

Phosphorus redistribution in P-doped polycrystalline silicon/tantalum silicide system during high temperature sintering

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We studied redistribution of phosphorus between layers of P-doped polycrystalline silicon and TaSi_2 during sintering of the silicide at 900°C . Because of the loss of phosphorus to the silicide, the sheet resistivity of polysilicon layers is increased. We attempted a systematic study of this effect using polysilicon layers of varying thicknesses (from less than 1000 to more than 6000 Å). The experimental results are in excellent agreement with our model which regards the concentrations of phosphorus in both polysilicon and silicide as dilute solutions and assumes that during sintering of the silicide these solutions come to equilibrium. From the equilibrium condition of uniform chemical potential with respect to the solute, we were able to determine the distribution coefficient of P between the two solvents.

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At the present stage of integrated circuit processing the resistance of polysilicon interconnects sets limits for further miniaturization. In order to decrease this resistance one uses polysilicon/silicide gates and interconnects. In such gates a heavily doped polysilicon layer adjacent to the gate oxide ensures the desired metal-oxide-semiconductor (MOS) properties, while a layer of silicide on top of polysilicon provides low resistance. In light of this development the exchange of impurities between polysilicon and silicides at elevated temperatures becomes a matter of interest. The polycrystalline nature of silicides suggests that the solubilities of various impurities and dopants in a silicide should be comparable to those in polysilicon. In this case the dopants will readily diffuse into the silicide. On the other hand, certain heavy impurities, e.g., Cu, Fe, or Ta, which are naturally abundant in the silicide, may diffuse into polysilicon and accumulate at the latter interface with the oxide. Such effects are responsible for a peculiar degradation of the MOS properties of polysilicon/silicide gates at intermediate stages of the transistor fabrication process.¹ Redistribution of impurities between the silicide and polysilicon layers can also be a useful effect. It has been shown, for example, that one can implant arsenic into the silicide and have it diffuse into the undoped polysilicon layer to form an ohmic contact.² Similar situations can be expected with other dopants, provided their solubilities in polysilicon and silicide are comparable.

In this work we study a system of phosphorus-doped polysilicon and tantalum silicide. We will show that the TaSi_2 layer absorbs a significant share of phosphorus from the polysilicon during the high-temperature sintering of the silicide (1 h at 900°C). It is not evident *a priori* whether this time should be sufficient for establishing an equilibrium concentration of phosphorus in the two phases (TaSi_2 and poly). The "mopping up" effect of the silicide could conceivably be governed by the kinetics of phosphorus diffusion across the boundary so that the final phosphorus concentration after sintering would still not correspond to equilibrium. Our results, however, indicate unambiguously that the equilibrium is, in fact, established, and is determined by the condition of uniform chemical potential of phosphorus in both phases.

Thus, from the experimental data we are able to determine the built-in difference in the distribution coefficient or "work function" for the dopant atoms in two solvents.

Polysilicon layers of various thicknesses were LPCVD deposited on top of 1000-Å-thick layers of silicon dioxide. The polysilicon layers were doped with phosphorus by diffusion from a PBr_3 source at 950°C . Sheet resistivity of the samples was measured and the duration of diffusion was adjusted to ensure saturation doping level. Then layers of tantalum silicide, 2500-Å thick, were cosputtered on polysilicon surface and sintered at 900°C for 60 min. To prevent out-

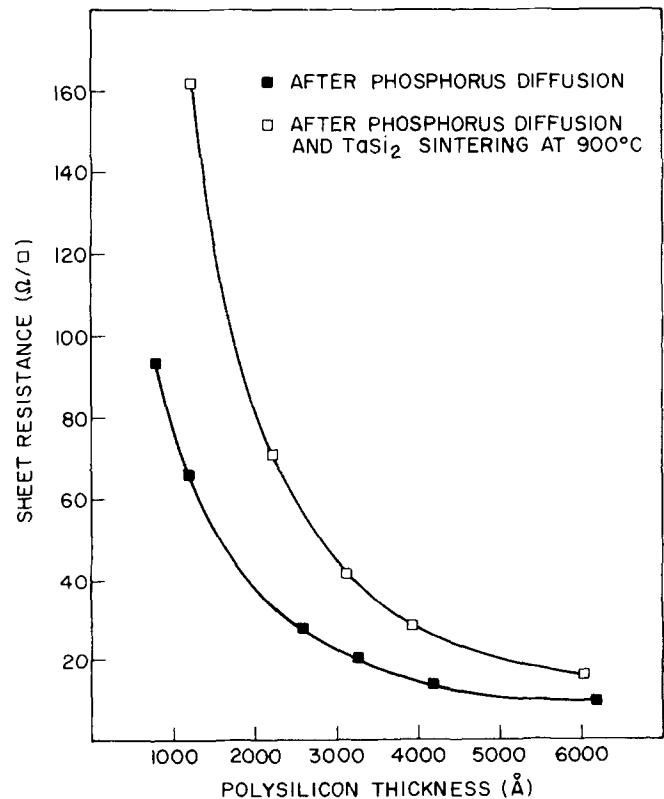


FIG. 1. Sheet resistance of polysilicon layers plotted as a function of layer thickness.

diffusion of impurities during sintering, the structure was covered with a protective layer of CVD oxide (1200-Å thick). After the sintering the silicide was chemically etched away (BHF, etching rate ≈ 200 Å per min). At this point the thickness and the sheet resistivity of the samples were measured again. Thickness measurements were made on Nanospec/AFT interferometer to the accuracy of better than 50 Å, and the resistivity was measured by a four probe method (relative accuracy of about 5%).

Results of the measurements are shown in Fig. 1. The sheet resistance of phosphorus doped polysilicon layers is plotted as a function of layer thickness. Resistivities obtained after diffusion of phosphorus (marked with filled squares) lie on a hyperbola corresponding to a bulk resistance of $6.1 \times 10^{-4} \Omega \text{ cm}$. This indicates that the polysilicon layers were doped to the saturation level ($\approx 6 \times 10^{20} \text{ cm}^{-3}$).³

Sheet resistances of the same samples after the tantalum silicide has been deposited, sintered, and then chemically removed, are shown by open squares. During the silicide etch about 100–200 Å of polysilicon was lost. It is clear from the figure that resistances of the polysilicon layers grew after the TaSi₂ sintering, the difference being especially pronounced for thin samples.

After the initial phosphorus diffusion the polysilicon layers were doped to a saturated density n_0 (per cm³). The value of n_0 is not expected to vary with the layer thickness (d). The sheet conductivity σ_0 of a polysilicon layer is given by

$$\sigma_0 \equiv \frac{1}{\rho_0} = \alpha e n_0 d \mu, \quad (1)$$

where e is the electron charge, μ the electron mobility in polysilicon, d the layer thickness, and $\alpha \lesssim 1$ describes the fraction of dopant atoms which are electrically active.

According to Eq. (1) the conductivity σ_0 should be a linear function of d provided the mobility and α do not vary with layer thickness. Experimentally, this is indeed the case. In Fig. 2 we plot σ_0 vs d . The experimental points lie closely on a straight line, whose slope is proportional to n_0 . Strictly

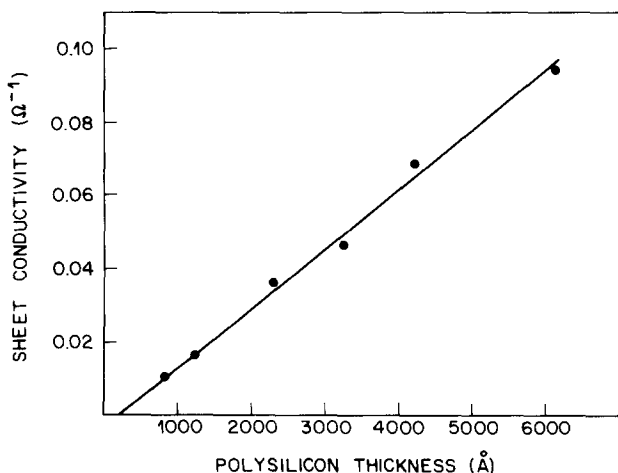


FIG. 2. Sheet conductivity of polysilicon layers after phosphorus diffusion (before silicide deposition and sintering).

speaking, this line does not cross the abscissa at the origin and therefore, corresponds not to Eq. (1) but rather

$$\sigma_0 = \alpha e n_0 \mu (d - d_0), \quad (1a)$$

where d_0 is of order 200 Å. This means that the polysilicon layers are not uniformly conducting but contain a constant thin resistive sublayer near the boundary. The nature of this sublayer will be discussed in detail elsewhere.³ For the sake of simplicity, the effect of d_0 will be neglected below.

During the high temperature sintering some fraction of the dopant escapes into the silicide. As discussed in Sec. I, we believe that the final ratio of dopant concentrations in the polysilicon and the silicide corresponds to equilibrium. Proceeding on this assumption we calculate the expected conductivity of polysilicon layers after the redistribution of phosphorus and find an excellent agreement with our observations.

Even when the solution of phosphorus in polysilicon or silicide is saturated, it is still a dilute solution in the sense that the ratio of the number of P atoms to the number of the solvent atoms is small. This allows us to use simple expressions of the theory of dilute solutions⁴ to describe the equilibrium. At the high temperatures of sintering our system represents two solutions in contact, the solutions being of the same substance in two different solvents. The solvents—silicide and polysilicon—can be regarded as immiscible, so that the equilibrium condition is that the chemical potentials of the solute (phosphorus) in the two solutions should be equal. This condition can be written in the form (Ref. 4, p. 271):

$$\frac{n_1}{n_2} = e^{(\psi_2 - \psi_1)/kT} \equiv \xi^{-1}(T), \quad (2)$$

where n_1 and n_2 are the concentrations of phosphorus in polysilicon and silicide, respectively. It is important that at a constant pressure the right-hand side of Eq. (2) is a function of temperature only. The quantities ψ_1 and ψ_2 characterize the phosphorus solubility in polysilicon and silicide, respectively, at a given temperature and pressure. The difference $\psi_1 - \psi_2$ can be interpreted as a work-function difference (by analogy with carrier diffusion in inhomogeneous semiconductors).

On the other hand, assuming that no phosphorus was lost during the redistribution, we can write

$$n_1 d + n_2 d_s = n_0 d, \quad (3)$$

where d_s is the thickness of silicide layers (2500 Å). Solving Eqs. (2) and (3) for n_1 we find

$$n_1 = \frac{n_0 d}{d + \xi d_s}. \quad (4)$$

Whence the sheet resistivity of polysilicon after the impurity redistribution and subsequent removal of silicide, is given by

$$\rho_1 \equiv \frac{1}{\sigma_1} = \frac{d + \xi d_s}{\alpha e \mu n_0 d^2}. \quad (5)$$

In Fig. 3 we plot $\rho_1 d^2$ vs d . The result is a straight line, as predicted by Eq. (5). The intercept of this line with the abscissa occurs at $-d = \xi d_s = 4600$ Å. From the known silicide thickness $d_s = 2500$ Å (for all samples) we can estimate ξ to be 1.84. Repeating these experiments at different tempera-

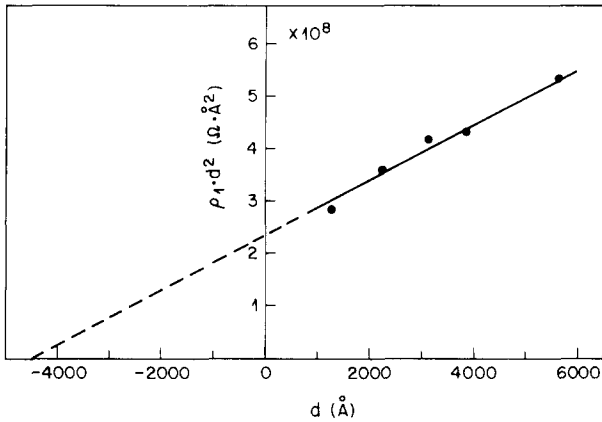


FIG. 3. Sheet resistance of polysilicon layers after sintering and subsequent removal of tantalum silicide. According to Eq. (5), we plot $\rho_s d^2$ vs d .

tures we should be able to trace the function $\xi(T)$. Our simple technique gives a means of determining experimentally the solubilities of various dopants in polysilicon–silicide and, in principle, other binary systems.

One should, of course, remember that the assumption of achieved equilibrium is essential here. The close agreement of Eq. (5) with experimental data corroborates this assumption for our experiments in which the phosphorus impurities were allowed 60 min to redistribute themselves at 900 °C. At a lower temperature the equilibration may take much longer.

Equation (5) is valid whether or not the electron mobility in polysilicon has changed after sintering. Since the grain structure of polysilicon was formed during the initial phosphorus diffusion at 950 °C, it is not likely to change during the sintering, and, therefore, we can expect that the electron mobility is the same before and after sintering. We can, in fact, test this hypothesis by comparing the slopes in Figs. 2 and 3. In both cases the slopes are determined by the same quantity $\gamma = \alpha e n_0 \mu$ (in Fig. 3 the slope equals $1/\gamma$). From

Fig. 2 we find $\gamma_1 = 1.7 \times 10^{-5} \Omega^{-1} \text{Å}^{-1}$, and Fig. 3 gives $1/\gamma_2 = 5.3 \times 10^4 \Omega \text{Å}$. Whence $\gamma_1/\gamma_2 = 0.9$, which means that the effective mobility $\alpha\mu$ has increased after sintering by about 10%.

We studied the system of phosphorus doped polysilicon/tantalum silicide at high temperatures. We found that a strong diffusion of phosphorus from polysilicon into the silicide occurs during 1-h silicide sintering at 900 °C. The impact of the loss of phosphorus to the silicide is particularly noticeable in thinner layers. It turns out that the redistribution of phosphorus between the polysilicon layer and the silicide is well described by a model which regards the concentrations of phosphorus in both phases as dilute solutions and assumes that toward the end of the sintering stage these solutions come to equilibrium. The equilibrium condition with respect to the solute requires uniformity of the chemical potential of phosphorus throughout the polysilicon/silicide system. On the basis of this model we were able to determine the built-in chemical potential (“work-function”) difference from our measurements of the sheet resistivity of polysilicon layers after sintering as a function of the layer thickness.

We would like to emphasize that the assumption of the equilibrium is not *a priori* evident, but rather it is our conclusion which follows from the good agreement between the experimental results and theoretical predictions. Our preliminary results show that the assumption of equilibrium after 1 h at 900 °C sintering is not valid for the silicide/P-doped polysilicon system if the silicide is implanted with As prior to sintering. It is speculated that a pileup of arsenic on the silicide/polysilicon boundary may significantly slow down the diffusion of phosphorus across the boundary. It should be interesting to pursue further experiments with varying temperatures of sintering.

¹N. Lifshitz and S. Luryi, IEEE Trans. Electron Devices, July 1983.

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⁴L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980), Vol. 1.