Absence of Surface States in Oxidized Si†

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A simple one-dimensional model of an oxide film on the surface of a semiconductor is used to calculate the surface-state energy as a function of the film width. As this width increases above a critical value, the surface state disappears from the semiconducting gap. Application is made to the Si-SiO$_2$ system, and a semiquantitative estimate of the critical width is given.

It has been known for some time that surface states are removed from a semiconductor upon oxidation.[1] Indeed, optical absorption experiments on cleaved (111) surfaces of Ge show a detectable decrease of absorption as the surface is gradually oxidized.[2] Preliminary experiments point at the same kind of behavior on other surfaces of Ge and in Si.[3] In this Letter we apply the two-surface Green's-function theory recently developed by our group[4] to a simple one-dimensional model of the above situation. We consider the system semiconductor-oxide-film-vacuum and calculate the energy of the film states as a function of the film width L. At a critical width L_c these film states disappear from the gap of the semiconductor.

The secular equation (12) of I reduces, when the film and the two media are periodic, to

$$(\mathcal{G}_{ex}{}^2+\mathcal{G}_s\mathcal{G}_v)\tanh\kappa_{ox}L+\mathcal{G}_{ox}(\mathcal{G}_s+\mathcal{G}_v)=0, \qquad (1)$$

where $\mathcal{G}_i$ (i = s, ox, v for semiconductor, oxide, and vacuum, respectively) is defined as in García-Moliner, Heine, and Rubio,[5] i.e., $\mathcal{G}_i(E)=G_i(E;0,0)$, a matrix element of the usual Green's function in position representation (we take as our origin the midpoint of the film), and κ_{ox} is a wave-vector characteristic of the oxide.

For the semiconductor we take a two-band approximation with a small gap of the bonding type ($V_s=-\frac{1}{2}E_{gs}$). This yields an energy-momentum law[5] $\xi^{\pm}(q)=\pm(V_s{}^2+g_s{}^2q^2)^{1/2}$ (g_s is the reciprocal lattice vector) which allows us to define a wave vector κ_s for energies in the gap by

$$g_s\kappa_s=(V_s{}^2-\xi^2)^{1/2}. \qquad (2)$$

The corresponding Green's function is[5]

$$\mathcal{G}_s(\xi)=-\frac{1}{g_s}\frac{\xi+V_s}{(V_s{}^2-\xi^2)^{1/2}}=\frac{1}{2|W_s|^{1/2}}\left(\frac{E_{gs}-2\xi}{E_{gs}+2\xi}\right)^{1/2}, \qquad (3)$$

where all the energies have been referred to the midgap, and W_s represents the energy at the bottom of the valence band, as shown in Fig. 1. As a typical case, we have taken Si, with $E_{gs}=4.08$ eV and $W_s=-10.20$ eV.[6] In the absence of any better information about the electronic structure of semiconducting oxides, we have assumed a Green's function of the form given by Eq. (3), corresponding to a bonding gap as well, with data for SiO$_2$ from Loh,[7] i.e., $E_{g\,ox}=11.0$ eV and $W_{ox}=-25.0$ eV. The wave vector κ_{ox} of Eq. (1) is defined as in Eq. (2), but with the SiO$_2$ data. Finally, the vacuum level has been put at $W=4.95$ eV above the midgap, i.e., approximately the value of the work function for SiO$_2$ given by Law.[8] Then $\mathcal{G}_v=(W-\xi)^{1/2}/2$.

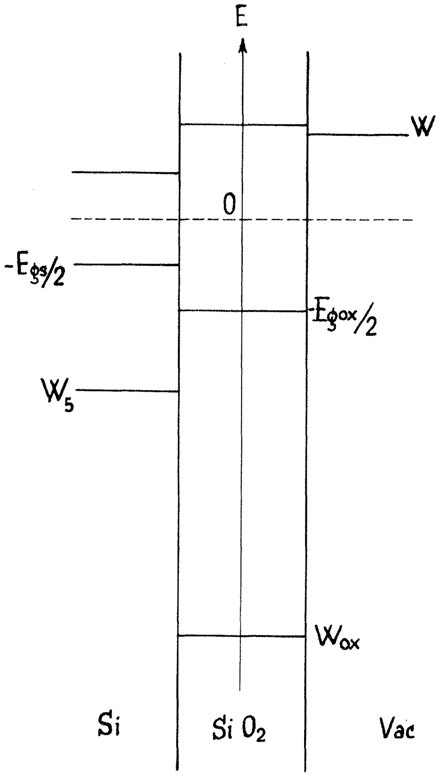

FIG. 1. Energy diagram for the Si-SiO$_2$-vacuum system.

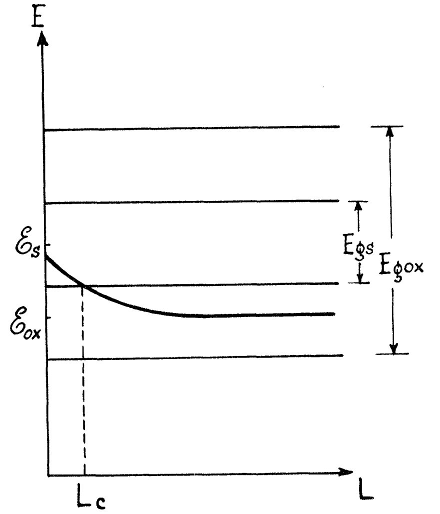

FIG. 2. Surface-state energy (heavy line) versus oxide-film width for the Si-SiO$_2$-vacuum system. The semiconductor and oxide gaps are shown.

Now we put all these data into Eq. (1) and calculate ξ as a function of L. The situation is sketched in Fig. 2. For $L=0$, Eq. (1) reduces to $\mathcal{G}_s+\mathcal{G}_v=0$, which has a solution at $\xi(0)=-0.61$ eV$\equiv\xi_s$ (surface-state energy of a clean Si surface). For $L=\infty$, Eq. (1) gives $(\mathcal{G}_{ox}+\mathcal{G}_v)(\mathcal{G}_s+\mathcal{G}_{ox})=0$, with two solutions (in principle): (a) $\mathcal{G}_{ox}+\mathcal{G}_v=0$ (SiO$_2$-vacuum surface), which gives $\xi(\infty)=-3.19$ eV$\equiv\xi_{ox}$ (inside the gap of SiO$_2$, but outside the gap of Si), and (b) $\mathcal{G}_s+\mathcal{G}_{ox}=0$ (Si-SiO$_2$ interface). This last equation does not have any solutions, as was to be expected from Shockley's theorem.[9]

The point to notice now is that as one goes from $L=0$ to $L=\infty$, the surface level is removed from the gap of the semiconductor. Hence, there should be an intermediate, critical width L_c such that the surface state is just at the bottom of the semiconducting gap, i.e., such that $\xi(L_c)=-2.04$ eV. To estimate this critical width, notice that $\mathcal{G}_s(-2.04)=\infty$; therefore, in the neighborhood of $L=L_c$, Eq. (1) simplifies to

$$\tanh\kappa_{ox}(\xi)L\simeq-\mathcal{G}_{ox}/\mathcal{G}_v.$$

For $\xi=-2.04$ eV, this gives $\tanh\kappa_{ox}L_c=0.78$, or $\kappa_{ox}L_c=1.05$. Using now the definition of κ_{ox} (i.e., Eq. (2) with the SiO$_2$ data, and $\xi=-2.04$ eV), we get $L_c\simeq4$ Å.

Hence, for $L>L_c$ the film state lies inside the valence band of the semiconductor, so that no discrete solution is possible for the whole system Si-SiO$_2$-vacuum. What we emphasize in this Letter is the existence of a critical width of the oxide film for the removal of surface states. As to the value $L_c\simeq4$ Å, although it should be taken with caution given the crudeness of the model used, it is roughly in agreement with experiment.[3]

Until more reliable information about the electronic structure of semiconducting oxides is available, it will be difficult to do better, but we should, perhaps, point out that $L_c\simeq4$ Å is in any case a lower estimate for the critical width, the reason being that a three-dimensional model yields a doubly degenerate band of surface states.[10] The width of the oxide film must then increase until all the states in the band have disappeared from the gap of the semiconductor. Furthermore, this degeneracy is lifted in a realistic model if the atomic rearrangement in the vicinity of the semiconductor surface[11] is taken into account. This can be attempted in several ways, e.g., by adding a thin film of disordered material to the semiconductor, or else by allowing for changes in the structure factor. Work on these problems, as well as on the metal-oxide-semiconductor system, is in progress in our group. In any case, the doubly degenerate band is split into two bands of surface states, which would correspond more closely to the experimental situation.[12] Then the critical width for removal of surface states would increase even more.

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Spin-Wave Dispersion Relation in Dysprosium Metal*

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The spin-wave dispersion relation for the c direction of dysprosium metal in the ferromagnetic phase at 78°K and in the helical magnetic phase at 98°K has been measured by triple-axis neutron spectrometry. The energy gap measured in the ferromagnetic phase at $\vec{q}=0$ is in poor agreement with that calculated from the macroscopic magnetostriction and crystal-field anisotropy constants. The Fourier-transformed exchange interaction $J(\vec{q})-J(0)$ in the ferromagnetic phase posses a peak near the wave vector that gives the periodicity of the helical structure just above the Curie temperature.

The spin-wave dispersion relation for the c direction of dysprosium metal in its ferromagnetic phase at 78°K and in its helical magnetic phase at 98°K has been measured by triple-axis neutron spectrometry. The measurements were carried out on the neutron spectrometer located at the Oak Ridge High Flux Isotope Reactor. Neutrons with energies in the range 10-16 meV were used. In addition to the usual constant-$\vec{q}$ and constant-E modes of operation, numerous mixed scans (both q and E varied) were employed. The specimen is a single crystal grown in this laboratory of dysprosium enriched (96.8%) in the low-neutron-capturing isotope ^{163}Dy, and it weighs approximately 28 g. The neutron-capture cross section at 1 Å is estimated to be 100 b.

Dysprosium possesses a simple helical magnetic structure below T_N, 179°K, and a ferromagnetic structure below T_c, about 87°K.[1] Thus with dysprosium one has a unique opportunity to study the exchange and anisotropy interactions over a relatively wide temperature range in both types of magnetic structures in the same metal. Of particular interest is the mechanism responsible for the magnetic phase transition and the extent to which the exchange interactions on either side of this transition differ. In the present Letter we report the results of measurements which were made primarily to examine the latter point.

The measured dispersion curves are shown in Figs. 1 and 2. For the ferromagnetic phase (78°K), the <u>relative</u> uncertainty of the measurements is estimated to be ~0.02 meV at small q and ~0.05 meV near the zone boundary. For the helical phase the errors at present are generally larger (0.04-0.10 meV).

The interpretation of these data has been based on the frozen-lattice model which leads to the following expression for the magnon energies along the c axis in the ferromagnetic phase[2,3] at $T=0$°K:

$$\hbar\omega(\vec{q}) = S\{[J(0)-J(\vec{q}) + 2P_2S(\tfrac{1}{2})/S^2][J(0)-J(\vec{q}) + C^{\gamma}(\lambda^{\gamma})^2/S^2 + 36P_6{}^6S(\tfrac{5}{2})/S^2]\}^{1/2}, \tag{1}$$

with

$$S(n) = S(S-\tfrac{1}{2})(S-1)\cdots(S-n).$$

Here S is the total angular momentum on each ion; $J(\vec{q})$ is the Fourier transform of the exchange interaction; P_2 and $P_6{}^6$ are the axial and hexagonal crystal-field anisotropy parameters; λ^{γ} is the parameter which specifies the lowest order single-ion magnetoelastic interaction, and C^{γ} is an elastic constant. The hexagonal anisotropy and magnetoelastic parameters usually occurring in the first bracket have been ignored here in comparison with P_2.

The energy gap at $\vec{q}=0$ measured in the ferromagnetic phase is 1.40 ± 0.05 meV. From Eq. (1) this gap theoretically is given by

$$\hbar\omega(0) = S^{-1}\{3K_2[36K_6{}^6 + C^{\gamma}(\lambda^{\gamma})^2]\}^{1/2}, \tag{2}$$

where we have replaced P_2 and $P_6{}^6$ by the measured macroscopic anisotropy constants K_2 and