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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 pro-
duced determines the strength of chemisorption bonding. This orbital has
affinity with the conductivity electrons of the crystal. Therefore, the localiza-
tion of such an electron on the orbital is an electron transition from the con-
ductivity 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 locali-
zation 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 ad-
sorbent. 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), be-
comes 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 hy-
drogen 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 semicon-
ductors 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 chemi-
sorption 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 unoc-
cupied and occupied chemisorbed levels. There are two more forms of chemi-
sorption, 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 tran-
sitions 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 chemi-
sorption 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 con-

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sidering the chemisorbed particles as defects on the semiconductor surface.

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