Ion neutralization near a disordered binary alloy surface

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Abstract. Ion neutralization near the surface of a disordered binary alloy is investigated within
the framework of the approximate many-level method. The disordered binary system is described
by the one-dimensional tight-binding model and the coherent potential approximation. The
results obtained show that the substrate's electronic structure and the concentration percentages
of the two components play important roles in the resonance charge transfer.

1. Introduction

In the recent past, ion neutralization scattering from surfaces has received considerable
attention from both experimentalists [1–3] and theoreticians [4–6]. A variety of analytical
techniques have been used in the study of surfaces. These include secondary-ion mass
spectrometry (SIMS) [7] and ion surface scattering (ISS) [8] for compositional and structural
analysis as described by Taglauer and Heiland [9] and ion neutralization spectroscopy
(INS) [10]. Theories of resonance transfer of electrons in ion–surface collisions have been
presented by a number of authors [11–14]. Many papers have reported ion neutralization
scattering from different substrates [15–18].

Growing interest has been devoted to the study of alloys since a specific behaviour
is to be expected from the alloy system if used as a catalyst. The behaviour of an alloy
is mainly determined by the alloy's surface composition. Thus, it is significant to study
the ion neutralization near the surface of a disordered binary alloy (DBA). So far, most of
the experimental and theoretical studies have been performed on the *ion–ordered substrate*
systems [15–18]. The purpose of the present paper is to calculate the ion orbital occupancy
of a positive ion at a DBA surface in the case of resonance charge transfer by extending the
ion–ordered substrate systems to *ion–DBA* systems.

The model and formalism are given in section 2, and the calculated results and discussion
are presented in section 3.

2. Model and formalism

The model used here consists of an incident positive ion and a DBA substrate (figure 1).
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
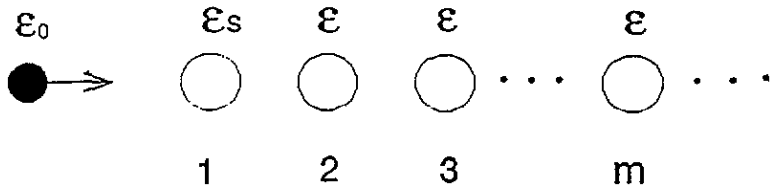energy. Taking $|m\rangle$ to be the atomic orbital centred on the mth substrate atom, then the

Figure 1. The one-dimensional tight-binding model of an ion–DBA system. ϵ_0 is the ion orbital energy, and $\epsilon_s = D_e + \sigma_s(E) - \sigma_b(E) + \epsilon$ and $\epsilon = \epsilon_V + \sigma_b(E)$ are the effective orbital energies of the effective medium corresponding to the DBA.

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 time dependent interaction potential, which has the pulse like form

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

The parameter λ is inversely proportional to the effective time of interaction between the ion and the solid. As in [5, 19], the intra-atomic Coulomb repulsion (U) is neglected. Although the ion energy level ϵ_0 is generally time dependent due to the image interaction, we simply take it as a constant value as usually treated [5, 19–23]. 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

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

Using perturbation theory, the solution to equation (4) can be written as

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

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

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

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 [24]

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

where E_F is the Fermi energy level, the factor of two represents the double occupancy of the ion orbital and $\rho_s(E)$ represents the surface density of states for the DBA substrate. As shown previously [18], $|d_0(E, t)|^2$ 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.

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 DBA chain. Following Parent *et al* [25, 26], the disordered binary material is presented by an effective medium by introducing the coherent potential, which may be calculated in a self-consistent manner. The coherent potential approximation (CPA) theory is used to treat the binary system $A_x B_{1-x}$, which is composed of the atoms A and B, with the atomic energies ϵ_A and ϵ_B and concentrations x and $1 - x$, respectively. Further, it is assumed that an electron is allowed to transfer between nearest-neighbour sites with the effective transfer energy J_e ($J_e = x^2 J_A + x(1 - \bar{x})(J_A + J_B) + (1 - x)^2 J_B$). The Hamiltonian corresponding to this system is [25]

$$H_e = H_V + \sum_{m=1}^{\infty} \sigma_b \big(|m\rangle\langle m| + (D_e + \sigma_s - \sigma_b)|1\rangle\langle 1|\big) + J_e(|0\rangle\langle 1| + \text{HC}) \tag{9}$$

where

$$H_V = \epsilon_V \sum_{m=1}^{\infty} |m\rangle\langle m| - J_e \sum_{m=1}^{\infty} (|m\rangle\langle m + 1| + \text{HC}) \tag{10}$$

is an ordered Hamiltonian which describes a virtual crystal with a mean atomic energy $\epsilon_V = x\epsilon_A + (1 - x)\epsilon_B$. $(D_e + \sigma_s - \sigma_b)$ is the surface perturbation. σ_b and σ_s are the bulk and

surface coherent potential of the semi-infinite system, respectively. They are determined by the self-consistent equations

$$\sigma_b + (\epsilon_A - \epsilon_V - \sigma_b)G_b(m, m)(\epsilon_B - \epsilon_V - \sigma_b) = 0 \tag{11}$$

$$\sigma_s + (\epsilon_A - \epsilon_V - \sigma_s)G_s(1, 1)(\epsilon_B - \epsilon_V - \sigma_s) = 0. \tag{12}$$

The surface Green function (GF) for this system is

$$G_s(1, 1) = \frac{G_b(1, 1)}{1 - (D_e + \sigma_s - \sigma_b)G_b(1, 1) - J_e G_b(1, 0)} \tag{13}$$

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

$$G_b(m, n) = G_b(m, m)u^{|m-n|} \tag{14}$$

$$G_b(m, m) = \frac{u}{J_e(u^2 - 1)} \tag{15}$$

where

$$u = Z - \sqrt{Z^2 - 1} \tag{16}$$

$$Z = \frac{E + i0^+ - \epsilon_V - \sigma_b}{2J_e}. \tag{17}$$

The SDOS is [27]

$$\rho_s(E) = -\frac{1}{\pi} \operatorname{Im} G_s(1, 1) \tag{18}$$

which consists of two parts: one corresponding to the band (ρ_s^b), the other corresponding to localized surface states (ρ_s^s) outside the band. The local DOS in the vicinity of E_s is [25]

$$\rho_s^s(E) = I_s \delta(E - E_s) \tag{19}$$

where E_s, the localized surface state energy, is determined by the real poles of $G_s(1, 1)$ outside the band; I_s is the intensity of surface states, which is given by the residue of $G_s(1, 1)$ at E_s. Using equations (17) and (18) in equation (8) and taking $t \to \infty$ gives $n(\infty)$, the final expected occupancy of the ion orbital.

$$n(\infty) = 2 \int_{E_L}^{E_U} \rho_s(E)|d_0(E, \infty)|^2 \, dE + 2I_s|d_0(E_s, \infty)|^2 \qquad (E_s \leqslant E_F) \tag{20}$$

where E_L (E_U) is the lower (upper) edge of the band. Without loss of generality, we choose the Fermi energy (E_F) at the upper edge of the band.

In the limit of $x = 0.0$ (corresponding to a pure B crystal), the model used here will be the same as that used in Sulston and Davison's paper [24].

3. Results and discussion

The numerical calculations of the ion occupancy near the surface of a DBA have been performed using the methods of section 2. The parameter values (in atomic units) are chosen as follows: $\epsilon_A = 0.0294$, $\epsilon_B = 0.0$, $J_A = J_B = 0.0184$. The energy zero is chosen to be at the vacuum level. The surface state energies E_s and the intensities I_s, corresponding to different perturbations D_e and concentration $x = 0.5$, are given in table 1. The units of intensities are in electrons. D_e and E_s are both in atomic units.

Table 1. Values of surface state energies E_s and intensities I_s corresponding to different perturbations for $x = 0.5$.

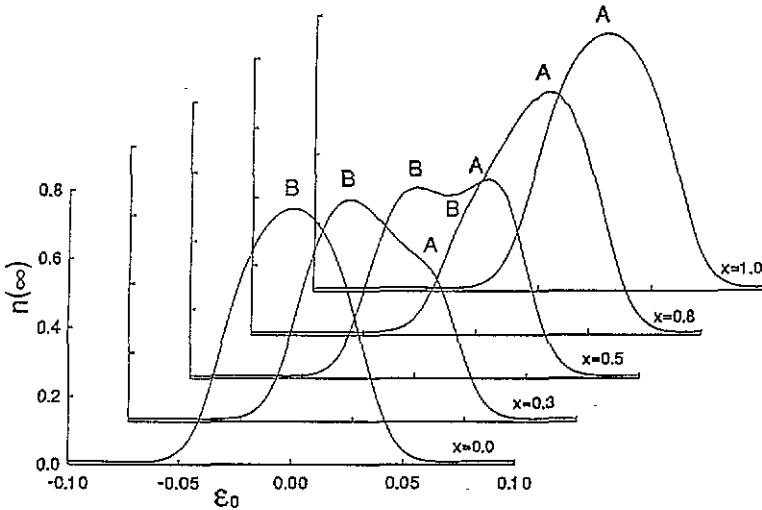| D_e	0.0	−0.0294	−0.0368
I_s	0.0	0.3829	0.422
E_s	no surface state	−0.0383	−0.044

Figure 2. $n(\infty)$ versus ϵ_0 with different x for $V_0 = 0.05$, $\lambda = 0.02$, $D_e = 0.0$ and no surface state.

Figure 2 shows the variation of the ion occupancy $n(\infty)$ with ϵ_0 for different concentrations x of type A atoms. When $x = 0.0$, corresponding to a pure B substrate, the curve has only one peak (labelled B) with a maximum value of 0.75 at $\epsilon_0 = 0.0$, which coincides with the centre (0.0) of the band. When $x = 0.3$, the curve exhibits a primary peak (labelled B) at $\epsilon_0 = -0.002$ and a slight shoulder (labelled A) on the right-hand side of the primary peak, corresponding to the contribution of atoms B and atoms A to the SIN, respectively. Increasing the concentration x of atoms A, we find that when $x = 0.5$, the curve exhibits two peaks which have almost the same heights, indicating atoms A have almost the same contribution to the SIN as atoms B; when $x = 0.8$, the height of peak B decreases dramatically, and that of peak A increases. This shows that the ion neutralization most likely occurs by picking up an electron from the band of A. Finally, when $x = 1.0$, peak B disappears completely; only peak A exists. So we can obtain the concentration

ratio of atoms A and B, according to the SIN curves. From figure 2, we can find that the maximum value of $n(\infty)$ decreases as the concentration of impurity increases, supposing that the concentration of impurity is relatively smaller.
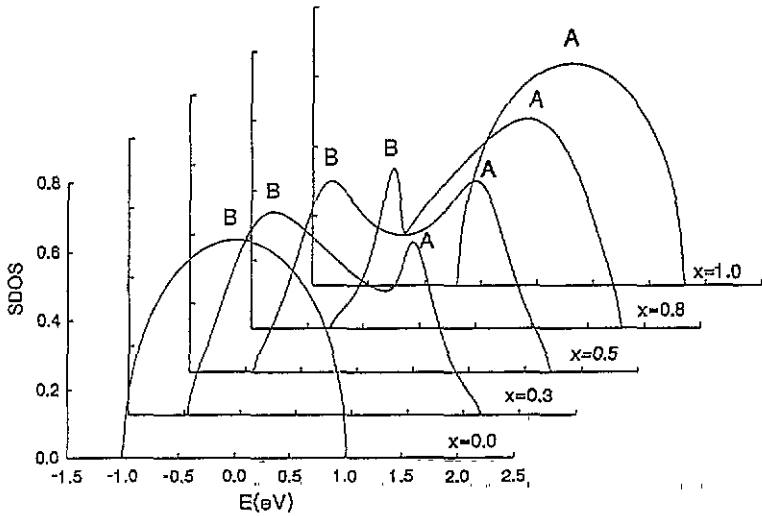

Figure 3. *The SDOS of the semi-infinite chain of* A_xB_{1-x} *alloy for different* x.
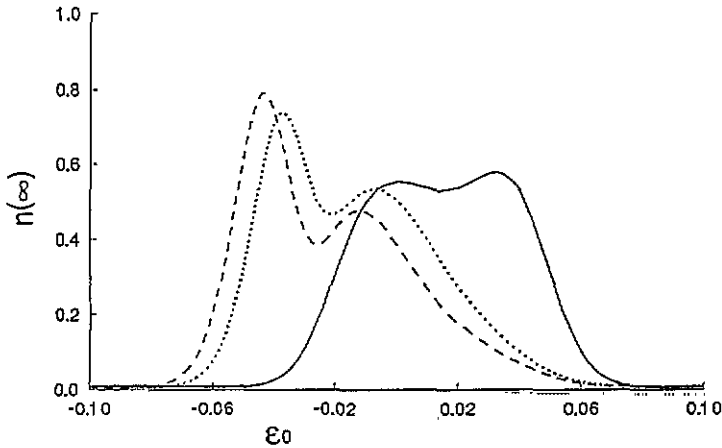

Figure 4. $n(\infty)$ versus ϵ_0 with different E_s for $x = 0.5$, $V_0 = 0.05$, $\lambda = 0.02$. No surface state (solid line); $E_s = -0.0383$ (dashed line); $E_s = -0.044$ (dotted line).

Figure 3 is the SDOS for five different concentrations of atoms A. The peaks labelled A and B correspond to the contributions of atoms A and B, respectively. When compared with figure 2, the ion occupancy curves are seen to resemble those of the SDOS, thus indicating the possibility of obtaining SDOS information from the ion orbital occupancy curves.

Figure 4 shows the graphs of ion occupancy $n(\infty)$ versus ϵ_0 for $x = 0.5$ and different perturbations D_e. It is clear that, for any particular choice of ϵ_0, $n(\infty)$ depends strongly on the value of D_e, and that the range of values of ϵ_0 which give high $n(\infty)$ varies dramatically with D_e. In the case of $D_e = 0.0$, significant amounts of neutralization can occur only if ϵ_0 is aligned with the occupied band. As $|D_e|$ increases, a localized state emerges from the lower band edge and moves to lower energies, with the peak in the curve simultaneously shifting to correspond to this energy. It is also significant that the maximum value of $n(\infty)$ increases with the creation and greater intensity of a localized state (i.e. large $|D_e|$), due to the fact that electrons in these states are more localized at the surface, making them more likely to be transferred to the ion than bulk state electrons, which are delocalized throughout the solid. The result suggests that SIN may be useful experimentally as a probe to determine the position of surface states, by bombarding the disordered binary crystal 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.

Note, in figure 4, that all the curves have two peaks. When $D_e = 0.0$ (no surface state exists), the two peaks corresponding to the contribution of the band states of atoms A and B have almost the same height. When $D_e = -0.0294$ and $D_e = -0.0368$, the curves both have one satellite peak corresponding to the band states and one primary peak centred around the localized surface state. With increasing $|D_e|$, the height of the primary peak grows and that of the satellite peak decreases.

In the limit of $x = 0.0$, the calculated results display the same behaviour as in [24].

From the discussion above, we can summarize our results as follows: (1) the greater the intensity of a localized state, the higher is the maximum value of $n(\infty)$; (2) the maximum value of $n(\infty)$ decreases as the concentration of the impurity increases; (3) bombarding the surface with ions and measuring the percentage of neutralized ions enables the concentration ratio of the binary alloy and the surface state energy to be obtained and provides information on the SDOS of the substrate; (4) the concentration of the substrate alloy has a significant influence on the ion neutralization process; in the limit of $x = 0.0$, the neutralization properties of an *ion–A_xB_{1-x}* system are the same as those of the *ion–pure metal* system shown in [24].

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