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FORMS OF CHEMISORPTION ON SEMICONDUCTORS

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Abstract

When considering the chemisorbed particles as defects of the semiconductor surface, this leads to the conclusion that various forms of chemisorption may exist: electrically neutral and charged, valence-saturated and radical, "weak" and "strong", reversible and irreversible. The mechanism of appearance of these forms and their role in chemisorption have been discussed.

The investigation of chemisorption on semiconductors is of interest on account of their wide application as catalysts. Being a necessary stage in catalytic processes, chemisorption is a chemical reaction in itself leading to the formation of bonds between the gas particles and the crystal surface due to the forces of exchange interaction between them. The formation of a chemisorption bond expresses itself in the appearance of new surface electron levels in the energy spectrum of the adsorbent-adsorbate system. Thus, when in chemisorbed state, the particle may be considered a surface defect. This conception, for which we are indebted to WOLKENSTEIN,1) entails many conclusions which can be proved experimentally and a great part of the investigations on catalysis upon semiconductors during the last decade is associated with confirmation or refutation of the above mentioned conception.2,3) The present work does not aim at discussion of the results of these studies. Our purpose is to consider the various forms of gas chemisorption on semiconductors according to the above conception.

The chemisorbed particles are considered as surface defects on the basis of a strict quantum mechanical treatment of the simplest cases of chemisorption.4~7) The adsorption of a monovalent electropositive atom leads to the formation of a quasimolecular orbital in immediate neighbourhood of the atom and the adsorption center. Being localized on this orbital, the valency electron is (to a greater or smaller extent) drawn into the lattice and the energy produced determines the strength of chemisorption bonding. This orbital has affinity with the conductivity electrons of the crystal. Therefore, the localization of such an electron on the orbital is an electron transition from the conductivity band to the local level caused by chemisorption. It should be taken into consideration that this level may be both occupied and unoccupied. This is the first distinction between the various forms of chemisorption. The localization of an electron or a hole on the level depends on the nature of lattice and the adsorbed particle as well as on the Fermi level position on the surface. The preliminary presence of electrons (holes) in the crystal is not necessary for they may appear during chemisorption.[8] This form of chemisorption is electrically charged. When the electrons and holes of an adsorbent do not participate in the chemisorption bond, the particle (together with its adsorption center) is electrically neutral. Therefore, the chemisorption forms may be charged and electrically neutral. The difference between them expresses itself in their effect on the work function and the electric conductivity of the adsorbent. The work function is influenced not only by the charged, but by the electrically neutral form as well for with the appearance of the latter there appears a dipole moment due to the deformation of the electron cloud of the particle. Only the charged form affects the electric conductivity causing changes in the concentration of current carriers in the subsurface layer.

The participation of current carriers in the formation of a chemisorption bond causes a change in the valence state of the adsorbed particle. A particle having a valence-unsaturated characer before adsorption (*i.e.*, a radical), becomes valence-saturated after the localization of an electron or hole of the semiconductor near it.[9] Thus, the conductivity electrons and holes play the part of free valencies of the crystal, positive and negative ones, respectively. On the contrary, with the transition of a valence-saturated particle (*e.g.* a hydrogen molecule) to the electrically charged form of chemisorption, it reaches an ion-radical state. The localization of the free valence of the crystal can be accompanied by its saturation at the expense of rupture of some bonds in the chemisorbed molecule, in particular, by dissociation of the molecule.[10]

The difference in the valency state of the chemisorbed particles is the second distinction between the various forms of chemisorption. From this point of view there are valence-saturated and radical forms of chemisorption. It is clear that this subdivision, although associated with the subdivision in electrically neutral and charged forms, does not coincide with it. The reactivity of chemisorbed particles changes due to the change in the valency state. The radical forms should possess higher reactivity than the valence-saturated. Here, the specificity of chemisorption and that of the catalytic action of semiconductors are closely associated.[11]

The various forms of chemisorption differ also in the strength of bonding between the chemisorbed particle and the lattice. When no electron or hole of the semiconductor participate in the bond, the chemisorption form may be called "a weak form" since capturing of an electron by an acceptor level (or of a hole by a donor level) always leads to strengthening of the chemisorption bond.[12] In other words, localization of the current carriers means transition of a particle into the state of "strong bonding" with the surface. As the binding energy of the "weak form" could be considerable, the term "weak form" is conventional.

The "weak" and "strong" forms do not necessarily coincide with the previous forms. The "strong form" is not always charged, *e.g.*, when the particle is adsorbed on an ionized electrically positive defect on the surface, the "weak form" will be the charged one. The localization on an electron makes it "strong" but electrically neutral.[13]

The difference between neutral and charged, valence-saturated and radical, "strong" and "weak" forms is associated merely with the presence of unoccupied and occupied chemisorbed levels. There are two more forms of chemisorption, reversible and irreversible, associated with the rate of capturing of electrons by the levels and their removal from the latter.[14,15] As can be shown,[1] only the neutral form of chemisorption participates in the exchange with the gaseous phase. On the other hand, the neutral and the charged forms pass continuously into each other, due to electron transitions. When the transitions of electrons proceed rapidly with respect to the exchange between the neutral form and the gas, the ratio of the two forms remains in quasiequilibrium during adsorption and desorption, *i.e.* it follows the changes of the Fermi level. On the contrary, when the exchange between the neutral form and the gaseous phase is the fast stage, equilibrium between the neutral and the charged forms is reached only with the establishment of adsorption equilibrium. Desorption will increasingly disturb the initial ratio of the two forms: at first, the neutral form leaves the surface and then (depending on the rate of discharging) the charged form too. The electron transitions can be hindered to a degree causing the neutral form to behave (for a certain time) as a reversible one, and the charged form as an irreversible one.

In conclusion, we should like to note that a variety of forms of chemisorption on semiconductors may exist: 1) electrically neutral and charged; 2) valence-saturated and radical; 3) "weak" and "strong"; and 4) reversible and irreversible. These forms are, however, associated by the same way of considering the chemisorbed particles as defects on the semiconductor surface.

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