

Theory of bound states associated with n -type inversion layers on silicon*

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The ground state and two excited states of an electron bound to a charged impurity located at the interface between silicon and silicon dioxide have been investigated. The interface was taken to be parallel to a (001) plane and a static electric field perpendicular to the surface was assumed. Calculations of the electron binding energies as functions of electric field were made for a bare charged impurity with screening by free carriers neglected. In addition, the oscillator strength for electric-dipole transitions was calculated. It was found that the binding energy increases with increasing electric field and approaches that of the corresponding state of a two-dimensional hydrogenlike atom in the limit of infinite electric field.

I. INTRODUCTION

The development of metal-oxide-semiconductor (MOS) devices has stimulated a great deal of interest in the basic properties of inversion layers at semiconductor boundaries. A number of these properties are influenced by the presence of impurities and their associated electronic bound states. We have investigated using a variational technique the ground state and two excited states of an electron bound to a bare charged impurity located at the interface between silicon (001) and silicon dioxide.

Theoretical investigations of the wave functions and binding energies of donor states localized at or near semiconductor surfaces without inversion layers have been carried out by Karpushin¹ and by Bell *et al.*² The effect of n -type inversion layers and electric subbands has been studied by Stern and Howard³ for InAs and Si(001) surfaces. They considered the screening produced by the inversion-layer charge carriers, but restricted their numerical results to the two-dimensional limit. In the present paper we eliminate the latter restriction, but neglect the effect of screening.

For the case of an n -type impurity at a semiconductor-oxide interface where the potential energy rises discontinuously to infinity, the ground state is, in hydrogen-atom nomenclature, the $2p_0$ level.² In addition, the first excited states to which a transition might be observed in optical absorption are the $3d_{\pm 1}$ and $4d_{\pm 1}$ states. This result is due to Levine⁴ who showed that a state cannot exist unless $l+m$ is an odd integer and that both l and m must differ by ± 1 in an electromagnetic transition. Here we consider only the $3d_{\pm 1}$ excited states.

As has been stated, we consider the Si(001) surface orientation. With such an orientation, the constant-energy ellipsoids can be divided into two kinds, namely, those for which the major axis is

perpendicular to the surface and those for which the major axis is parallel to the surface. We will consider ellipsoids of the first type, since they lead to the lowest-lying bound states.¹ We introduce a coordinate system in which the z axis is directed into the depth of the semiconductor along a normal to the surface and place the n -type impurity at the Si-SiO₂ interface.

In a previous publication,⁵ we studied the effect of an electric field normal to the interface on the $2p_0$ and $3d_{\pm 1}$ bound states using the variational trial functions of Karpushin¹ and Bell *et al.*² Although these trial functions are reasonably good for small electric fields, they are not satisfactory at high fields. In particular, they do not lead to the correct limiting values for the binding energies at high fields. In the present paper, we overcome this difficulty by using a new type of trial function. The binding energy of the impurity ground state which we calculate is compared to the recent experimental data of Hartstein and Fowler.⁶

II. THEORETICAL DEVELOPMENT

We consider two contiguous semi-infinite half-spaces, one of p -type silicon and the other of SiO₂, with a common boundary parallel to a (001) plane of the silicon. We assume that the potential energy of an electron undergoes a discontinuous jump as the electron passes from the silicon into the SiO₂. This discontinuity in energy is about 3 eV (Ref. 3); however, we shall assume that the discontinuity is infinite and that the electronic wave functions vanish at the boundary. In the region of the inversion layer, there is an electric field present which in general is a complicated function of the distance from the interface. To a good first approximation³ one can take the electric field to be constant, a procedure which we adopt in this paper.

We assume that an impurity ion of charge $+Ze$ is located at the boundary between the silicon and

the SiO₂. For this situation, Karpushin¹ has shown that in the absence of an external electric field the lowest-lying bound states associated with a (001) interface on silicon are primarily derived from the energy ellipsoids whose major axes are perpendicular to the interface. This situation continues to hold in the presence of an electric field. We therefore consider only the ellipsoids just mentioned. We also neglect intervalley interactions between the two ellipsoids perpendicular to the surface. Finally, we operate within the framework of the effective-mass approximation.

In the light of the foregoing discussion, we employ the Hamiltonian

$$H = -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \gamma \frac{\partial^2}{\partial z^2} + U(\vec{r}) + \frac{\delta}{z} + \kappa \mathcal{E}z, \quad (1)$$

where $\gamma = m_t/m_l$, $\delta = (\epsilon_2 - \epsilon_1)/4Z\epsilon_2$, $\kappa = \hbar^4(\epsilon_1 + \epsilon_2)^3/4Z^3m_t^2e^5$, \mathcal{E} is the external electric field, m_t and m_l are the transverse and longitudinal effective masses, respectively, and ϵ_1 and ϵ_2 are the dielectric constants of the SiO₂ and silicon, respectively. In Eq. (1), energy is measured in units of the effective Rydberg, $R^* = 2m_t e^4 Z^2 / \hbar^2 (\epsilon_1 + \epsilon_2)^2$ and length in units of the effective Bohr radius, $a_0^* = \hbar^2 (\epsilon_1 + \epsilon_2) / 2Z m_t e^2$. For the silicon-silicon dioxide system with $Z = 1$, $R^* = 42.3$ meV and $a_0^* = 21.8$ Å. The potential energy $U(\vec{r})$ takes into account the interaction of the electron with the impurity ion and with the image of the impurity ion and also the screening of the impurity-ion potential by electrons in the inversion layer. In the present paper, we neglect screening and take $U(\vec{r})$ to have the Coulomb form

$$U(\vec{r}) = -2/r, \quad (2)$$

where $r = (x^2 + y^2 + z^2)^{1/2}$. The term involving δ in Eq. (1) represents the interaction of the electron with its own image. Our Hamiltonian consists of that of Karpushin with the addition of the electric field term.

We shall be particularly interested in the regime of large electric fields where the electric subband energies are large compared to the impurity binding energy. The problem is then analogous to the problem of an impurity in a high magnetic field⁷ and the problem of separating the electronic and nuclear motions in the theory of molecules and solids.⁸ We use the same sort of adiabatic approach that has proven useful in the latter two problems.

Let us write the Hamiltonian in the form

$$H = H_0 + H_1, \quad (3)$$

where

$$H_0 = -\gamma \frac{\partial^2}{\partial z^2} + \frac{\delta}{z} + \kappa \mathcal{E}z, \quad z \geq 0, \quad (4a)$$

$$H_1 = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + U(\vec{r}). \quad (4b)$$

Let the eigenfunctions of H_0 be denoted by $f_\lambda(z)$. We expand the eigenfunctions $\psi(\vec{r})$ of H in terms of the functions $f_\lambda(z)$:

$$\psi(\vec{r}) = \sum_\lambda \chi^{(\lambda)}(x, y) f_\lambda(z). \quad (5)$$

To determine the functions $\chi^{(\lambda)}(x, y)$, we substitute Eq. (5) into the Schrödinger equation for $\psi(\vec{r})$, multiply from the left by $f_{\lambda'}^*(z)$ and integrate over z from 0 to infinity. We obtain

$$\sum_\lambda \langle \lambda' | H_1 | \lambda \rangle \chi^{(\lambda)}(x, y) = (E - E_{0\lambda'}) \chi^{(\lambda')} (x, y), \quad (6)$$

where E and $E_{0\lambda'}$ are the eigenvalues of H and H_0 , respectively,

$$\begin{aligned} \langle \lambda' | H_1 | \lambda \rangle = & \int_0^\infty dz f_{\lambda'}^*(z) H_1 f_\lambda(z) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \delta_{\lambda\lambda'} \\ & + \int_0^\infty dz f_{\lambda'}^*(z) U(\vec{r}) f_\lambda(z), \end{aligned} \quad (7)$$

and we have assumed that the $f_\lambda(z)$ are normalized to unity. Equations (6) constitute a system of differential equations which determine the functions $\chi^{(\lambda)}(x, y)$.

The expansion given by Eq. (5) is quite general and could be applied at any electric field. At high electric fields where the differences between the eigenvalues $E_{0\lambda}$ are large compared to the impurity-binding energy, however, we anticipate that one term in Eq. (5) will dominate and the others will be small correction terms. In the present paper we proceed even further and assume that the wave function $\psi(\vec{r})$ consists of only a single term

$$\psi(r) = \chi^{(\lambda_0)}(x, y) f_{\lambda_0}(z), \quad (8)$$

where $f_{\lambda_0}(z)$ is the electric subband wave function of lowest energy. For $f_{\lambda_0}(z)$ we choose the variational form of Fang and Howard⁹

$$f_{\lambda_0}(z) = (b^3/2)^{1/2} e^{-bz/2}, \quad z > 0. \quad (9)$$

For the lowest subband λ_0 , there is a series of bound states. We shall discuss the ground state and the lowest excited states that are coupled to the ground state by electric-dipole transitions. The overall wave functions for these states have the symmetries of hydrogenic $2p_0$ and $3d_{\pm 1}$ states, respectively. For these states, we choose the $\chi^{(\lambda_0)}(x, y)$ to have the variational forms

$$\chi_{2p_0}^{(\lambda_0)}(x, y) = (a_2^2/2\pi)^{1/2} e^{-a_2\rho/2}, \quad (10a)$$

$$\chi_{3d_{\pm 1}}^{(\lambda_0)}(x, y) = (a_3^4/12\pi)^{1/2}(x \pm iy)e^{-a_3\rho/2}, \quad (10b)$$

where $\rho = (x^2 + y^2)^{1/2}$.

In the spirit of the adiabatic approximation, one would determine the parameter b by minimizing the expectation value of H_0 . We shall generalize the situation by determining all variational parameters through minimizing the expectation value of the total Hamiltonian H . This procedure leads

$$E_{2p_0} = \frac{1}{4}(a_2^2 + \gamma b_2^2) + \frac{1}{2}\delta b_2 + \frac{3\mathcal{E}\kappa}{b_2} - 2a_2^2 b_2^3 \left[\frac{3a_2^3 - 12a_2 b_2^2}{2X_2^7} \ln \left(\frac{b_2(X_2 - b_2)}{a_2(X_2 + a_2)} \right) + \frac{a_2^5 + 10a_2^3 b_2^2 - 13a_2^2 b_2^3 - 6a_2 b_2^4 + 2b_2^5}{2a_2 b_2^2 X_2^6} \right], \quad (11)$$

$$E_{3d_{\pm 1}} = \frac{1}{4}(a_3^2 + \gamma b_3^2) + \frac{1}{2}\delta b_3 + \frac{3\mathcal{E}\kappa}{b_3} - \frac{a_3^4 b_3^3}{6} \left[\frac{60a_3^5 - 615a_3^3 b_3^2 + 270a_3 b_3^4}{X_3^{11}} \ln \left(\frac{b_3(X_3 - b_3)}{a_3(X_3 + a_3)} \right) + \frac{6a_3^9 + 197a_3^7 b_3^2 - 420a_3^6 b_3^3 - 674a_3^5 b_3^4 + 529a_3^4 b_3^5 + 80a_3^3 b_3^6 + 8a_3^2 b_3^7 + 4b_3^8}{a_3^3 b_3^2 X_3^{10}} \right], \quad (12)$$

where $X_i = (a_i^2 + b_i^2)^{1/2}$ for $i=2, 3$. The values of the variational parameters a_i, b_i in each case were obtained from the equations

$$\frac{\partial E_{2p_0}}{\partial a_2} = \frac{\partial E_{2p_0}}{\partial b_2} = 0, \quad (13a)$$

$$\frac{\partial E_{3d_{\pm 1}}}{\partial a_3} = \frac{\partial E_{3d_{\pm 1}}}{\partial b_3} = 0. \quad (13b)$$

In order to obtain the binding energies, we must obtain the expectation value of the Hamiltonian without the impurity term. It is sufficient to consider the Hamiltonian H_0 given by Eq. (4a). We use the variational trial function given by Eq. (9). The expectation value of the Hamiltonian H_0 calculated with this trial function is given by

$$E_s = \frac{1}{4}\gamma b^2 + \frac{1}{2}\delta b + 3\mathcal{E}\kappa/b, \quad (14)$$

from which one determines the optimum value of b by minimizing E_s . From the minimized values of E_{2p_0} , $E_{3d_{\pm 1}}$, and E_s , the binding energies are calculated from the equations

$$E_{2p_0}^B = E_s - E_{2p_0}, \quad (15a)$$

$$E_{3d_{\pm 1}}^B = E_s - E_{3d_{\pm 1}}. \quad (15b)$$

We have calculated the variational parameters and the binding energies for the $2p_0$ and $3d_{\pm 1}$ states for electric fields ranging from zero up to 10^{10} esu. The results are tabulated in Table I. The binding energies are plotted as functions of

to different values for b for the $2p_0$ and $3d_{\pm 1}$ states which we designate by b_2 and b_3 , respectively.

III. RESULTS

A. Energies

The evaluation of the expectation values E_{2p_0} and $E_{3d_{\pm 1}}$ is straightforward. The results are

the electric field in Fig. 1. We see that the binding energies increase monotonically with increasing electric field and approach asymptotic limiting values at very large fields. The limiting values at high fields correspond to the binding energies of two-dimensional hydrogenlike atoms. The binding energies of the $2p_0$ and $3d_{\pm 1}$ states increase by factors of over 10 and 4, respectively, from zero field to very high fields. Associated with the increases in binding energies are decreases in the

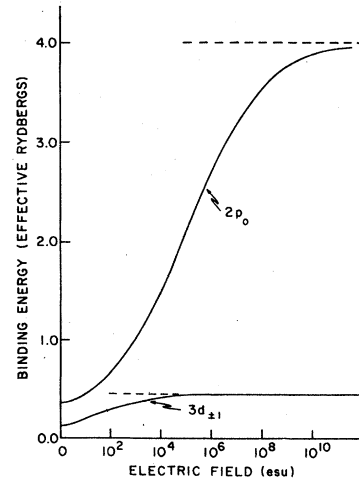


FIG. 1. Binding energies vs electric field for the $2p_0$ and $3d_{\pm 1}$ states. The dashed lines are the two-dimensional values.

TABLE I. Variational parameters a and b and binding energy E^B for the $2p_0$ and $3d_{\pm 1}$ states as functions of electric field \mathcal{E} . The units are indicated in parentheses.

\mathcal{E} (esu)	a ($1/a_0^*$)	b ($1/a_0^*$)	E^B (\mathcal{R}^*)	a ($1/a_0^*$)	b ($1/a_0^*$)	E^B (\mathcal{R}^*)
1	0.91	1.64	0.38	0.60	0.69	0.14
10	0.93	1.72	0.46	0.67	0.89	0.20
10^2	1.05	2.20	0.66	0.83	1.59	0.27
10^3	1.34	3.80	1.01	1.04	3.37	0.35
10^4	1.78	7.68	1.51	1.20	7.40	0.41
10^5	2.29	16.34	2.11	1.29	16.20	0.44
10^6	2.81	35.26	2.70	1.32	35.19	0.44
10^7	3.25	76.16	3.20	1.33	76.12	0.44
10^8	3.57	164.4	3.55	1.33	164.4	0.44
10^9	3.84	354.5	3.80	1.33	354.5	0.44
10^{10}	3.88	763.9	3.90	1.33	763.9	0.44

effective Bohr radii in the plane of the oxide-semiconductor interface. The effective Bohr radii are inversely proportional to the variational parameters a_2 and a_3 and decrease by factors of over 4 and 2 in going from zero field to very high fields for the $2p_0$ and $3d_{\pm 1}$ states, respectively.

B. Oscillator strength

Using the variational wave functions which we have obtained, we have calculated the oscillator strength for the transition $2p_0 \rightarrow 3d_{\pm 1}$ as a function of the electric field. When atomic units are used, the oscillator strength for a transition between states i and j produced by an electromagnetic wave with electric vector in the α direction takes the form

$$f_{ij}^{\alpha} = \frac{4|\langle j | p_{\alpha} | i \rangle|^2}{E_j - E_i}, \quad E_j > E_i, \quad (16)$$

where p_{α} is the α component of the electron momentum. We shall consider the radiation incident normally on the oxide-semiconductor interface so

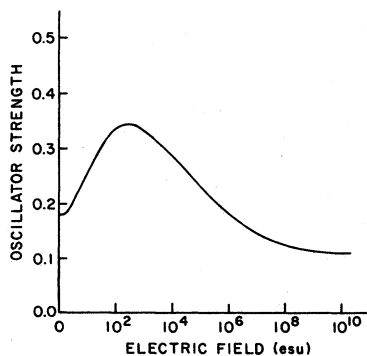


FIG. 2. Oscillator strength vs electric field for the $2p_0 \rightarrow 3d_{\pm 1}$ transition.

that the electric vector is parallel to the surface.

We take $\alpha = x$. The required momentum matrix element is found to be

$$\langle 3d_{\pm 1} | p_x | 2p_0 \rangle = -\frac{32}{\sqrt{6}} \frac{a_2^2 a_3^2 (b_2^3 b_3^3)^{1/2}}{(a_2 + a_3)^3 (b_2 + b_3)^3}. \quad (17)$$

The results for the oscillator strength are plotted as a function of electric field in Fig. 2. We see that the oscillator strength initially increases with increasing electric field, reaches a maximum, and then gradually decreases.

IV. DISCUSSION

In our previous paper⁵ on this subject, we employed the variational trial functions of Karpushin¹ and Bell *et al.*² to investigate the effect of an electric field normal to the SiO_2 -Si interface. These trial functions do not have the form specified by Eq. (8) and do not give the correct limiting values for the binding energies at high fields—namely, $4.0\mathcal{R}^*$ for the $2p_0$ state and $0.444\mathcal{R}^*$ for the $3d_{\pm 1}$ states. The trial functions used in the present paper, on the other hand, give the correct limiting values of the binding energies.

These limiting values are the binding energies of the appropriate states of a two-dimensional hydrogenlike atom. It should be noted that the two-dimensional value is closely approached for the $2p_0$ state only at very high electric fields in the 10^9 – 10^{10} -esu range. Such fields are in fact not realizable in the SiO_2 -Si system since the energy barrier between the SiO_2 and Si is only ~ 3 eV. Physically achievable fields may reach as high as 10^9 esu (3×10^5 V/cm), where the $2p_0$ state binding energy is intermediate between the two-dimensional and three-dimensional limits. Thus, the use of the two-dimensional binding energy in discussing the properties of inversion layers may be some-

what misleading. Furthermore, some of the theoretical assumptions made are untenable at the very high electric fields.

The calculations reported in this paper are based on a number of simplifying assumptions. We have already alluded to our use of an infinite potential barrier at the SiO_2 -Si interface. It would be desirable, particularly at the higher electric fields, to use a finite barrier of ~ 3 eV. One would then have to allow penetration of the electron into the oxide. In the present work we have assumed that the impurity ion is located exactly at the interface. In an experimental situation, however, the impurity will, in general, be situated at some finite distance from the interface. This possibility is taken into account in the Stern-Howard formalism and is currently being investigated by detailed calculations. Another point which should be raised is that the interface is not a mathematical plane, but in fact is a somewhat diffuse entity extending over a region of $5 - 10 \text{ \AA}$.¹⁰ This might be taken into account by using a position-dependent dielectric constant which varies smoothly from the value for silicon to that for SiO_2 across the transition region. Another assumption which we have made is to ignore the presence of the constant energy ellipsoids whose major axes are parallel to the interface. Taking into account these ellipsoids would lead to additional higher-lying bound states and some modification of the bound states already considered due to intervalley coupling. We have also assumed that the electric field due to the inversion layer is a constant, whereas, in reality, this is not so. Nevertheless, the work of Stern and Howard³ indicates that the variation of the electric field over the dimension of a bound state is rather small. Finally, we note that our use of the effective-mass approximation may lead to some error, particularly at the higher electric fields where the bound-state wave functions are compressed very close to the interface.

Let us now compare our theoretical results with

the experimental results of Hartstein and Fowler⁶ who have measured the conductivity of n -channel silicon metal-oxide-semiconductor field-effect transistor (MOSFET) devices in which Na^+ ions were diffused through the oxide to the oxide-semiconductor interface. Over a certain temperature range, the peak conductivity can be described by an activation energy which Hartstein and Fowler identify as the binding energy of an impurity band. This binding energy for the case of a narrow impurity band should be identifiable with the binding energy of an isolated impurity that we have considered in the present paper. By varying the substrate bias Hartstein and Fowler were able to vary the electric field in the inversion layer and thus were able to study the activation energy as a function of electric field. They found that in a sample with $5 \times 10^{11} \text{ cm}^{-2}$ oxide charge density the activation energy varied from 18 meV at zero substrate bias to 25 meV at -15 -V substrate bias. The corresponding electric fields are estimated to be 19.9 and 60.4 esu, respectively. From Fig. 1, we see that our calculated binding energies for the $2p_0$ ground state at these two electric fields are $0.50 \mathcal{R}^*$ and $0.60 \mathcal{R}^*$, respectively, or 21 and 25 meV, respectively. Thus, our theoretical results agree rather well with experiment.

In fact, the good agreement with experiment is probably fortuitous because of the many approximations we have made. For example, the impurity ions are not exactly at the interface, and the interface itself is not a geometrical plane as we have assumed. We have neglected whatever screening and impurity banding are present in the experimental situation. Also, at the relatively low electric fields in the experiments, our variational wave function can probably be improved. All of these aspects are now being investigated.

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