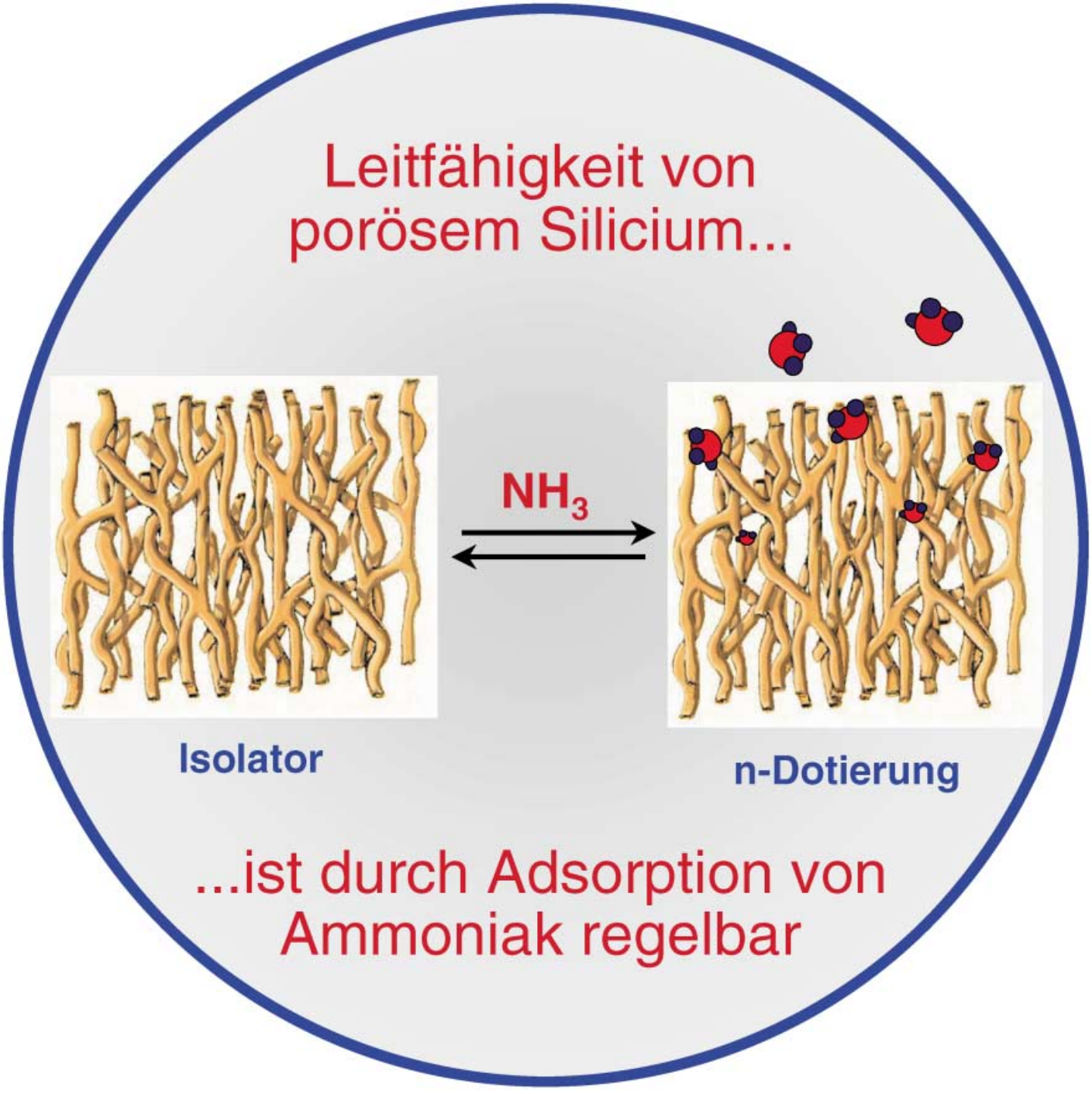
Zuschriften



Die Adsorption von Ammoniak führt zu einem bemerkenswerten Anstieg der Elektronenbesetzung im Leitungsband von mesoporösem Silicium. Diesen Effekt sowie den Isolator-Metall-Übergang, der bei hohen NH_3-Beladungen beobachtet wird, beschreiben E. Giamello et al. auf den folgenden Seiten.

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Electronic Transitions in Silicon

Reversible Insulator-to-Metal Transition in p^+-Type Mesoporous Silicon Induced by the Adsorption of Ammonia

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Several "classic" functional materials, when prepared in nanostructured forms, exhibit unique physical properties that present opportunities for new applications.[1–3] This is the case for mesoporous silicon, a material widely investigated for its peculiar photoluminescence, optical, and electronic properties.[4] These properties have been harnessed for a variety of challenging chemical sensor applications,[5] such as the quantification of reactive pollutant gases (for example, NO_2).[6] The present article reports the observation of a dramatic increase in the conduction-electron population in mesoporous silicon, which occurs upon adsorption of ammonia onto the surface. This effect has been monitored by EPR spectroscopy and is interpreted in terms of a reversible change from Langevin to Pauli paramagnetism, which corresponds to an insulator-to-metal transition.

Mesoporous silicon (m-PS) is prepared by electrochemically etching B-doped p^+-type crystalline silicon in HF solutions, where the boron content is typically of the order of 10^{19}–10^{20} atoms cm^{-3}. It possesses a dendritic structure, comprised of Si nanowires with diameters ranging from 5–12 nm and a specific surface area up to 600 $m^2 cm^{-3}$.

Despite the number of papers devoted to m-PS in recent years, a number of questions are still unanswered, for example, concerning the hole-based electrical conductivity of B-doped Si, which drops by several orders of magnitude upon the formation of pores, and renders the PS nearly an insulator. This loss of conductivity cannot be ascribed to any preferential removal of boron atoms during etching. The disappearance of the great majority of free holes has been interpreted by various, sometimes conflicting hypotheses.[7–11] There are a few examples of experiments in which the conductivity of porous Si samples increases. For example, contact between porous silicon and polar liquids causes such an increase, and this observation has been interpreted as the removal of carrier constriction.[12] Most interpretations of this phenomenon postulate that the reactivation of "trapped" holes is due to an increase in dielectric constant when the liquid fills the porous structure.[13] In the present work, it will be shown that the free carriers generated by NH_3 adsorption on B-doped porous silicon are indeed electrons. This interpretation is in agreement with the observation of Poindexter and co-workers[14] for the case of p- and n-type porous silicon when in contact with acetone.

Freshly prepared p^+ layers only show a weak EPR spectrum due to P_b centers (silicon dangling bonds at the Si/SiO_2 interface).[15] These centers have been thoroughly investigated in the past[16,17] and will not be commented upon further here. On dosing m-PS at room temperature with an amount of NH_3 corresponding to 2.7×10^{20} molecules per cm^3 of m-PS, and cooling the cell down to 77 K, a symmetric, intense EPR signal is observed. This signal

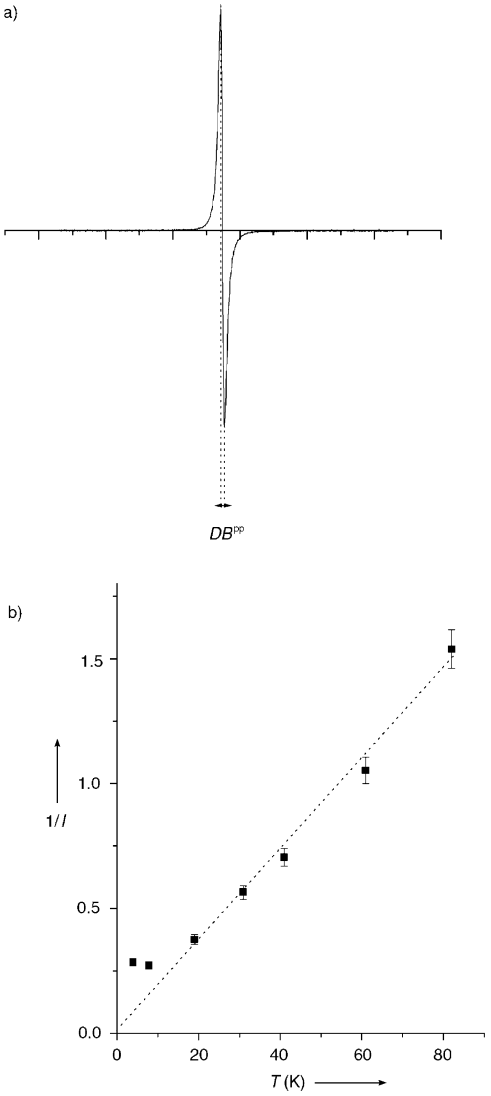

Figure 1. a) EPR spectrum of mesoporous silicon (m-PS) dosed with ammonia (2.7×10^{20} molecules per cm^3 m-PS) measured at 10 K (B^{PP} = peak-to-peak separation); b) the temperature dependence of the paramagnetic susceptibility χ, measured in terms of $1/I$ versus T.

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disappears upon removal of the adsorbate and it can be regenerated with a fresh dose of NH_3. The temperature dependence of this EPR signal has been investigated. The spectrum at 10 K is shown in Figure 1 a; the resonance has an isotropic g value of 1.9984 ± 0.0003, independent of temperature, and a Lorentzian line-shape. The peak-to-peak line width ($\Delta H_{pp} = 10$ G at 10 K) linearly decreases in the range 100–30 K while it remains constant from 30 to 4 K. The broadening of the line prevents observation of the signal at temperatures above 130 K. The intensity I of the EPR signal is a measure of the pure paramagnetic susceptibility of the sample (χ): Figure 1 b reports the temperature dependence of χ in the range 4–100 K, as a plot $1/I$ versus T. The data displays Langevin–Curie behavior down to about 20 K. A spin–lattice relaxation time of $(2.5 \pm 1) \times 10^{-6}$ s was derived from the saturation trend observed in the resonance at 10 K. This value is typical of conduction electrons in Si-based semiconductors.[18] The spin concentration (see Experimental Section) is estimated to be $5 \pm 3 \times 10^{17}$ spins cm^{-3}. The line shape, g value, and temperature dependence indicate that the EPR signal is associated with conduction-band (CB) electrons, as described by Poindexter et al.[14] for the case of p- and n-type porous silicon treated with acetone. The signal reported in Figure 1 a is therefore a true conduction electron spin resonance (CESR) signal. Any role that holes might have in determining such a signal is excluded, as is the case in silicon-based semiconductors, where holes are EPR-inactive unless a strong mechanical stress is applied to the solid.[19]

The intensity of the Lorentzian line has been studied as a function of the amount of adsorbed NH_3 in the range between 1×10^{19}–4×10^{20} molecules cm^{-3} of PS (data not reported), and a linear dependence is observed. A dramatic change in the EPR spectrum occurs when higher doses of NH_3 are adsorbed. The spectrum recorded at 77 K upon dosing of 6×10^{20} molecules cm^{-3} is displayed in Figure 2 a. Under these conditions a marked asymmetry in the resonance line is observed, corresponding to a Dysonian line-shape. The g value of the resonance is the same as that measured at lower ammonia doses and is constant with temperature. The Dyson profile is typically ascribed to the magnetic resonance of electrons in conducting materials when the electron concentration is high enough to produce the so-called "skin-depth effect". In this case the resonance of electrons is observed in a limited external portion of the material (skin) whose depth is given by:

$$\delta = \left(\frac{2 c^2 \varepsilon_0 \rho}{\omega} \right)^{1/2} \quad (1)$$

where ρ is the electrical resistivity and ω is the angular frequency of the radiation. The symmetric Lorentzian line shape gives way to the asymmetric Dysonian absorption when δ becomes small in comparison to the sample thickness.[20] In other words the line shape is expected to change from Lorentzian to Dysonian when the electrical conductivity of the material increases.

The above observations are consistent with the paramagnetic susceptibility reported in Figure 2 b. In parallel with the onset of the transition to a Dysonian line shape, a

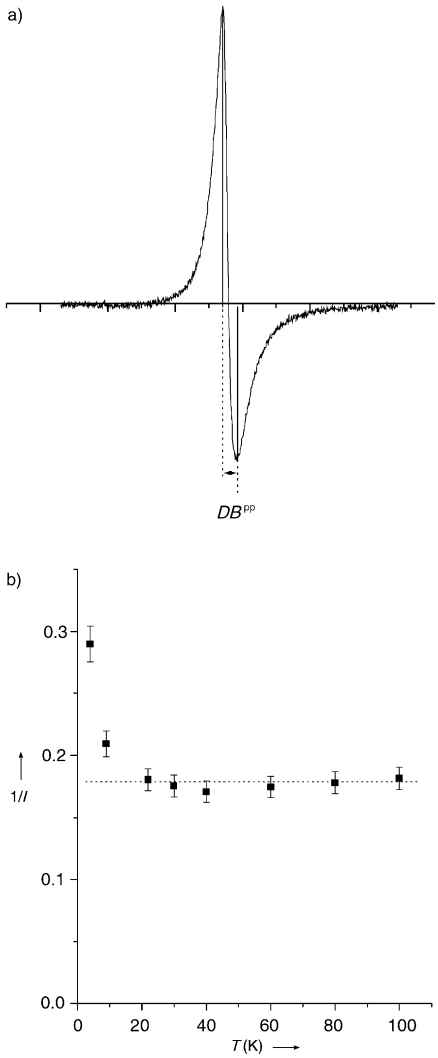

Figure 2. a) EPR spectrum of mesoporous silicon (m-PS) with a higher ammonia dosage (6×10^{20} molecules per cm^3 m-PS) measured at 77 K; b) the temperature dependence of the paramagnetic susceptibility χ, measured in terms of $1/I$ versus T.

temperature-independent (in the range 20–100 K) Pauli-like behavior is observed for χ. Below 20 K a deviation from linearity occurs, as observed in the case of low ammonia coverage (Figure 1 b), which could be ascribed to a magnetic phase transition. This phenomenon is currently under investigation in our laboratories.

According to standard formulas,[21] degeneracy of a free-electron gas and the concomitant onset of Pauli paramagnetism is expected to occur at about 100 K for an electron concentration of the order of 10^{19} cm^{-3}. Such a value can be considered a reasonable estimate of the electron density in m-PS in the conditions corresponding to the onset of the Dysonian ESR line. The generation of free carriers in the present samples is induced by the adsorption of ammonia. Remarkably, these free carriers are electronic in nature and their concentration depends on the amount of adsorbed ammonia. The coverage in ammonia is estimated to be of the order of a monolayer under circumstances leading to the

Dysonian line shape; note that the whole adsorbed amount in such conditions (40 mbar NH_3 pressure in the cell before cooling to 77 K) corresponds to about 4% of the porous volume. This rules out any explanation of the observed phenomena in terms of capillary condensation into the pores, and consequent changes in the dielectric properties of the sample. The remarkable changes observed are ascribed to effects associated with the chemical interaction between the porous system and the adsorbed molecules. Similarly, increases in absorption by free carriers have been observed by means of IR spectroscopy in the case of NO_2 acting as an adsorbate.[6]

Modifications of the surface conductivity in insulators and semiconductors brought about by redox interactions between the solid and an adsorbate are not unusual.[22] This implies the development of space charge in the solid, band bending, and possibly Fermi-level pinning to the energy of the surface state. The case described in the present paper has peculiar features in that: a) the modification of the electron population seems to involve all of the solid; b) the chemical properties of ammonia (a typical Lewis base) are very different from those of the molecules or ions which have previously been shown to modify surface conductivity.[23] In these latter cases, the molecules or ions involved are usually redox active with suitable electrochemical potential.

Regardless of the exact nature of the NH_3–porous silicon interaction, the phenomenon reported here is remarkable considering that the starting material (p^+ crystalline silicon) is a p-type semiconductor, which becomes pratically an insulator upon etching (p^+ mesoporous silicon) and, in turn, an n-type semiconductor upon adsorption of ammonia (Figure 3). Moreover the remarkable peculiarity of the case

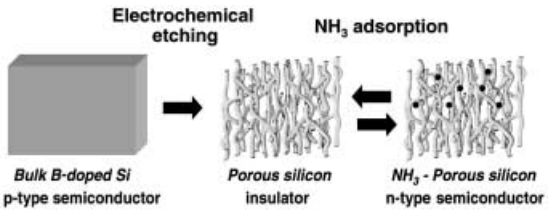

Figure 3. The electronic behavior of mesoporous silicon on the adsorption of ammonia.

here described is that the conversion is triggered by adsorption of a gas (a low-energy reversible process) and that, in principle, the electronic (and magnetic) properties of the solid can be tuned simply by varying the amount of adsorbed gas. The phenomenon is also intriguing considering that it has already been demonstrated that adsorption of an electron scavenger like NO_2 on the same type of m-PS employed in the present work, restores the original hole conductivity of the bulk B-doped Si.[11,12] Thus, the possibility of creating an n–p junction by gas adsorption appears very exciting.

In summary, we report evidence for the generation of conduction-band electrons in p^+-type porous silicon by the adsorption of NH_3 molecules. The g value of the observed CESR signal ($g = 1.9984$) is, within the experimental error, the same as that of conduction electrons in crystalline, polycrystalline, and porous silicon.[14–25] The number of free carriers increases with increasing NH_3 adsorption and, beyond a critical value, a true reversible insulator-to-metal transition[26] is observed with the onset of both a skin-depth effect and transition from a Langevin to Pauli paramagnetism.

Experimental Section

Porous silicon membranes were prepared in 25% HF/25% H_2O/50% EtOH solutions by anodization of boron-doped p^+-type c-Si(100) substrates ($B \cong 3 \times 10^{19}$ atoms cm^{-3}; resistivity = 5–15 mΩ cm). Etching was carried out at a current density of 250 mA cm^{-2} to produce $\approx$60% porosity membranes. At the end of anodization, the membrane was detached by means of a high-current pulse.

Measurements were performed with a Bruker ESP-300 spectrometer operating in the X-band mode (9.5 GHz). The sample (typically 5 mg) was cooled with a gas-flow cryostat operated from $T = 4.0$ to 300 K. DPPH ($g = 2.0036$) and a solid solution of Mn^{2+} ions in MgO ($g = 2.0064$) were used as standards for g-value calibration and quantitative evaluation of the number of carriers. The intensity of the EPR signal was obtained as the absorption curve area by a numerical integration of the data. In order to measure the number of molecules interacting with the solid, the volume of the EPR cell was carefully evaluated by means of a volumetric vacuum manifold.

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