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The Cabrera–Mott mechanism for silicon etching by fluorine atoms

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Abstract. A model for silicon etching by fluorine atoms is described. It can be used to explain how fluorine with a high heat of adsorption can penetrate into the SiF_x film on the surface. The electric field arising in this film causes the fluorine penetration to have non-activated character. The field strength and the etch rate are estimated.

In order to explain silicon etching it is necessary to give a clear description of the mechanism of the reaction between fluorine atoms and Si. The simplest etchants, F_2 plasma [1, 2] and F atoms [3], were chosen for the experiments, so that the interaction with silicon in its pure form could be observed. A straightforward experimental proof that a stationary SiF_x ($x = 1, 2, 3$) film with a thickness of $\approx 10 \text{ \AA}$ is formed on the etched surface has been reported [4]. The fluorine atoms are adsorbed on the SiF_x surface and then penetrate into the film where they form volatile SiF_4 molecules with a probability of 0.25. As a consequence of chemisorbed fluorine having a high heat of adsorption ($Q \approx 1.2 \text{ eV}$ [5]) it is hard to get it to penetrate into the film. It has been assumed [6] that penetration does occur as a result of the electric field arising in the film, but no estimations have been obtained that support the validity of making this assumption. A similar idea was proposed by Cabrera and Mott [7] to explain the initial stages of metal oxidation.

An electric field can be induced by electron tunnelling from the Si valence band to the adsorbed fluorine through the dielectric SiF_x film, as it is thin enough. This results in the generation of negative F ions on the surface, while holes accumulated on the Si– SiF_x interface. The field of this double layer, \mathcal{E} , reduces the surface barrier E_s against penetration of F^- into the film: $E'_s = E_s - e\mathcal{E}a$, where a is a distance between the surface and the adsorbed atom. Let Γ_t be the adsorption centre concentration, let Γ and N be the surface concentrations of atoms and ions, respectively. The kinetic equations describing the surface processes are then

$$\frac{dN}{dt} = \frac{\Gamma - N}{\tau_T(N)} - \frac{N}{\tau_S(N)} \quad \frac{d\Gamma}{dt} = \frac{\Gamma_t - \Gamma}{\tau_A} - \frac{N}{\tau_S(N)}. \quad (1)$$

The time parameters in (1) have the following meanings: τ_A is the adsorption time, $\tau_S(N) = \tau_S^0 \exp(E'_s/kT)$ is the time taken to overcome the surface barrier, $\tau_T(N)$ is the time taken for the electron resonance tunnelling (the opposite process is suppressed because of the short lifetime of a hole in its original state).

The stationary solution of the non-linear equations (1) supplies all the necessary information. Let us consider the solution in the limit $\tau_T \ll \tau_A$. For the field strength we have

$$\mathcal{E} \approx (1/ea)[E_S + kT[\ln(\tau_S^0/\tau_A) + \ln c]] \quad (2)$$

where c is a parameter of the order of 1. It is clear that \mathcal{E} depends weakly on the incident fluorine flux J_F and can be estimated as $\mathcal{E} \sim 10^7 \text{ V cm}^{-1}$. In the same limit $\tau_S = c\tau_A$. This means that the mechanism proposed here provides non-activated fluorine-atom penetration into the film.

The flux of SiF_4 molecules desorbing from the surface is $j_{\text{SiF}_4} = N/4\tau_S(N)$ and the etch rate is

$$v \approx (\sigma\Gamma_t/4n_{\text{Si}})J_F[1 - E_S/E_t + (kT/E_t) \ln(\tau_A/\tau_S^0)]. \quad (3)$$

Here $E_t = 4\pi e^2\Gamma_t a/\varepsilon$, ε is dielectric constant of SiF_x , n_{Si} is the bulk Si-atom concentration, and $\sigma \sim 10 \text{ \AA}^2$ is the cross section for F-atom trapping by the surface. Since $\tau_A = (\sigma J_F)^{-1}$, the dependence of v on J_F is nearly linear, as it should be [1–3]. This is a non-trivial consequence of the non-linear kinetic equations characterising the process.

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