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Adsorption on stepped surfaces: The adsorbate concentration profile and its induced work-function change

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A model for the work-function change caused by adsorption on stepped surfaces is studied and discussed. The equilibrium concentration profiles of adsorbed particles at step and terrace sites at different coverage and temperature is calculated by means of a Monte Carlo simulation. The obtained profiles allow us to evaluate the work-function changes by use of the Helmholtz equation and the experimental evidence which shows that the dipole moment of the adparticles depends on the adsorption site. Our results are in agreement with available experimental data and we point out that special care must be taken in order to interpret the work-function changes measured by use of polycrystalline samples and step-"contaminated" single crystals.

I. INTRODUCTION

The understanding of work-function changes [henceforth $\Delta\phi$] caused by the adsorption of foreign atoms and molecules on polycrystalline and single-crystal surfaces is a problem which has attracted considerable attention (Ref. 1 and references therein). Technological interest is mainly originated from the design of electron emitters (Ref. 2 and references therein). On the other hand, in the field of surface physical chemistry, $\Delta\phi$ measurements are a widely employed technique to study adsorbate-substrate interactions.[1,3–7]

Several models, based on the well-known Helmholtz equation,[1] have been proposed in order to explain adsorbate-induced work-function changes (Refs. 1, 8, 9, and references therein). On the other hand, there is much experimental evidence showing that $\Delta\phi$ depends not only on the crystallographic orientation of the substrate but also on the presence of surface defects.[1,3–7] These facts are of great importance in the case of adsorption on polycrystalline samples. Therefore, in order to contribute to the understanding of the influence of surface defects on $\Delta\phi$, we have considered it useful to study a model of adsorbed particles on stepped surfaces. Our motivation for the present work is fourfold: Firstly, surface atoms on steps represent the largest portion of possible defects on crystalline surfaces. In fact, ~1% of surface atoms belong to the steps if a single crystal is cut with an inclination of only 30′ with respect to the ideal crystallographic orientation. Secondly, the equilibrium population of adatoms on terraces and at step sites for various surfaces coverages depends on the temperature and on the substrate-adatom, adatom-adatom, and adatom-step interactions. The model used in this work to account for these facts constitutes an alternative approach to the study of the heterogeneous nucleation on cleavage steps (Ref. 10 and references therein) which takes the competitive capture of adatoms by clusters growing on the flat surface into ac-

TABLE I. Available experimental data found in the literature for the dipole moment of atoms at steps (P_S) and on terraces (P_T) sites, respectively.

Substrate	Adsorbate	P_S (D)	P_T (D)	Ref.
$[\mathrm{Ru}(0001)]_{(\text{s-k})}$	Xe	1.0	0.34	4
$\mathrm{Pd}_{(s)}[8(100)\times(110)]$	Xe	1.12	0.49	5
$\mathrm{Pt}_{(s)}[9(111)\times(111)]$	H	negative	positive	6
$\mathrm{W}_{(s)}[m(110)\times(110)]$	W	0.37		16
W(110)	W	0.30[a]	1.0	7
$\mathrm{Au}_{(s)}[m(111)\times(100)]$	Au	0.27		17
$\mathrm{Au}_{(s)}[m(111)\times(11\bar{1})]$	Au	0.20		17
$\mathrm{Pt}_{(s)}[m(111)\times(100)]$	Pt	0.63		17
$\mathrm{Pt}_{(s)}[m(111)\times(11\bar{1})]$	Pt	0.52		17

[a] Dipole moment of W atoms at the edges of W islands on W(110). This value could be compared with the dipole moment of W atom at the steps of the $\mathrm{W}_{(s)}[m(110)\times(110)]$ surface.

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count. Thirdly, adsorption experiments carried out with well-defined stepped surfaces reveal substantial differences between the dipole moment of adatoms at step and on terrace sites (see, for example, Table I). Therefore, the presence of steps would influence $\Delta\phi$ which can be calculated by use of the equilibrium distribution of adatoms. Fourthly, the growth mechanisms of metal atoms deposited on single-crystal metal surfaces are being extensively studied (see, for example, the reviews of Rhead[11] and Somorjai *et al.*,[12] and references therein). Since in these studies step-free patches cannot be isolated, the results of our Monte Carlo simulation would be also useful in order to evaluate the possible influence of steps on the growth mechanism.

The model for the adsorbate-induced work-function changes on stepped surfaces and the Monte Carlo procedure are described in Sec. II. The obtained results are presented and discussed in Sec. III, and the conclusions are stated in Sec. IV.

II. DESCRIPTION OF THE MODEL

A. The equilibrium distribution of the adsorbate on stepped surfaces

For uniformly distributed steps of one-atomic-layer height,[6] the deviation α of the stepped surface from a flat crystal is given by

$$\tan\alpha = 1/L_T , \tag{1}$$

where L_T is the terrace width, taking the nearest-neighbor distance as length unity. According to Eq. (1), if a single crystal is cut with a deviation of $\alpha = 1°$ from the desired crystallographic orientation, step sites represent $\sim 2\%$ of the surface available for adsorption. This concentration of surface defects is greater than the detection limit for surface impurities of conventional ultrahigh-vacuum techniques (i.e., Auger electron spectroscopy) and could certainly influence the adsorption-desorption kinetics, surface catalytic reactions, atomic and molecular scattering, adsorbate-induced work-function changes, etc.[6]

Just as in the usual lattice-gas model[13] we have assumed the substrate where the adsorption takes place as a two-dimensional lattice built up with square unit cells. Double occupancy of lattice sites is forbidden. Each adsorbate is bound to the surface with the binding energy U_0 and each pair of adparticles in nearest-neighbor sites contributes an amount W to the potential energy. Furthermore, each adparticle in the jth row parallel to the step experiences an additional potential energy $V(j)$ as a result of step placed at $j = 0$, given by

$$V(j) = V_0 W / j^3, \quad 1 \le j \le L_T , \tag{2}$$

where V_0 is a dimensionless parameter introduced in order to express $V(j)$ in the W energy scale. The dependence on j has been chosen considering both experimental evidences[14] and theoretical calculations[15] which indicate that for $j > 3$ the ratio $V(j)/V(1)$ is negligible. Let σ_{ij} be 0 or 1 according to whether the lattice site of coordinates (i,j) is empty or occupied by one adparticle, respectively. Then the Hamiltonian (H) of the system can be written as

$$H = -U_0 \sum_{i,j} \sigma_{ij} - W \sum_{\langle ij,i'j' \rangle} \sigma_{ij}\sigma_{i'j'} - \sum_{i,j} V(j)\sigma_{ij} , \tag{3}$$

where $\langle\ \rangle$ denote a nearest-neighbor pair of sites. The system described by Eq. (3) is analogous to an Ising ferromagnet.[13] Such a ferromagnet is semi-infinite (with boundaries at the step and at the terrace edge) and has an inhomogeneous magnetic field given by $V(j)$. In order to evaluate the equilibrium population of adparticles at step and terrace sites, Monte Carlo simulations on square lattices of size $153 \times L_T$ $(L_T \le 51)$ have been performed. Periodic boundary conditions in the direction parallel to the step have also been employed in order to avoid finite-size effects. The initial configuration (IC) is obtained covering the lattice sites with probability p. This procedure is equivalent to the condensation of incident atoms onto a cooled substratum. After the deposition the diffusion of adparticles at constant coverage (i.e., the so-called Kawasaki dynamics) is simulated. This method, instead of the Glauber approach, has been employed to avoid fluctuations in the number of adparticles in the low-coverage regime which is studied in detail. Additionally, most measurements on adsorbed layers are performed at constant coverage, i.e., dosing the sample with a preset exposure in langmuirs, rather than under equilibrium conditions with the gas phase.

At each time step the probability P_{hq} that a given particle at the site h jumps to a given q nearest-neighbor empty site is given by[13]

$$P_{hq} = \begin{cases} \exp(-\delta H / kT) & \text{if } \delta H > 0 , \\ 1, & \text{otherwise} , \end{cases} \tag{4}$$

where k is the Boltzmann constant, T the temperature, and δH the energy change due to the movement of one particle from h to q. Particle hopping between adjacent terraces is forbidden. Let us denote by effective movement (EM) when one particle actually jumps from one site to another one. After the deposition at random, the system is equilibrated at a preset temperature by allowing the adsorbate to perform 4000 EM's per occupied site. Average values of the properties under investigation are evaluated in the subsequent equilibrium configurations (EC's), each of them obtained after 2 EM's per particle. The data for each value of p, L_T, W/kT, and V_0 were obtained by averaging over 100 EC's. Let us now briefly discuss the main difference between the model studied in this work and the theory of heterogeneous nucleation on cleavage steps proposed by Gates and Robins[10] (henceforth GR). The kinetic model of GR is valid when there is no competitive capture of adatoms by terrace clusters.[10] On the contrary, we are concerned with the equilibrium distribution of the adparticles which, at certain temperature, is the consequence of adatom-adatom and adatom-step interactions. In the GR model it is also assumed that an atom trapped by one step does not leave it again and that immobile clusters are formed by the collision between trapped atoms.[10] Concerning this aspect of the problem, our approach is substantially different since atoms can leave step sites, and clusters stuck to the steps can be dissociated and moved by the displacement of individual

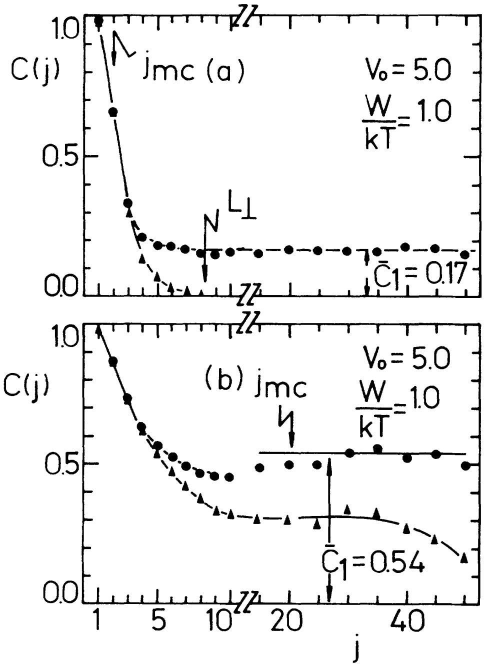

FIG. 1. (a) and (b) The concentration profiles of adatoms in the direction perpendicular to the step, as defined in the text, for two different values of $\bar{C}_1$. Results obtained by means of Monte Carlo simulations on lattices of size $(L=153)\times(L_T=51)$: ●, $C_1(j)$; ▲, $C_2(j)$. The arrows in the upper part of the figures indicate the position of the mass center (j_{MC}) of the cluster(s) in contact with the step placed at $j=0$, $L_\perp$ and $\bar{C}_1$ are also illustrated in the figures. In (b) $L_T=L_\perp$ and therefore the last has not been indicated.

atoms depending on the interaction energies and temperature.

B. The work-function change caused by adsorption

The adsorbate induced work function change on a flat surface ($\Delta\phi_f$) is proportional to the dipole moment (P_f) of the adparticle, i.e., the well-known Helmholtz equation[1,8]

$$\Delta\phi_f=-4\pi NP_f/A \ , \qquad (5)$$

where N is the number of particles adsorbed on the sample of area A. In the following discussion it is assumed that the dipole moment is positive (negative) when it is pointing away from (toward) the surface, causing the work function to decrease (increase). Equation (5) has to be modified in order to take the influence of steps into account. Let N_S and N_T be the number of particles adsorbed at step and on terrace sites, respectively, under equilibrium conditions at constant coverage and temperature. That is

$$N=N_S+N_T \ . \qquad (6)$$

Both N_S and N_T will be computed in Sec. III by means of a Monte Carlo simulation. Let P_S and P_T be the dipole moment of particles adsorbed at step and on terrace sites, respectively. Hence, for stepped surfaces, Eq. (5) becomes

$$\Delta\phi_S=-4\pi(N_SP_S+N_TP_T)/A \ . \qquad (7)$$

In order to easily estimate how the presence of spureous steps could influence the measured work function change upon adsorption, it is useful to combine Eqs. (5), (6), and (7) taking $P_T=P_f$; that is

$$\Delta\phi_S/\Delta\phi_f=1+N_S(P_S-P_T)/NP_T \ . \qquad (8)$$

As expected, the effect of steps could be easily detected if P_S is substantially different from P_T, and therefore the discussion will be focused on this case. It should be mentioned that available experimental data for $\Delta\phi_S$ on well-characterized stepped surfaces reveal that the above mentioned condition is fulfilled for all the adsorption systems which within our knowledge have been studied, as is shown in Table I. When $P_S\neq P_T$, the adsorption of atoms at step sites also slightly influence $\Delta\phi$ even in the case that steps sites would not be selectively populated ($V_0=0$ or $W/kT=0$), as will be discussed in Sec. III B. Nevertheless, a great variety of adsorbate-adsorbent systems exhibit selective growth of adparticles at step sites. In fact, since the earlier experiments of Bassett,[18] this preferential growth is the basis of the well known "surface decoration technique," which allows the detection of surface inhomogeneities (see, for example, Refs. 19 and 20). On the other hand, photoemission of adsorbed xenon (PAX) combined with thermal desorption mass spectrometry and $\Delta\phi$ measurements have unambiguously revealed the selective adsorption of Xe atoms at step sites on stepped-kinked Ru(0001), $[\mathrm{Ru}(0001)]_{(\mathrm{s\text{-}k})}$,[4] and stepped $\mathrm{Pd}_{(s)}$ $[8(100)\times(110)]$.[5]

It should also be mentioned that a few systems are expected to have a quite different behavior. For example, Davies *et al.*[21] have proposed that Ag atoms deposited on a stepped Pt(553) surface nucleate and grow on terrace sites while the step sites remain free. In contrast to the behavior of Ag, no selective blocking of either terrace or step sites has been detected by the same authors for Au/Pt(553).

III. RESULTS

A. The concentration profile of adsorbed particles

The concentration profile $C_1(j)$ of adparticles in the direction perpendicular to the step placed at $j=0$ is given by

$$C_1(j)=(1/L)\sum_{i=1}^{L}\sigma_{ij}, \quad 1\leq j\leq L_T \ , \qquad (9)$$

where L is the step length ($L=153$ in the Monte Carlo simulations). It is also useful to define the concentration profile $C_2(j)$ of particles which belong to the cluster(s) in contact with the step (a cluster is defined as a group of particles connected by nearest-neighbor distances). For this purpose, the summation of Eq. (9) must be restricted only to adparticles fulfilling the above mentioned condition. Figure 1 shows the dependence of both $C_1(j)$ and $C_2(j)$ on j (averaged over 100 EC's), for two different surface coverages. Close to the step, the higher concentration indicates the preferential growth of clusters in this region.

For $j<10$, $C_1(j)$ drops quickly when j increases, and usually for $j>10$ it reaches a constant value ($\bar{C}_1$) independent on j, as it is indicated in Fig. 1. Also $C_2(j)$ drops quickly for j close to the step and its interception with the j axis is a measure of the average cluster length ($L_\perp$) in the direction perpendicular to the step. As can be seen by comparing Figs. 1(a) and 1(b), $L_\perp$ depends on $\bar{C}_1$ and for a certain critical value, denoted by $\bar{C}_{1c}$, one has $L_\perp=L_T$ for the first time. Therefore, it is said that a percolating cluster(s) in the direction perpendicular to the step has been formed at $\bar{C}_{1c}$ or, in other words, the cluster(s) growing in contact with the step reaches for the first time the edge of the terrace at $\bar{C}_{1c}$ (for details of the percolation theory see, for example, the reviews of Stauffer[22] and Clerc *et al.*[23]). It should be mentioned that $\bar{C}_{1c}$ depends on V_0, W/kT and the terrace width L_T (if $L \gg L_T$ all the results do not depend on L, and one expects that this statement also holds in our cases where $L \geq 3L_T$). In the limit L, $L_T=\infty$, where only one percolation cluster can exit, the influence of the step potential can be neglected and $\bar{C}_{1c}$ takes the value of the critical concentration (ϕ_c) of the site-percolation model on the square lattice (for example, $\phi_c=0.5927$ and $\phi_c=0.55$ for $W/kT=0.0$ and $W/kT=1.0$, respectively[24]). Due to these circumstances the concentration profiles derived from Monte Carlo simulations are independent of L_T provided that $L_T>L_\perp$.

The coordinate of the mass center ($j_{\rm MC}$) of the cluster(s) growing in contact with the step can be evaluated from the concentration profile according to the following equation

$$j_{\rm MC}=\left[\sum_{j=1}^{L_T} jC_2(j)\right]\left[\sum_{j=1}^{L_T} C_2(j)\right]^{-1} . \tag{10}$$

As an example, the arrows in Fig. 1 indicate the position of $j_{\rm MC}$ in each case. It is interesting to describe the dependence of $j_{\rm MC}$ on $\bar{C}_1$ shown in Fig. 2. $j_{\rm MC}$ increases linearly with $\bar{C}_1$ (for $\bar{C}_1<0.4$), but it remains close to the step ($j_{\rm MC}<4$). This fact also indicates a preferential aggregation of particles close to the step in spite of the fact that $L_\perp \cong 20$ for $\bar{C}_1 \cong 0.40$. For $\bar{C}_1>0.4$, $j_{\rm MC}$ abruptly increases due to the approach to the percolation threshold $\bar{C}_{1c}$. For example, at $\bar{C}_1=0.54$, 84% of the evaluated samples exhibited percolating clusters in the direction perpendicular to the step. For $\bar{C}_1>\bar{C}_{1c}$, $j_{\rm MC}$ is close to $L_T/2$, as expected, since the growth is dominated by the percolating cluster(s).

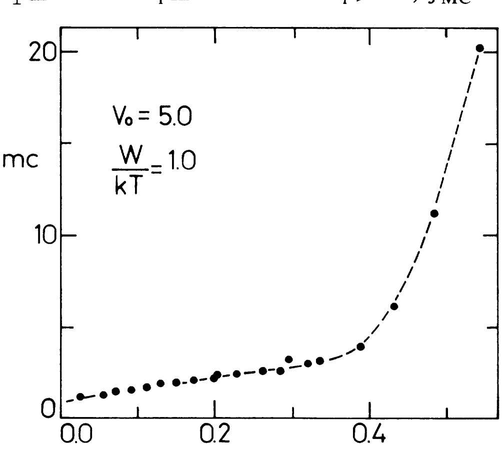

FIG. 2. The position of the mass center $j_{\rm MC}$ of the cluster(s) stuck to the step as a function of the adsorbate concentration beyond the influence of the step potential ($\bar{C}_1$). Results were obtained with lattice of size $(L=153)\times(L_T=51)$ and the parameters listed in the figure.

B. The adsorbate-induced work-function change

Let us define the coverage (Θ) as the mean of particles per lattice site, that is

$$\Theta=N/L\,L_T\ . \tag{11}$$

Now using Eqs. (6) and (7) with $A=LL_Tb^2$ (where b is the nearest-neighbor distance), one obtains

$$\Delta\phi_S=-(4\pi/b^2)[P_T\Theta+(P_S-P_T)n_S/L_T]\ , \tag{12}$$

where $n_S \equiv N_S/L=C_1(1)$ is the density of adsorbed particles at step sites. In general, for fixed values of V_0 and W/kT, n_S is a function of Θ and L_T; but for steps such that $L_T>L_\perp$ (see Fig. 1), n_S can be considered only as a function of $\bar{C}_1$. In Fig. 3 it is shown the Monte Carlo results of n_S versus Θ for different values of W/kT, obtained for $L=153$, $L_T=11$ and $V_0=5$. From these results, and as an example, $\Delta\phi_S$ has been computed using $P_S=1.0$ D, $P_T=0.4$ D (which are typical values, see Table I) and $b=5$ Å (see Fig. 4). For $W/kT=0$ one obtains $n_S=\Theta$, and Eq. (12) gives

$$\Delta\phi_S=-(4\pi/b^2)[P_T+(P_S-P_T)/L_T]\Theta\ . \tag{13}$$

That is, within the high-temperature regime, and due to the mobility of the adparticles, $\Delta\phi_S$ is expected to change linearly with the coverage. From Eq. (13) the effective dipole moment of the adparticles, related to the slope of the dashed line of Fig. 4, is given by $\bar{P}=P_T+(P_S-P_T)/L_T \cong 0.45$ D. That is, even in the case when there is not a selective population of particles at step sites, one would obtain an overestimation of P_T if the presence of steps were not taken into account. For $W/kT=0.1$, the results of n_S and $\Delta\phi_S$ shown in Figs. 3 and 4, respectively, are

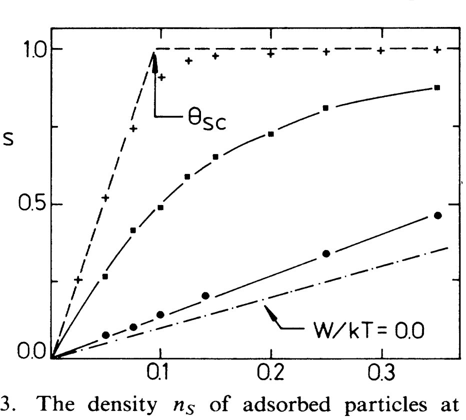

FIG. 3. The density n_S of adsorbed particles at the step against the coverage Θ for $V_0=5$ and different values of W/kT: ●, $W/kT=0.1$; ■, $W/kT=0.5$; and +, $W/kT=1.0$. The dash-dotted line corresponds to the case $W/kT=0$. The dashed line corresponds to the expected behavior for very large values of W/kT. The results were obtained using lattices of size $L=153$ and $L_T=11$.

close to those obtained for $W/kT=0$. For $W/kT=0.5$, an effective dipole moment $\bar{P}\cong 0.70$ D is obtained in the limit of zero coverage. For strong enough step-particle interaction (that is for large values of W/kT because of V_0 is a constant of Fig. 3), n_S has two different behaviors

$$n_S=\begin{cases} a\Theta \ \text{ for } 0\le\Theta\le\Theta_{SC} , \\ 1 \ \text{ for } \Theta_{SC}\le\Theta\le 1 , \end{cases} \tag{14}$$

where Θ_{SC} is the step saturation coverage $\Theta_{SC}=1/L_T$ ($\simeq 0.09$ in our case) and then $a=L_T$ (see the dashed lines in Fig. 3). Now from Eq. (12) one obtains

$$\Delta\phi_S=\begin{cases} -(4\pi/b^2)P_S\Theta \ \text{ for } 0\le\Theta\le\Theta_{SC} , \\ -(4\pi/b^2)[(P_S-P_T)/L_T+P_T\Theta] \\ \qquad\qquad\qquad \text{for } \Theta_{SC}\le\Theta\le 1 . \end{cases} \tag{15}$$

Accordingly, two regions of linear variation of the work function are clearly distinguishable in Fig. 4 for $W/kT=1.0$. This kind of behavior is in excellent agreement with available experimental data for the systems Xe/[Ru(0001)]$_{(\text{s-k})}$ (Ref. 4) and Xe/Pd$_{(s)}$[8(100)×(110)] (Ref. 5). From the slopes of the two straight lines shown in Fig. 4, the effective step $\bar{P}_S=0.96$ D and the terrace $\bar{P}_T=0.41$ D dipole moments have been calculated. For a large value of W/kT (or V_0), one would obtain $\bar{P}_S=P_s=1.0$ D and $\bar{P}_T=P_T=0.40$ D [see Eq. (15)].

It should be noticed that assuming $b=5$ Å, $P_S=1.0$ D and $P_T<P_S$ the repulsion energy between two nearest-neighbor dipoles at step sites (i.e., the strongest repulsion) is only about 0.12 kcal/mol, and it has been neglected in the model [see Eq. (3)]. In fact, this energy is roughly one half of the bulk nearest-neighbor interaction W_b between Xe atoms[25] and the approach will certainly be better for metallic adsorbates with larger W_b. On the other hand, our simulation is not appropriate for alkali atoms adsorbed on metal surfaces because in this case the dipolar repulsion is appreciable and it determines the structure of the adlayer.[26]

Let us now consider the ratio N_S/N which is directly related to $\Delta\phi_S/\Delta\phi_f$ [see Eq. (8)]. For large enough step-particle interactions, N_S/N has two well-defined behaviors [see Eq. (14)]; therefore one has

$$N_S/N=\begin{cases} 1 \ \text{ for } 0\le\Theta\le\Theta_{SC} , \\ 1/\Theta L_T \ \text{ for } \Theta_{SC}\le\Theta\le 1 . \end{cases} \tag{16}$$

N_S/N versus Θ is plotted in Fig. 5 for $W/kT=1$ and different values of V_0. For $V_0=5$ a behavior very close to those given by Eq. (16), is obtained. On the other hand, for $V_0=0$ one has $N_S/N=1/L_T$. Finally for a perfect flat surface without steps $N_S/N=0$.

In order to obtain some illustrative results, let us assume $P_S=1.0$ D and $P_T=0.5$ D (see Table I). In this case one has [see Eq. (8)]

$$\Delta\phi_S/\Delta\phi_f=1+(N_S/N) . \tag{17}$$

Now from Fig. 5 it follows that $\Delta\phi$ is very sensitive to the presence of steps for $\Theta\le 0.10$ and $3\le V_0\le 5$. For these cases, deviations as high as 65–95 % with respect to the $\Delta\phi$ values expected for an ideally flat surface ($N_S/N=0$) can be found. For $\Theta>0.10$ the difference is also appreciable. For a weaker potential energy ($V_0=1$) the deviations from the values corresponding to a flat surface are between 16 and 22 %, within the analyzed range of coverage ($0<\Theta\le 0.4$). All these results must be considered in order to interpret adsorbate induced work function changes on polycrystalline samples at low coverage. In fact, for such systems one should expect results strongly influenced by the preferential adsorption on surface defects as, for example, steps and grain boundaries. On the other hand, a new method for the study of two-dimensional phase transitions based on the temperature dependence of the work function of an adsorbate-covered metal surfaces has recently been proposed and applied to the Au/W(110) system.[3] The method is supported by the fact that the dipole moment of an Au atom on two-dimensional Au islands is negligible compared to that of an Au atom in the two-dimensional gas phase.[3] The present study pointed out that, as the authors have also stressed, such experiments must be carried out with step-free surfaces in order to obtain unambiguous results.

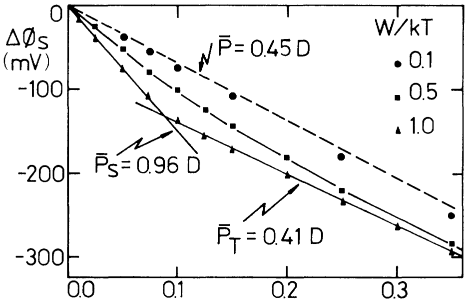

FIG. 4. The work-function change on a stepped surface versus coverage. The concentration profiles were evaluated with lattices of size ($L=153$)×($L_T=11$), $V_0=5$ and three values of W/kT as indicated in the figure. $\Delta\phi_S$ was calculated using Eq. (7) assuming $P_S=1.0$ D and $P_T=0.4$ D, and taking 5 Å as the nearest-neighbor distance between adatoms. The dashed line corresponds to $W/kT=0$ [Eq. (13)]. More details are given in the text.

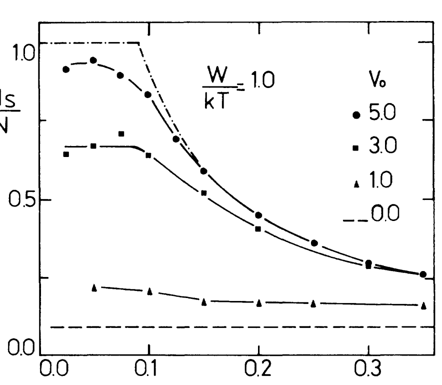

FIG. 5. The ratio N_S/N as a function of the coverage. The results were obtained using lattices with $L=153$ and $L_T=11$. The dash-dotted lines correspond to the expected behavior for very large values of V_0.

IV. CONCLUSIONS

A model for the heterogeneous nucleation of adparticles on cleavage steps is studied in the submonolayer regime by means of a Monte Carlo simulation. Taking both adatom-adatom and adatom-step interactions into account, the concentration profile in the direction perpendicular to the step as a function of the temperature and surface coverage $\overline{C}_1$ or Θ have been evaluated. Preferential nucleation is characterized by the fact that the mass center (j_{MC}) of the cluster(s) stuck to a step is found to remain close to it (within four nearest-neighbor distances for $\overline{C}_1 < 0.4$ in the case shown in Fig. 2) in a wide range of surface coverage. Increasing the coverage, an abrupt displacement of the mass center close to the terrace half-width is found. This behavior is due to the growth of percolation clusters between adjacent steps.

The concentration profiles derived from the simulations are employed to evaluate the adsorption-induced work-function changes on stepped surfaces ($\Delta\phi_S$). Essentially, at low and at high temperature, the coverage dependence of $\Delta\phi_S$ has two different behaviors (see Fig. 4). At low temperature there are two well-defined regions of linear variation of $\Delta\phi_S$ versus Θ; the low ($0 \le \Theta \le \Theta_{\mathrm{SC}}$) and the high ($\Theta_{\mathrm{SC}} \le \Theta \le 1$) coverage regime ($\Theta_{\mathrm{SC}}$ is the step saturation coverage), which are characterized by the influence of the step and the terrace dipole moments, respectively, in agreement with available experimental data. At high temperature there is only one region of linear variation of $\Delta\phi_S$ versus Θ ($0 \le \Theta \le 1$) with a different slope than the one obtained for a perfect flat surface.

On the other hand, all the obtained results should be relevant for the interpretation of the influence of steps on the thin film growth mechanism. In fact, Frank—van der Merwe and Stranski-Krastanov growth mechanisms,[11,12,21] expected for perfect flat surfaces, could turn into the Volmer-Weber growth mechanism due to the nucleation of adatoms at steps during the early stage of film growth. This effect suggests us to tentatively propose the "defect induced Volmer-Weber growth mechanism."

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