

Chemisorption of NO₂ at Boron Sites at the Surface of Nanostructured Mesoporous Silicon

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The interaction of NO₂ with mesoporous silicon (m-PS), obtained by the electrochemical etching of p⁺-type crystalline silicon in HF solutions, has the nature of adsorption on definite surface sites, involving most of the boron atoms present in the sample, brought to the surface by the etching mechanism. Adsorption brings about the release of hole carriers to the solid, which absorb in the IR according to the Drude model for a free-charge-carrier gas: this renders the phenomenon measurable, notwithstanding the very low concentration of surface sites. Adsorption follows a Langmuir isotherm; that is, the involved sites are apparently equal and noninteracting. This, as well as the insensitivity of IR modes of surface SiH_x species to the increase in carrier concentration, strongly indicates that the outermost layers of m-PS crystallites have an insulator behavior. Estimation of the enthalpy of adsorption suggests that a chemisorption process is involved: this is confirmed by the kinetics of desorption being lower than that of adsorption.

Introduction

Electrochemical etching in HF solutions of B-doped p⁺-type crystalline silicon (c-Si), with a boron content typically of the order of 10¹⁹–10²⁰ atoms cm⁻³, leads to porous systems with dendritic structure and specific surface areas up to 600 m² cm⁻³.¹ The properties of this mesoporous silicon (m-PS) have attracted much attention in the past decade in the realm of solid-state physics and electronics, in particular as concerns morphology and the very low electrical conductivity. The latter cannot be ascribed to any preferential removal of boron atoms during etching, because the ratio between boron and silicon in m-PS does not significantly change with respect to the substrate.^{2,3} Current interest in porous silicon also concerns its application in biological systems⁴ and as an ingredient for nanocomposites.⁵

Notwithstanding a large number of papers, several aspects are still obscure. For instance, the dramatic loss in conductivity (which, inter alia, renders m-PS transparent in the IR) has not yet received a commonly accepted explanation. Several hypotheses have been put forward, mainly in terms of solid-state physics.^{2,6} A “chemical” interpretation, that is, the reaction of bulk B atoms with hydrogen atoms coming from the etching solution with formation of Si–H–B species inside the Si nanocrystallites,^{3,7} has been disproved on the basis of joint computational and IR results.^{8,9} Another chemical interpretation hypothesizes 3-coordination of boron atoms at the surface of the nanocrystallites.¹⁰ We have found¹¹ that NMR spectra concerning ¹¹B support this latter type of interpretation as they show that nearly all B species in m-PS exist as either surface

or subsurface entities. Chart 1 represents the corresponding possible structures which take into account that the surface is hydrogenated: in **a** the surface B atom is simply trigonal and has no tendency to accept electrons from the bulk. In **b** (of which **b'** is only a resonance structure), the B atom is underneath a surface Si atom, carrying no H atom; the B/naked Si couple, being neutral, does not accept electrons from the bulk.

The presence of B atoms at the surface is in agreement with a proposed mechanism of etching, by which erosion of the c-Si structure stops when a B atom gets near to the surface.¹⁰ From the point of adsorption, it is most noticeable that such surface centers (in both versions **a** and **b**) have a Lewis acidic character and may in principle act as sites.

The concentration of carriers in m-PS is affected by the presence of polar liquids,^{12–19} probably because of a dielectric effect of the liquids filling the voids of the mesostructure.

Other mechanisms of carrier reactivation are however possible. p⁺-Type m-PS increases^{20–23} enormously its electrical conductivity in the presence of a few parts per billion of NO₂. At such densities of the gas phase,^{24,25} no variations in the dielectric properties of the voids may be considered. An adsorption phenomenon is to be invoked in which each adsorbed NO₂ molecule traps one electron, because of its remarkable electron affinity, and releases a hole into the bulk.

The present paper brings evidence in favor of this mechanism by studying the IR spectra of the system at different NO₂ equilibrium pressures. Adsorbed molecules are not visible in IR per se, but the presence of generated holes shows up as a change in background absorption due to the free-carrier gas, interpreted in terms of the Drude theory.²⁶ Ancillary electron paramagnetic resonance (EPR) measurements have also been carried out.

Experimental Section

Sample Preparation. Porous silicon membranes have been prepared in 25% HF/25% H₂O/50% EtOH solutions by anod-

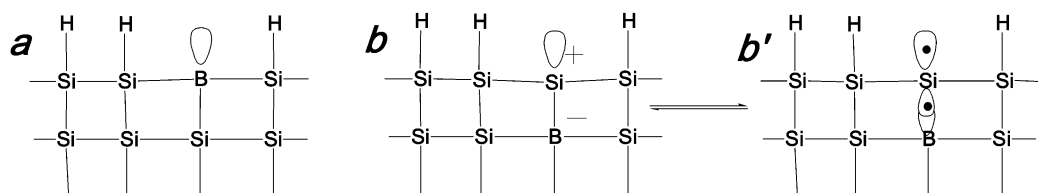
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CHART 1



ization of boron-doped p⁺-type c-Si(100) substrates ($B \approx 3 \times 10^{19}$ atoms/cm³; 5–15 mΩ cm resistivity). Etching cycles have been applied with a current density of 250 mA/cm² in order to produce ≈60% porosity membranes. Etch stops have been introduced in every cycle in order to allow for replenishment of the solution inside the pores to avoid porosity gradients. At the end of anodization, the membrane has been detached by means of a high current pulse.²⁷ Due to its brittleness, the m-PS membrane has been deposited for IR measurements onto a lightly doped, double-polished silicon wafer, transparent in the mid-infrared region. Measurements were performed on samples with thickness between 40 and 60 microns and a porosity of 60%, which corresponds to a surface area of about 600 m²/cm³.

FTIR Measurements. m-PS samples were placed in a homemade vacuum cell and connected to a vacuum frame permitting operations under controlled atmosphere. Samples were first outgassed under a dynamic vacuum (10⁻¹ Pa) at room temperature; successively, pure nitrogen dioxide was dosed. The spectra here reported are those recorded 15 min after NO₂ admission, when constant values of pressure and absorbance were achieved, that is, under apparent equilibrium conditions.

IR spectra have been collected on a Bruker Equinox 55 spectrometer operating in the transmission mode, equipped with an MCT cryodetector. Spectral resolution was 2 cm⁻¹, and 64 interferograms were collected for each spectrum. The measurement compartment was purged with decarbonated dry air.

Computation of Carrier Concentration and Mobility from IR Spectra. Absorbance spectra have been simulated by means of SCOUT software²⁸ in the range 2000–600 cm⁻¹. The dielectric function of m-PS has been evaluated by the effective-medium approximation proposed by Bruggemann:²⁹ with respect to the original formulation, the matrix material and the particle material are represented by undoped c-Si and air, respectively, and the volume fraction is replaced by the porosity. From membrane thickness and the dielectric constants of air and undoped c-Si, the absorbance spectra are calculated as a set of interference fringes: comparison with the spectra of the as-prepared sample yields a good fit, which improves by marginally changing the volume fraction. To take into account the presence of free carriers, the c-Si dielectric function is modified according to the Drude model,³⁰ where charge carriers are treated as a gas of free particles with a characteristic scattering time τ . The susceptibility of the material depends on two parameters: Ω_p (plasma frequency) and Ω_τ (damping frequency, related to τ), which are proportional to the carrier concentration p and the mobility μ , respectively:

$$p = \frac{4\pi^2 c^2 \epsilon_0 m}{e^2} \Omega_p^2 \quad (1)$$

$$\mu = \frac{e}{mc} \frac{1}{\Omega_\tau} \quad (2)$$

where e indicates the electron charge and m the effective mass of the carriers, set to 0.37 times the electron mass at rest.

Fitting of the experimental spectra has been carried out by varying Ω_p and Ω_τ , until agreement was obtained between experimental and calculated spectra in the region where free carrier absorption is evident (below 2000 cm⁻¹). From eqs 1 and 2, the free carrier concentration p and the mobility μ have been calculated.

EPR measurements were performed on a Bruker ESP-300 spectrometer equipped with a TE100 rectangular cavity and operating in the X-band mode (9.5 GHz). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) ($g = 2.0036$) and a solid solution of Mn²⁺ in MgO ($g = 2.0064$) have been used as standards for g -value calibration.

Results

Curve a in Figure 1 shows the IR spectrum taken under a vacuum and at room temperature of a m-PS sample as-prepared.

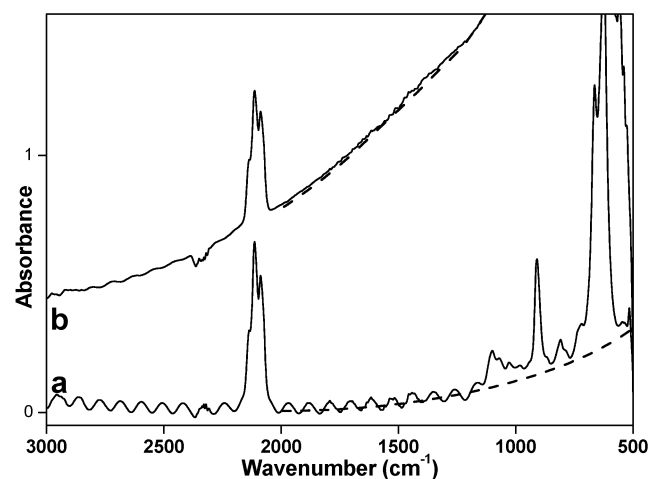


Figure 1. Infrared spectra of p⁺-type PS in vacuo (curve a) and under 0.25 mbar of pure NO₂ (curve b). Broken lines show the behavior of baselines.

Three features are seen: (i) the presence of interference fringes, due to the limited thickness of the m-PS membrane; (ii) definite bands due to surface SiH_x species³¹ (with $x = 1, 2, 3$: an envelope around 2100 cm⁻¹, a sharp absorption at 912 cm⁻¹, and a strong doublet at 667 and 622 cm⁻¹); (iii) a limited increase in the background at low frequency, masked to some extent by the presence of the SiH_x modes, described in Figure 1 by the broken curve. This background absorption is due to residual untrapped free carriers, for which a concentration $p_0 = 0.24 \times 10^{19}$ holes/cm³ and a mobility $\mu = 170$ cm² V⁻¹ s⁻¹ are calculated.

NO₂ dosage causes a loss of transparency of the sample, shown by the increase of the background absorption. For example, curve b is taken under an equilibrium pressure of 0.25 mbar: from the background profile, values for carrier concentration and mobility are calculated as $p = 1.60 \times 10^{19}$ holes/cm³ and $\mu = 85$ cm² V⁻¹ s⁻¹.

As a consequence of the increased absorption, interference fringes are smeared out. The frequencies of the molecular modes

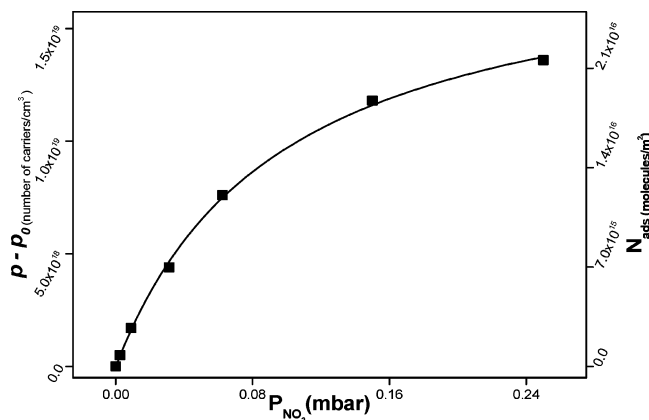


Figure 2. Number of generated carriers as a function of the pressure of the adsorbed NO₂ (left-hand scale) and corresponding number of molecules for surface area unit (right-hand scale).

are unaffected, and at the most, their intensities are slightly lowered. The spectrum after prolonged room-temperature outgassing coincides with the starting one; that is, the interaction is reversible. The time required to outgas the sample is more than twice that required to achieve the equilibrium during the adsorption.

Spectra like that of curve b have been recorded for several equilibrium NO₂ pressures (P_{NO_2}) in the range of 2.0×10^{-3} to 2.5×10^{-1} mbar. At higher pressures, surface reactions take place leading to the irreversible oxidation of the sample. The corresponding values of p are reported in Figure 2 as a function of P_{NO_2} (left-hand scale): a saturation effect is seen, indicating a maximum concentration of carriers in the neighborhood of 1.6×10^{19} holes/cm³.

Discussion

Taking into account that etching basically consumes Si atoms, leaving boron behind,^{2,3,10} the potential concentration of carriers in m-PS is evaluated to be close to that of the starting material ($\approx 3 \times 10^{19}$ holes/cm³). The residual concentration of carriers p_0 being 0.24×10^{19} holes/cm³, it results that about 8% of the carriers are actually untrapped. Notwithstanding such a remarkable concentration of carriers, the m-PS system does not practically conduct current; the discussion of this fact is, however, outside the scope of the present paper.

The carrier concentrations estimated in the presence of relatively large NO₂ pressures are of the order of the original B content; that is, equilibrium pressures of NO₂ around 1 mbar, too low to affect the dielectric properties of the systems, suffice to reactivate nearly all carriers. This speaks in favor of an adsorption mechanism. If a 1:1 correspondence between adsorbed molecules and injected holes is assumed, the number of adsorbed molecules may be determined from the increase in concentration of holes $p - p_0$. This is most important, because, the actual number of B atoms in the 40 μ membrane being at the most 3×10^{16} , it is difficult to envisage other means of measuring such small adsorbed amounts. For this reason, adsorbed NO₂ molecules cannot be detected directly in the IR spectrum, and only the giant intensity related to the absorption of the free-carrier gas allows their detection.

The diagram $(p - p_0)$ versus NO₂ equilibrium pressure (Figure 2) thus represents the isotherm describing the adsorption process: the number of NO₂ molecules for unit surface area, denoted as N_{ads} (right-hand scale in Figure 2), equals $p - p_0$ divided by the surface exposed by a volume unit of m-PS (~ 600 m² cm⁻³).

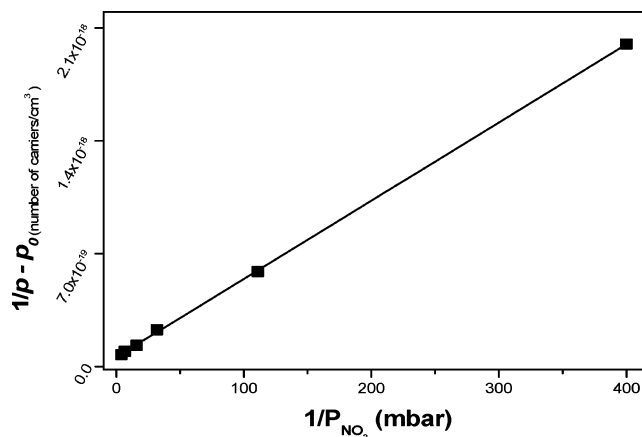


Figure 3. Data of Figure 2 plotted in the linearized form of the Langmuir model.

The isotherm in Figure 2 has a Langmuir³² shape: the corresponding data have been therefore fitted through the equation

$$N_{\text{ads}} = \frac{N_{\text{ads}}^{\text{max}} K P_{\text{NO}_2}}{1 + K P_{\text{NO}_2}} \quad (3)$$

where $N_{\text{ads}}^{\text{max}}$ is the total number of surface sites and K is the equilibrium constant of the adsorption process.³¹ The Langmuir equation may be linearized in a doubly reciprocal version:

$$1/N_{\text{ads}} = 1/N_{\text{ads}}^{\text{max}} + (1/KN_{\text{ads}}^{\text{max}})(1/P_{\text{NO}_2}) \quad (4)$$

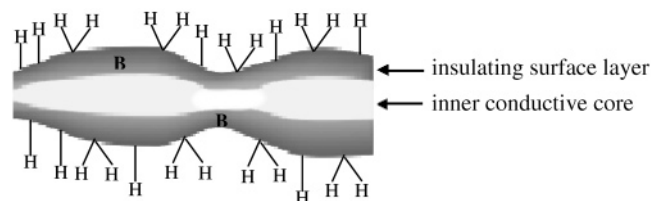
Figure 3 shows that data plotted in this way yield a straight line: data in Figure 2 conform to the Langmuir model, with $N_{\text{ads}}^{\text{max}} = (1.8 \pm 0.1) \times 10^{19}$ sites/cm⁻³ (corresponding to 2.2×10^{16} molecules/m²), and $K = 12.1 \pm 0.3$ mbar⁻¹ = 12100 ± 300 bar⁻¹. In the Langmuir model, all adsorption sites are assumed to be equivalent and noninteracting: it is known that these are rather loose requirements, that is, that even systems not strictly ideal in the thermodynamic sense may conform to a Langmuir isotherm. In any case, the plot in Figure 3 strongly supports the concept that NO₂ adsorption on the PS surface has a localized nature, taking place on definite sites, all basically similar and noninteracting.

This result is in contrast with the standard description of ionic adsorption on semiconductors basically due to Wolkenstein,³³ that implies a collective behavior of the solid, that is, long-range transmission of electronic effects. Indeed, although we are not dealing with an oxide semiconductor, it is feasible to assume that the increase in p should change the electronic properties of the surface. There is, however, independent evidence that the surface seems to be electronically independent from the core properties of m-PS. As shown by IR spectroscopy, at the surface SiH_x species are present (bands around 2100 cm⁻¹ in Figure 1). The Si-H vibrations depend in principle on the electronic state of the Si atom involved, so that the Si-H frequencies witness any change of these. For instance, the Si-H_x vibrations of groups linked to O atoms are subjected to sizable hypsochromic shifts³⁴ (up to 50 cm⁻¹), depending on the number of surrounding O atoms. With semiconducting oxides, like ZnO or TiO₂, adsorption of electron donor molecules (e.g., CO) perturbs the successive adsorption of the same species, and the CO stretching frequency is seen to shift with coverage.³⁵ Finally, with conducting solids (metals), the vibrations of adsorbed species bring about the change in the dipole moment

of the molecule, but also in the image dipole created by the conduction electrons: this phenomenon affects any IR mode substantially and leads to specific "surface dipole selection rules".³⁶

One should expect a similar mechanism to be operative also with conducting m-PS. Spectra in Figure 1 show, contrary to expectations, that none of the Si-H modes is perturbed in frequency by the presence of free carriers. This strongly suggests that the outermost layers of m-PS have an insulating nature, in contrast with the core which maintains a semiconducting behavior: Chart 2 illustrates pictorially the proposed structure of m-PS.

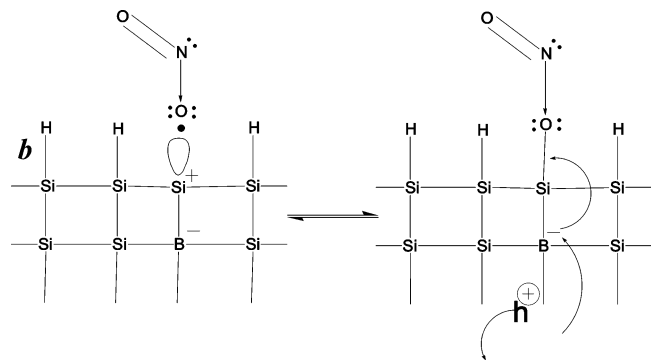
CHART 2



The outermost insulating layers do not transmit electronic effects from adsorption site to adsorption site, so that a Langmuir isotherm is observed, and their electron properties are not influenced by the presence of a conductive core. Electron transfer between surface sites and semiconducting core is instead possible.

Concerning the adsorption site, both structures **a** and **b** (Chart 1) account for the observed reactivity. Chart 3 reports case **b**, case **a** being entirely similar: adsorption of NO₂ onto the empty orbital of the surface Si atom abstracts one electron originally belonging to the B atom, which in turn takes an electron from the valence band, so forming a hole.

CHART 3



The structure of adsorbed NO₂ is hypothetical, because its IR modes are not available to detection: preliminary quantum mechanical calculations¹¹ indicate reactivity through the O-end prevailing over that through the N-end, also possible. EPR measurements show that no signal is developed upon NO₂ contact. This is not in contrast with hole formation, because holes in p⁺ Si are only visible in EPR if the sample is subjected to uniaxial stress.³⁷ On the other hand, it speaks in favor of the diamagnetic nature of adsorbed NO₂, as depicted in Chart 3, because adsorption of similar small amounts of NO₂ on other solids, for example, zeolites, where the molecule maintains its paramagnetic state, gives rise to perfectly visible signals.³⁸

As concerns the energetic aspects of the interactions, the following consideration may be done. *K* being the equilibrium constant of the adsorption process, the corresponding ΔG° is $-RT \ln K = -23.3 \pm 0.1$ kJ (bar). As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$,

an estimate of the standard enthalpy of adsorption ΔH° may be made by assuming a reasonable value for the standard entropy change of adsorption ΔS° . This latter is negative, because the adsorbed state is more ordered than the gas. The standard molar entropy of NO₂ is 240.4 J mol⁻¹ K⁻¹,³⁹ assuming as a rule of thumb that all translational contributions to entropy have been lost in adsorption, ΔS° is ≈ -157 J mol⁻¹ K⁻¹. The corresponding value for ΔH° is ≈ 70 kJ mol⁻¹, a value corresponding to the actual occurrence of chemical bonds between the surface and the adsorbate, in line with the proposed nature of the interaction.

The application of the Drude model to absorption spectra yields, besides the concentration of carriers *p*, their mobility μ . The value for hole mobility extracted in this way is very close to those measured for c-Si with a similar number of carriers: moreover, a decrease of the mobility is seen when the concentration of carriers increases, as expected.⁴⁰

Finally, a comment on the time dependency of the experiments is appropriate. Adsorption measurements attain steady (equilibrium) condition after some 15 min: this is ascribed to a slow diffusion of NO₂ into the m-PS void structure, constituted by a complex system of irregularly shaped channels, not interconnected, ranging between 5 and 30 nm.^{41,42} As already noted, the time required to evacuate the system and restore the sample conditions before another NO₂ dosage is definitely longer than that required to reach the equilibrium. The reason probably is that removal of the adsorbed NO₂ is an endothermic and hence activated process: the substantial ΔH° value (in the neighborhood of 70 kJ mol⁻¹) is reflected directly in the difficulty with which NO₂ molecules are desorbed. The activated nature of evacuation is yet another piece of evidence about the nature of a surface chemisorption interaction.

Conclusions

The interaction of NO₂ with m-PS has the nature of adsorption on definite surface sites, involving most of the boron atoms present in the sample. The presence of B in a surface or a subsurface situation brings support to a proposed etching mechanism. The release of hole carriers as a consequence of the adsorption process renders the phenomenon available to IR study, notwithstanding the very low concentration of surface sites. The occurrence of a Langmuir adsorption isotherm as well as the insensitivity of SiH modes of molecular surface SiH_x species to the increase of carrier concentration strongly suggest that the outermost layer of the m-PS crystallites has an insulator behavior, so that electronic effects are not transferred from site to site. Estimation of the enthalpy of adsorption suggests that a chemisorption process is involved: this is confirmed by the kinetics of desorption being lower than that of adsorption. Adsorbed NO₂ is probably in a diamagnetic state.

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