

Confinement effects on phosphorus donors embedded in silicon nanocrystals

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Abstract

Magnetic resonance of shallow donor center phosphorus is used to track size-related changes of energy band structure in silicon powders. Small conduction band upshifts of several meV are determined for nanocrystals of approximately $d = 100$ nm diameter and smaller. These are interpreted as the onset of the quantum confinement-induced variations of silicon band structure. The conduction band upshift is experimentally found to follow the $1/d^{1.2}$ dependence in the investigated size range. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicon low-dimensional structures possess a variety of interesting electronic properties. It has been shown [1] that the decreasing size of crystallites leads to quantum confinement effect which enlarges the band-gap energy [2,3], and which can possibly also lead to change of its character from indirect to direct [4]. Both effects should be detectable by optical methods due to an increased efficiency of the emission and its gradual shift to higher energies upon size reduction. In line with that expectation visible luminescence in specially prepared silicon nanocrystal structures has been reported [5,6]. Unfortunately, low-dimensional structures are also characterized by a large surface-to-volume ratio. Surface-related effects obscure observation and conclusive identification of quantum-confinement-related effects. Consequently, to our knowledge, the onset of the size-induced changes of the energetic structure of silicon has been traced experimentally.

In this study we present experimental evidence of band structure changes in the relatively ‘large’ crystallites for

which the theory-predicted conduction band upshift should be of the order of a few meV only. The experiment has been conducted on silicon nanocrystals prepared by mechanical milling. The size confinement is monitored by its effect on the electronic structure of phosphorus impurity as monitored by electron paramagnetic resonance (EPR). Substitutional phosphorus in silicon forms an effective-mass-theory (EMT) donor center; the extended character of its electronic wave function renders this center sensitive to variations of electronic structure of the conduction band minimum. Phosphorus donor in silicon is paramagnetic in its neutral charge state P^0 and is well-studied by EPR. It has cubic symmetry which is advantageous for randomly oriented grains. From the EPR spectrum the details of the wave function — spin localization on the phosphorus nucleus and mutual overlap of neighboring donors can be concluded. At the same time the observed spectrum is exclusive for a substitutional donor and therefore only the bulk of the nanocrystal is monitored. In this way, the volume and the surface effects can be separated. This in a clear advantage to other less discriminative techniques.

2. Silicon powders

For the current experiment two kinds of phosphorus-doped silicon have been used: Czochralski (CZ)

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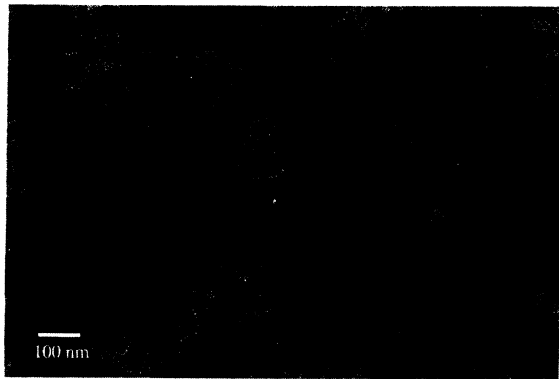


Fig. 1. Scanning electron microscopy picture of Si-powder before oxidation.

$[P] \approx 5 \times 10^{15} \text{ cm}^{-3}$ and float-zoned (FZ) $[P] \approx 1.5 \times 10^{17} \text{ cm}^{-3}$. Nanocrystals have been prepared by mechanical ball milling for 1 h in ethanol (ZrO_2 balls and crucible). The milling step was followed by sedimentation of 15 h in order to remove the largest silicon grains. After that centrifuged sedimentation has been applied for size segregation. The actual size distribution was directly measured by scanning electron microscopy (SEM) (Figs. 1 and 2) and fitted with usual function $\exp(-\ln^2(d/x)/2w^2)$. For the particular set of powders investigated in this study the maxima of size distributions were determined at $x_B = 200 \text{ nm}$ for big, $x_{MB} = 110 \text{ nm}$ for medium big, $x_{MS} = 100 \text{ nm}$ for medium small and $x_S = 60 \text{ nm}$ for small nanocrystals. Further size reduction was achieved by oxidation; the powders were annealed at 1000°C in open air for time duration from 5 min to 3 h. By such a procedure the silicon core size was reduced by the formation of a SiO_2 layer. At the same time silicon surface was replaced by Si/ SiO_2 interface.

The crystallinity of silicon powders was controlled by X-ray diffraction. Characteristic diffraction patterns of silicon crystal were clear and strong for as-milled and oxidized nanocrystals. Their intensity gradually decreased upon heat-treatment indicating the size reduction of the silicon core. After prolonged oxidation the X-ray pattern vanished completely as all the silicon has been transformed into SiO_2 .

In addition to Röntgen diffraction, grain crystallinity was confirmed by other experiments. Raman spectroscopy revealed a strong first-order Stokes peak around 521 cm^{-1} . The line at 480 cm^{-1} which is characteristic of amorphous Si [7] was not observed. Also from transmission electron microscopy (TEM) related techniques of bright field/dark field (BF/DF) and selected area diffraction pattern (SADP) we obtained clear support that both as-milled and oxidized silicon grains retain their crystal structure. A TEM image of an oxidized silicon grain used

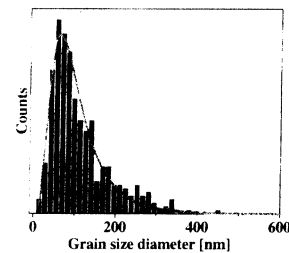


Fig. 2. Grain size distribution of one of the smallest powders obtained by ball milling, sedimentation, ultrasonic vibration and centrifuged sedimentation. The maximum of grain size distribution peaks at 60 nm. Almost no grains are bigger than 300 nm.



Fig. 3. Transmission electron microscopy picture of Si-grain after 1 h of oxidation at 1000°C . The SiO_2 thickness around the silicon core corresponds to approximately 80 nm. Evidence of crystallinity of the entire grain core is manifested by diffraction fringes in bright field/dark field method. The surrounding SiO_2 is amorphous.

in the present study is shown in Fig. 3; both the crystalline Si core and the external layer of SiO_2 developed by oxidation can be readily seen. By TEM we could also monitor how fast the SiO_2 layer develops at the surface of silicon grains. We conclude that the growth process proceeds according to the well-established formula $d_{\text{SiO}_2} = 10.78 \times \sqrt{t}$, where d_{SiO_2} is the oxide layer thickness (in nanometers) and t is the oxidation time (in min) [8]. From BF/DF and SADP we learn also that the SiO_2 layer is amorphous.

3. Experimental results

The EPR measurements were performed at a temperature of $T = 4.2 \text{ K}$ in a superheterodyne EPR spectrometer operating at 23 GHz in the K-microwave band and tuned to detect the dispersive part of the signal. The EPR of P donor in bulk Si has been extensively investigated [9]. The spectrum consists of 2 lines separated due to the

hyperfine interaction. The hyperfine constant A , which is equal to the separation between the two resonance lines, is proportional to the localization of electron wave function on phosphorus nucleus and is given by the Fermi contact term: $A = (\mu_0/4\pi)g_e\mu_B g_N\mu_N|\Psi(0)|^2$. For P in bulk silicon it has $A = 4.2$ mT value. At higher doping levels an exchange interaction between individual P impurities appears. This shows in the EPR spectrum as components developing between the hyperfine lines at moderate concentrations ($[P] \leq 10^{16} \text{ cm}^{-3}$) and originating from donor pairs and larger clusters [10]. The spin Hamiltonian appropriate for a pair of donor atoms can be written as [11]

$$\mathcal{H} = g\mu_B B(S_1 + S_2) + A(I_1 S_1 + I_2 S_2) + J(S_1 S_2), \quad (1)$$

where S_1 , S_2 and I_1 , I_2 are the electron and nuclear spins of the two donors, respectively, A is the hyperfine interaction constant, and J is the exchange coupling. At high concentrations ($[P] \geq 10^{17} \text{ cm}^{-3}$) the two-lines spectrum characteristic for an isolated donor decreases considerably and a strong Lorentzian-shaped line appears in the center of the spectrum. It exhibits exchange narrowing and evidences the donor-impurity band formation. The EPR spectrum of the bulk CZ-Si : P material used to prepare powders for this study is presented in Fig. 4. Also, EPR spectrum measured for powder sample prepared from this material is shown. As can be seen, in the EPR spectra of Si nanocrystals the lines originating from isolated donors are shifted towards the center and have a clearly asymmetric form, with the broadening also towards the center. This indicates a smaller hyperfine interaction for P donors embedded in the nanocrystals when compared to those in the bulk, and, also, size distribution within a given powder. Systematic EPR measurements of oxidized samples showed that a clear dependence exists between the value of the hyperfine splitting parameter A and an average volume of the

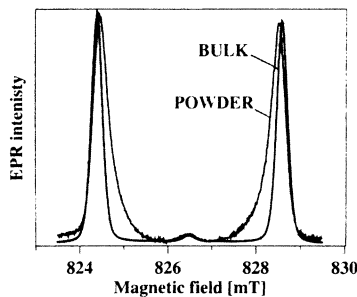


Fig. 4. EPR spectrum of the CZ-Si : P ($[P] = 5 \times 10^{15} \text{ cm}^{-3}$) bulk and nanocrystal sample. The hyperfine lines in powder sample are moved to the middle manifesting lowering of hyperfine splitting. The maximum of grain size distribution of powder before oxidation is $d \approx 200$ nm. Microwave frequency is $\nu = 23.11997$ GHz.

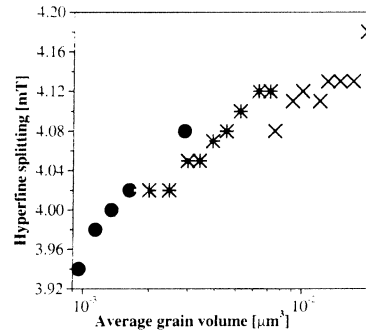


Fig. 5. Hyperfine splitting parameter for four different powders after oxidation versus average grain volume. For bulk silicon $A = 4.2$ mT. For powders the hyperfine parameter decreases with diminishing grain size. Oxidized powders has been marked with x-big; (*)-medium big; (+)-medium small and (o)-small ones.

silicon grain — see Fig. 5. A decrease of up to 6.5% for the smallest grains has been observed.

By inspecting the EPR spectra of the nanocrystals we also note that the central lines originating from mutual interaction between donors have a slightly higher intensity than in the bulk material used for preparation of the powders. For the smallest nanocrystals the exchange interaction becomes very strong. An increased mutual interaction and a decreased hyperfine constant were observed consistently in all the nanocrystals investigated in the current study. For nanocrystals prepared from FZ-Si with a higher P -concentration ($[P] = 1.5 \times 10^{17} \text{ cm}^{-3}$), the signal from the isolated donors disappeared completely upon oxidation and a single central line, with a strong exchange narrowing dominated the spectrum.

4. Discussion

Before we assign the observed changes of the EPR spectrum of silicon powders (lowering of the hyperfine and increase of the exchange interactions) to the quantum confinement-induced perturbation of the ground state of P donor, we will first consider alternative mechanisms that could possibly account for the observed effects. The enhanced mutual interaction between phosphorus atoms could also be explained by an increase of P concentration caused by diffusion and the strain fields generated during mechanical milling, annealing and/or oxidation. In order to check this possibility non-oxidized silicon grains were heat-treated in argon atmosphere. In this way, grain reduction by oxidation is excluded, but thermal migration is allowed. No effect of heat treatment in an argon atmosphere on the EPR spectrum has been found. Also devoted measurements of oxidized silicon wafers by secondary ion mass spectroscopy (SIMS)

[12,13] showed that P indiffusion into silicon grain due to impurity pile-up at the Si–SiO₂ interface is negligible and cannot account for the effects observed here. Additional verification of importance of pile-up has been performed by oxidation of much bigger grains for times exceeding up to 100 h. In these powders the evaluated pile-up to grain core volume ratio is larger in comparison to samples used in our experiment. No traces of enhanced mutual interaction has been found by EPR.

Yet another possible explanation which has to be considered is the hydrogen passivation which could change the initial ratio between the isolated P impurities and their complexes. Hydrogen can easily be introduced into Si grains during oxidation, and passivation of donors renders them non-paramagnetic and non-detectable by EPR. We have made computer simulation of this process. The basic assumption of the program algorithm was to keep equal probability of passivation of all donors, the isolated ones and the ones forming pairs or larger aggregates. The simulation showed that the relative number of interacting donors would drop upon passivation, in contrary to experimental observation.

Based on the above, we conclude that the observed decrease of the hyperfine and increase of the exchange interactions of P donors in silicon nanocrystals reflects changes of the electronic structure of the donor centers, which appear upon grain size reduction.

Following the observation that the hyperfine splitting depends on the average volume of the grain, we attempt to analyze the effect in terms of the size confinement. Since P donor is well described by EMT we apply this formalism in our analysis of the effect. We describe the shallow donor electron wave function as a linear combination of envelope function, which is the solution of hydrogen-like Schrödinger equation, and propagating wave through the crystal modulated by Bloch function:

$$\Psi(r) = \sum_{j=1}^6 x^{(j)} F^{(j)}(r) u^{(j)}(r) e^{ik \cdot r} \quad (2)$$

$|x^{(j)}|^2$ is the probability of finding an electron in the j th valley $j = 1, \dots, 6$, as a consequence of the six-fold CB degeneracy in silicon. The 1s donor ground state is split by the cubic crystal field into the symmetric-singlet A_1 and asymmetric doublet E and triplet T_2 . The separations of these energy levels have been directly measured by optical spectroscopy [14].

On basis of the EMT formalism we will derive an expression for the lowering of the hyperfine splitting and explain qualitatively the increased mutual interaction between donors. The ground state A_1 is symmetric with equal probability of finding the electron in all the 6 CB minima $x = \frac{1}{\sqrt{6}}(1, 1, 1, 1, 1, 1)$. It is the only state that has non-vanishing localization on the nucleus and, consequently, the only one contributing to the hyperfine interaction. The increased mutual interaction can be ex-

plained on the basis of admixing higher lying states which are anisotropic and are characterized by a more extended character. For simplicity we consider a tetragonal perturbation which can be characterized by a single parameter. Such a situation is similar to the symmetry perturbation induced in bulk Si : P by an application of a uniaxial stress along $\langle 100 \rangle$ [15]. The interaction term of donor electron Hamiltonian with respect to the center of gravity has the form of the so-called valley-orbit matrix (6×6):

$$H_{\text{vo}} = -\Delta_2 \begin{vmatrix} -2x & 1+\delta & 1 & 1 & 1 & 1 \\ 1+\delta & -2x & 1 & 1 & 1 & 1 \\ 1 & 1 & x & 1+\delta & 1 & 1 \\ 1 & 1 & 1+\delta & x & 1 & 1 \\ 1 & 1 & 1 & 1 & x & 1+\delta \\ 1 & 1 & 1 & 1 & 1+\delta & x \end{vmatrix} \quad (3)$$

The six-fold degeneracy of the CB is now lifted and we get 2 eigenvalues of the states, one corresponding to the ground state A_1 :

$$E_{A_1} = \Delta_2 \left[-(2+\delta) + \frac{1}{2}x - \frac{3}{2}\sqrt{x^2 + \frac{4}{3}x + 4} \right] \quad (4)$$

and the second to one of the admixed excited states E :

$$E_E = \Delta_2 \left[-(2+\delta) + \frac{1}{2}x + \frac{3}{2}\sqrt{x^2 + \frac{4}{3}x + 4} \right]. \quad (5)$$

The hyperfine splitting is given by the expression: $A \sim |F^{(j)}(0)|^2 |u^{(j)}(0)|^2 |\sum_{j=1}^6 x^{(j)}|^2$. If we consider that CB degeneracy lifting affects only electron probability in the valleys then the reduction of hyperfine interaction can be expressed in terms of the $x^{(j)}$ and the perturbation parameter $x_E = \Delta_2 x$ (meV) ($\Delta_2 = 2.17$ meV). We get then, for $j = 1, 2$:

$$(x^{(j)})^2 = \frac{1}{4} \left[1 - \frac{x_E + 2/3}{\sqrt{x_E^2 + (4/3)x_E + 4}} \right] \quad (6)$$

and for $j = 3, 4, 5, 6$:

$$(x^{(j)})^2 = \frac{1}{8} \left[1 + \frac{x_E + 2/3}{\sqrt{x_E^2 + (4/3)x_E + 4}} \right]. \quad (7)$$

For the hyperfine splitting reduction we obtain the following dependence on the perturbation parameter:

$$\frac{A'}{A} = \frac{1}{6} |\sum x^{(j)}|^2 = \frac{1}{2} \left[1 + \frac{2 + \frac{1}{3}x_E}{\sqrt{x_E^2 + \frac{4}{3}x_E + 4}} \right]. \quad (8)$$

In our interpretation the perturbation of valley-orbit matrix is due to quantum confinement combined with

shape asymmetry of small grains. We assume further that the grains have shapes of cigars ($d_{\perp} \times d_{\perp} \times d_{\parallel}$). From SEM pictures of the powders we calculate the average asymmetry parameter defined as ratio of the shorter side to the longer side of grain $\gamma_0 = d_{\perp}/d_{\parallel}$ is $\gamma_0 \approx 0.6$.

Many experimental and theoretical publications derive expressions for enlarging the energy band gap [16–18,20] when diminishing grain size. The enlargement is made up of a downshift of the VB and an upshift of CB [2]. Since in our study we are dealing with EMT shallow donor, then only the upshift of CB will affect electronic structure of phosphorus. For the assumed cigar-shaped grains, the upshift in perpendicular directions will exceed that one along the axis. In our analysis we take the general expression for CB upshift to be $\Delta E_{CB} = \alpha/d^{\beta}$ [17]. In line with the tetragonal perturbation we assume further that the grains are oriented in such a way that their longitudinal axis coincides with one of the $\langle 100 \rangle$ crystallographic directions. The correlation between the tetragonal perturbation in the valley-orbit matrix and the perturbation induced by quantum confinement takes the form: $3x_E = \Delta E(d_{\perp}) - \Delta E(d_{\parallel}) = (1 - \gamma^{\beta})\alpha/\gamma^{\beta}d_{\parallel}^{\beta}$. Knowing now the expression for the perturbation and for the hyperfine splitting, we can simulate our experimental results using α and β as fitting parameters, keeping the asymmetry parameter $\gamma = 0.6$. We find that the β parameter derived from fittings is not sensitive to the particular choice of γ . For all the powders; small, medium (big and small) and big, we get consistent results for β which are collected in the Table 1. Since homogeneity of grains was best for smallest powder, we consider the result $\beta = 1.2$ to be the most reliable. The α parameter changed from powder to powder and showed dependence on γ . For the fitting obtained for the smallest grains with γ taken from SEM pictures the explicit upshift of CB has the form $\Delta E_{CB}[\text{meV}] = 800/d^{1.2}[\text{nm}]$. This is far less rapid than expected from a simple EMT approximation. Expression for CB upshift is experimental result obtained for larger grains with broader size distributions than the theoretical calculations has been performed. Extrapolation of band-gap behaviour from small nanocrystals up to bulk material has been postulated by Delley et al. [19]. Our result is similar to that which has been calculated by pseudo-potential method by Ögüt et al. [1] for few nm Si grains. We note that our approximation holds for relatively small perturbations only, i.e., for relatively large grains. For large perturbations — $x \gg 1$ the 2 CB valleys distinguished by the perturbation become fully populated and the hyperfine splitting approaches in its limiting value $A' \rightarrow \frac{2}{3}A$. Any further upshift of CB, and thus an increased non-equivalence of the 6 CB minima, will not affect the hyperfine splitting A . Therefore for still smaller grains another experimental techniques should be more appropriate [20].

Finally we note that the second effect, an increased mutual interaction between donors, can be elucidated in

Table 1

Fitting parameters $\beta(\Delta E_{CB} \propto 1/d^{\beta})$ for different silicon nanocrystals

Powder type	Parameter β
Big	1.17
Medium big	1.17
Medium small	1.27
Small	1.2

terms of the admixing of the excited states E. The overlap between electron wave functions increases then due to the extended p-like character of the state E.

5. Summary

We show experimental evidence that the electronic structure of a shallow donor center phosphorus in silicon is changed when placed in a nanocrystal environment. The observed effects can be understood within the EMT by the ground state perturbation induced by the size confinement when combined with the asymmetry of the grains. The use of surface insensitive monitoring allows thus to observe the onset of the quantum confinement: it is shown to take place for relatively large grains of approximately 50–100 nm size. We conclude that in this range the confinement-induced CB upshift follows $\Delta E_{CB} \propto d^{-1.2}$ dependence.

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