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The wetting of oxide films on silicon and the monitoring of fixed charge

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Abstract. The wetting of thin oxide films on silicon by water is affected by fixed charge near the outer surface of the oxide. We show that existing data can be analysed to give both the depth and concentration of these fixed charges. The precise values indicate depths of a few ångstroms and concentrations of a few times 10^{13} cm^{-2}. There are hints that the values depend on the temperature at which the oxide is grown. We conclude that the wetting angle offers a further method of measuring fixed charge.

1. Introduction

It is a well known observation that, immediately after the removal of the oxide film on silicon, water does not wet the silicon surface whereas the growth of a mere 40 Å or so of oxide gives a surface which can be wetted completely. The phenomenon was studied in detail by Williams and Goodman (1974), who discussed possible explanations without a satisfying conclusion. Stoneham and Tasker (1985) noted that the results could be fitted rather well by assuming simply that there was some fixed charge in the oxide, close to the outer (oxide–atmosphere) surface. The fixed charge, because of the polarisation it creates, affects the difference in interfacial energy as one replaces the atmosphere (with low dielectric constant) by a medium – water – with high dielectric constant. In the present paper we perform a range of calculations which assess the phenomenon as a technique for measuring fixed charge, i.e. we ask what can be learned about fixed charges by monitoring the change of wetting angle with oxide thickness.

2. General expressions

Our calculations are those of continuum electrostatics and mechanics. We note that the wetting angle is given in terms of the interfacial energies by

$$\cos\theta = \Delta\sigma/\sigma_w \tag{1}$$

where σ_w is the water surface energy (equal to the surface tension for a liquid) and $\Delta\sigma$ is the difference between the oxide–atmosphere and oxide–water surface energies:

$$\Delta\sigma = \sigma_{OA} - \sigma_{Ow} \tag{2}$$

This difference, $\Delta\sigma$, consists of two terms. One, $\Delta\sigma_0$, is the surface energy difference for an 'ideal' charge-free oxide. The other, $\Delta\sigma_I$, arises because of the polarisation associated with fixed charges in the oxide, i.e. the so called image terms of Stoneham and Tasker (1985).

In the limit of a very thick oxide, with a single charge Qe at distance x from the outer surface of the oxide, the polarisation energy contributes the following term to the energy difference when water is put on the surface:

$$Q^2u(x) = (Q^2e^2/4\varepsilon_s x)\left(\frac{\varepsilon_s - \varepsilon_w}{\varepsilon_s + \varepsilon_w} - \frac{\varepsilon_s - \varepsilon_A}{\varepsilon_s + \varepsilon_A}\right). \tag{3}$$

Here ε_s is the dielectric constant of silicon dioxide, ε_A that of the atmosphere and ε_w that of water. We shall take $\varepsilon_s = 4.6$, $\varepsilon_A = 1$ and $\varepsilon_w = 80$ in our calculations. If there is a density of charges $\rho(x)$ per unit area, and if they are widely spaced (in practice, separations greater than their depth x suffice) then the charges at this depth contribute

$$\Delta\sigma_I = \rho(x)Q^2u(x) \tag{4}$$

to the difference in surface energies.

This standard image expression, equation (3), does not suffice for the thinner oxide layers of interest to us. We may follow the methods of Smythe (1939) to show that, for thickness t, $u(x)$ goes over to

$$\frac{e^2}{2\varepsilon_s}\int_0^{\infty} dk\left(\frac{\alpha+\beta-2\alpha\beta}{\alpha\beta-1} - \frac{\alpha_0+\beta-2\alpha_0\beta}{\alpha_0\beta-1}\right) \tag{5}$$

with

$$\begin{aligned}\alpha &= [(\varepsilon_w - \varepsilon_s)/(\varepsilon_w + \varepsilon_s)]\exp(-2kx) \\ \alpha_0 &= [(\varepsilon_A - \varepsilon_s)/(\varepsilon_A + \varepsilon_s)]\exp(-2kx) \\ \beta &= [(\varepsilon_{Si} - \varepsilon_s)/(\varepsilon_{Si} + \varepsilon_s)]\exp[-2k(t-x)].\end{aligned} \tag{6}$$

This integral reduces to $u(x)$ in the limit $t \to \infty$, i.e. $\beta \to 0$.

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3. Trends and orders of magnitude

3.1. Large-thickness limit

We note from the general form of equation (3) that $\Delta\sigma_I$ varies as Q^2/x multiplied by a function of the dielectric constants. This presumes the charges are far enough apart to be regarded as independent. Several points follow. First, charges close to the outer surface dominate because of the factor $1/x$. Secondly, large nominal charges Q have a large effect. For a charge $2e$ at depth $x = 1$ Å one finds

$$Q^2/4\varepsilon_s x \simeq 3.13 \text{ eV} \tag{7}$$

which, with a density of 10^{13} cm^{-2}, yields

$$\Delta\sigma_I \sim 90 \text{ erg cm}^{-2}. \tag{8}$$

Thirdly, so long as the charges can be regarded as independent, their sign is immaterial. There could be all positive charges ($Q = +2$), all negative ($Q = -2$) or equal numbers of each. There is no reason to require a dipole layer or a change in work function to match $\Delta\sigma_I$, although there may be a correlation of $\Delta\sigma_I$ and work function for other reasons. Finally, the dependence on ε_w (the dielectric constant of the liquid) is significant but not great. Going from water ($\varepsilon_w = 80$) even to a liquid of low dielectric constant, $\varepsilon_w = 2$, reduces $\Delta\sigma_I$ by a factor of four only. So, whilst there is an advantage in a liquid with large ε_w, other liquids (especially with $\varepsilon_w \gtrsim 20$) could be used if convenient. We now turn to the dependence on ε_w for smaller oxide thicknesses.

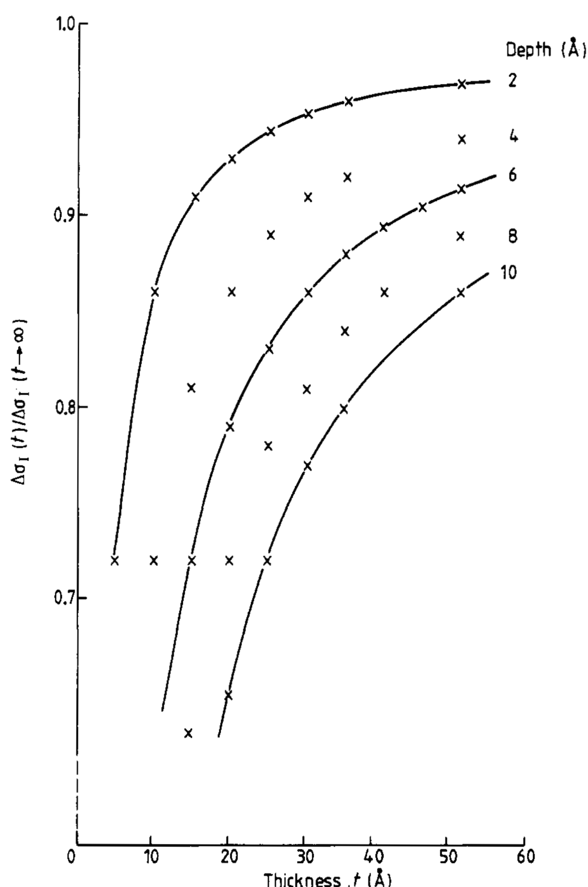

Figure 1. Variation of $\Delta\sigma_I(t)/\Delta\sigma_I(t\to\infty)$ with thickness t. The crosses use the full calculation based on equation (5) and the curves are from approximation (9).

3.2. Dependence on oxide thickness

Suppose there is charge fixed at depth x from the outer oxide surface. We can use equation (5) to predict the dependence of $\Delta\sigma_I$ on the oxide thickness and also on the value of ε_w, i.e. on whether the test liquid affects the degree of depth discrimination possible. Clearly we cannot consider thicknesses t less than x, but normally we may assume $x \leqslant 5$ Å and $10 \text{ Å} \leqslant t \leqslant 50$ Å as the range of interest.

It is easily verified that $\Delta\sigma_I$ is a monotonic increasing function of t. Thus, for our chosen values of ε, we find the trend shown in figure 1. We may verify also that the qualitative form is insensitive to ε_w, just as we find only a modest dependence of $\Delta\sigma_I(t=\infty)$ on ε_w. If we look at the values $\Delta\sigma_I(\varepsilon_w, t)/\Delta\sigma_I(\varepsilon_w = 80, t)$ for various thicknesses, we find a very slight dependence on the chosen value of thickness, t. This is less than 2–3% for thicknesses in the range 20–50 Å, even for large changes in ε_w to values of 2–6. To a good approximation, $\Delta\sigma_I$ can be factorised into terms depending separately on Q, on x and t, and on ε_w.

3.3. Dependence on position of the fixed charge

The results show readily that the closer the charge is to the outer surface (i.e. the smaller x is), the more rapidly $\Delta\sigma_I(t)$ saturates with oxide thickness. We have looked at an extensive range of results with $2 \leqslant x \leqslant 10$ Å and thicknesses of 10–50 Å, together with the limiting values at very large thickness. We find that a simple analytic form, namely

$$\frac{\Delta\sigma_I(t)}{\Delta\sigma_I(\infty)} = 1 - 0.7\,\frac{x}{t}, \tag{9}$$

describes the data. Clearly there are ranges of x and t for which this would be inapplicable, and it would need revision for other dielectric constants, but the fit is surprisingly good overall (see figure 1). Collecting terms, we find

$$\Delta\sigma_I \simeq (20 \text{ erg cm}^{-2})Q^2\left(\frac{1}{x} - \frac{0.7}{t}\right)\rho(x) \tag{10}$$

for the water/silicon dioxide/silicon system, with charges solely at depth x. The charge is in units of the electronic charge, x and the oxide thickness t are in Å, and $\rho(x)$ is in units of 10^{13} cm^{-2}.

3.4. Comparison with experiment

We turn to the data of Williams and Goodman (1974). Their data are in two groups, namely cos θ as a function of thickness for samples grown at room temperature and for samples grown at 600 °C. The data lie close to a common curve, but it is useful to analyse them separately.

In our analysis, we note that $Y(t)$, defined experimentally by

$$Y(t)=\frac{\cos(\theta(t))-\cos(\theta(t=0))}{\cos(\theta(t\rightarrow\infty))-\cos(\theta(t=0))}, \quad (11)$$

is given theoretically by our expression

$$Y(t)=1-0.7\frac{x}{t} \quad (12)$$

if there is a single layer of charge at depth x. We may use the form

$$x=t(1-Y(t))/0.7 \quad (13)$$

to evaluate x from the data read from the curves of Williams and Goodman (1974). We find the following results (figure 2 shows the fit).

(i) For the case of growth at room temperature $x\sim 5.4$ Å with a standard deviation of 0.9 Å (the error being, in part, from our measurement of data from the published figures).

(ii) For growth at 600 °C we find $x\sim 3.2$ Å with a standard deviation of 0.7 Å. We would not wish to read too much into our fits, since they involve both physical assumptions and problems of detailed measurement. Moreover, the deviations may suggest a more complex charge distribution. Nevertheless, there is a clear hint of a shift in the charge with growth temperature. The slight discrepancies in curve shape in figure 2 could readily be accommodated by having two or more layers of charge, but we felt this would go beyond the level of detail appropriate to our analysis.

We may also use the depths deduced to obtain charge densities. Using a surface tension of water of 73 deg cm^{-1}, we find values of ρQ^2 to fit the data. With ρ measured in 10^{13} cm^{-2} and Q electronic charge units, we find $\rho Q^2\sim 32$ for the room-temperature material and $\rho Q^2\sim 18$ for that grown at 600 °C. Thus, if $Q=-4$ (as for Si vacancies of full nominal charge) one would have charge densities of 2×10^{13} cm^{-2} and 1.2×10^{13} cm^{-2} in the two cases. In the possibly more likely case of oxygen defects with $Q=+2$ for oxide vacancies, charge densities of 8×10^{13} cm^{-2} and 4×10^{13} cm^{-2} are found. These are significant densities, but are well within the range of physically reasonable values.

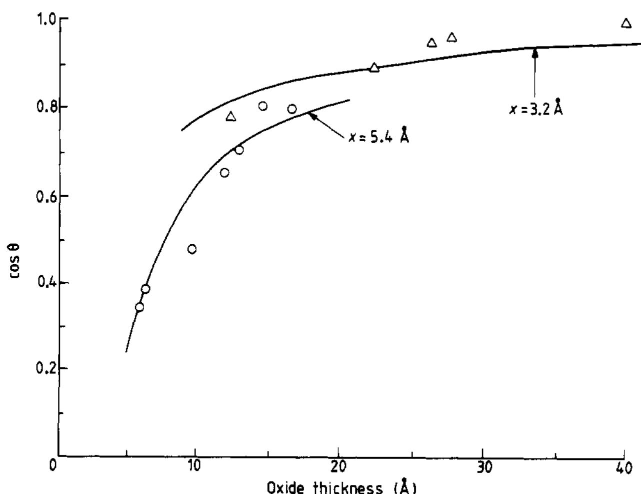

Figure 2. Fits to the data of Williams and Goodman (1974): O, film grown at room temperature, charges assumed at depth 5.4 Å; △, film grown at 600 °C, depth 3.2 Å.

3.5. Relation to other oxide charges

Charges in oxide grown thermally on silicon have been of considerable interest since they can affect device characteristics. General reviews are given by Deal (1974), Cheng (1977) and Helms (1981). The charges are normally classified into four groups. One includes the mobile ionic charge, notably alkali ions, and is unlikely to be the source of the charges we describe. A second group contains the oxide-trapped charge, due to electrons and holes associated with bulk oxide defects. Again, this component is unlikely to contribute to the charges we have described, partly because we consider very thin oxide, and partly because significant densities of oxide-trapped charge usually result from processes not relevant here (e.g., involving ionising radiation or avalanche injection). The third group includes interface-trapped charges, localised at the silicon/oxide boundary itself. This is, of course, the opposite side of the oxide from the charges which affect wetting. The fourth contribution is the so called fixed oxide charge. It is usually within a few tens of ångstroms of the silicon/oxide interface, and is known to depend on the oxidation conditions. The apparent dependence of wetting on growth temperature and the fact that, for the thin films considered here, the fixed charge might extend through the whole film both suggest a connection between the fixed charges we discuss and the fixed oxide charge. The two are not identical in that only those charges which remain close to the outer surface affect wetting whereas the ones usually monitored are apparently those closer to the silicon/oxide interface. Nevertheless, it would be of interest to see if fixed oxide charges measured by capacitance–voltage analyses do correlate with those affecting wetting as the growth conditions are modified.

4. Conclusions

We conclude that the observed changes in the wetting of oxide films are a result of fixed charges close to the outer surface. These charges may have either sign, and indeed both positive and negative charges may be present. If the wetting is monitored as a function of oxide thickness one can deduce depths and concentrations of the fixed charge. We make this analysis from the data of Williams and Goodman (1974) and conclude the data are consistent with charge concentrations of a few times 10^{13} cm^{-2} a few ångstroms below the surface. The data suggest that these charges might be fewer and closer to the outer surface in films grown at higher temperatures.

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