Gas Adsorption on Tungsten Exposed to a Mixture of Nitrogen and Oxygen

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The adsorption process of a mixture of nitrogen and oxygen on tungsten has been studied by field-emission microscopy. The observations of work function and field-emission-microscopy patterns suggest that when the tungsten surface at 300 K is exposed to this mixture the preferential adsorption of nitrogen, the replacement of adsorbed nitrogen by oxygen, and the adsorption of oxygen take place sequentially.

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Although the adsorption of simple gas on tungsten has been extensively studied, the adsorption of a gas mixture on tungsten has not. In the case of a gas mixture, whether or not surface processes such as selective adsorption, replacement, and catalytic reaction take place is an essential problem to be solved. In this paper, the selective adsorption and the replacement in the adsorption system of a mixture of nitrogen and oxygen on tungsten by using field-emission microscopy (FEM) are reported. Because FEM shows a high sensitivity for the changes of work function in a very short time of measurements (only a few seconds), it is an incisive method by which to study the adsorption process in several steps.

A standard FEM setup was used. In order to reduce the effect of residual gas desorbed from the glass wall of the setup, it was first exposed to a mixture of nitrogen and oxygen (1:1) at 5×10^{-8} Torr for one day. The setup was evacuated by an ion pump until the residual pressure fell down below 2×10^{-10} Torr. The clean surface was obtained by heating the tungsten tip at 2900 K. The temperature of the tip was measured by a W-Re thermocouple. Before the gas adsorption, the cleanliness of the tip was always checked by observing its FEM pattern. A typical pattern from clean tungsten is shown in Fig. 1(a). Since the FEM patterns are enlarged on a screen by the cold emission originating from identifiable lattice planes on the tip and since the tungsten tip has a (110) lattice plane perpendicular to the axis, its pattern is compared with a (110) cubic stereographic projection. The most obvious feature in Fig. 1(a) is a large dark rectangle seen around the central part of the pattern. Keeping the symmetry of the (110) cubic stereographic projection, the FEM patterns change under different coverages and different temperatures. Some examples of such FEM patterns are also shown in Figs. 1(b)–1(e). Figures 1(b) and 1(c) are the typical patterns of the nitrogen-saturated tungsten tip at 300 K and of the tip after 1000-K heating, respectively. Figures 1(d) and 1(e) are the typical patterns of the oxygen-saturated tungsten tip at 300 K and of the tip after heating at 1550 K, respectively. These patterns are used as the standard ones for the assignment of the observed FEM patterns of the gas mixture.

While the gas mixture was introduced into the FEM tube, the viewing voltages were intermittently applied on the tip, adjusting the emission current always to the constant value. From the applied voltages, the values of work function of the associated tip were obtained by a relation of

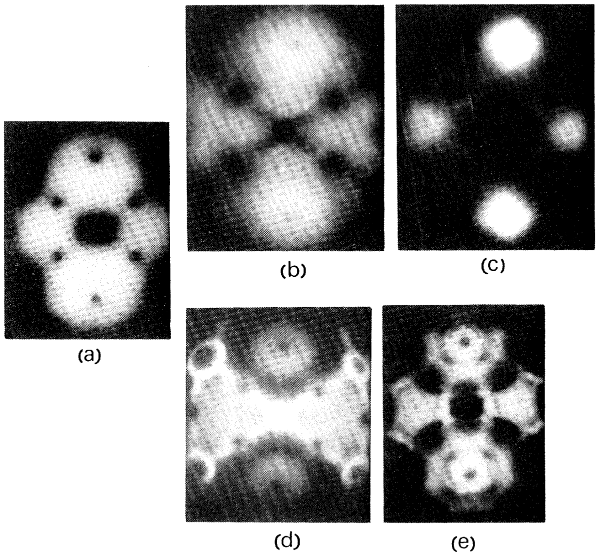

FIG. 1. FEM patterns used as standards for the assignment. (a) Clean tungsten tip (~1000-Å radius). (b) Tungsten tip saturated with nitrogen at 300 K. N_2 exposure is 34 L; $\varphi = 4.99$ eV. (c) Pattern obtained by heating N_2-saturated tip shown in (b) at 1000 K; $\varphi = 4.52$ eV. (d) O_2-saturated tungsten tip at 300 K. O_2 exposure is 18 L; $\varphi = 5.54$ eV. (e) Pattern obtained by heating O_2-saturated tip shown in (d) at 1550 K; $\varphi = 5.56$ eV.

$\varphi = \varphi_0(V/V_0)^{2/3}$, where φ (φ_0) is work function of the gas-covered (clean) tip and V (V_0) is the applied voltage at constant current on the gas-covered (clean) tip.[1]

In Fig. 2 the value of work function is shown as a function of exposure, where exposure is expressed by langmuirs (L) (1 L = 1×10^{-6} Torr sec). Two steps can be seen in the curve. The first step of the curve is found to be saturated near 29 L (4.95 eV). The FEM pattern observed at this work-function value was analogous to that shown in Fig. 1(b). When this tip was heated up to 1000 K, the pattern observed became analogous to that shown in Fig. 1(c). All the patterns obtained at other temperatures were analogous to those associated with the nitrogen-tungsten adsorption system. Therefore, it seems that during the first step of the adsorption process nitrogen is adsorbed preferentially on tungsten. Since both nitrogen and oxygen are adsorbed atomically on tungsten,[2] the observations seem to suggest that nitrogen having three lone-pair $2p$ electrons is more active for the adsorption than oxygen with two lone-pair $2p$ electrons.

The second step of the curve seems to approach the saturated value of 5.58 eV near 50.0 L. This value is close to that of the tip saturated with oxygen, 5.54 eV. The observed FEM pattern under this condition was analogous to that at the saturation of oxygen shown in Fig. 1(d). Moreover, the pattern obtained at 1500 K by heating the tip with this oxygenlike pattern became analogous to that shown in Fig. 1(e), and all the patterns obtained at other temperatures were also analogous to those associated with the oxygen-tungsten adsorption system, with a good agreement of work-function values. Therefore, it seems that at the saturation of the second step the surface is covered by oxygen. The second step in the work-function curve shows a rapid increase, during which the FEM patterns obtained could not be assigned as any nitrogen- or oxygen-associated ones. Rerently, it has been reported that the adsorbed nitrogen is replaced by oxygen on the evaporated tungsten film,[3] and so the replacement possibly occurred during the rapid increase. It should be remarked that the FEM patterns observed during the rapid increase suggest a nitrogen-oxygen–coadsorbed state or a precursory complex state before the replacement. Since the work-function value due to the oxygen-adsorbed surface is much higher than that due to the nitrogen-adsorbed surface above described, the rapid increase will be considered as due to oxygen adsorbed after it has removed the initially adsorbed nitrogen from the surface. Since the electronegativity of oxygen is higher than that of nitrogen, the replacement may take place as a result of a charge-transfer mechanism, in which the bonding of adsorbed nitrogen is weakened by the impinging oxygen.

Bhattacharya, Broughton, and Perry[4] reported no preferential adsorption. The admission rate of the gas mixture in their experiment might be higher than that in the present experiment. When the rate was adjusted more highly (1×10^{-7} Torr/min) than that above mentioned (2×10^{-8} Torr/min), the work-function change as shown in Fig. 3 was obtained. Two-step processes such as those observed in the lower rate of admission of the mixture were not observed here. The work function quickly approached 5.54 eV, i.e., the

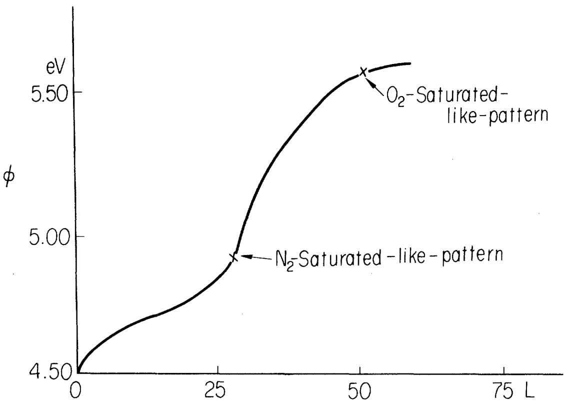

FIG. 2. Work-function change during adsorption of mixture of N_2 and O_2 as a function of exposure. Admission rate is 2×10^{-8} Torr/min.

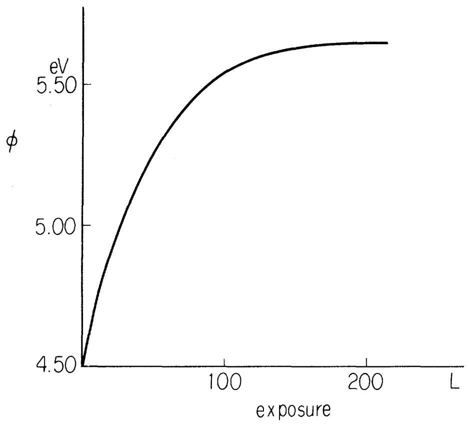

FIG. 3. Work-function change at admission rate of 1×10^{-7} Torr/min.

value for the oxygen-saturated tip. During this change no nitrogenlike pattern appeared; rather, an oxygenlike pattern appeared. Moreover, in the case of the lower rate of admission, when the admission was stopped on the way and the pressure was kept very low (~ 10^{-8} Torr), the replacement did not take place and only nitrogenlike patterns were obtained. So it seems that the replacement requires a certain critical quantity of impinging oxygen. Then, in the higher rate of admission, nitrogen will be easily replaced by oxygen in sufficient quantities as soon as nitrogen is adsorbed; on the other hand, in the lower rate of admission, nitrogen will continue to be adsorbed until the nitrogen-saturated surface is formed. Under the present experimental conditions, we may thus overlook the nitrogen-adsorbed surface, or we may observe only the oxygen-adsorbed surface as reported in Ref. 4. The critical quantity of oxygen needed may be determined by changing the oxygen pressure.

It is concluded that in the adsorption of the mixture of nitrogen and oxygen the preferential adsorption of nitrogen, the replacement of the adsorbed nitrogen by oxygen, and the adsorption of oxygen take place in sequential order.

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Nature of Melting and Superionicity in Alkali and Alkaline-Earth Halides

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A parameter-free theory is shown to provide an explanation for both melting in alkali halides, and superionicity in alkaline-earth halides, in terms of different types of instabilities of the perfect lattice.

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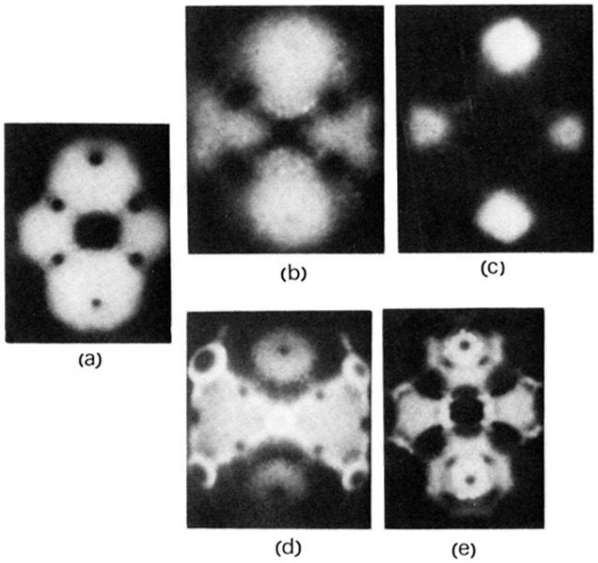
In a recent Letter[1] I reported results of parameter-free equation-of-state calculations for two alkali halides using the pair potentials of Gordon and Kim.[2] An intriguing result of this work was the *prediction* of a lattice instability which seemed to correlate with melting.[3] New, more accurate calculations for sixteen alkali halides[4] along with a detailed analysis of high-temperature thermal-expansion data[5] provide additional evidence that this instability plays a role in causing solids to melt. To further test the theory, I have applied it to a material which becomes superionic before it melts (CaF_2). In this case the results reveal a high-temperature instability of a different sort which is consistent with known properties of the superionic transition. Specific results for NaCl are used here to contrast with those for CaF_2 in explaining the two different types of instabilities.

The free energy of a crystal whose structure is given by its volume, V, may be written,[6]

$$F(V,T)=U(V)+\tfrac{1}{2}\sum_i h\nu_i + kT\sum_i \ln[1-\exp(-h\nu_i/kT)], \qquad (1)$$

where U is the ground-state electronic, or static, contribution to F and the last two terms are contributions due to crystal vibrations or phonons. The frequencies, ν_i, are classical frequencies of small-amplitude oscillations about the perfect lattice positions given by V, and the summation is over all normal modes of the system. The derivation of Eq. (1) assumes that the vibrational energy levels of the system are those of harmonic oscillators with frequencies ν_i (quasiharmonic approximation). Once the potentials are known U, $\{\nu_i\}$, and F can be determined for any volume and temperature, T, we choose. The frequencies


(a) (b) (c) (d) (e)

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