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Confinement Effects of Phosphorus Donors Embedded in Silicon Microcrystals

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Due to their extended electronic structure shallow donors are believed to be very sensitive to confinement effects. Our interest is to investigate the influence of size on the properties of shallow donor phosphorus in mechanically milled silicon microcrystals. The crystallinity of powders is confirmed by X-ray diffraction and the size as determined by scanning electron microscopy was found to be 0.25 μm for smallest to 4 μm for largest microcrystals. In the current experiment we use electron paramagnetic resonance to measure the hyperfine interaction between donor electron and P nucleus. The hyperfine constant and mutual overlap of donor wave functions exhibit significant dependence on grain size and subsequent annealing. By photoluminescence spectroscopy the appearance of a strong band around 1515 nm which shifts to higher energies with diminishing grain size has been established.

Introduction. The interest in silicon low-dimensional structures stems from a variety of their interesting electronic properties. It has been shown [1] that the decreasing size of crystallites leads to a quantum confinement effect which enlarges the bandgap [2] and changes silicon band structure from indirect to direct [3]. Our research is focused on confinement effects in mechanically milled silicon microcrystals; these are monitored by their effect on the electronic structure of phosphorus impurity. This center is chosen in view of its shallow donor character with significantly delocalized electron wave function. Since the P° center in silicon is paramagnetic, we can use EPR to measure the hyperfine interaction whose magnitude is proportional to the localization of the electron wave function on the P nucleus [4]. If the grain size became comparable with the donor electron Bohr radius (approx. 2 nm) the electron wave function would be influenced with a consequent change of the magnitude of the hyperfine interaction.

Also photoluminescence (PL) efficiency and energy should be affected by the quantum confinement. In view of that we have investigated PL from silicon microcrystallites ([1, 3]).

Experimental Results and Discussion. For the current experiment two kinds of silicon doped with phosphorus have been used: Czochralski (CZ) $[P] \approx 6 \times 10^{15}$ cm^{-3} and float-zone (FZ) $[P] \approx 7 \times 10^{17}$ cm^{-3}. Microcrystals have been prepared by mechanical milling for 10 min to 2 h, followed by sedimentation of 20 min to 5 h. In this way segregation in size in the range of one order of magnitude from original powder into three types of grains could be achieved: as-milled with grain size of 700 nm (medium), the ones which stayed in the liquid with size of 315 nm (small) and the ones of size

3900 nm which dropped to the bottom of the container during sedimentation (big). Subsequently, powders were annealed at 1000 °C in open air for times varying from 10 min to 100 h. The annealing was performed in order to reduce surface effects by passivation and also to reduce the silicon core size by creation of a SiO_2 layer.

The crystallinity of silicon milled powders has been confirmed by X-ray diffraction. Characteristic diffraction patterns were clear and strong for as-milled powders and showed decreasing intensity after prolonged heat-treatment indicating size reduction of the silicon core. The actual average size of particular microcrystals was measured by Scanning Electron Microscopy (SEM) and determined to be in the range of 0.25 to 4 μm. As expected for mechanical milling the size distribution showed a long taii toward larger grains.

The EPR measurements were performed in a superheterodyne K-band spectrometer in dispersion mode at temperature T = 4.2 K. The EPR spectrum of P donors in bulk Si consists of two lines with the separation determined by the magnitude of the hyperfine interaction. The spin Hamiltonian of the system is

$$\mathcal{H} = \mu_B \mathbf{B}\bar{\bar{g}}\mathbf{S} - g_N\mu_N \mathbf{B}\mathbf{I} + \mathbf{S}\bar{\bar{A}}\mathbf{I}\,. \tag{1}$$

At moderate concentrations ($[P] = 10^{16}\ cm^{-3}$) low intensity lines appear in between; they originate from mutual overlap of electron wave functions of individual donors. At high concentrations ($[P] > 10^{17}\ cm^{-3}$) the two lines characteristic of an isolated donor become small and a strong Lorentzian shaped line appears in the middle due to motional narrowing.

The hyperfine constant A describes the interaction between electron and nuclear spins and is proportional to the localization of electron wave function on phosphorus nucleus: $A = \frac{\mu_0}{4\pi} g_e\mu_B g_N\mu_N\, |\Psi(0)|^2$. For P in bulk silicon the value of the hyperfine splitting is A = 4.2 mT [4].

In the current experiment lowering of the hyperfine interaction with diminishing crystallite size and upon annealing has been observed in silicon microcrystals. Fig. 1 presents annealing time dependence of the hyperfine parameter A as measured for three powders with different crystal sizes. For all powders the value of A is by 0.7 to 4.7% smaller than in bulk material. From the figure we note that the smaller the initial grain size of the powder, the steeper the dependence. We have also observed that the EPR

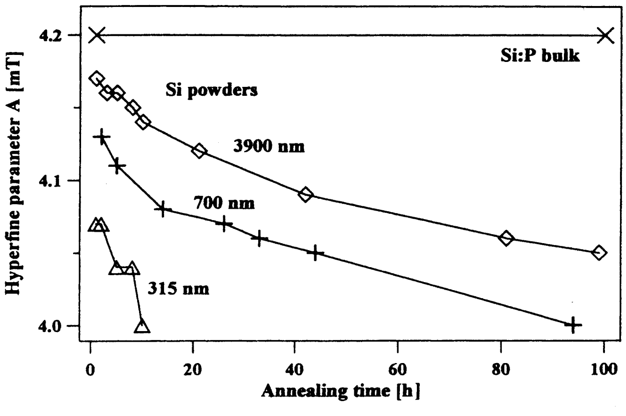

Fig. 1. Hyperfine interaction parameter versus annealing time (1000 °C in air) for three different silicon microcrystals with grain sizes of 315, 700 and 3900 nm

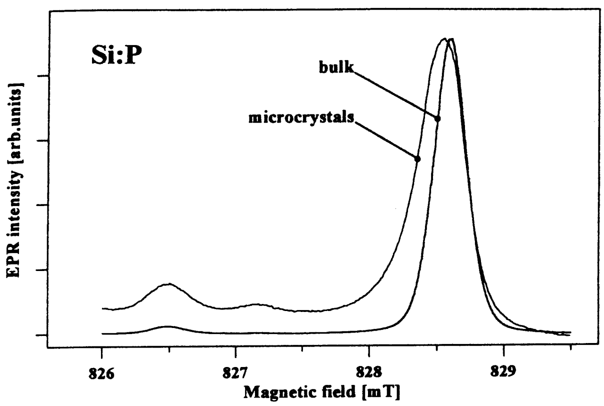

Fig. 2. EPR spectrum of the CZ-Si:P microcrystal sample: one of the two hyperfine lines and small peaks originating from mutual overlap between individual donors are shown as measured in bulk and Si-powder (with size $d \approx$ 315 nm). Microwave frequency is $\nu = 23.11997$ GHz

signal intensity strongly decreases with annealing time for the smallest powders. It may be thought of as related to creation of an SiO_2 layer on the surface of grains, thus, effectively shrinking the volume of the silicon core which contributes to our measurements. EPR spectra of CZ-Si:P measured for bulk and for microcrystal samples (size $d \approx 315$ nm) are shown in Fig. 2. The EPR line from Si microcrystals has an asymmetric shape tailing toward lower values of the hyperfine constant A. We ascribe that effect to the size distribution of microcrystals resulting in a spread of the hyperfine constant values. In our interpretation lowering of A is due to the reduction of electron localization on P nucleus induced by volume confinement. For the grain sizes of a few hundreds of nanometers, such a perturbation of the electron wave function will affect only paramagnetic centers located in the vicinity of the grain border; these will contribute to the low-A tail of the observed line shape. The majority of centers will be located in the central part of the microcrystal with standard A constant. Variation of the hyperfine interaction was also observed in SiGe alloys by Feher [5]. He observed an increase in width of the P line due to a spread of the hyperfine interaction from one donor to another.

By inspecting the EPR spectra of the microcrystals we also note that the middle lines originating from mutual overlap between donors [6] show an increased intensity in comparison with the bulk sample of the same material. Consistent effects were also observed in microcrystals prepared from FZ-Si with higher P concentration ([P] = 7×10^{17} cm^{-3}), where the side P lines disappeared completely and one major motionally narrowed line appeared. We conclude therefore that the reduction of the grain size and the annealing treatment enhance mutual interaction between donor electrons. If we compare three EPR spectra of Si:P due to bulk sample, as-milled microcrystals and powders after heat treatment at 1000 °C, the EPR pattern will continuously change from the one characteristic for original concentration to that which is usually observed for bulk Si:P sample with twice higher doping [7].

Also PL of the mechanically milled microcrystals has been investigated. PL spectra were recorded at $T = 4.2$ K upon excitation of Ar-ion laser (wavelength $\lambda = 514$ nm). Annealing of the samples at 1000 °C in water for 10 min was performed in order to passivate the surface. After that short heat treatment silicon powders display a strong PL signal around 1515 nm. At this wavelength a PL spectrum has been observed before in dislocated bulk Si [8]. Accordingly we relate the observed PL to dislocations

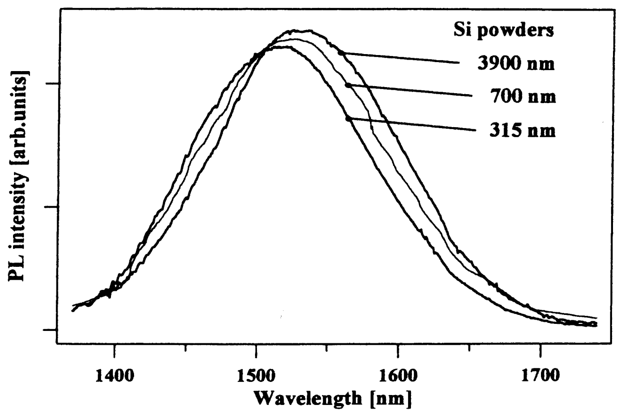

Fig. 3. PL spectra from Si microcrystals with sizes of 315, 700, 3900 nm after 10 min annealing at 1000 °C in water vapor

generated in the microcrystals by mechanical milling and subsequent annealing. The present investigation shows that in the microcrystals the observed PL band exhibits a clear blueshift from 1520 to 1510 nm upon size reduction: the effect is illustrated in Fig. 3. Further studies are necessary to establish whether this shift is due to the quantum-confinement related bandgap change of the silicon microcrystal, or is induced by variation of the strain field around a dislocation upon size reduction or annealing.

References

[1] S. ÖĞÜT, J.R. CHELIKOVSKY, and S.G. LOUIE, Phys. Rev. Lett. **79**, 1770 (1997).
[2] L.E. BRUS, J. Chem. Phys. **80**, 4403 (1984).
[3] T. TAKAGAHARA and K. TAKEDA, Phys. Rev. B **46**, 15578 (1992).
[4] W. KOHN and J.M. LUTTINGER, Phys. Rev. **97**, 883 (1955).
[5] G. FEHER, Phys. Rev. **114**, 1219 (1959).
[6] C.P. SLICHTER, Phys. Rev. **99**, 479 (1955).
[7] S. MAEKAWA and N. KINOSHITA, J. Phys. Soc. Jpn. **20**, 1447 (1965).
[8] N.A. DROZDOV, A.A. PATRIN, and V.D. TKACHEV, Soviet Phys. – J. Exper. Theor. Phys. Lett. **23**, 597 (1976).