PHYSICAL REVIEW B VOLUME 58, NUMBER 16 15 OCTOBER 1998-II

Ion neutralization on composite catalysts

Y. G. Weng*
Physics Department, Zhengzhou University, Zhengzhou 450052, China

Z. X. Yang and G. H. Wei
Surface Physics Laboratory (National Key Laboratory), Fudan University, Shanghai 200433, China

X. Q. Dai and S. Y. Wei
Physics Department, Henan Normal University, Xinxiang 453002, China

T. Zhang
Henan Association for Science and Technology, Zhengzhou 450003, China

(Received 29 December 1997; revised manuscript received 15 April 1998)

Ion neutralization near the surface of the composite catalysts Pt (or Ni)/ZnO is investigated by means of the Green-function method and the approximate many-level approach within the framework of the tight-binding model. The catalyst metal film is represented by a one-dimensional finite chain of *d* orbitals, the semiconductor support ZnO is characterized by a linear semi-infinite chain of alternating *s* and *p* orbitals, and the effects of a substitutional impurity atom at the surface of a substrate are studied using the Koster-Slater model. The calculated results show that the electronic structures of both the supported metal film and the support ZnO play important roles in the resonant charge-transfer process, upon which the impurity atom at the surface also exerts significant effects. [S0163-1829(98)05639-2]

I. INTRODUCTION

In recent years, ion neutralization at the surface of a solid has received considerable attention from both experimentalists and theoreticians, because it plays a fundamental role in a variety of analytical techniques used in surface analysis, such as ion scattering spectrography (ISS) for the compositional and structural analysis,[1] ion neutralization spectrography (INS),[2] etc. The surface-ion neutralization (SIN) process is one of the key processes in ISS analysis.[3] The essence of SIN can be captured in a two-level model,[4,5] in which SIN may be viewed as a very brief binary collision involving resonant charge transfer between an incoming ion and a target atom at the surface of a solid. On the basis of the two-level exact solution, Davison and co-workers presented a more realistic many-level method,[6,7] which has been used to investigate the resonant charge transfer of a positive ion scattering from a metal surface,[7] a contaminated metal surface,[8] an ionic crystal surface etc.[9,10]

Other investigations on the SIN process have been reported,[11,12] but very few theoretical studies have been related to the composite system. It is well known that nearly all the industrially important catalytic reactions use supported catalysts of the synergetic type or ‘‘dual function catalysts,’’[13] such as Pt/ZnO, Ni/ZnO, and Ni/Al_2O_3, etc. Their catalytic functions are obviously different from those of bulk metals or oxides; therefore, they can be used to meet the special needs of some catalytic reactions. Both experimental and theoretical scientists have paid great attention to these composite systems.[13] In these composite catalysts, Pt and Ni metal films are called the active components which generally dominate the activity and selectivity of catalysts, while the oxide ZnO and Al_2O_3 are called supports which not only can improve the strength of catalysts and disperse the active components, but also play an important role in affecting their catalytic functions.

The catalytic functions of the composite catalysts are determined mainly by their surface electronic structure. Thus it is significant to study ion neutralization at the surface of the composite catalysts. The purpose of the present paper is to calculate the ion orbital occupancy in the SIN processes on the composite catalysts Pt (or Ni)/ZnO in various cases within the framework of the approximate many-level method. The model and calculation methods are given in Sec. II, the results and discussion are presented in Sec. III, and the main conclusions are summarized in Sec. IV.

II. MODEL AND CALCULATION METHODS

A. Two-level model

In the two-level model,[4,5] it is supposed that, in a target atom at the substrate surface, there is only one isoenergetic occupied orbital which is denoted by ket $|1\rangle$; its energy is ϵ_1. An incident positive ion has an empty valence orbital $|0\rangle$ whose energy ϵ_0 is not very different from ϵ_1; the resonant charge transfer between them occurs in the SIN process. The time-dependent Schrödinger equation for the interaction, in atomic units $(\hbar=1)$, is

$$i|\psi'(t)\rangle=\mathcal{H}(t)|\psi(t)\rangle. \tag{2.1}$$

The time-dependent Hamiltonian is

$$\mathcal{H}(t)=\epsilon_0|0\rangle\langle 0|+\epsilon_1|1\rangle\langle 1|+V(t)(|0\rangle\langle 1|+\text{H.c.}), \tag{2.2}$$

where the time-dependent interaction potential $V(t)$ is supposed to take the pulse like form

$$V(t)=V_0e^{-\lambda|t|}, \quad \lambda>0. \tag{2.3}$$

The parameter λ is inversely proportional to the effective time of the interaction between the ion and the substrate, and V_0 is the maximum interaction strength which occurs at the moment of closest approach ($t=0$). As in Refs. 7, 14, and 15, the intra-atomic Coulomb repulsion is neglected. Although the ion energy level ϵ_0 is generally time dependent due to the image interaction, we simply treat it as a constant.[7,14,15] Using perturbation theory, the solution can be written in the form

$$|\psi(t)\rangle=d_0(t)e^{-i\epsilon_0 t}|0\rangle+d_1(t)e^{-i\epsilon_1 t}|1\rangle. \tag{2.4}$$

The ion-neutralization probability is $|d_0(t)|^2$; then $d_0(t)$ can be solved from the above time-dependent Schrödinger equation exactly, and expressed in terms of Bessel functions of complex order.[14] For convenience of later discussion, we rewrite $d_0(t)$ as $d_0(\epsilon_{1,}t)$, and take the limit $t\rightarrow\infty$; then the item $d_0(\epsilon_{1,}\infty)$ can be expressed as

$$d_0(\epsilon_{1,}\infty)=\lim_{t\rightarrow\infty}d_0(\epsilon_{1,}t)=\frac{\pi\xi_0[J_{-\nu_-}(\xi_0)J_{\nu_-}(\xi_0)+J_{-\nu_+}(\xi_0)J_{\nu_+}(\xi_0)]}{2\cosh(\pi\omega/2\lambda)}, \tag{2.5}$$

where $\omega=\epsilon_0-\epsilon_1, \quad \xi_0=V_0/\lambda, \nu_\pm=(i\omega\mp\lambda)/(2\lambda)$.

B. Approximate many-level method

In fact there is more than one eigenstate at the substrate surface, which comprises a complete set of eigenstates.[6,7] It is supposed that the two-level results could be extrapolated and applied to the resonant charge transfer between the incident ion empty orbital $|0\rangle$ and every eigenstate $|\chi_k\rangle$ at a substrate surface whose eigenenergy is ϵ_k; then the corresponding SIN probability $P(\epsilon_k,t)$ should be $|d_0(\epsilon_k,t)|^2$. Generally the electronic state $|\psi_s\rangle$ at the substrate surface is not one of the eigenstates $|\chi_k\rangle$, but can be expressed as

$$|\psi_s\rangle=\sum_k \langle\chi_k|\psi_s\rangle|\chi_k\rangle, \tag{2.6}$$

where $|\langle\chi_k|\psi_s\rangle|^2$ is the relative intensity I_k of the component $|\chi_k\rangle$. Therefore, the total SIN probability $P(t)$ for the electronic state $|\psi_s\rangle$ at the substrate surface should be the summation of every $P(\epsilon_k,t)$ weighted by its component intensity I_k statistically:

$$P(t)=\sum_k I_kP(\epsilon_k,t)=\sum_k I_k|d_0(\epsilon_k,t)|^2. \tag{2.7}$$

If the eigenstates are continuous and form a band, then the corresponding SIN probability should be expressed in the integral form

$$P(t)=\int_{E_L}^{E_U}\rho_s^b(E)|d_0(E,t)|^2dE, \tag{2.8}$$

where $E_L(E_U)$ is the lower (upper) edge of the band, and $\rho_s^b(E)$ is the surface density of states in the band. As shown previously, $|d_0(E,t)|^2$ represents the SIN probability in the corresponding two-level model, except using E in place of ϵ_1. Furthermore, if there exist both discrete eigenstates and a continuous band at the substrate surface, we can introduce a single surface density of states (SDOS) $\rho_s(E)$ to represent the weight factor in the integral on both discrete eigenstates and continuous band at the substrate surface. Then $\rho_s(E)$ consists of two parts: $\rho_s^b(E)$ corresponds to the continuous band, and $\rho_s^s(E)$ corresponds to the discrete localized surface states outside the band,

$$\rho_s(E)=\rho_s^b(E)+\rho_s^s(E). \tag{2.9}$$

Here $\rho_s(E)$ can be calculated from the substrate surface Green function $G(1,1,E)$,[16]

$$\rho_s(E)=-\frac{1}{\pi}\operatorname{Im}G(1,1,E), \tag{2.10}$$

and $\rho_s^s(E)$ is given by

$$\rho_s^s(E)=\sum_i I_i\delta(E-E_i), \tag{2.11}$$

where the energy E_i of the localized surface state $|\chi_i\rangle$ is determined by the real poles of $G(1,1,E)$ outside the band; I_i is the intensity of the surface state $|\chi_i\rangle$, and can be calculated by the residue of $G(1,1,E)$ at $E=E_i$. The local $\rho_s^s(E)$ in the vicinity of E_i is $I_i\delta(E-E_i)$. By means of $\rho_s(E)$, $P(t)$ can be expressed in the general form

$$P(t)=\int_{-\infty}^{E_f}|d_0(E,t)|^2\rho_s(E)dE, \tag{2.12}$$

where E_f is the Fermi energy level, and $E_i<E_f$. The approximate many-level solution of the ion orbital occupancy $N(t)$ can be written as

$$N(t)=2\int_{-\infty}^{E_f}|d_0(E,t)|^2\rho_s(E)dE, \tag{2.13}$$

where 2 represents the double occupancy of the ion orbital. If we take limit $t\rightarrow\infty$, we can obtain the approximate many-level expression of the final expected ion-orbital occupancy,

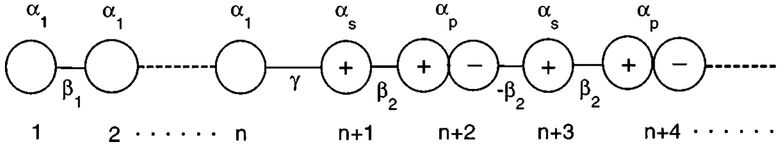

FIG. 1. One-dimensional schematic representation of the Pt (or Ni)/ZnO composite system.

$$N(\infty)=\lim_{t\to\infty}N(t)=2\int_{-\infty}^{E_f}|d_0(E,\infty)|^2\rho_s(E)dE, \quad (2.14)$$

where $d_0(E,\infty)$ is the same as that in Eq. (2.5) of the two-level model, except using E in place of ϵ_1. Sulston and Davison[7] reported that the approximate many-level method can give qualitatively correct results for most cases except for large values of V_0 and λ^{-1}, or very wide bandwidths. For narrow bands, it can give both qualitatively and quantitatively good results. If the band is not narrow enough, for an incident ion with orbital energy ϵ_0, we should calculate the above integral between the lower limit $\epsilon_0-\delta$ and the upper limit $\epsilon_0+\delta$, where δ is a suitable small positive number. Thus qualitatively we can obtain an approximate many-level result for the band under the condition of resonant charge transfer.

C. Model and surface Green-function calculation

The model used here consists of an incident positive ion and a composite system Pt (or Ni)/ZnO (as shown in Fig. 1). The metal film is modeled by one-dimensional finite chain of d orbitals with site energy α_1 and bond energy β_1. The film contains n layers of metal atoms lying between $1\leqslant m\leqslant n$ (m is the site serial number). The bond of energy γ attaches the film to the first Zn cation ($m=n+1$) in the semiconductor support ZnO, which is depicted by a semi-infinite chain of alternating s and p orbitals with corresponding site energies α_s and α_p, and bond energies $\pm\beta_2$.

The Hamiltonian $\mathcal{H}_1$ corresponding to the one-dimensional infinite chain of d orbitals, with site energy α_1 and bond energy β_1, is

$$\mathcal{H}_1=\sum_m \alpha_1|m\rangle\langle m|+\beta_1\sum_m (|m\rangle\langle m+1|+\text{H.c.}). \quad (2.15)$$

The corresponding Green function $G_1(i,j,E)$ between the ith and jth atoms of the infinite chain of metal atoms can be derived from Eq. (2.15). From $G_1(i,j,E)$, the surface Green function $G_{1S}(1,1,E)$ of the semi-infinite chain and the Green function $G_{1f}(i,j,E)$ of a metal film containing n atoms in Wannier representation can be derived by the Dyson equation approach as

$$G_{1S}(1,1,E)=\frac{G_1(1,1,E)}{1+\beta_1G_1(1,0,E)}, \quad (2.16)$$

$$G_{1f}(i,j,E)=G_1(i,j,E)-\beta_1[\lambda_1G_1(i,0,E)+\lambda_2G_1(i,n+1,E)], \quad (2.17)$$

where $\lambda_1=[AG_1(1,j,E)-BG_1(n,j,E)]/(A^2-B^2)$, $\lambda_2=[AG_1(n,j,E)-BG_1(1,j,E)]/(A^2-B^2)$, $A=1+\beta_1G_1(n,n+1,E)$, and $B=\beta_1G_1(1,n+1,E)$.

The substitutional impurity atom contained in the metal film is described by the Koster-Slater model.[17] The effective level of the impurity atom is taken to be the difference between the substitutional impurity free atomic orbital energies α_i and α_1: $\triangle\epsilon_i=\alpha_i-\alpha_1$. From $G_{1f}(i,j,E)$, and using the Dyson equation approach, the Green function $G_{1f}^i(i,j,E)$ of a contaminated metal film can be derived as

$$G_{1f}^i(i,j,E)=G_{1f}(i,j,E)+\frac{\triangle\epsilon_iG_{1f}(i,i_m,E)G_{1f}(i_m,j,E)}{1-\triangle\epsilon_iG_{1f}(i_m,i_m,E)}, \quad (2.18)$$

where i_m represents the site of impurity atom in the metal film.

The Hamiltonian $\mathcal{H}_2$ corresponding to the one-dimensional infinite chain of alternating s and p orbitals, with corresponding site energies α_s and α_p, and bond energies $\pm\beta_2$, is

$$\mathcal{H}_2=\sum_m [\alpha_s|2m\rangle\langle 2m|+\alpha_p|2m+1\rangle\langle 2m+1|+\beta_2(|2m\rangle\langle 2m+1|-|2m-1\rangle\langle 2m|+\text{H.c.})]. \quad (2.19)$$

The corresponding Green function $G_2(i,j,E)$ of the infinite chain of ZnO can be derived from Eq. (2.19).[9] In terms of $G_2(i,j,E)$, the surface Green function $G_{2S}(n+1,n+1,E)$ of the semi-infinite chain of ZnO can be calculated by the Dyson equation approach as

$$G_{2S}(n+1,n+1,E)=\frac{G_2(n+1,n+1,E)}{1+\beta_2G_2(n+1,n,E)}. \quad (2.20)$$

Using $G_{1f}(i,j,E)$ and $G_{2S}(n+1,n+1,E)$, the surface Green function $G(1,1,E)$ of the composite system Pt (or Ni)/ZnO can be derived by the Dyson equation approach[13] as

$$G(1,1,E)=G_{1f}(1,1,E)+\frac{\gamma^2G_{1f}(1,n,E)G_{1f}(n,1,E)G_{2S}(n+1,n+1,E)}{1-\gamma^2G_{1f}(n,n,E)G_{2S}(n+1,n+1,E)}, \quad (2.21)$$

and the surface Green function $G^i(1,1,E)$ of the contaminated composite system with impurity atom residing in the metal film can be derived as

$$G^{i}(1,1,E)=G^{i}_{1f}(1,1,E)+\frac{\gamma^{2}G^{i}_{1f}(1,n,E)G^{i}_{1f}(n,1,E)G_{2S}(n+1,n+1,E)}{1-\gamma^{2}G^{i}_{1f}(n,n,E)G_{2S}(n+1,n+1,E)}, \tag{2.22}$$

which is similar to Eq. (2.21) except using $G^{i}_{1f}(i,j,E)$ of the contaminated metal film in place of $G_{1f}(i,j,E)$ of the pure metal film.

III. RESULTS AND DISCUSSION

In numerical calculations, the parameter values (in atomic units) are chosen as follows: $\alpha_s=0.0625$, $\alpha_p=-0.0625$, and $\beta_2=0.1382$ for ZnO support; and $\alpha_1=-0.0838$ and $\beta_1=0.0671$ for a Pt film[18] (or $\alpha_1=0.0$ and $\beta_1=0.0349$ for a Ni film[13]). The bond energy γ is taken to be the average of β_1 and β_2: $\gamma=(\beta_1+\beta_2)/2$. The parameters for calculating the ion-orbital occupancy $N(\infty)$ are chosen as $\lambda=0.02$, the maximum interaction strength $V_0=0.05$, and Fermi energy $E_f=0.0625$.[19] All the values in the following figures and tables are expressed in atomic units. For convenience and without losing generality, we suppose that there are three layers of metal atoms (Pt or Ni, $n=3$) in the film throughout following discussions.

In Fig. 2, the SDOS graph of the semi-infinite chain of ZnO is shown by the solid line. The Zn cation resides at the surface site, the forbidden energy gap (FEG) lies between -0.0625 and 0.0625, and the energy zero is taken to be at the middle of the FEG. The SDOS graph of the semi-infinite chain of Ni atoms is shown by the short-dashed line; its band extends from -0.07 to 0.07, most of the band overlapping the range of the FEG. The SDOS graph of the semi-infinite chain of Pt atoms is shown by the dot-dashed line, and its band extends from -0.218 to 0.051, nearly half of the band overlapping the range of the FEG.

The variations of the ion-orbital occupancy $N(\infty)$ versus the incident ion empty orbital energy ϵ_0 at the surfaces of the above substrates are shown in Fig. 3; ZnO by solid line, Ni by the short-dashed line, and Pt by the dot-dashed line. It can be seen that the graph of $N(\infty)$ versus ϵ_0 in Fig. 3 has a strong resemblance to the corresponding SDOS graph shown in Fig. 2.

Actually it is difficult for Pt (or Ni) to form an isolated metal film composed of only several layers of atoms, so it is necessary to use support ZnO to form a Pt/ZnO (or Ni/ZnO) composite catalyst. For the convenience of comparison, the SDOS graph of the Pt/ZnO system is shown in Fig. 4(a), and the corresponding graph of $N(\infty)$ versus ϵ_0 is shown in Fig. 4(b). In Fig. 4(a), the band extends from -0.218 to -0.0625; there are two peaks in the band, and their positions E_r are listed in Table I . There is only one surface state inside the FEG; its position E_s and intensity I_s are also listed in Table I. In Fig. 4(b), there exist three peaks in the graph whose positions E_m and peak values N_m are listed in Table I. From Figs. 4(a) and 4(b) and Table I, it can be seen that $N(\infty)$ will attain its local maximum value N_m when ϵ_0 approaches either the peak position E_r in the band, or the surface states E_s inside the FEG. In other words, the E_m inside the FEG corresponds to the surface state E_s, otherwise it corresponds to the SDOS peak position E_r in the band approximately.

Theoretically, the surface states E_s of the corresponding isolated Pt film should be within the band of Pt bulk; these E_s and their intensities I_s are also listed in Table I for comparison. There is only one of them inside the FEG, which is consistent with the SDOS graph of the Pt/ZnO system in Fig. 4(a). Comparing the graph of $N(\infty)$ versus ϵ_0 on the Pt/ZnO system in Fig. 4(b) with that on the surface of Pt (or ZnO) bulk in Fig. 3, we find that the FEG of support ZnO plays an important role in the SIN process on the Pt/ZnO composite system.

In Fig. 5, the graph of $N(\infty)$ versus ϵ_0 on a pure Ni/ZnO system is shown by the solid line. All three peaks are inside the FEG; their positions E_m and peak values N_m are listed in Table II. Theoretically, the surface states E_s of the corresponding isolated Ni film should be within the band of Ni bulk; these E_s and their intensities I_s are also listed in Table II for comparison. All of these E_s are inside the FEG, which are consistent with the surface states E_s on the Ni/ZnO sys-

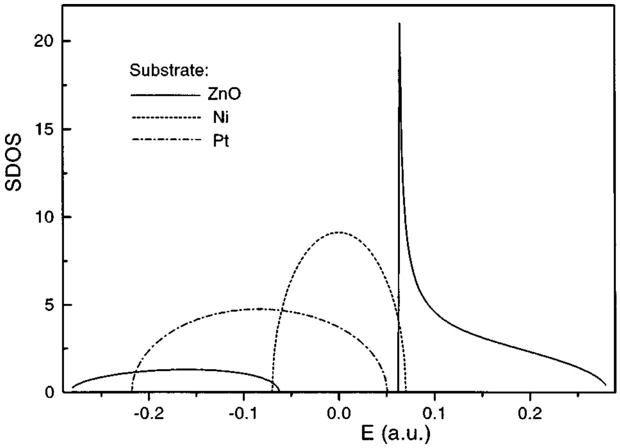

FIG. 2. SDOS of the semi-infinite chain of (a) ZnO (solid line), (b) Ni atoms (short-dashed line), and (c) Pt atoms (dot-dashed line).

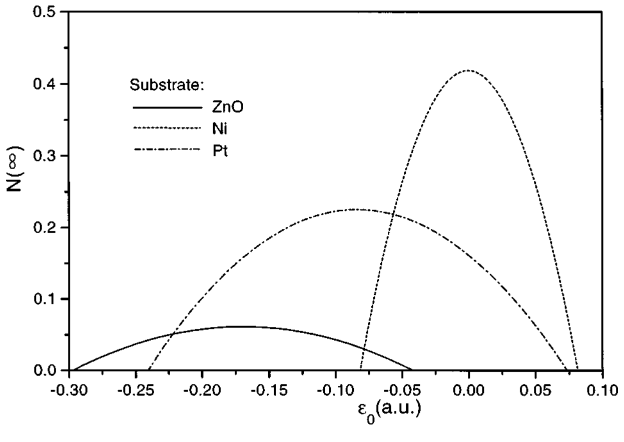

FIG. 3. $N(\infty)$ vs ϵ_0 at the surface of (a) ZnO (solid line), (b) Ni (short-dashed line), and (c) Pt (dot-dashed line).

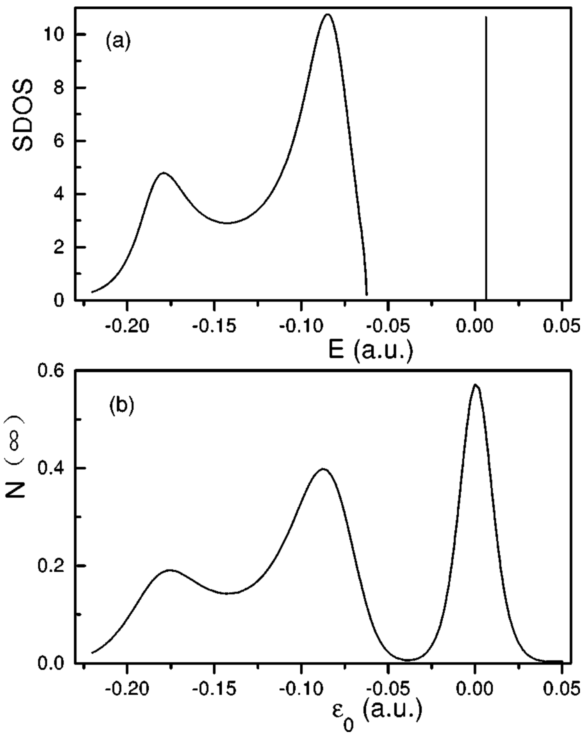

FIG. 4. (a) SDOS of the Pt/ZnO composite system ($n=3$). (b) $N(\infty)$ vs ϵ_0 at the surface of the Pt/ZnO composite system ($n=3$).

tem listed in Table II. From Fig. 5 and Table II, it can be seen that the peak position E_m inside the FEG corresponds to the surface state E_s on the Ni/ZnO system; in addition, the peak value N_m reflects the relative value of the intensity I_s.

Comparing the graph of $N(\infty)$ versus ϵ_0 on the Ni/ZnO system in Fig. 5 with that on the Pt/ZnO system in Fig. 4(b), and comparing the values listed in Table II with that in Table I, it can be seen that under the condition of the same support ZnO, the active Ni and Pt film components play different roles in the SIN process, respectively. As shown in Fig. 2, most of the band on the surface of Ni bulk overlaps the range of the FEG, but only half as much as the band on the surface of Pt bulk overlap the range of the FEG. Theoretically, the surface states of the metal film should be within the band of the corresponding metal bulk; in other words, the band position relative to the FEG determines the range of the surface states of the metal film, which in turn determines the SDOS on the composite system and affects the SIN process. All three surface states E_s of an isolated Ni film are inside the FEG, but only one of the surface states of an isolated Pt film is inside the FEG, which is consistent with the graphs of $N(\infty)$ versus ϵ_0 on the Ni/ZnO system in Fig. 5 and the Pt/ZnO system in Fig. 4(b). Therefore, the surface electronic structures of both the supported metal (Pt or Ni) film and the support ZnO play important roles in the SIN process.

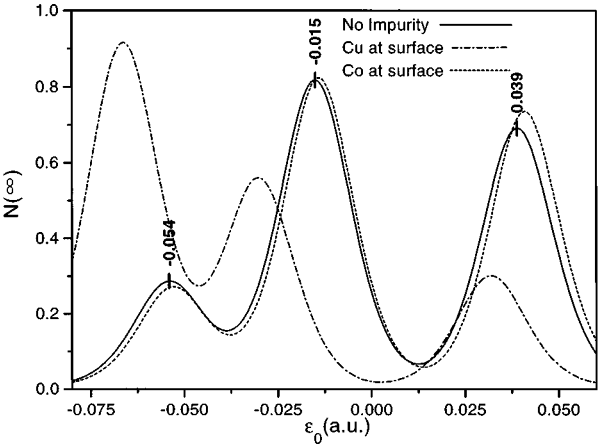

FIG. 5. $N(\infty)$ vs ϵ_0 at the surface of the Ni/ZnO composite system ($n=3$) for the case of (a) pure Ni film (solid line), (b) impurity Cu atom residing at the surface (dot-dashed line), and (c) impurity Co atom residing at the surface (short-dashed line).

In Fig. 5, there are another two curves of $N(\infty)$ versus ϵ_0: one corresponds to the case of an impurity Cu atom residing at the surface of the Ni/ZnO system, which is shown by the dot-dashed line; the other corresponds to the case of impurity Co atom residing at the surface of the Ni/ZnO system, which is shown by the short-dashed line. The peak positions E_m and peak values N_m in three cases are all listed in Table III for comparison. In numerical calculations, the free orbital energies α_i of impurity atoms are chosen to be -0.0408 a.u. for Cu, and 0.0022 a.u. for Co, respectively.[18] From Fig. 5, it is easy to see that if $\Delta\epsilon_i=\alpha_i-\alpha_1<0$ (as in the case of Cu), the peak positions E_m will shift to lower energy compared with the pure case, and the peak values N_m of the lower energy will be increased; conversely, if $\Delta\epsilon_i>0$ (as in the case of Co), the peak positions E_m will shift to higher energy, and the peak values N_m of the higher energy will be increased. The greater $|\Delta\epsilon_i|$ is, the more the peak positions E_m will shift, and the more the peak values N_m will be changed.

The graphs of ion occupancy $N(\infty)$ versus λ^2 for different interaction potential V_0 on the surface of the Ni/ZnO system are shown in Fig. 6. It can be seen that the oscillatory behavior persists for various values of V_0, which is in qualitative agreement with the experiment[20] and the result of Ref. 7. Since λ is inversely proportional to the effective time of the interaction, λ^2 is proportional to the kinetic energy of the incident ion; then the oscillatory behavior has a simple physical interpretation. When the ion kinetic energy is fairly

TABLE I. Surface parameters of the Pt/ZnO system ($n=3$).

Peak	Pt film		Pt/ZnO system			
No.	E_s	I_s	E_s (or E_r)	I_s	E_m	N_m
1	−0.179	0.250	(−0.179)	-	−0.175	0.190
2	−0.084	0.500	(−0.085)	-	−0.088	0.398
3	0.011	0.250	0.001	0.308	0.0	0.572

TABLE II. Surface parameters of the Ni/ZnO system ($n=3$).

Peak	Ni film		Ni/ZnO system			
No.	E_s	I_s	E_s	I_s	E_m	N_m
1	−0.049	0.250	−0.053	0.156	−0.054	0.292
2	0.0	0.500	−0.015	0.453	−0.015	0.836
3	0.049	0.250	0.040	0.382	0.039	0.703

TABLE III. Peak positions E_m and peak values N_m on the Ni/ZnO system ($n=3$).

Impurity at surface	Peak 1 E_m	Peak 1 N_m	Peak 2 E_m	Peak 2 N_m	Peak 3 E_m	Peak 3 N_m
Pure	−0.054	0.292	−0.015	0.836	0.039	0.703
Cu	−0.066	0.942	−0.032	0.564	0.030	0.301
Co	−0.053	0.273	−0.014	0.824	0.041	0.735

large, the effective time of the interaction will be so short that only a single transfer process of an electron from the substrate can neutralize the ion. When λ^2 decreases and the effective time of the interaction will be extended, it is possible for the transferred electron to have enough time to jump back to the substrate surface. The effective time of the interaction will become longer and longer when λ^2 decreases, and it is possible for the above charge transfer to occur more times, which is an attenuation process. If the charge transfer occurs an odd number of times, the ion leaving the substrate surface will be neutralized; if it occurs an even number of times, the ion leaving the substrate surface will remain ionized. Therefore, the graph of ion occupancy $N(\infty)$ versus λ^2 displays an oscillatory behavior. Obviously, the stronger the interaction strength V_0, the higher the maximum peak value of $N(\infty)$ versus λ^2, which corresponds to a single transfer process, will be, and the greater the value of the corresponding peak position λ^2 will be. This can be used to estimate the relative value of V_0.

IV. CONCLUSION

From the above calculated results and discussion, we can obtain the following conclusions.

(1) SIN on the composite system may be used as a useful experimental probe to determine the positions of the surface states E_s, and estimate their relative intensities I_s. The graph of $N(\infty)$ versus ϵ_0 on the substrate has a strong resemblance to the corresponding SDOS graph. The peak position E_m inside the FEG corresponds to the surface state E_s, and the peak value N_m reflects the relative value of its intensity I_s approximately; whereas the E_m outside the FEG corresponds to the SDOS peak position E_r in the band.

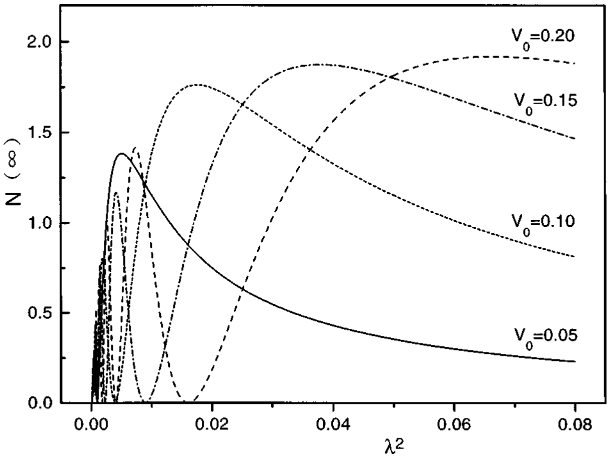

FIG. 6. $N(\infty)$ vs λ^2 at the surface of the Ni/ZnO composite system ($n=3, \epsilon_0=0.0$ a.u.) for various maximum interaction strengths: (1) $V_0=0.05$ (solid line), (2) $V_0=0.10$ (short-dashed line), (3) $V_0=0.15$ (dot-dashed line), and (4) $V_0=0.20$ (dashed line).

(2) The surface electronic structures of both the supported metal (Pt or Ni) film and the support ZnO play important roles in the SIN process on a composite system. In particular, the FEG of the support ZnO plays an important role in the SIN process on a composite system.

(3) The existence of an impurity atom at the surface of the Ni/ZnO composite system has significant effects on the corresponding SIN process.

(4) The graphs of $N(\infty)$ versus λ^2 on the composite system display an oscillatory behavior for various interaction strengths V_0. This can be used to estimate the relative value of V_0.

ACKNOWLEDGMENT

The work reported here was supported by the Surface Physics Laboratory (National Key Laboratory), Fudan University, China.

---

*Author to whom correspondence should be addressed. Electronic address: wengyg@mail.zzu.edu.cn

[1] John C. Tully, Phys. Rev. B **16**, 4324 (1977).

[2] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

[3] D. P. Smith, Surf. Sci. **25**, 171 (1971).

[4] S. G. Davison, K. W. Sulston, and A. T. Amos, J. Electroanal. Chem. **204**, 173 (1986).

[5] S. G. Davison, Z. L. Miskovic, A. T. Amos, B. L. Burrows, F. O. Goodman, and K. W. Sulston, Prog. Surf. Sci. **48**, 193 (1995).

[6] A. T. Amos, S. G. Davison, and K. W. Sulston, Phys. Lett. A **118**, 471 (1986).

[7] K. W. Sulston, S. G. Davison, and A. T. Amos, Solid State Commun. **62**, 781 (1987).

[8] J. J. Xie and T. Zhang, Surf. Sci. **268**, 158 (1992).

[9] G. H. Wei, Z. X. Yang, S. Y. Wei, X. Q. Dai, M. Wang, and T. Zhang, Surf. Sci. **317**, 270 (1994).

[10] G. H. Wei, Z. X. Yang, X. Q. Dai, S. Y. Wei, M. Wang, and T. Zhang, Phys. Lett. A **193**, 293 (1994).

[11] Z. X. Yang, G. H. Wei, X. Q. Dai, L. D. Wan, M. Wang, and T. Zhang, Phys. Rev. B **52**, 8483 (1995).

[12] Z. X. Yang, S. Y. Wei, T. Zhang, and Y. G. Weng, Phys. Lett. A **217**, 349 (1996).

[13] S. G. Davison, C. M. Bose, and K. W. Sulston, Surf. Sci. **200**, 265 (1988).

[14] K. W. Sulston, A. T. Amos, and S. G. Davison, Surf. Sci. **197**, 555 (1988).

[15] A. Yoshimori and K. Makoshi, Prog. Surf. Sci. **21**, 251 (1986).

[16] D. Kalkstein and P. Soven, Surf. Sci. **26**, 85 (1971).

[17] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1208 (1954).

[18] P. Nordlander, S. Holloway, and J. K. Nǿrskov, Surf. Sci. **136**, 59 (1984).

[19] R. Dorn, H. Lüth, and M. Büchel, Phys. Rev. B **16**, 4675 (1977).

[20] R. L. Erickson and D. P. Smith, Phys. Rev. Lett. **34**, 297 (1975).