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Effect of impurity on ion neutralization

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The influence of a substitutional impurity atom on the ion neutralization near the (100) surface of a simple cubic substrate is investigated using the Green's-function method. Ion neutralization is studied within the framework of the approximate many-level method. The pure metal substrate is described by the three-dimensional tight-binding scheme, and the impurity is described by the Koster-Slater model. The effects of the impurity site, orbital energy, and impact site on ion neutralization are discussed in detail. Calculations show that the ion occupancy depends strongly on the impact site, and the impurity can play a potentially dominant role in surface-ion neutralization.

I. INTRODUCTION

In recent years, many theoretical and experimental studies have been reported on dynamical charge-transfer processes at solid surfaces. They are interesting as basic problems of quantum mechanics and also very important for practical applications. There are three mechanisms (resonant, quasiresonant, and Auger transition) for charge transfer. Resonant charge transfer is a fairly pervasive mechanism and this has led to an increasing theoretical interest in the topic.[1-4] In the present paper, we are concerned with the resonant charge-transfer process.

For discussion of the charge-transfer probability in the resonant transfer process, the time-dependent Anderson Hamiltonian[5,6] is often used based on the classical trajectory approximation.[7-9] The Hartree-Fock approximation, for example, is often used to treat the electron-electron interaction. For the simplified models, the intraatomic Coulomb energy is neglected, or rather taken to be infinite. Kasai and Okiji[10] developed for time-dependent Anderson-Newns (TDAN) model[2] beyond the Hartree-Fock approximation by means of the Heisenberg equations of motion within the wide-band limit.[11]

Because surface-ion neutralization can be regarded as being similar to "dynamic" chemisorption, it is natural that the TDAN model has played a large role in many investigations of charge transfer. Kawai,[12] for example, used the Heisenberg equations of motion for the TDAN Hamiltonian to derive an integral-differential equation of motion, within the so-called local time approximation, which led to the ion-neutralization probability. The qualitative behavior of the results was unchanged, to a certain extent, by the time dependence of the Coulomb repulsion and the ionic energy level. In terms of the TDAN model, Davison and co-workers[3,13,14] presented a many-level method based on the two-level one to investigate the resonance charge-transfer process. Calculations show that the surface state can play a potentially dominant role in surface-ion neutralization. Wei *et al.*[15-18] and Xie and Zhang[19] studied charge transfer during reflection of ions from different substrate surfaces using the single-orbital approximation.[13]

Considerable progress has been made in the theoretical understanding of the process of ion neutralization on a pure substrate.[13-16] Experimentally, it may not be possible to remove all the impurities or defects near the surface of a crystal sample, and the presence of an impurity atom affects the charge transfer between the ion and solid dramatically. Thus, it is significant to study the ion neutralization near the surface of a contaminated substrate. Xie and Zhang[19] employed a one-dimensional tight-binding model to investigate the impurity effects on the ion-neutralization probability using the many-level method. The purpose of the present paper is to investigate the effect of impurity on the surface-ion neutralization in the case of resonance charge transfer by extending one-dimensional systems to three-dimensional systems. Thus, different impurity locations and different scattering sites (such as atop, bridge, or centered sites) can be considered in this model. To our knowledge, the features of the neutralization process on such a model have not been studied before. We only consider the situation of a single impurity. For the substrate containing several impurities, it can be transferred to a disordered binary alloy which we[16,18] have discussed.

The model and formalism are given in Sec. II, and the calculated results and discussion are presented in Sec. III.

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II. MODEL AND FORMALISM

The model used here consists of an incident positive ion and a contaminated metal substrate (Fig. 1) that is characterized by a semi-infinite simple cubic crystal. We consider the situations of the ion striking normally the atop (A), bridge (B), and centered (C) sites on the (100) face.

Let the ket $|0\rangle$ denote the ion orbital and ϵ_0 at $t=t_0(\rightarrow -\infty)$ the corresponding energy. Taking $|m\rangle$ to be the atomic orbital centered 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 the 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

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

where $V(t)$ is the time-dependent interaction potential, which has the *pulselike* form

$$V(t)=V_0e^{-\lambda|t|}\;,\quad \lambda>0\;. \tag{3}$$

The parameter λ is inversely proportional to the effective time of interaction between the ion and the solid. As in Refs. 2, 13, and 20, 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.[2,8,9,13,20] 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 Eq. (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

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

The occupancy of the ion orbital is

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

In the case of $N\rightarrow\infty$, the total ion-orbital occupancy is given approximately by[13]

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

where E_F is the Fermi energy level, the factor of 2 represents double occupancy of the ion orbital, and $\rho_s(E)$ represents the surface density of states for the contaminated metal substrate. As shown previously,[15] $|d_0(E,t)|^2$ in Eq. (8) represents the ion-orbital occupancy in the corresponding two-level problem. The presence of $\rho_s(E)$ in Eq. (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 Eq. (8) numerically, the surface density of states (SDOS) was taken to be that of a three-dimensional semi-infinite contaminated metal crystal. The Hamiltonian corresponding to this system is

$$H=H_0+H_1\;, \tag{9}$$

where

$$H_0=-\beta\sum_{i,j(\neq i)}|i\rangle\langle j| \tag{10}$$

is the Hamiltonian for the pure semi-infinite solid with $-\beta$ being the two-center hopping integral of the solid atoms, and the sum is over only the nearest-neighbor substrate atoms. The energy zero is defined to be the orbital energy of the solid atom. A substitutional impurity at the lth site of the solid will be represented by the Koster-Slater model,[21]

$$H_1=\varepsilon|l\rangle\langle l|\;, \tag{11}$$

where ε is the effective orbital energy of the impurity. In Wannier representation, the surface Green's function (GF) for this system is

$$G(i,j;z)=G_0(i,j;z)+\varepsilon\frac{G_0(i,l;z)G_0(l,j;z)}{1-\varepsilon G_0(l,l;z)}\;, \tag{12}$$

where

$$G_0(i,j;z)=\frac{a_0^2}{(2\pi)^2}\int_{\mathrm{SBZ}}d^2\mathbf{k}_\parallel e^{i\mathbf{k}_\parallel\cdot(\mathbf{R}_i-\mathbf{R}_j)}G_0(\mathbf{k}_\parallel,Z) \tag{13}$$

is the surface GF of the (100) face of a simple cubic crystal without surface perturbation. The integral is over the

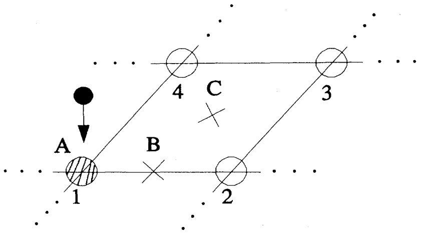

FIG. 1. Ion and semi-infinite contaminated metal system. Solid circle, ion; hatched circle, impurity atom.

surface Brillouin zone. $Z=E+i0^+$, $\mathbf{k}_\parallel$ is the two-dimensional wave vector parallel to the surface, $\mathbf{R}_i$ and $\mathbf{R}_j$ are the position vectors on the surface of the ith and jth sites, respectively. $G_0(\mathbf{k}_\parallel,z)$ is the surface GF in the mixed Bloch-Wannier representation,

$$G_0(\mathbf{k}_\parallel,z)=\beta(\mu-\sqrt{\mu^2-1})\ , \tag{14}$$

where

$$\mu=\frac{E}{2\beta}+\cos(k_x a_0)+\cos(k_y a_0)+i0^+\ . \tag{15}$$

a_0 is the lattice constant and $\mathbf{k}_\parallel=(k_x,k_y)$. For simplicity, we choose $a_0=1$. From Fig. 1, the GF of site 1 is

$$G(1,1)=G_0(1,1)+\varepsilon\frac{G_0(1,l)G_0(l,1)}{1-\varepsilon G_0(1,1)}\ . \tag{16}$$

When the impurity atom is at site 1, the GF's of A, B, and C binding are,[22] respectively,

$$G_A=\frac{G_0(1,1)}{1-\varepsilon G_0(1,1)}\ , \tag{17}$$

$$G_B=\tfrac{1}{2}[G(1,1)+2G(1,2)+G(2,2)]\ , \tag{18}$$

and

$$G_C=\tfrac{1}{4}[G(1,1)+4G(1,2)+2G(1,3)+2G(2,2)+G(3,3)+4G(2,3)+2G(2,4)]\ . \tag{19}$$

The SDOS is[23]

$$\rho_s(E)=-\frac{1}{\pi}\,\mathrm{Im}G[G=G_A,G_B,G_C,G(1,1)]\ , \tag{20}$$

which consists of two parts, one corresponding to the band (ρ_s^b), the other corresponding to localized surface states (ρ_s^i) induced by the impurity (we call them impurity states) outside the band. The local density of states in the vicinity of E_i is[24]

$$\rho_s^i(E)=I_s\delta(E-E_i)\ , \tag{21}$$

where E_i, the localized impurity-state energy, is determined by the real poles of G outside the band, and I_s is the intensity of impurity states, which is given by the residue of G at E_i. Using Eqs. (17) and (18) in Eq. (8) and taking $t\to\infty$ gives $n(\infty)$, the final expected occupancy of the ion orbital:

$$n(\infty)=2\int_{E_L}^{E_F}\rho_s(E)|d_0(E,\infty)|^2dE+2I_s|d_0(E_i,\infty)|^2\quad(E_i\le E_F)\ , \tag{22}$$

where E_L is the lower edge of the band. Without loss of generality, we choose the Fermi energy (E_F) to be at the center of the conduction band.

III. RESULTS AND DISCUSSION

The numerical calculations of the ion occupancy near a contaminated metal surface have been performed using the methods of Sec. II. The interaction potential V of an ion with the substrate is the same for sites A, B, and C.[22] The parameter values (in atomic units) are chosen as follows: $\beta=0.0061$, $\lambda=0.02$, and $V_0=0.05$. The energy zero is chosen to be at the center of the band. The values of impurity state energies E_i and the intensities I_s, corresponding to different scattering sites and impurity orbital energies ε, are listed in Tables I and II. They are calculated in atomic units.

TABLE I. Values of impurity-state energies E_i and intensities I_S corresponding to different scattering sites for $\varepsilon=-0.0294$.

Scattering site	E_i	I_s
A	-0.0369	0.5647
B	-0.0369	0.2938
C	-0.0369	0.2022

Figure 2 shows the graphs of ion occupancy $n(\infty)$ versus ϵ_0 for different impurity orbital energies. It is clear that, for any particular choice of ϵ_0, $n(\infty)$ depends strongly on the value of ε, and that the range of values of ϵ_0, which give high $n(\infty)$, varies dramatically with ε. In the case of the impurity with a repulsive potential ($\varepsilon>0$), the maximum value of $n(\infty)$ decreases as the impurity atom orbital energy ε increases. The reason is that the impurity-state energy is above the band and has no contribution to surface-ion neutralization (because E_F is at the center of the band). Therefore, our discussion will be concentrated on the case of the impurity with an attractive potential ($\varepsilon<0$). When $\varepsilon=-0.0074$, no impurity state exists. As ε 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 $|\varepsilon|$), 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 orbital than band-state electrons, which are delocalized throughout the solid. The result suggests that surface-ion neutralization may be useful experimentally as a problem to determine the position of impurity states, by bombarding the contaminated metal crystal surface with a species of ion whose orbital energy ϵ_0 lies below the lower edge of the solid band, 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 impurity state with energy not too different from ϵ_0.

TABLE II. Values of impurity-state energies E_i and intensities I_S corresponding to different impurity atom orbital energies ε for $l=1$.

ε	E_i	I_s
-0.0515	-0.0533	0.9201
-0.0294	-0.0369	0.5647
-0.0074	no	
0.0074	no	
0.0294	0.0369	0.5647

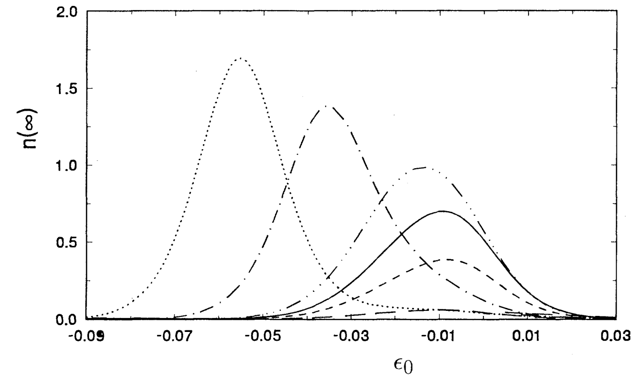

FIG. 2. $n(\infty)$ vs ϵ_0 with different impurity energies ε for $l=1$, $V_0=0.05$, and $\lambda=0.02$. No impurity atom (solid line), $\varepsilon=0.074$ (short dashed line); $\varepsilon=0.0294$ (long dashed line), $\varepsilon=-0.0074$ (double dotted-dashed line), $\varepsilon=-0.0294$ (dot-dashed line), and $\varepsilon=-0.0515$ (dotted line).

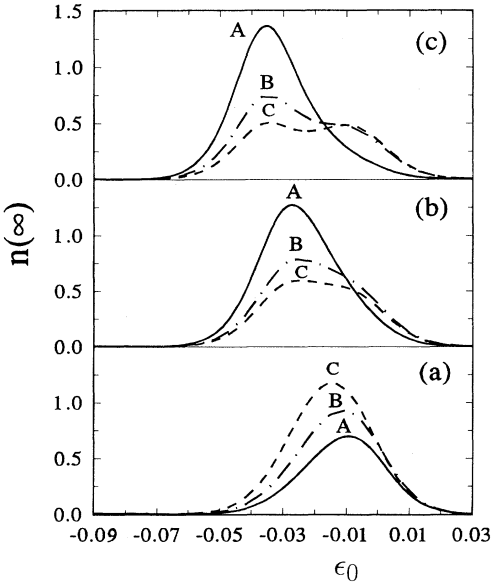

FIG. 3. $n(\infty)$ vs ϵ_0 with different scattering sites and impurity orbital energies. $V_0=0.05$, $\lambda=0.02$. Curve *A* (ion striking site *A*). Curve *B* (ion striking site *B*). Curve *C* (ion striking site *C*).

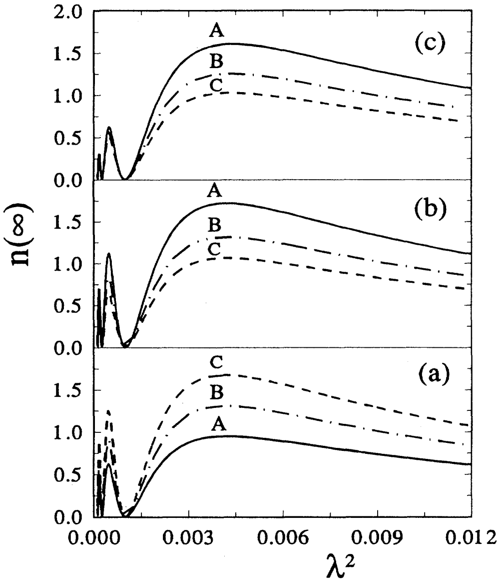

FIG. 4. $n(\infty)$ vs λ^2 with different scattering sites and impurity orbital energies. $V_0=0.05$, $\lambda=0.02$. Curve *A* (ion striking site *A*). Curve *B* (ion striking site *B*). Curve *C* (ion striking site *C*).

Figure 3 shows the variation of the ion occupancy $n(\infty)$ with ϵ_0 for different scattering sites and impurity orbital energies. When $\varepsilon=0.0$ [Fig. 3(a)], corresponding to no impurity atom, the three curves are different, showing that the ion occupancy depends strongly on the impact site. The peak value of curve *C* is obviously larger than those of curves *A* and *B*, indicating that the ion neutralization most likely occurs when the ion strikes the centered site (*C*). When $\varepsilon=-0.0206$ [Fig. 3(b) and no impurity state], in contrast to Fig. 3(a), the three curves change dramatically. This shows that the impurity atom has a very important influence on surface-ion neutralization. The peak value of curve *A* is largest. The reason is that the impurity atom is at site *A* (site 1). When $\varepsilon=-0.0294$ [Fig. 3(c)], curves *B* and *C* both have two peaks, one (at $\epsilon_0=-0.0369$) corresponds to the impurity state ($E_i=-0.0369$), the other (at $\epsilon_0=-0.01$) to the band states. The two peaks of curve *C* have almost the same contribution to surface-ion neutralization. Curve *B* has a primary peak (at $\epsilon_0=-0.0369$) and a shoulder (at $\epsilon_0=-0.01$). The height of the former is obviously larger than that of the latter, indicating the contribution of the impurity atom to surface-ion neutralization is greater than that of the band. Curve *A* has only one peak (at $\epsilon_0=-0.0369$), corresponding to the impurity state, indicating the contribution to surface-ion neutralization for the atop scattering site is primarily due to the impurity atom.

Figure 4 shows the ion occupancy $n(\infty)$ versus λ^2 for different scattering sites and impurity orbital energies.

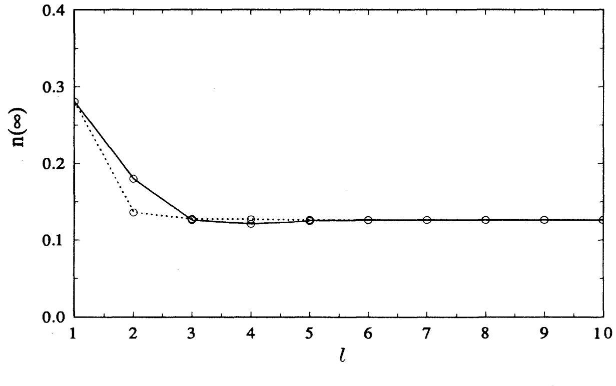

FIG. 5. $n(\infty)$ vs impurity site l for $V_0=0.05$, $\lambda=0.02$, $\epsilon_0=-0.0355$, $\varepsilon=-0.0515$. Along the direction of 12 (solid line); along the direction of 13 (dotted line).

All the curves display an oscillatory behavior. This result is similar to Ref. 19 (Fig. 3). From Fig. 4, the ion neutralization probability has obvious differences when the ion strikes different sites (A, B, C); when $\varepsilon=0.0$ [Fig. 4(a)], corresponding to no impurity atom, the ion-orbital occupancy is largest when the ion strikes site C. However, when $\varepsilon=-0.0206$ [Fig. 4(b)] and -0.0294 [Fig. 4(c)], the ion occupancy is less than that of $\varepsilon=0.0$. This indicates that the impurity atom has a very significant influence on surface-ion neutralization. These results are in agreement with those of Fig. 3.

Figure 5 shows the ion occupancy $n(\infty)$ versus impurity site l for the ion striking site A. When the impurity ion is at site A, the ion orbital occupancy has a maximum, indicating the influence of the impurity on surface-ion neutralization is strongest. When the impurity is the nearest neighbor to the scattering site, the influence of the impurity on surface-ion neutralization is less than that of an impurity at scattering site. When the impurity is the next-nearest neighbor (NNN) to the scattering site, it has almost no effect on surface-ion neutralization.

From the discussion above, we can summarize our results as follows: (1) The impurity atom has a very significant influence on the surface-ion neutralization when it is located close to the ion scattering site. The influence will weaken rapidly with the impurity location far away from the ion scattering site. When the impurity atom reaches the NNN site, there will be no effect on the surface-ion neutralization at all. (2) For an impurity with an attractive potential, when the ion scattering is at the atop site, the maximum value of $n(\infty)$ increases as the impurity atom orbital energy ε decreases, and an opposite tendency is observed for an impurity with a repulsive potential. (3) Bombarding the surface with ions and measuring the percentage of neutralized ions enables the impurity-state energy to be obtained and provides information on the substrate. (4) The curve of ion occupancy $n(\infty)$ versus λ^2 displays an oscillatory behavior. (5) The ion occupancy depends strongly on the impact site. It has obvious differences for ions striking different sites, such as atop, bridge, or centered sites.

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