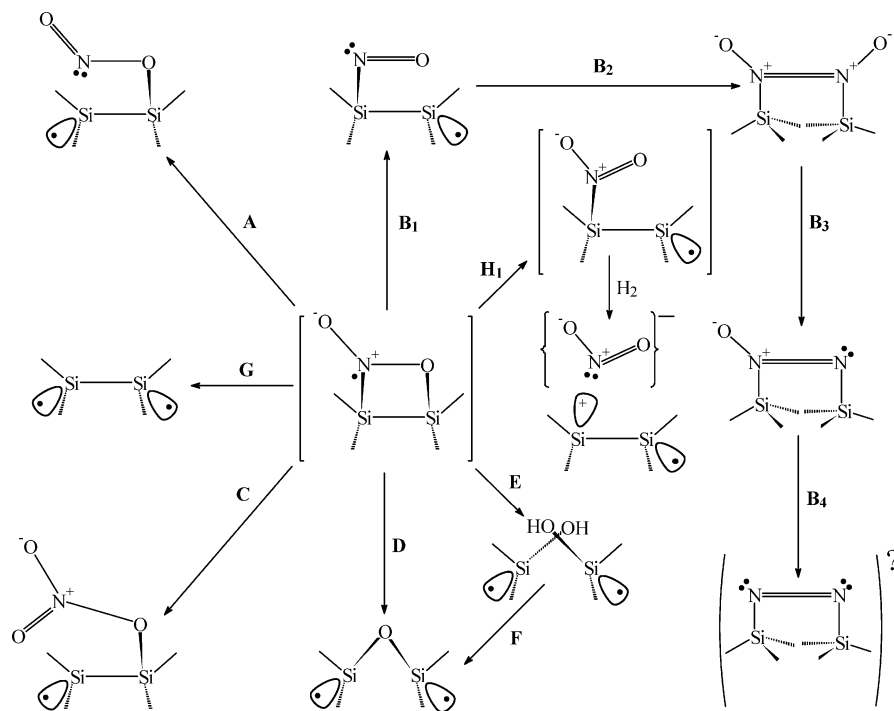
The processes involved should be explained. Most of them are made possible by heat—internal molecular energy transformation arising from the fact that IC is the target of free molecule attacks.

A. The formation of covalent silicon nitrite will happen if excessive energy is delocalized in a $\text{N}-\text{Si}$ bond in IC. After breaking the $\text{N}-\text{Si}$ bond, the oxygen atom terminating IC returns an electron ensured by the nitrogen atom in NO_2 to nitrogen and a double covalent bond between the atoms concerned is formed.

B₁. Nitroso silicon may be synthesized on the condition that the oxygen atom terminating IC is captured by strong reducing agents on the PS surface $-\text{Si}-\text{H}_x$ groups situated near IC. The interaction between hydrogen-terminated silicon atoms and IC probably proceeds along two different lines:



The latter will take place, if the excess of energy is too large for stable nitroso silicon to exist. The former will dominate, if the amount of energy to break the bonds is still not sufficient to destroy the whole IC. Also it highlights that eq 7b virtually reflects process G. Nitroso silicon can be synthesized by NO directly attacking the surface too. It is the case, because a NO molecule can break an ordinary covalent $\text{Si}-\text{Si}$ bond. It is explained primarily by the fact that it possesses an unpaired electron situated at a high-energy π_x^* loosening orbital (Figure 5).

SCHEME 2: Transforming the Intermediate Complex to Final Products

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