

Metallized submonolayers of atoms adsorbed on a nonconducting substrate

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When atoms are adsorbed on the surface of nonconducting ionic crystal, a delocalization of their electrons, which are drawn into the crystal, is possible. This results in an anomalous dependence of the heat of adsorption on the surface coverage and on the N -shaped I - V characteristic of the "surface metal".

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It is usually customary to assume that the adsorption of atoms on the surface of a crystal leads to a lowering of its conductivity, since the adatoms behave like traps with respect to the current carriers. Below, we shall examine the opposite situation, when the adsorption of atoms increases the surface conductivity of the crystal and can result in the appearance of a surface metal at intermediate degrees of surface coverage. Such a metal differs from the normal metal in that its "density" depends strongly on the temperature and pressure of the ambient gas, and therefore it should exhibit several anomalies of both quantitative and qualitative nature compared with a normal metal. Thus, the I - V characteristic of this metal can be N -shaped. On the other hand, delocalization of the adatom electrons results in a new mechanism of the dependence of the heat of adsorption on the surface coverage compared to the usual dipole-dipole repulsion.

The described effects are possible for the adsorption of electropositive atoms (Cs, etc.) on the surface of an ionic crystal when the adsorption centers are anions. Such an adsorption model, which was proposed in Ref. 1, assumes that the adatom electron is drawn from it into the crystal. Because of Coulomb attraction to the anion, the electron is localized in the ground state in the vicinity of the anion. Therefore, the adatom plays the role of a surface donor. If the distance d between the adatoms is reduced, the overlapping of the orbits of their electrons, which are drawn into the crystal, becomes appreciable. As usual, we must expect that at the critical value $d_c = \alpha r$, where r is the orbit radius and $\alpha \sim 1$, a delocalization of the electrons must occur. The fact that here the crystal is two-dimensional, in principle, does not prevent its metallization: at low temperatures the adatoms form a regular structure on the substrate, and direct experiments on freshly cleaved Ge surfaces² indicate that a metallic, two-dimensional conductivity exists in ordered systems down to very low temperatures.

If there is no surface-conduction band in the crystal spectrum for zero coverage, then we can use the continuous-medium approximation to determine the state of the adatom electron in the case of shallow electron levels. Since the electron wave function Ψ is zero at the crystal surface, Ψ corresponds to the lowest energy of an iso-

lated electron, which is equal to 0 outside the crystal and inside the crystal is the same as a p -type hydrogenlike wave function polarized perpendicularly to the crystal surface. It follows from this that $r = 2\epsilon_s/mc^2$, where m is the effective electron mass, $\epsilon_s = (\epsilon_i + \epsilon_e)/2$, and ϵ_i and ϵ_e are, respectively, the dielectric constants of the crystal and its surroundings. Calculation of the exact value of α involves large difficulties that have not been overcome even in the thoroughly studied three-dimensional case. The system-polarizability divergence condition, which is calculated in the approximation of van der Waal interaction between atoms ($d \gg d_c$), gives sufficiently good agreement ($\alpha \sim 0.3$). If the two-dimensional analog of this approach is used, a value of 0.2 would be obtained for α . In any case, these results for r and α indicate that the metallization conditions of surface donors cannot be significantly more stringent than those for volume donors, and the former are much more favorable than the latter for large ϵ_e (the crystal is bounded by a liquid).

When $d \ll d_c$, the delocalized electrons of the adatoms fill a surface layer with a thickness of the order of the shielding radius r_D . Their energy E_e is calculated in the Fermi-Thomas approximation. Since for sufficiently large r_D the energy of interaction of the adions with the lattice does not depend on their number, we obtain the following expression for the decrease of the heat of adsorption with filling

$$\delta Q = \frac{\partial E_e}{\partial n} = 7,7 \frac{e^2}{\epsilon_i a_B} (n a_B^2)^{4/5}, \quad a_B = \frac{\epsilon_i}{m e^2}, \quad n = d^{-2}. \quad (1)$$

This law is significantly different from the commonly accepted $\delta Q \sim n^{3/2}$ law which is valid for a dipole-dipole interaction between adatoms. For $\epsilon_e = 1$, $\epsilon_s = 10$, $m = 0.2 \times 10^{-27}$ g, and $n \approx a_B^{-2}$ we obtain from Eq. (1) a rather large value for δQ , ~ 0.5 eV.

It should be noted that because of the decrease of Q with filling, some other form of chemisorption, which is not accompanied by electron delocalization, can be energetically more favorable starting with a certain value of n . For example, the adsorption centers can be cations (the model of Ref. 3). The adatom electron in this case must be apportioned between the adatom and the acceptor and cannot be delocalized. Therefore, the Fermi level will remain unchanged despite an increase in surface coverage.

The current flow through the metallized layers of adatoms decreases simultaneously due to Joule heating the degree of surface coverage and the ordering of the adatom arrangement. The first effect involves a reduction in the number of carriers, the second one decreases their mobility. In both cases the Joule heating increases the resistance of the crystal. On the other hand, at a given potential difference the increase in resistance reduces the evolution of Joule heat, which results in a trend toward a lower resistance. Therefore, the Joule heating leads to considerable nonlinearity of the I-V characteristic of the system and produces a tendency toward instability of the homogeneous state of the adatom system.

Consider a crystal film with a thickness $2R$. It is assumed that current is flowing along both its surfaces $z = \pm R$. The penetration depth of the current into the crystal is small compared with R . Therefore, the heat-conductivity equation and its boundary conditions can be written in the form

$$\kappa \frac{d^2 T}{dz^2} = 0, \quad -\kappa \frac{dT}{dz} \Big|_{z=\pm R} = -\lambda [T(\pm R) - T_0] + eUnE^2, \quad (2)$$

where κ is the heat conductivity of the crystal, λ is the heat-transfer coefficient between the crystal and the medium, T_0 is the ambient temperature, and E is the electric-field intensity. The concentration of adatoms and the equivalent concentration of electrons, if we ignore the dependence of the heat of adsorption Q on the degree of coverage, are given by the expression

$$\gamma = \frac{n}{n_0} = \exp \left\{ Q \left[\frac{1}{T(\pm R)} - \frac{1}{T_0} \right] \right\}, \quad (3)$$

where n_0 is the concentration in the absence of a current. The temperature dependence of electron mobility U is ignored because of its weakness.

An analysis of Eqs. (2) and (3) shows that the I-V characteristic can have an N shape. If $(Q/T_0) \gg 1$, then the current maximum will correspond to $n \approx 1/3n_0$. For $U = 100 \text{ cm}^2/\text{V} \cdot \text{sec}$, $R = 3 \times 10^{-6} \text{ cm}$, $n_0 = 4 \times 10^{14} \text{ cm}^{-2}$, $\lambda = 8 \times 10^{-4} \text{ J/cm}^2 \text{ deg} \cdot \text{sec}$, $T_0 = 300^\circ \text{ K}$, and $Q/T_0 = 19$ this value is reached when $E = 2.5 \text{ V/cm}$ and $T(R) = 1.06 T_0$. As E increases the decreasing branch of the I-V characteristic again begins to increase because of the increase of λ with T .

An N -shaped I-V characteristic in materials with metallic conductivity is a new result. Until now, such I-V characteristics have been observed only in semiconductors; however, this effect in our case is completely different. A submonolayer of adatoms, which has metallic conductivity in weak fields, in strong fields can be divided into domains with a higher density of adatoms that have a metallic conductivity, and with a lower density of adatoms that have semiconducting properties. We call such domains adsorption-current domains. The N -shaped character of the I-V characteristic can also appear as a transient behavior of the current.

Although the above-developed theory is not directly applicable to homopolar semiconductors, the conductivity involving adatoms directly makes it possible to explain the experimental data of Ref. 4. According to these data, when Cs is adsorbed onto a very clean surface of p -type Ge, the surface conductivity σ initially decreases with an increase in the degree of coverage η , and then starts to increase sharply. The decrease of σ can be attributed to the fact that the Cs atoms, which are easily ionizable, act like surface donors and therefore compensate for the conductivity caused by acceptors. With a further increase of η the conductivity involving the Cs atoms directly becomes possible as soon as some of these atoms are ionized because of electron transitions to the acceptor levels. But the conductivity σ via the impurity band, which is formed from the atomic levels of Cs, will definitely be lower than the original σ_0 if the number of carriers remains equal to the number of ionized Cs atoms. The fact that σ is much larger than σ_0 for large η can be explained by assuming that the Cs electrons become delocalized. It would be desirable to conduct similar experiments on ionic crystals or homopolar semiconductors with an oxidized surface.

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