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Ion neutralization at an Si- or Ge-type semiconductor surface

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Abstract. The approximate many-level method is used to study ion neutralization near the surface of an Si- or Ge-type semiconductor. The tight-binding approximation is employed to model the semiconductor as a one-dimensional chain of sp hybrids. Calculations show that the electronic structure and the component of the substrate surface, by introducing the surface density, play important roles in the ion resonance charge transfer.

1. Introduction

The study of the process of surface ion neutralization (SIN) has long been a centre of attention in both theoretical and experimental investigations. The interest in such processes arises because of the fundamental role they play in a variety of analytical techniques used in the study of surfaces. These include secondary-ion mass spectrometry (SIMS) [1] and ion surface scattering (ISS) [2] for compositional and structural analysis as described by Taglauer and Heiland [3] and ion neutralization spectroscopy (INS) [4] and its modern version metastable quenching spectroscopy (MQS) [5] which provide information on the electronic properties of the surface. Various theoretical methods have been applied to study the charge-exchange scattering of an ion at a solid surface. The earliest theoretical work on SIN was that of Hagstrum [4], who gave the ion survival rate as being proportional to $\exp(-v_0/v)$, where v_0 is characteristic velocity of the ion and v is its velocity normal to the surface. Kawai [6, 7] used the Heisenberg equations of motion for the time-dependent version of the Anderson–Newns model (TDAN) Hamiltonian to derive an integral–differential equation, whose solution, within the so-called local time approximation, led to the ion-neutralization probability. In a similar vein, Makoshi and co-workers [8–10] investigated the effects of the intra-atomic Coulomb repulsion in the TDAN model on the ion–solid charge transfer, within the Hartree–Fock approximation. The charge state of the scattered ion was calculated self-consistently in the wide-band limit. It was observed that there was not much difference in the neutralization probability between gradual and sudden switching on and off of the interaction potential. Additionally, the qualitative behaviour of the probability is not changed, to any noticeable extent, by the time dependence of the Coulomb repulsion and the ionic energy level. Sebastian *et al* [11] calculated the ionization/neutralization probability by solving the differential equation for the time-evolution operator of the electronic system, under the assumption that the atom/ion moves along a classical trajectory. McDowell [12] developed two equivalent techniques for calculating the neutralization probability of ions impinging on solid surfaces, both starting from the Heisenberg equations of motion. In qualitative agreement with experiment, the neutralization probability was observed to oscillate as a

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function of the energy of the incident ion. Battaglia and coworkers [13, 14] performed an investigation of positive-ion neutralization at surfaces using first-order perturbation theory. Davison and coworkers [15, 16] presented a many-level method based on the two-level one to investigate the resonance charge-transfer process. Xie and Zhang [17] investigated the ion neutralization near a contaminated metal surface using the many-level method.

So far very few theoretical studies have been related to the system which consists of an ion and a semiconductor substrate. The purpose of the present paper is to calculate the ion orbital occupancy of a positive ion at an Si- or Ge-type semiconductor surface in the case of resonance charge transfer.

2. Model and formalism

The model used here consists of an incident positive ion and an Si- or Ge-type semiconductor substrate. We consider the situation of the ion striking the end atom (atom 1) of a linear chain of N atoms.

Let the ket $|0\rangle$ denote the ion orbital and ϵ_0 at $t = t_0(\to -\infty)$ the corresponding energy. Taking $|m\rangle$ to be the atomic orbital centred on the mth substrate atom, then the kth molecular orbital (MO) of the solid has the form $|\chi_k\rangle = \sum_{m=1}^{N} C_{km}|m\rangle$, where N is the number of atoms in the substrate. Then, before the interaction occurs, the ion–substrate system is described by Hamiltonian

$$H_0 = \epsilon_0|0\rangle\langle 0| + \sum_{k=1}^{N} \epsilon_k|\chi_k\rangle\langle\chi_k|. \tag{1}$$

The time-dependent Hamiltonian characterizing the scattering process is

$$H = H_0 + H_1(t) = \epsilon_0|0\rangle\langle 0| + \sum_{k=1}^{N} \epsilon_k|\chi_k\rangle\langle\chi_k| + V(t)(|0\rangle\langle 1| + |1\rangle\langle 0|) \tag{2}$$

where $V(t)$ is the interaction potential. It has the form

$$V(t) = V_0\,\mathrm{e}^{-\lambda|t|} \qquad \lambda > 0. \tag{3}$$

The parameter λ is inversely proportional to the effective time of interaction between the ion and the solid. Here we neglected the intra-atomic Coulomb repulsion (U) on the impinging ion as usually treated [18, 19]. Although the ion energy level ϵ_0 is generally time dependent due to the image interaction, we simply take it as a constant value [7, 15, 18–21]. V_0 is the maximum interaction strength, which occurs at the moment of closest approach ($t = 0$), and λ is related to the kinetic energy E and mass m of the incoming ion by $\lambda = \mu(2E/m)^{1/2}$, μ being a constant of proportionality.

The time-dependent Schrödinger equation for the interaction process, in atomic units ($\hbar = 1$), is

$$\mathrm{i}|\Psi_j(t)'\rangle = H(t)|\Psi_j(t)\rangle. \tag{4}$$

Using perturbation theory, the solution to (4) can be written in the form

$$|\Psi_j(t)\rangle = a_{0j}(t)\,\mathrm{e}^{-\mathrm{i}\epsilon_0 t}|0\rangle + \sum_{k=1}^{N} a_{kj}(t)\,\mathrm{e}^{-\mathrm{i}\epsilon_k t}|\chi_k\rangle \tag{5}$$

which is subject to the initial conditions $a_{0j}(-\infty) = 0$ and $a_{kj}(-\infty) = \delta_{kj}$. The probability of the originally empty ion orbital being filled by the electron from the jth MO is

$$P = \lim_{t\to\infty} |a_{0j}(t)|^2. \tag{6}$$

In the case of resonance transfer treated here, the positive ion has an empty orbital, whose energy lies in the forbidden energy gap (FEG) and in the vicinity of the surface state. The occupancy of the ion orbital is

$$n(t) = 2\sum_{j=1}^{N} |a_{0j}(t)|^2. \tag{7}$$

In the case of $N \to \infty$, the total ion-orbital occupancy is given approximately by [22]

$$n(t) = 2\int_{-\infty}^{E_F} \rho_s(E)|d_0(E,t)|^2\,\mathrm{d}E \tag{8}$$

where E_F is the Fermi energy level, 2 represents double occupancy of the ion orbital and $\rho_s(E)$ represents the surface density of states for the semiconductor substrate. $|d_0(E,t)|^2$ in equation (8) represents the ion-orbital occupancy in the corresponding two-level problem. The presence of $\rho_s(E)$ in equation (8) introduces the substrate electronic structure in such a way as to transform the two-level result into an approximate solution to the many-level case. The expressions for $d_0(E,t)$ are

$$d_0(E,t) = (V_0/\mathrm{i})^{1/2}(V_0/\lambda)^{-\nu_-}\xi^{\nu_-}[a_-J_{\nu_-}(\xi) + b_-J_{\nu_-}(\xi)] \qquad (t \leqslant 0) \tag{9}$$

$$d_0(E,t) = (V_0/\mathrm{i})^{1/2}(V_0/\lambda)^{\nu_+}\xi^{-\nu_+}[a_+J_{\nu_+}(\xi) + b_+J_{\nu_+}(\xi)] \qquad (t > 0) \tag{10}$$

$$d_0(E,t) = \frac{\pi\xi_0[J_{-\nu_-}(\xi_0)J_{\nu_-}(\xi_0) + J_{-\nu_+}(\xi_0)J_{\nu_+}(\xi_0)]}{2\cosh(\pi\omega/2\lambda)} \qquad (t \to \infty). \tag{11}$$

Here

$$\omega = \epsilon_0 - E \qquad \xi_0 = V_0/\lambda \qquad \nu_\pm = (\mathrm{i}\omega \mp \lambda)/2\lambda \qquad \xi = \xi_0\mathrm{e}^{-\lambda|t|} \qquad b_- = 0$$

$$a_- = (\mathrm{i}V_0)^{-1/2}(V_0/2\lambda)^{-\nu_+}\Gamma(\nu_-) \tag{12}$$

$$a_+ = [J_{\nu_-}(\xi_0)J_{-\nu_-}(\xi_0) + J_{-\nu_+}(\xi_0)J_{\nu_+}(\xi_0)]/D \tag{13}$$

$$b_+ = [J_{\nu_-}(\xi_0)J_{\nu_-}(\xi_0) - J_{\nu_+}(\xi_0)J_{\nu_+}(\xi_0)]/D \tag{14}$$

where

$$D = [J_{\nu_+}(\xi_0)J_{-\nu_-}(\xi_0) + J_{-\nu_+}(\xi_0)J_{\nu_-}(\xi_0)]/a_-. \tag{15}$$

For the purpose of evaluating equation (8) numerically, the surface density of states (SDOS) was taken to be that of a one-dimensional semi-infinite sp hybrid chain [23, 24] as in figure 1. Associated with each atom in the chain are two sp hybrid orbitals of equal energy ϵ, labelled 1 and 2. The index m labels the sites in the lattice, and $|mi\rangle$, $i = 1, 2$ denote the Wannier states associating with the orbitals. There are two types of interaction term: the overlap integral $-J_1(J_1 > 0)$ between states 1 and 2 on the same atom and $-J_2(J_2 > 0)$ between

state 2 on the site m and state 1 on the site $(m+1)$. The Hamiltonian corresponding to this system is

$$H=\sum_{m=1}^{\infty}[\epsilon(|m1\rangle\langle m1|+|m2\rangle\langle m2|)-J_1(|m2\rangle\langle m1|+\mathrm{HC})-J_2(|m+1;\,1\rangle\langle m2|+\mathrm{HC})]+D|11\rangle\langle 11| \tag{16}$$

where D corresponds to the surface perturbation. The surface GF for this system is

$$G_s(11,11)=\frac{G_b(11,11)}{1-J_2G_b(11,02)-DG_b(11,11)} \tag{17}$$

where G_b is the GF in Wannier representation for the infinite chain

$$G_b(m1,n1)=G_b(m2,n2)=-\frac{Z-\epsilon}{2J_1J_2}I_{|m-n|} \tag{18}$$

$$G_b(m1,n2)=\frac{1}{2J_1J_2}(J_1I_{|m-n|}+J_2I_{|m-n-1|}) \tag{19}$$

where

$$I_{|m-n|}=\frac{2u^{|m-n|+1}}{u^2-1} \tag{20}$$

$$u=Z_1-\sqrt{Z_1^2-1} \tag{21}$$

$$Z=E+\mathrm{i}0^+ \tag{22}$$

$$Z_1=\frac{(Z-\epsilon)^2-J_1^2-J_2^2}{2J_1J_2}. \tag{23}$$

The surface density of states is [25]

$$\rho_s(E)=-\frac{1}{\pi}\,\mathrm{Im}\,G_s(11,11). \tag{24}$$

This SDOS consists of two parts: one corresponding to the valence and conduction bands (ρ_s^b), the other corresponding to localized surface states (ρ_s^s) outside the bands. The local DOS in the vicinity of E_s is [26]

$$\rho_s^s(E)=I_s\delta(E-E_s) \tag{25}$$

where E_s is the localized surface state energy, which can be determined by the real poles of $G_s(11,11)$ outside the bands, and I_s is the intensity of surface states, which is given by the residue of $G_s(11,11)$ at E_s. Using equations (24) and (25) in equation (8) and taking $t\to\infty$ gives $n(\infty)$, the final expected occupancy of the ion orbital.

$$n(\infty)=2\int_{E_L}^{E_U}\rho_s(E)|d_0(E,\infty)|^2\,\mathrm{d}E+2I_s|d_0(E_s,\infty)|^2 \qquad (\text{for } E_s\leqslant E_F) \tag{26}$$

where E_L, E_U is the lower and upper edge of the valence band, respectively. Without losing generality, we choose the Fermi energy (E_F) at the centre of the FEG.

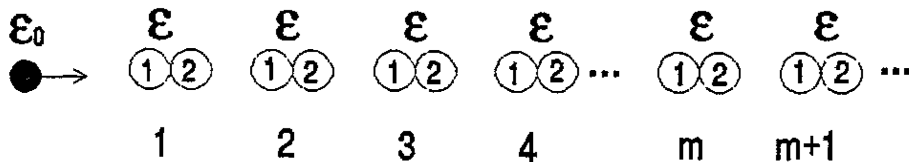

Figure 1. The model of an Si- or Ge-type semiconductor, which is represented by a semi-infinite chain of sp hybrids.

3. Results and discussion

In the numerical calculations, we take Si as an example. The parameter values [27] (in atomic units) are chosen as follows: $\epsilon = 0.0$, $J_1 = 0.0205$, $J_2 = 0.0410$. The energy zero is chosen to be at the centre of the forbidden energy gap (FEG). The values of perturbation D corresponding to different surface state energies E_s and the intensities I_s are $D = 0.0$, -0.0092, -0.0276, $E_s = 0.0$, -0.0068, -0.0179, $I_s = 0.75$, 0.72, 0.41, respectively. The units of intensities are in electrons. D and E_s are both in atomic units.

Figure 2 shows the ion occupancy $n(\infty)$ versus ϵ_0 with different surface state energies. The final ion orbital occupancy is largest when ϵ_0 is identical with the surface state energy. Additionally, the height of the peak grows as the intensity of the surface state increases. We can also see that the peak in the curve shifts to lower energies with decreasing D, reflecting the position of the surface state. For the three cases of $D = 0.0$, -0.0092, -0.0276, three localized surface states (LSSs) are found in the FEG. The curves have three satellite peaks corresponding to the contribution of the band states (-0.0615 to -0.0205) and three primary peaks centred around the LSS. The result suggests that SIN may be useful experimentally as a probe to determine the position of surface states, by bombarding the semiconductor surface with a species of ion whose orbital energy ϵ_0 lies outside the solid's band region, and measuring the percentage of such ions which are neutralized. If the percentage is quite high, i.e. the average orbital occupancy is large, then one can deduce that there exists a surface state with energy not too different from ϵ_0.

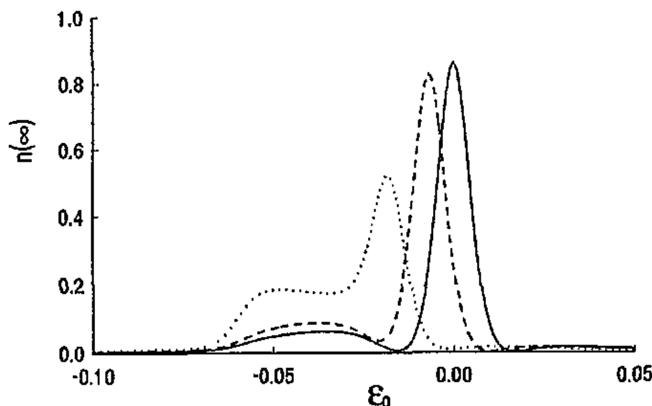

Figure 2. $n(\infty)$ versus ϵ_0 for $V_0 = 0.02$, $\lambda = 0.01$, $E_s = 0.0$ (the solid line), -0.0068 (the dashed line), -0.0179 (the dotted line).

Figure 3 shows the ion occupancy $n(\infty)$ versus λ^2 with different surface state energies. For the same value of V_0 (which governs the interaction strength), all the curves have corresponding maxima and minima, but quantitatively different heights. For the different values of V_0 (figure 4), the greater V_0 is, the greater the oscillation is.

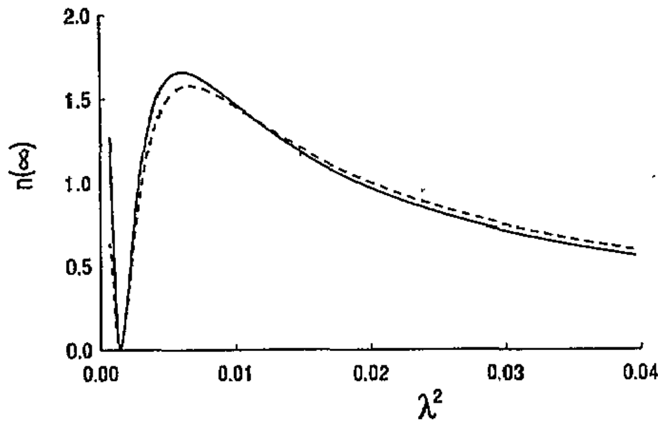

Figure 3. $n(\infty)$ versus λ^2 for $V_0 = 0.06$ and $\epsilon_0 = -0.0068$. $E_s = 0.0$ (the solid line), -0.0179 (the dashed line).

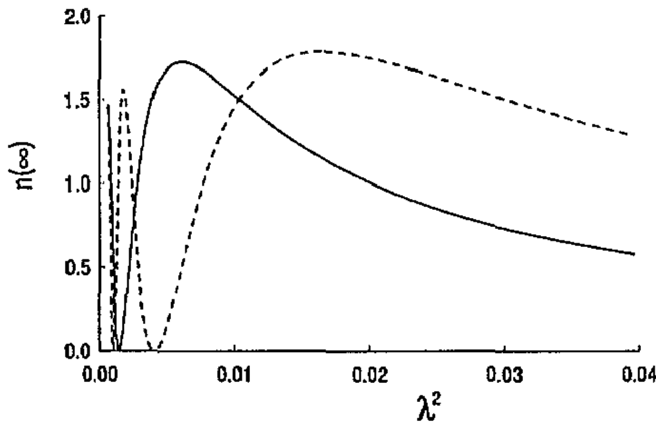

Figure 4. *$n(\infty)$ versus λ^2 for $\epsilon_0 = -0.0068$ and $E_s = -0.0068$. $V_0 = 0.06$ (the solid line),* 0.10 (the dashed line).

A plot of the ion orbital occupancy, as a function of λ^2, is shown in figure 4, and displays an oscillatory behviour in qualitative similarity to the experimentally observed pattern [28]. *Since λ is proportional to the ion velocity and, hence, inversely proportional to the effective* time of interaction, the oscillatory behaviour has a simple physical interpretation. When the ion has a fairly large velocity, the collision time is only long enough for an electron to transfer from the solid, neutralizing the ion. For a somewhat lower velocity (i.e. longer

collision), the transferred electron has enough time to jump back to the solid atom, so the ion leaves the surface still ionized after the double exchange. With a still longer interaction, the ion can be neutralized after three charge exchanges have occurred, and so on. Thus the $n(\infty)$ versus λ^2 curve will exhibit a sequence of relative maxima at those points for which the ion velocity is such that an odd number of electron-transfer events is most likely to occur. An important aspect of figure 4 is the fact that the electronic energy ϵ_0 of the ion orbital is equal to the energy E_s of the localized surface state, indicating that the aforementioned oscillatory feature does indeed persist when the ion is neutralized by an electron from the surface state, rather than a delocalized bulk state.

The above explanation of the oscillation in the $n(\infty)$ versus λ^2 curve is confirmed by examining the variation in time of the occupancy of the ion orbital (figure 5), for several values of λ. When $\lambda = 0.08$, the occupancy is originally zero, and increases monotonically to a final value of about 1.55, indicating that the interaction time is short enough that, once the electron has transferred to the ion orbital, it stays there and is unable to return to the solid. When $\lambda = 0.02$, which corresponds to a longer collision time, the ion orbital has a small occupancy, then increases nearly to 1.6, drops down to 0.1, rises again to 1.45 and then decreases to an asymptotic value of about 1.4. This feature implies that one expects the electron to transfer to the ion, back to the solid and then back again to the ion, where it remains as the ion leaves the surface. Reducing λ to 0.015, giving an even longer collision time, produces further oscillation in time of the occupancy, demonstrating that longer interactions (smaller λ) give rise to more electron exchange during that period.

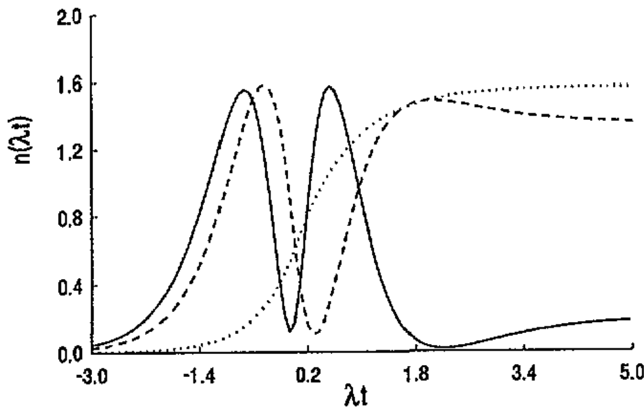

Figure 5. $n(t)$ versus λt for $V_0 = 0.05$, $E_s = \epsilon_0 = -0.0068$. $\lambda = 0.015$ (the solid line), 0.02 (the dashed line), 0.08 (the dotted line).

4. Summary

The ion occupancy near an Si- or Ge-type semiconductor surface has been calculated using the many-level method. The calculated results show that (1) the greater the intensity of a localized state or the smaller $|\epsilon_0 - E_s|$ is, the higher the maximum value of $n(\infty)$ is and (2) $n(\infty)$ versus λ^2 and $n(t)$ versus t both have oscillatory behaviours. These results for ion neutralization at a semiconductor surface are similar to those for ion neutralization at a metal substrate [22].

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