Regular Mixing in a Two-Dimensional Lattice System: The Coadsorption of N and O on Ru(0001)

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The coadsorption of N and O on Ru(0001) has been studied by scanning tunneling microscopy; by this technique we can distinquish between the two atomic adsorbates. N and O form a dense intermixed 2×2 phase in equilibrium with a dilute lattice gas. The two-dimensional "vapor pressure" of N, i.e., its concentration in the lattice gas, has been determined for various ratios of N and O in the dense phase by adjusting the total coverage of N and O. The resulting vapor pressure curve indicates a positive enthalpy of mixing, due to relatively weak N-O interactions in the dense phase.   [S0031-9007(98)07374-8]

Lattice models are well established for the theoretical description of multicomponent systems like liquid mixtures, alloys, solid solutions, etc. [1,2]. Because of their discrete nature, which allows the explicit calculation of thermodynamic properties within statistical concepts, lattice models very often provide an appropriate and feasible mathematical description of these systems [3]. Nowadays, powerful computers allow the simulation of such models even for complicated systems [4]. Direct experimental verification of thermodynamic properties of such a system has, however, so far been lacking and will be presented in this paper.

By applying scanning tunneling microscopy (STM) to the two-dimensional (2D) lattice system of coadsorbed O and N atoms on a Ru(0001) surface, we were able to directly determine the atomic configurations of this binary mixture. N and O atoms are shown to form two phases coexisting on the surface, a dense inter-mixed 2×2 phase in equilibrium with a dilute lattice gas phase. The thermodynamic quantities like the composition of the dense phase as well as the concentrations of the components in the lattice gas phase, i.e., their 2D partial pressures, were derived by simply counting the individual atoms.

N and O were coadsorbed on the Ru(0001) surface by dissociative adsorption of NO [5,6] where all adatoms occupy equivalent hcp sites of the substrate lattice. The NO dissociation results in equal total amounts of N and O, while the atomic compositions of the different phases and hence also the partial pressures in the lattice gas phase vary with the overall coverage. By varying the exposure to NO, it became possible to derive the 2D N partial pressure for various ratios of N and O in the dense phase. The thus derived data indicate a positive enthalpy of mixing, reflecting the interactions of the adsorbates in the dense phase. These experimental results are compared with predictions from a simple lattice model for a binary mixture in 2D, from which a weak attractive third nearest neighbor ($3nn$) interaction between the O and N atoms is derived.

The STM experiments were performed in a UHV chamber with a base pressure below 1×10^{-10} mbar, described in detail in [7]. The Ru(0001) sample was cleaned by Ar^+ sputtering, followed by several annealing and oxidation cycles [8]. Coadsorption of N and O was achieved by adsorbing NO at 375 K. At this temperature NO completely dissociates into O and N adatoms [5,6,9,10]. Since the desorption of nitrogen and oxygen starts only at temperatures above 500 K, equal amounts of O and N are covering the surface. In order to vary the total N/O ratio in some experiments, N was preadsorbed by exposure to N_2 molecules excited at the filament of the ion gauge [8]. The STM images were recorded at room temperature (T_R).

Figure 1(a) shows the Ru(0001) surface after exposure to 0.3 L NO. Two phases can be distinguished. Well-ordered islands of a dense phase are embedded into a dilute disordered lattice gas. The well-ordered patches exhibit a 2×2 periodicity with respect to the substrate lattice, as discussed in detail in [11]. Upon closer inspection [inset in Fig. 1(a)], two different species are discernible in the 2×2 structure. Most of the features appear black, corresponding to an apparent depth of 0.5 Å. About 6% of the spots appear gray (0.35 Å depth) and are randomly distributed among the 2×2 sites. In contrast, in the lattice gas phase the gray spots represent the majority of the features. They are identified with chemisorbed N atoms; in the absence of neighboring adatoms, their mean residence time on the adsorption site before moving to a neighboring one is 45 s at 300 K [6,11], i.e., about equal to the recording time of the STM images (60 s). On the other hand, the islands of the dense phase of mostly black indentations can be assigned to the known 2×2 phase of O/Ru(0001). Only a fraction of $x_N = 6\%$ of the O atoms are substituted by (gray) N atoms, "dissolved" in this 2×2 O/Ru(0001) phase where both atoms occupy hcp sites of the substrate lattice with a local coverage of $\theta = 0.25$ [12,13], referred to the 1×1 substrate lattice.

Contrary to the N atoms in the lattice gas, isolated O atoms are more mobile; they exhibit a hopping frequency of about 16 jumps per sec, which is close to the horizontal
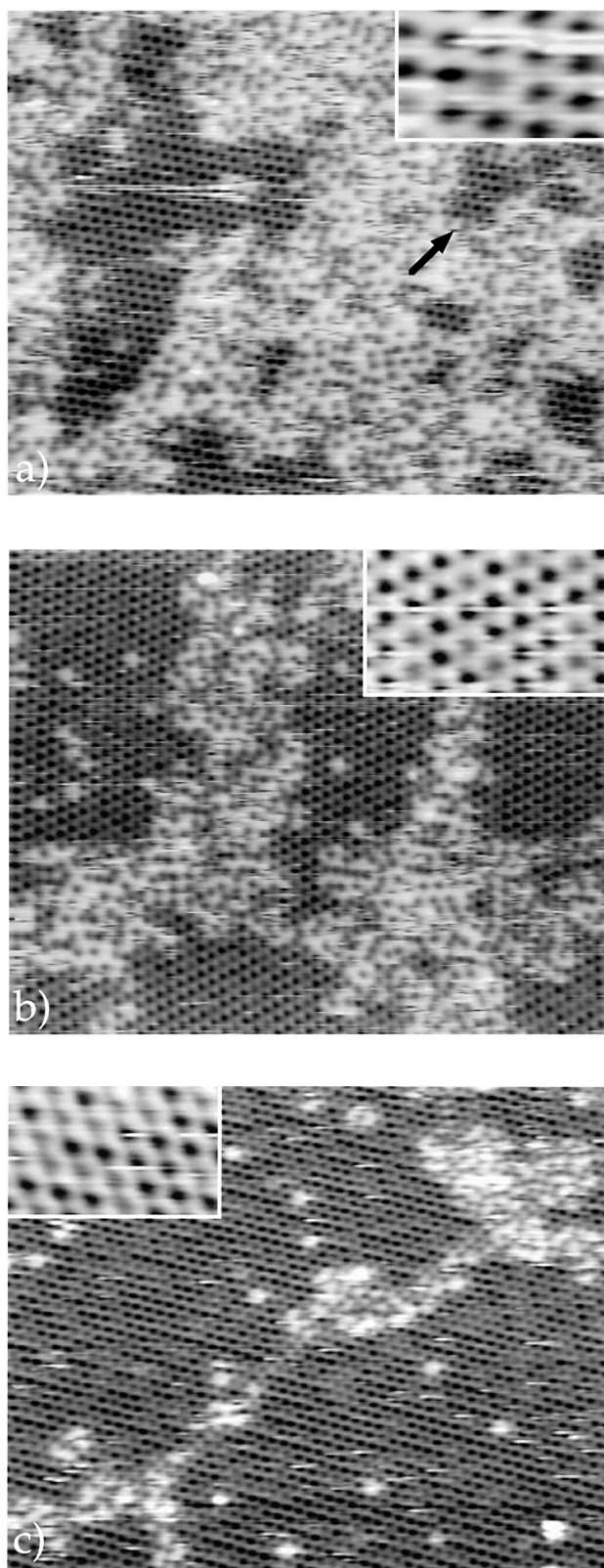
FIG. 1. STM images of Ru(0001) after exposure to NO (270 Å × 270 Å). The insets show details of the 2 × 2 phase of the corresponding images. The black indentations constitute O atoms, and the gray ones N atoms. (a) 0.3 L NO; $U_T = -0.13$ V, $I_T = 1$ nA. (b) 0.35 L NO; $U_T = -0.13$ V, $I_T = 1$ nA. (c) 0.45 L NO; $U_T = -0.13$ V, $I_T = 1$ nA.

(fast) scan frequency of our STM. Thus, most of the O atoms in the lattice gas move between successive scan lines and are therefore imaged only as black streaks along the fast scan direction (cf. [11]). One of them is marked with an arrow in Fig. 1(a). The density of O atoms in the gas phase is much smaller than that of the N atoms ($\theta_{\text{N-gas}} = 0.09$). For each exposure the fraction of N in the dense phase (x_N) as well as the concentration of N atoms in the lattice gas phase were determined by averaging over several STM images. Only perfect 2 × 2 areas or complete lattice gas areas were used for the determination of those numbers. The borders of the 2 × 2 islands were excluded from this analysis.

It is important to note that there exist continuous fluctuations of atoms to and from the island edges. This manifests itself by a continuous change of the shapes of the 2 × 2 islands between subsequent STM images (not shown here). This observation, together with the high mobility of both adsorbed species, strongly indicates that the distribution of N and O between islands and lattice gas in Fig. 1(a) is in thermal equilibrium. To ascertain the establishment of such an equilibrium between the two phases of different densities, the adsorption of NO was carried out at 375 K, followed by 10 min of annealing at that temperature before recording the STM images. Additionally, we performed experiments where the NO adsorption took place at about room temperature, which did not change the compositions of the different phases, namely, the respective concentrations of N and O. Hence, we assume that the morphology in Fig. 1(a) is not the result of a kinetic process of nucleation and growth. It is the consequence of the *phase equilibrium* between the two-component 2 × 2 phase and its dilute gas phase, i.e., an O-rich dense phase and a N-rich lattice gas.

Therefore, the composition of the dense phase is determined by the composition of the dilute phase. The driving force for the mixing of the N atoms into the dense 2 × 2 phase is the partial pressure of N in the gas phase, i.e., the concentration of this species in the lattice gas. We therefore expect the fraction of N in the 2 × 2 phase to increase with increasing N partial pressure in the gas phase. This becomes evident from Fig. 1(b). After adsorption of 0.35 L of NO, the area covered by islands of the 2 × 2 phase increased considerably. Consequently, the 2D volume of the lattice gas diminished, and the coverage of N in the lattice gas now amounts to $\theta_{\text{N-gas}} = 0.12$, which results in a considerably higher N pressure compared to that in Fig. 1(a). As expected, the portion of nitrogen in the dense phase rose to $x_N = 22\%$. Further increase of the NO dose (0.45 L) and hence higher N gas pressure ($\theta_{\text{N-gas}} = 0.15$) led to an even higher mole fraction of N in the dense phase [$x_N = 40\%$; Fig. 1(c)]. At this coverage the lattice gas is mostly restricted to small stripes at antiphase domain boundaries, but it is well discernible from the ordered 2 × 2 islands. It is noteworthy that the

nitrogen atoms are still homogeneously distributed in the 2×2 phase without obvious coverage gradients towards the island edges, which supports that the system reached equilibrium.

To derive a vapor pressure curve where the N partial pressure is plotted versus the N mole fraction in the dense phase, we transcribed the N coverage into the 2D partial pressure. The pressure of the lattice gas is defined as the negative partial derivative of the free energy of the lattice gas with respect to its 2D volume. The pressure is caused by both the interactions of the particles as well as by the entropic repulsion resulting from the blocking of lattice sites, due to the finite volume of the particles. For the case of a lattice gas on a 1×1 lattice in 2D without interactions, the pressure is given by $p = -kT \ln(1 - \theta)$, where k is the Boltzmann constant and T the temperature [3,14]. Thus, for low coverages the pressure increases approximately linearly with the coverage, while it diverges for coverages close to the saturation coverage of $\theta = 1$. For N/Ru(0001), however, repulsive N-N interactions up to the next-nearest neighbors lead to the stabilization of a 2×2 structure at $\theta_N = 0.25$ [8]. This implies the divergence of the pressure already at this coverage. The inclusion of an effective blocking volume of four lattice sites per N atom alters the above pressure formula to $p = (-kT/4) \ln(1 - 4\theta)$, which is equivalent to the normalization of the coverage by a factor of 4. The formula exhibits the expected limiting behavior ($p \propto \theta$ for $\theta \to 0$ and $p \to \infty$ for $\theta \to 0.25$) and is therefore assumed to provide an appropriate estimate of the thermodynamic pressure. An exact result for the relation between thermodynamic pressure and coverage cannot be given explicitly, as the effective blocking volume continuously increases from one lattice site at low coverages towards four sites upon approaching $\theta_N = 0.25$. However, since the measured N coverages vary only between $\theta_N = 0.09$ and $\theta_N = 0.15$, the deviation from linearity between coverage and pressure stays well below 20%. Interactions between the N atoms are neglected because they would lead only to second-order corrections of p [3] and are well below thermal energies at distances exceeding the 2×2 positions [8].

Figure 2 shows the N partial pressure data for various mole fractions of N in the dense phase (open circles). We also included results from experiments where about $\theta_N = 0.1$ of nitrogen was preadsorbed on the surface before dosing NO (closed circles). The data points fit well with the results obtained by pure NO adsorption, which further substantiates that the two phases are in thermodynamic equilibrium. The pressure is normalized with respect to p_N^0, which is the vapor pressure of a fictive 2×2 phase, consisting only of N atoms (see below). We were unable to extend the experimental vapor pressure curve in Fig. 2 towards N fractions above $x_N = 40\%$ because the lattice gas areas became
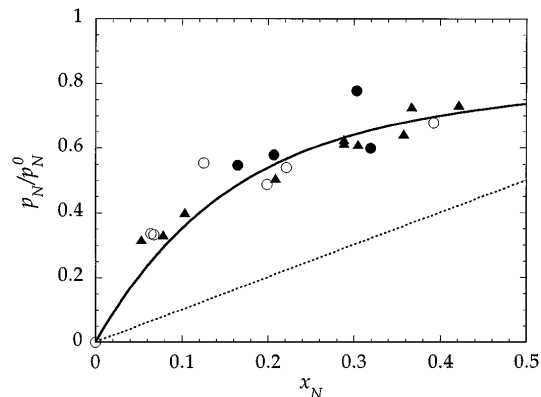

FIG. 2. N partial pressure in the lattice gas vs mole fraction x_N in the dense 2×2 phase. Open circles: Results from STM images after NO adsorption. Closed circles: Experimental results with additional N preadsorption. Dotted line: Raoult's law. Full line: Fit to the experimental data within the lattice model with $\omega = -13$ meV. Triangles: Results of the Monte Carlo simulation. The pressure is normalized with respect to the p_N^0 of the above fit (see text).

too small to obtain sufficient accuracy for a statistical evaluation.

The strong positive deviation of the vapor pressure curve from Raoult's law (indicated by the dotted line in Fig. 2), i.e., the high N partial pressure at low mole fractions, indicates a *positive enthalpy of mixing*. It costs energy to mix an N atom into the 2×2 O matrix.

To perform a more quantitative analysis of the data, we compared the vapor pressure curve in Fig. 2 with the theoretical one of a binary mixture on a lattice. Guggenheim [2] calculated the respective vapor pressure curves for a "regular mixture," i.e., including pairwise *nn* interactions of the particles. He employed the mixing entropy of an ideal mixture within the Bragg-Williams approximation. This approach allows double occupation of single sites by different particles in the gas phase and neglects corrections of the entropy, due to clustering of the particles in the dense phase. Furthermore, the dense phase in the model constitutes a 1×1 phase on the underlying lattice and not a 2×2 as in the experiment. This should, however, have no influence on the mixing entropy in the dense phase: In the case of a 2×2 structure, the mixing entropy is defined by the possible configurations of the particles on only one of the four possible sublattices. Within this model, the partial pressure of N varies with the mole fraction according to

$$\frac{p_N}{p_N^0} = x_N \exp[(1 - x_N)^2 c\omega/2kT], \qquad (1)$$

where c is the number of nearest neighbors (six 2×2 neighbors in our case) [2,3,14]. p_N^0 gives the vapor pressure of a dense phase consisting only of N atoms which can be regarded as scale factor. The shape of the vapor pressure curve is solely determined by the parameter ω, which reflects the net energy balance of

the interactions between the atoms in the dense phase upon intermixing: $\omega = E_{OO} + E_{NN} - 2E_{NO}$, where E_{OO} is the $3nn$ interaction energy of two O atoms, E_{NN} that of the N atoms, and E_{NO} corresponds to the N—O "bond" in the 2×2 structure. For a positive deviation from Raoult's law, ω has to be negative; i.e., O—O and N—N $3nn$ interactions are more attractive (negative) than the N—O $3nn$ interaction, and oxygen and nitrogen prefer to be surrounded by atoms of the same kind. A value of $\omega = -13$ meV (with $c = 6$ and $kT_R = 25$ meV) fits the experimental data well, as shown by the solid line in Fig. 2.

Employing the experimentally determined ω, we want to derive the N—O $3nn$ interactions. From the vapor pressure of oxygen 2×2 islands on Ru(0001), Wintterlin *et al.* estimated an O—O $3nn$ interaction energy of $E_{OO} = -25$ meV [13]. Trost *et al.* gave a lower limit for the effective N—N $3nn$ interaction of $E_{NN} = -18$ meV [8]. Considering these interactions and the above determined ω, the energy balance results in an attractive N—O $3nn$ interaction weaker than -15 meV. However, the above E_{NN} was obtained from the correlation function of the N atoms in an N lattice gas and hence includes the entropic forces, due to site blocking of atoms. From comparison with the effective interactions of a hard-sphere model where already the purely entropic part of the interactions amounts of about -10 meV at T_R, the real attraction between the N atoms is expected to be much weaker [8]. A realistic value might be $E_{NN} \approx -10$ meV. Employing this more realistic value for the N—N $3nn$ interaction results in $E_{NO} \approx -11$ meV. But even zero $3nn$ interaction between the N atoms would suggest a weak attraction between N and O in 2×2 positions.

The mixing entropy favors a random distribution of N and O atoms in the dense phase because of the "maximum disorder" of such a configuration. However, interactions between the particles might favor clustering, which changes the configurational degeneracy of the system and hence the entropy. Additionally, the above model allows double occupancy of sites, which is certainly forbidden in the real system. It is also noteworthy that the model intrinsically includes site blocking in the dense 2×2 phase up to second nearest neighbors. To check the validity of the model, we performed equilibrium Monte Carlo simulations of a lattice model with two kinds of adsorbed particles, employing the Metropolis algorithm. As an input we used pairwise interactions between the atoms, which are repulsive up to the second nearest neighbors in order to stabilize the 2×2 structure and to suppress $\sqrt{3}a_0$ and $1a_0$ distances in this phase, which is in accordance with the experimental findings. Further details can be found in [13]. The $3nn$ interactions were set to $E_{OO} = -25$ meV, $E_{NN} = -4$ meV, and $E_{NO} = -8$ meV, which results in $\omega = -13$ meV at room temperature. The triangles in Fig. 2 show the results of the simulation. Note that there were no adjustable parameters such as scale factors in the simulation. The results agree well with the experimen-

tal values, which substantiates the validity of the above theoretical approximation for our system. This is also in accordance with theoretical estimations by Hill [3], which show that the influence of the configurational entropy is fairly small in mixtures, at least, if one does not consider critical phenomena.

In conclusion, it was shown that the coadsorption system of O and N on the surface lattice of Ru(0001) represents a 2D example of a binary mixture of interacting particles. A dense intermixed phase is in equilibrium with its surrounding lattice gas vapor, for which the thermodynamic variables like pressure and mole fraction were obtained by analyzing the system on atomic scale. By applying a simple lattice model for the equilibrium thermodynamics of a regular binary mixture, the $3nn$ interaction energy of N and O was determined to be slightly attractive, of the order of fractions of kT_R. Effects on the entropy caused by the nonzero interactions of the particles are negligible. Even the allowance of double occupation of lattice sites in the model has no obvious effect on the entropy. Therefore, our experiments provide support for the simplifying lattice models underlying the explanation of many physical systems like, e.g., the vapor pressure curves of regular binary mixtures of simple liquids.

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