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V. A. Shishkin

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Abstract

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PHYSICAL CHEMISTRY

V. A. Shishkin

THE EFFECT OF THE SURFACE ON THE SHAPE AND BEHAVIOR OF MOLECULAR PATTERNS

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The nature of molecular patterns (m.p.), i.e., emission images appearing on the screen of an electron projector during condensation, on a point, of small amounts of vapors or gases, remains unresolved to the present day. None of the proposed hypotheses explains the whole body of accumulated experimental data ($^{1-4}$). To understand the nature of molecular patterns, it is at least necessary to know: the form of the bonding of the molecules that give rise to the observed m.p. with the surface and their geometrical position on it; the mechanism of electron transfer from the emitter to the molecule; the magnitude and character of the change in the symmetry of the electron clouds of molecules and of individual bonds in fields of $\sim 1 \cdot 10^8$ V/cm; and the character of the interaction of the electron beam with the charge distribution within the molecule.

For obvious reasons, obtaining answers to all the questions posed by carrying out direct experiments or model experiments does not yet appear possible. We have chosen an indirect route for studying the influence of the electrical properties of molecules, the influence of external factors (temperature, field, and pressure), and the nature of the surface on the shapes and behavior of m.p. for a broad range of substances.

The present article is devoted to the last question, i.e., to an experimental study of the influence of the electronic type of a solid body (metal, semiconductor, dielectric), crystallographic inhomogeneity, and surface relief on the shapes and behavior of m.p. The remaining questions will be treated in subsequent publications.

Influence of the electronic type of the emitter. In studying the adsorption of CO_2, divinyl, and ferrocene on Si and Ge tips, a control tube with a tungsten tip was simultaneously sealed in. The experiments showed that the

Fig. 1

Figure 1: Fig. 1

shapes of the observed molecular patterns on these semiconductors do not differ in any way from those observed on a metallic tungsten tip and obey the same regularities. However, the number of m.p. and their contrast with the surrounding background on Ge and Si were lower than on W (see Fig. 1).

In another series of experiments, before admitting C_3F_6, the tungsten tip was held in an atmosphere of N_2 or O_2. It is known that such treatment leads to the formation of a strongly bound chemisorbed layer that completely saturates the free bonds of the surface atoms. It turned out that the shapes of the m.p. do not depend on whether the adsorbed layers lying below them are formed by C_3F_6 molecules or by molecules of residual gases. At the same time, the contrast of the m.p. in this case is maximal. This indicates a dependence of the contrast on the work function of the emitter. Finally, heating a tungsten tip in an O_2 atmosphere with an anode field applied leads to the formation of a surface covered with crystallites. These crystallites collect in light rings around 100 and 110. The shapes of m.p. on such protrusions* also do not differ in any way from those observed on a clean tungsten surface.

Influence of crystallographic inhomogeneity. In experiments on the adsorption of various gases on W and H_2 and divinyl on Ge, no difference was found in the behavior or forms of molecular patterns at faces differing both in packing density and in work function*. True, at the beginning molecular patterns are observed more often around 111 and 100 ( ), where the frequency of their appearance is higher. However, this advantage is more likely connected with the higher emission capacity of these regions and the smaller local radii of curvature which, according to the ionograms obtained (6), these faces possess. As filling proceeds (especially in a strong field), redistribution of the adsorbed layer occurs and, judging by the emission pattern, the surface is uniformly covered with molecular patterns.

Fig. 1. *a* –H_2 on Ge. Only simple disks are observed. The contrast of the molecular patterns with the background is weak; *b* –ferrocene on a Si emitter not cleaned of the oxide film

Influence of the microrelief of the surface. Experiments on the adsorption of O_2, N_2, H_2, and C_2F_4 on tungsten tips reconstructed in the field confirm the preferential appearance of molecular patterns on regions with smaller radii of curvature. On these protrusions, which, according to (7), have heights of up to 12 Å, the course of adsorption differs from that described for atomically smooth

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* According to Gomer (5), these crystallites are oxides (WO_3). In the absence of a field, WO_3 is a dielectric.

Fig. 2

Figure 2: Fig. 2

planes. Molecular patterns can appear already at $p < 1 \cdot 10^{-7}$ mm Hg. The molecular patterns themselves are larger, and their concentration is so great that molecular patterns from two neighboring molecules are often not resolved.

Analogous results were also observed during adsorption on the above-mentioned ridges formed during reconstruction of the tip in an oxygen atmosphere or during heating in hydrocarbon vapors. In studying many complex or readily decomposed organic compounds (for example, CS_2), it was found that parasitic protrusions form by themselves during observation. The low temperature at which these protrusions disappear ($< 800^\circ$ K) apparently indicates that they are formed from decomposition products. The behavior of molecular patterns on parasitic protrusions, especially during adsorption of large linear molecules, is more complex; the frequency of disappearance of mutual transformations of molecular patterns at the same pressure is much higher here than on flat regions. The images overlap one another, and their shapes are often strongly distor—

···reduced. Sometimes very complex forms are observed; however, the short lifetime makes it difficult to determine their shapes and mutual transformations precisely. In the adsorption of benzene it was noticed that the number of "rosettes" on such a protrusion is greater than on flat regions. In the experiment with toluene, as one parasitic protrusion grew, the voltage required to maintain a constant current decreased. At the end of the experiment the anode voltage was only 1.1 kV ($I = 5 \cdot 10^{-7}$ A) instead of 14.5 kV at the beginning. As the microtip grew, the molecular patterns became less and less sharp, and at 1.1 kV it was already impossible to notice the separation of the "double leaf."

Fig. 2. Possible cases of the formation of submicroprotrusions on the surface of an emitter: **a** —a C_3F_6 molecule adsorbed on top of a layer strongly bound to the surface; **b** —an O_2 molecule adsorbed on a protrusion of the lattice; **c** —a large phthalocyanine molecule (14.5 Å) adsorbed "standing up" on a clean surface.

Thus, no effect has been found of the crystallogeometric inhomogeneity of the surface and of the electronic type of emitter on the shapes and behavior of molecular patterns, whose contrast relative to the background increases with the work function of the emitter. Only the microrelief of the surface has a substantial influence on the shapes and behavior of molecular patterns. It is most natural to relate this influence to a local enhancement of the field near microprotrusions, as well as to a change in its symmetry. Indeed, the high brightness of molecular patterns can be explained either by a lower local work function at the site of adsorption of the molecule, or by the presence of a stronger local field. Since active gases increase the work function, the first explanation is ruled out, and

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* Recently this was confirmed by Melmed and Müller on 10 metals ([1]).

the conclusion remains that a necessary condition for observing molecular patterns is the presence of a strong local field near the molecule. Although under conditions of a strong field one may imagine the formation of microprotrusions by the molecules themselves,* the presence of lattice protrusions facilitates their formation. Figure 2 presents three possible cases of the creation of a strong local field near a molecule.

In conclusion, the author considers it a pleasant duty to express gratitude to Corresponding Member of the Academy of Sciences of the USSR S. Z. Roginsky for valuable advice and constant attention to the work.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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* The formation of such protrusions will be considered in the next publication.

Note: Figure translations are in progress. See original paper for figures.

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