Impurity Bands in n-type Si/SiO$_2$ Metal-Oxide Semiconductors

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We calculate the density of states (DOS) for Na$^+$ impurity bands in n-type Si/SiO$_2$ metal-oxide-semiconductor structures with a Hubbard-type model and using as a basis Martin and Wallis single-impurity states. We show that the intrasite correlation energy increases with the applied electric field on the junction. The same occurs with the bandwidth and with the energy corresponding to the maximum in the DOS. This effect is enhanced by an increase in the impurity concentration, N_{ox}. The asymmetry of the DOS explains why the measured binding energy for finite N_{ox} is smaller than in the single-impurity case.

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It is well known that electrons in inversion layers (IL) of metal-oxide-semiconductor (MOS) structures are a good way to study transport properties of disordered systems such as metal-nonmetal transition, weak localization, quantum Hall effect, etc.[1] Another relevant question concerns the existence of an impurity band in those structures, associated with an activated transport regime at low temperatures. In fact, the occurrence of an impurity band in n-type Si/SiO$_2$ MOS has been observed by Hartstein and Fowler (HF)[2] and more recently by Glaser *et al.*[3] The band is usually generated by the presence of Na$^+$ ions that are randomly located near the interface in the oxide region and which bind electrons in the semiconductor.

The electronic states associated with Na$^+$ impurities in Si/SiO$_2$ MOS have been studied theoretically in the past by several authors.[4-7] Among other factors, the states depend on the electric field that is applied perpendicular to the junction in order to form the depletion layer. Unlike impurity bands in doped semiconductors, the position of the Fermi level, which in that case depends only on the impurity concentration, in the case of MOS is determined by the gate voltage and by the substrate bias. Therefore, the Fermi level can be made to scan the impurity band, which allows, in consequence, an external control of the filling factor, i.e., the average number of electrons per impurity. Another interesting feature from a theoretical point of view is the possibility of varying the electronic intrasite (impurity) interaction potential with the gate voltage. In a Hubbard-type model Hamiltonian representing the impurity electrons, it would correspond to external control of the correlation U and its ratio to the bandwidth Δ.

In a first attempt to calculate the density of impurity states (DOS) associated with an IL, da Cunha Lima *et al.*[8] used a tight-binding model based on a single-impurity state given by the two-dimensional effective-mass approximation of Stern and Howard.[4] However, more realistic treatments exist for the one-impurity problem,[5-7] which take into account important corrections, such as an image-charge potential due to a large difference between the dielectric constants of the oxide and semiconductor, the spatial extension in the z direction (normal to the interface) of the electron wave function, and the dependence of the bound state on external applied field. In the present calculation we used the variational solution due to Martin and Wallis.[5] It does not consider screening of the impurity potential due to IL electrons. However, for the purpose of calculating the impurity band this is a reasonable assumption, since the latter is determined generally by measurement of the activated conductivity and in this case the Fermi level lies below the first subband. On the other hand, a variational solution for the single-impurity problem makes the DOS calculation much easier. A more accurate treatment should consider the screening due to a finite density of states at the Fermi level. Nevertheless, these states

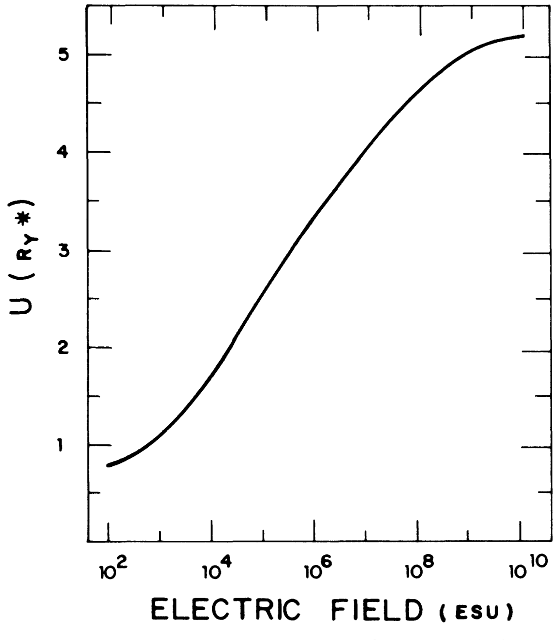

FIG. 1. Correlation energy U as a function of the applied electric field.

would correspond to electrons in the impurity band, certainly localized, which screen the impurity potential very weakly.

In the model considered here we include electron-electron correlation via a Hubbard-type Hamiltonian:

$$H=\sum_{i\sigma}\varepsilon a^{\dagger}_{i\sigma}a_{i\sigma}+\sum_{i\neq j}V_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+\tfrac{1}{2}U\sum_{i\sigma}n_{i\sigma}n_{i-\sigma}, \qquad (1)$$

where $a^{\dagger}_{i\sigma}$ and $a_{i\sigma}$ refer to creation (annihilation) operators of an electron with spin σ in the bound states described by a Martin and Wallis wave function, ψ_i, centered at the impurity i,

$$\psi_i(\mathbf{r},z)\equiv\phi_i(\mathbf{r})\xi(z) = (a^2/2\pi)^{1/2}e^{-ar/2}(b^3/2)^{1/2}ze^{-bz/2}. \qquad (2)$$

The single-impurity Hamiltonian depends on the electric field through the carrier concentration of the depletion layer $N_{\rm depl}$. The dependence of the DOS on the electric field comes out through the variational parameters a and b. V_{ij} is the hopping matrix element

$$V_{ij}\equiv\int dz\int d^2r\,\psi_i(\mathbf{r},z)V_i(\mathbf{r},z)\psi_j(\mathbf{r},z), \qquad (3)$$

where V_i is the interaction potential between the electron and an impurity located at site $\mathbf{R}_i$. We assume that the impurities lie at $z=0$.

The DOS is now obtained by the calculation of the single-particle Green's function via a method previously developed by Kishore[9] and applied to doped semiconductors by Ferreira da Silva, Kishore, and da Cunha Lima.[10] The configurational average uses the diagrammatic summation of Matsubara and Toyozawa.[11] Defining

$$G^{\pm}_{ij,\sigma}(t)=i\theta(t)\langle[a_{i\sigma}n^{\pm}_{i-\sigma},a^{\dagger}_{j\sigma}(t)]_+\rangle, \qquad (4)$$

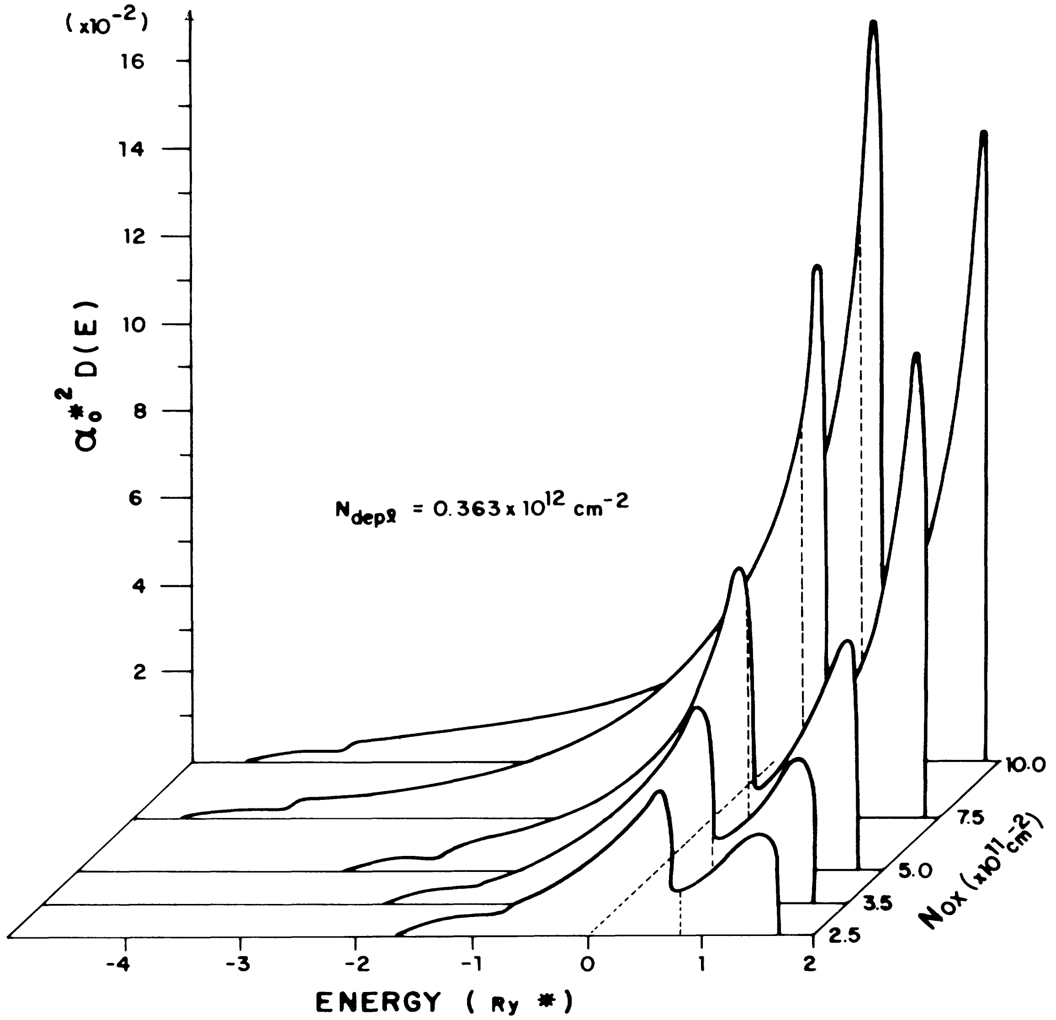

FIG. 2. The calculated density of impurity states. Oblique dashed line gives the energy of the single-impurity ground state; vertical dashed lines give the minimum of the first unperturbed subband.

with $n_{i\sigma}^{+} \equiv a_{i\sigma}^{\dagger} a_{i\sigma}$ and $n_{i\sigma}^{-} = 1 - n_{i\sigma}^{+}$, we have for the single-particle Green's function the sum of G^{+} and G^{-}. The lowest-order approximation in Kishore's method[9] gives an equation of motion for $G^{\pm}$ in first order of U,

$$(\omega - E^{\pm}) G_{ij,\sigma}^{\pm}(\omega) = n_{-\sigma}^{\pm} \delta_{ij} + \sum_{l \neq i} V_{il} G_{lj\sigma}^{\pm}(\omega), \tag{5}$$

where $E^{+} = \varepsilon + U$, $E^{-} = \varepsilon$, and we have assumed $n^{\pm}$ as site independent. The configuration-averaged diagonal elements for impurities in a plane are[12]

$$\langle G_{ii,\sigma}^{\pm}(\omega) \rangle_{\text{av}} = [n_{-\sigma}^{\pm}/(\omega - E^{\pm})] \xi^{\pm}(\omega), \tag{6}$$

$$\xi^{\pm} = [1 - \eta^{\pm}(\omega)]^{-1}, \tag{7}$$

$$\eta^{\pm}(\omega) = [N_{\text{ox}} \xi^{\pm}(\omega)/(2\omega)^2 (\omega - E^{\pm})^2] \int d^2k \, V^2(\mathbf{k}) \{1 - [N \xi^{\pm}(\omega)/(\omega - E^{\pm})] V(\mathbf{k})\}^{-1}, \tag{8}$$

where N_{ox} is the number of impurities per square centimeter and $V(\mathbf{k})$ is the 2D Fourier transform of the hopping potential $V(\mathbf{R})$ in Eq. (3). Equations (7) and (8) are now solved numerically to obtain the density of states for the upper and lower Hubbard bands, D^{+} and D^{-}:

$$D^{\pm}(\omega) = -(N/\pi) \sum\nolimits_{\sigma} \text{Im} \langle G_{ii,\sigma}^{\pm}(\omega + i0^{+}) \rangle_{\text{av}}. \tag{9}$$

The problem is then reduced to the calculation of U and $V(\mathbf{k})$.

By use of the usual atomic units appropriate for the (100) n-type Si/SiO$_2$ IL, $\mathcal{R}^* = 43.6$ meV and $a_0^* = 21.7$ Å, we obtain

$$V(\mathbf{k} = \mathbf{q}/a^*) = -(E_b + q^2) \phi^2(q) a_0^{*2} \mathcal{R}^*, \tag{10}$$

where E_b is the binding energy for the single impurity and $\phi(q)$ is given by

$$\phi(q) = \int e^{-i\mathbf{q}\cdot\mathbf{x}} \phi(r = x a_0^*) d^2x. \tag{11}$$

After performing the integral above, we get

$$V(k) = -(E_b + a^{*2} k^2) \pi [2a^2 (\tfrac{1}{4} + a_0^{*2} k^2/a^2)^3]^{-1} a_0^{*2} \mathcal{R}^*. \tag{12}$$

The intrasite correlation energy $\langle ii | V(\mathbf{r}_1 - \mathbf{r}_2) | ii \rangle$ is calculated numerically by use of a potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ that takes into account the image charge due to the difference in the dielectric constants of the semiconductor and the oxide.[13] As a result we obtain a correlation energy U depending on the applied electric field, as shown in Fig. 1. In the range realizable in the experiments, U is greater than E_b, which explains why the upper Hubbard band is not observed, as already pointed out by da Cunha Lima and Ferreira da Silva.[12] It is worthwhile to say that U does not go to the 2D limit of $4.17\mathcal{R}^*$ for very high field. This is due to the addition of the image term in the interaction potential.

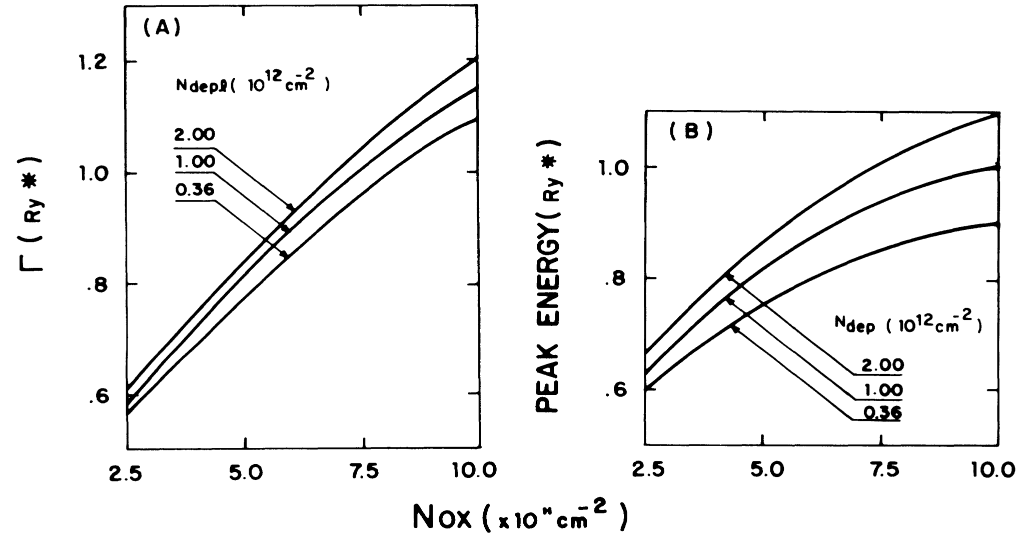

FIG. 3. The dispersion Γ and the energy of maximum DOS of the lower Hubbard band as functions of impurity concentration.

The calculated DOS is shown in Fig. 2. We have chosen $N_{\mathrm{depl}}=0.36\times 10^{12}$ cm^{-2} in order to compare with the results obtained by Hartstein and Fowler.[2] The zero in energy corresponds to the single-impurity ground state. We have also assigned the position of the IL first subband. The peak of the lower band is displaced to the right of the zero of energy, which explains why the measured binding energy for finite N_{ox} is smaller than for the single impurity. We can also observe that for $N_{\mathrm{ox}}=5.0\times 10^{11}$ cm^{-2}, the lower band has already merged into the conduction band. HF found, by extrapolation, $E_b=0$ for $N_{\mathrm{ox}}=17.0\times 10^{11}$ cm^{-2}, a value that our results show to be too large. By fitting a Gaussian, HF obtained for $N_{\mathrm{ox}}=3.5\times 10^{11}$ cm^{-2} the maximum of the DOS equal to 3.4×10^{13} cm^{-2} eV^{-1} and a bandwidth $\Gamma=1.8$ meV. Our calculations give, taking into account the double degeneracy of the first subband, $D(E)_{\max}=2.32\times 10^{13}$ cm^{-2} eV^{-1} and a dispersion $\Gamma=5.1$ meV. The last value is in disagreement mainly because the shape of the band is very asymmetric and a Gaussian becomes a very poor approximation. In addition, it is important to mention some uncertainty in the experimental data available.[14]

Finally, we have investigated the effect of the applied field (or N_{depl}) in the DOS. The results are shown in Fig. 3 for the bandwidth (dispersion in the lower subband) and the energy of the maximum DOS. In Fig. 3(a) we observe the broadening of the impurity band with the increase of the electric field. This effect has, in fact, been observed by HF. As shown in Fig. 3(b), the position of the maximum of the DOS goes to higher energies as N_{depl} increases. In both Figs. 3(a) and 3(b) we can observe that increasing the impurity concentration results in enhancing the effect of the applied field.

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