Influence of the grain structure on the Fermi level in polycrystalline silicon: A quantum size effect?

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It has been observed by several authors that metal-oxide-semiconductor devices with polycrystalline Si (poly-Si) gates behave differently depending on the doping species in poly-Si: the work-function difference between the silicon substrate and the gate (ϕ_{PS}) is higher when the gates are doped with arsenic than when they are doped with phosphorus. As a function of the doping devel, this difference becomes first noticeable at $\sim 10^{19}$ cm^{-3}, and then it increases for heavier doped materials, reaching 120 meV near the dopant solubility limit. We believe that the different behavior of ϕ_{PS} can be explained by different grain textures at the poly-Si/SiO_2 interface. Our transmission electron microscopy of the films indicates that while P-doped material consists of large ($\gtrsim 3000$ Å) grains, As-doped poly-Si preserves its as-deposited columnar structure, even after a high-temperature anneal. Moreover, at the interface with the gate oxide an as-deposited microstructure with very small ($\lesssim 100$ Å) "embrionic" grains is preserved. On the basis of these observations, we suggest a model for the different behavior of ϕ_{PS}. The model is based on a quantum size effect which becomes important for such small grain dimensions at the interface in As-doped poly-Si. This effect drastically reduces the number of states available in the conduction band at low energies and thus forces a more complete filling of the impurity band. The resulting shift of the Fermi level provides a qualitative explanation for the observed puzzling difference between the work functions of As- and P-doped poly-Si.

Polycrystalline silicon (poly-Si) gates have become an important element of the modern technology. In dealing with the poly-Si material it is usually assumed that its band structure is similar to that of a single-crystal Si, and the work-function difference ϕ_{PS} between the Si substrate and a poly-Si gate is usually estimated on that basis. The ϕ_{PS} is an important parameter of the metal-oxide-semiconductor system, because it determines the threshold voltage of a field-effect transistor. It is usually measured as the difference in the positions of the Fermi levels in the Si substrate and in poly-Si of the gates at the so-called "flatband condition."[1]

In a recent work[2] we correlated the ϕ_{PS} with both the doping level and carrier concentration in poly-Si (the substrate doping was kept constant and the electron concentration in poly-Si was determined by the Hall method). The poly-Si was doped by ion implantation either with arsenic or phosphorus, with the doping level varying from mid 10^{19} to high 10^{20} cm^{-3}. We found that at moderate doping levels the ϕ_{PS} values for As and P doping are identical when plotted as a function of the electron Hall concentration. This is, of course, as expected, since the Fermi level is supposed to be determined only by the carrier concentration.[3] However, at high concentrations the two curves begin to diverge (Fig. 1), so that at concentrations near the dopant solubility limits[4] the difference in ϕ_{PS} between As- and P-doped materials reaches $\gtrsim 0.12$ eV.

This puzzling difference has not been explained, although we had suggested[2] that it may be related to a difference in the grain size in the As- and P-doped poly-Si. It is known that the presence of P in high concentrations promotes the grain growth in poly-Si, while As has no such effect.[5] The presence of this effect in our structures is demonstrated in Fig. 2, which shows the grain texture of the two materials as seen in a transmission electron microscope (TEM). The poly-Si films 4000 Å thick were deposited at 625 °C. They were implanted with the respective dopants (dose: 1×10^{16} cm^{-2}) and annealed for 1 h at 900 °C. The difference between the two films is glaring. P-doped poly-Si consists of large (3000 Å) grains which form a smooth interface with the adjacent SiO_2. As-doped poly-Si preserves its as-deposited structure which consists of smaller (700 Å) columnar grains. Moreover, it is clearly seen in the micrograph that the texture of the As-doped film in the area *adjacent to the gate oxide* is different from the rest of the film: it represents a mesh of smaller grains. Note that the layer of poly-Si adjacent to the gate oxide is the region whose properties directly influence the work-function difference. Let us take a closer look at this particular region. The planar TEM micrograph in Fig. 2(c) was prepared by etching away the Si substrate from the structure shown in Fig. 2(b). Then the top As-doped poly-Si layer was etched to form a wedge. One

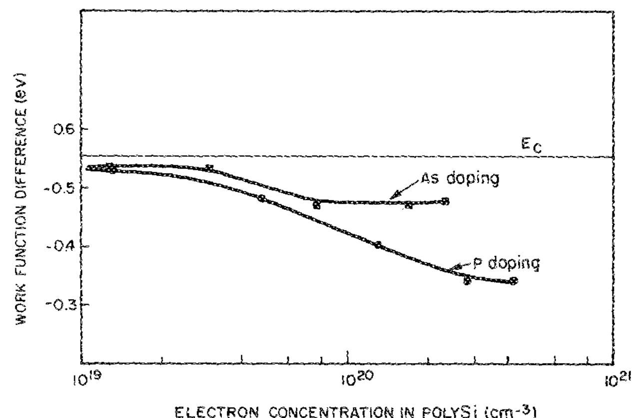

FIG. 1. Dependence of the Fermi level in poly-Si gates doped with As and P, as measured by the C-V method, on the electron concentration. For reader's convenience, the energy values are referred to the midgap level in the substrate—rather than to the substrate Fermi level.

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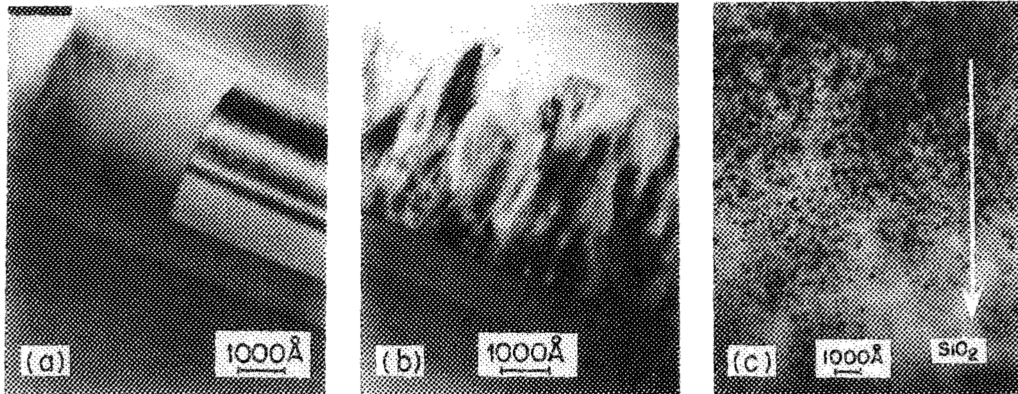

FIG. 2. Transmission electron micrographs of the poly-Si layers deposited on the gate oxide. (a) Cross-sectional TEM of P-doped poly-Si. (b) Cross-sectional TEM of As-doped poly-Si. (c) Planar TEM of As-doped poly-Si. The Si substrate was removed and poly-Si was etched to form a wedge. The wedge-thinning direction is shown by an arrow.

can see the grain size diminishing towards the thinner side of the wedge (in the direction of the SiO_2 interface). At the interface, the grain size is of the order of 100 Å. No such structure exists in the P-doped poly-Si, which strongly suggests that the small grains may be responsible for the observed difference in ϕ_{PS}.

Another indication that this might be the case comes from experiments[6] with As-doped poly-Si gates whose grain structure was formed during poly-Si deposition at 900 °C—prior to As implantation and anneal. The structure of those films was similar to that in Fig. 2(a), with large grains (3000 Å) and a smooth interface with the gate oxide. When compared to poly-Si gates deposited at a standard 625 °C, a consistent difference of 100 meV ϕ_{PS} was observed[6] (both lots were implanted with identical doses of As and annealed at 900 °C). This result also suggests that it is the grain structure, rather than the doping species, which is responsible for the observed ϕ_{PS} difference. Let us emphasize again that the data in Fig. 1 are plotted in terms of the *carrier concentration*, not of the doping level. This appears to rule out any explanation based on the different tendencies of As and P to segregate to the grain boundaries, the different solid solubilities of the two dopants, or the larger surface-to-volume ratio in fine-grain structures leading again to a greater amount of segregated arsenic.

In this work we attempt to qualitatively explain the effect of small grains on the position of the Fermi level in poly-Si and, therefore, on the value of ϕ_{PS}. We also explain why this difference occurs only at higher doping levels. Before discussing our model let us briefly review several phenomena important for a better understanding of the problem.

(1) *Band-gap narrowing at high-doping levels*. The value of 1.12 eV, usually quoted for the room-temperature energy gap in Si, is relevant only under light-doping condition. At high dopant concentrations the band gap undergoes considerable narrowing due to the local fields of charged impurity centers and because of many-body effects.[7] According to the experimental results quoted in Ref. 7, at a dopant concentration of 2×10^{20} cm^{-3} the gap narrowing is of the order of 250 meV. The depth of the Fermi sea at this concentration is 100 meV. This would bring the position of the Fermi level relative to the midgap point of the substrate in our system to $\approx$0.4 eV, which is in a reasonable agreement with 0.38 eV observed experimentally for P-doped material (Fig. 1). The movement of the Fermi level downward at high concentrations, seen in Fig. 1, is thus accounted for by the band-gap narrowing effect, and it is reasonable to conclude that the behavior of the Fermi level in a large-grain P-doped poly-Si is similar to that in a single-crystal Si. It is, therefore, the behavior of As-doped materials which should find an explanation.

(2) *The impurity band*. At low doping densities the dopant atomic wave functions do not overlap and the impurity-bound electron states form a degenerate level within the energy gap. At higher doping levels, when the wave functions of separate dopant atoms begin to overlap, the level widens into an impurity band.[8] A detailed discussion of the impurity band behavior as a function of the donor concentration in silicon can be found in Ref. 9. The width of this band increases with the dopant concentration and at the doping density of $\approx 10^{20}$ cm^{-3} it becomes $\approx$0.3 eV. The impurity band is approximately centered at the same energy as the original donor level.

(3) *Grain boundaries in poly-Si*. Polycrystalline silicon can be viewed as an agglomeration of single-crystal Si grains separated by grain boundaries. These boundaries are the loci of an orientational misfit; their properties are not well understood. It is known, however, that they contain charged traps. It is also known that *n*-type dopants and some other impurities tend to segregate to the grain boundaries.[5,10] Therefore, the grain boundaries present a potential barrier for the free-carrier transport; cf. the review[11] and references therein. In general, this barrier results from two contributions: (i) The potential variation in the depletion region near the grain boundary, arising from the field of charges trapped at the boundary; this barrier, studied extensively in *p*-type poly-Si,[12,13] becomes negligible at high doping densities. (ii) The *core* barrier, which is a property of the grain-boundary material itself, rather than the doping level or the state of charged traps. It was found experimentally[14] that grain boundaries in As- and P-doped poly-Si are best modeled by narrow (7 Å) rectangular barriers of height 0.66 eV.

(4) *Quantum size effect in small grains*. It is, therefore, reasonable to assume that a conduction-band electron is strongly confined by the potential barriers at the grain boundaries of the *n*-type poly-Si. Then we can view a small grain as a three-dimensional potential well formed by the grain boundaries. The energy spectrum of an electron confined in such a well will be different from that of a free electron in the conduction band. Because of the quantum size effect the continuous spectrum of a free electron becomes discrete and the density of states in the conduction band at low energies is

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depressed. Modeling a poly-Si grain as a cube of side $a \sim 100$ Å we can estimate the electron energy levels from the expression

$$E_{n_1,n_2,n_3} = \frac{\pi^2\hbar^2}{2a^2}\left(\frac{n_1^2+n_2^2}{m_t}+\frac{n_3^2}{m_l}\right)$$
$$\simeq 4[\text{meV}][5(n_1^2+n_2^2)+n_3^2], \qquad (1)$$

where m_t and m_l are the longitudinal and the transverse electron masses in the grain, and the quantum numbers n_j ($j = 1,2,3$) assume the values $n_j = 1,2,...$ It is easy to see from Eq. (1) that the density of states in the conduction band is drastically reduced by the quantum size effect. At electron concentrations of 2×10^{20} cm^{-3} a 100-Å grain contains 200 electrons, but below 100 meV (which is the Fermi level calculated without confinement) there is room for only 72 of them in the conduction band (including the twofold spin and the sixfold valley degeneracy). It should be, of course, noted that the measured Hall concentration refers to the bulk of poly-Si layers, which is not necessarily identical to that at the SiO_2 interface. Figure 3 displays the dependences of the Fermi level on the electron concentration in the conduction band, calculated with and without the confinement effect for $T = 300$ K. We see that at the concentrations of order 2×10^{20} cm^{-3}, the shift of the Fermi level is about 0.1 eV.

We can now summarize our model. Position of the Fermi level in poly-Si is determined by filing of both the conduction-band and the impurity-band states. In the case of large grains, the Fermi level is determined mainly by filling of the conduction-band states, and the measured ϕ_{PS} is well accounted for by the band-narrowing effect.[2] However, for grains as fine as those observed near the gate oxide in case of As doping, the quantum size effect comes into play: the conduction-band density of states is reduced and electrons are distributed mainly on the impurity-band levels. As a result, the Fermi level moves higher. This difference in the position of the Fermi levels for the two gates (As and P doped) manifests itself in the measured ϕ_{PS} difference. Positions of the bands and the Fermi level at different carrier concentrations are schematically illustrated in Fig. 4. To give a quantitative account of the bands and levels shown in Fig. 4, one would have to know accurately the densities of states in both the impurity and the conduction bands distorted by many-body effects and short-range potential fluctuations. Since such information is unavailable at present, we feel it would not be meaningful to go beyond the qualitative arguments presented above.

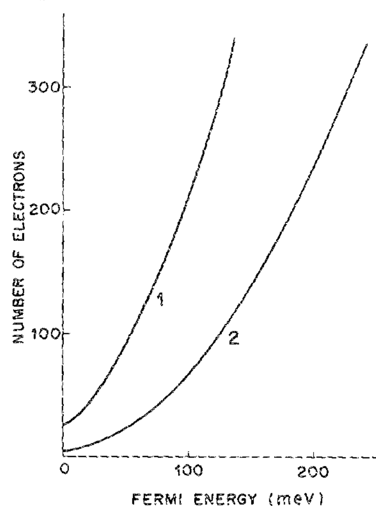

FIG. 3. Relation between the Fermi level at 300 K and the number of carriers in a cube 100×100×100 Å, calculated for the "classical" case (bulk-Si, curve 1) and the quantum confined case (curve 2).

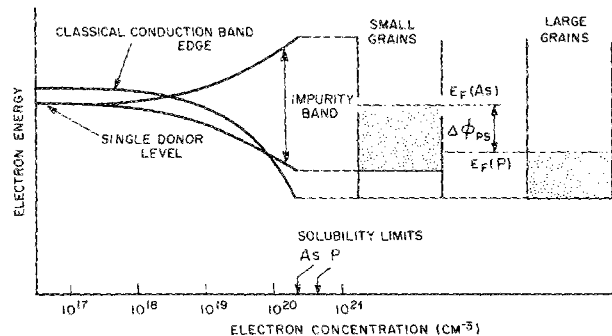

FIG. 4. Schematic illustration of the behavior of energy levels and bands in polycrystalline silicon at different concentrations.

It should be emphasized that our model is by no means unique; there may be other explanations (which we have not been able to contrive). We have shown that the structural properties of poly-Si may influence its band structure, and, therefore, the MOS properties of poly-Si gates. The discrepancy between the work functions of poly-Si gates heavily doped with As and P, which manifests itself in different flatband voltage values on the same substrate,[2] can be explained by a peculiar grain structure in As-doped poly-Si which leads to a quantum size effect on the work function of a poly-Si sublayer—in the area adjacent to the oxide—which is responsible for the MOS characteristics. The prevalence of ultrasmall grains in that structure near the interface with SiO_2 is demonstrated by transmission electron microscopy. It is rather amusing that such a mundane object as a poly-Si gate may exhibit a large quantum size effect at room temperature.

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[4] These limits (approximately 2×10^{20} cm^{-3} for As and 4.5×10^{20} cm^{-3} for P; cf. Ref. 2) are different from the usual "metallurgical" solubility limits and have the following meaning: they represent the highest active carrier concentration at room temperature which can be obtained by implanting and annealing a high dose of the respective dopant atoms.

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