Excitation of nonequilibrium conductivity due to adsorption of hydrogen atoms on zinc oxide

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Nonequilibrium conductivity has been observed when hydrogen atoms are adsorbed on an epitaxial ZnO film. The effect is caused by nonequilibrium ionization of the surface states in the chemisorption events.

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Hydrogen atoms, adsorbed on zinc oxide, form shallow donor-type surface states, so that the adsorption is accompanied by an increase in the conductivity of the material (see, for example, Ref. 1 and the references give there). It is traditional to assume that the ionization of adatoms on a surface occurs in an equilibrium manner, and the electron density in the C band can be determined on the basis of Fermi–Dirac statistics[1]. Since the adsorption levels are very shallow (~ 0.1 eV[1]), the equilibrium between the adsorption states and the C band at relatively low temperatures is prevented even during the adsorption kinetics.

It is known, however, that the extothermic adsorption is accompanied by considerable energy release (~ 1 eV in the ZnO–H system[1]). The rapid dissipation of such a large energy in the crystal during a relatively low-intensity multiphonon process is difficult. Therefore, the released energy can, in principle, "live" a fairly long time ($\gtrsim 10^{-13}$ sec) on the surface in the form of a vibrational excitation of the Zn–H chemical bond formed during adsorption. The adsorption state can be electronically excited (ionization) by means of an electron-vibrational interaction.[2] This means that in addition to an equilibrium component there can also be a nonequilibrium component of the conductivity variation during adsorption, i.e.,

$$\Delta \sigma \ = \ \Delta \sigma_a \ + \ \Delta \sigma_a^* . \tag{1}$$

The equilibrium component $\Delta\sigma_a$ increases monotonically as the surface is filled by the atoms to some stationary value determined by the atom density on the surface and by the temperature of the sample.[1] Conversely, the nonequilibrium component $\Delta\sigma_a^*$, which is proportional to the chemisorption rate, must be maximum at the outset of the chemisorption process and approach zero as the system approaches the steady state. The goal of our work was to detect experimentally the nonequilibrium (adsorbo) conductivity.

As is clear from the foregoing, the adsorboconductivity $\Delta\sigma_a^*$ must be looked for in the initial portion of the adsorption process. The experimental difficulty of isolating the $\Delta\sigma_a^*$ component is associated, however, with the inertia of the supply of the gas that is to be adsorbed to the sample, i.e., the "prolongation" of the initial adsorption stage because of instrumentation effects. To overcome this difficulty, we used an atomic beam method, which made it possible to establish "instantaneously" a steady-state
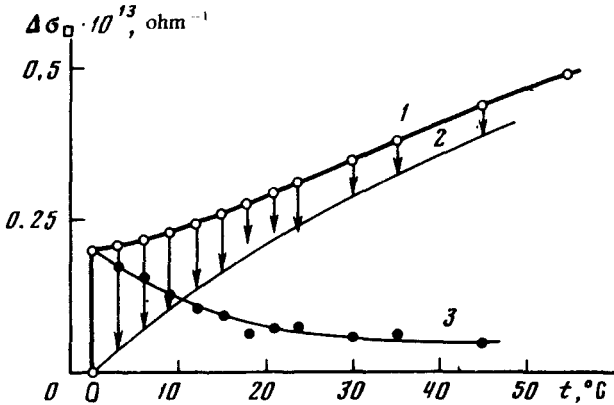
FIG. 1. Kinetics of variation of the conductivity of a ZnO film in a hydrogen atom beam for a sample temperature of 95 K, a source temperature of 293 K, and an atom beam density of $j = 5 \times 10^{13}$ cm^{-2} sec^{-1}: 1, total change in conductivity; 2, equilibrium component; 3, nonequilibrium component.

atom flux to the sample by opening the shutter blocking the beam. The three-chamber, high-vacuum system with an atomic beam, shaped by a multichannel source and sites, was described in Ref. 4. The H atoms were produced by means of a HF discharge in spectroscopically pure hydrogen. The ZnO sample (an epitaxial film on sapphire[3]) was subjected to a prolonged aging process in a high vacuum ($P \sim 8 \times 10^{-7}$ Torr) at a temperature of $T = 253$ K, and then it was quickly cooled to liquid nitrogen temperature (to reduce the equilibrium component of the conductivity). The shutter was then removed from the slit and the hydrogen atom beam was allowed to strike the sample. The beam density j was 0.5×10^{14} cm^{-2} sec^{-1}. The conductivity variation was recorded by a ED-05M electrometer (with a sensitivity of 10^{-15} A).

Figure 1 shows the kinetics of the conductivity variation of the ZnO film in the atomic hydrogen beam at a sample temperature of $T_0 = 95$ K and a source temperature of $T_s = 293$ K (curve 1). At the moment the atom beam is exposed the conductivity increases suddenly, and then it varies relatively slowly[4]. Shutting off (modulating) the beam in the initial part of the proces leads to a rapid synchronous decrease of $\Delta\sigma$ to the values on curve 2 (indicated by arrows). The short-lived part of $\Delta\sigma$, defined by the length of the arrows, decreases rapidly with time and disappears in the late stages of the process (curve 3). The observed kinetic behavior of $\Delta\sigma$ indicates that there are two components of $\Delta\sigma$, in accordance with Eq. (1). The latter can be rewritten in the following manner:

$$\Delta\sigma_\square = \mu_s e \, (1 - f \,) N + \mu_s e \, \eta_e \tau \, \frac{dN}{dt} \, . \tag{2}$$

Here $\Delta\sigma_\square$ is the specific surface conductivity,[5] μ_s is the mobility of the carriers, f is the Fermi function, N is the surface density of adatoms, η_e is the probability of electron excitation during adsorption, and τ is the lifetime of nonequilibrium electrons in the C band. As follows from (2), in the initial part of the process, when N is small and the derivative dN/dt is large, the second (nonequilibrium) term makes the major con-

tribution. The nonequilibrium conductivity decreases with time (the chemisorption rate decreases), and the filling of the surface with adatoms increases, so that the first (equilibrium) term in Eq. (2) is the dominant term in $\Delta\sigma$. This accounts for the observed behavior of the kinetic curve of $\Delta\sigma$. Since $\Delta\sigma_a^*$ is determined by the nonequilibrium electrons in the C band, a cessation of adsorption (interruption of the atom beam) at the outset of adsorption, when $\Delta\sigma_a^*$ dominates, leads to a decrease of $\Delta\sigma$ in a very short time (of the order of τ). However, a cessation of adsorption in its late stages, when $\Delta\sigma_a$ predominates, leads to a very slow decrease of $\Delta\sigma$ as a result of desorption of atoms.

In the case of Langmuir adsorption, we represent (2) in the following form

$$\Delta\sigma_\Box = \mu_s e (1-f) N_0 [1 - \exp(-\Omega_a j t)] + \mu_s e \eta_e \tau \Omega_a j N_0 \exp(-\Omega_a j t) \qquad (3)$$

or

$$\Delta\sigma_\Box = \Delta\sigma_{\Box(a)}(t) + \Delta\sigma_{\Box(a)}^*(0) \exp(-\Omega_a j \tau), \qquad (4)$$

where Ω_a is the adsorption cross section, j is the flux density of atoms to the sample. N_0 is the surface density of adsorption centers, and $\Delta\sigma_\Box^*(a)(0)$ is the initial surge of nonequilibrium conductivity. Using curve 3 in Fig. 1 and the expression for $\Delta\sigma_{\Box(a)}^*(t)$. we calculate from (4) the cross section for adsorption of a H atom on zinc oxide: $\Omega_a = 6 \times 10^{-16}$ cm^2. Setting $N_0 = 10^{15}$ cm^{-2}, we obtain an estimate for $\eta_e \tau (\eta_e \tau = 7 \times 10^{-12}$ sec).

In the given analysis of the experimental data we ignored the possible excitation of nonequilibrium conductivity in the atom recombination reaction that occurs together with adsorption: $\Delta\sigma_{\Box(r)}^* = \mu_s ej\tau^* \Omega_r^* (1-f)N$, where Ω_r^* is the cross section of the atom recombination reaction with electron excitation and τ^* is the lifetime of the excited charge carriers. During the initial surge of adsorboconductivity $\Delta\sigma_{\Box(r)}^* = 0$ since $N = 0$. Subsequently, $\Delta\sigma_{\Box(r)}^*$ does not contribute appreciably to the conductivity, since an abrupt decrease in the conductivity (during the time τ^*) due to blocking of the atom beam in the late stages of the process when N is large is not observed.

The discovery of nonequilibrium conductivity effect in the adsorption of gas particles on the surface of a solid indicates that there is a relaxation of the chemical energy by means of the electron system, rather than just the phonon system of the crystal. This can have a considerable influence on the existing concepts of energy transfer mechanisms at the boundary between a gas and a solid [catalysis, selective (laser) activation of adsorption and catalytic processes, adsorptive isotope separation, plasma etching of semiconductors, etc.]

In conclusion, we wish to thank V. L. Bonch-Bruevich for useful discussions of the results of this work.

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[1] The electron equilibrium is only slightly perturbed by the recombination reaction of atoms into a molecule that occurs simultaneously with the adsorption.[2]

[2] Bonch-Bruevich pointed out the possibility of nonequilibrium ionization of adatoms as early as 1950.[3]

[3] We wish to thank A. M. Bagamdova for kindly providing the film sample.

[4] A beam of H_2 molecules produced no effects.

[5] $\Delta\sigma_\Box = (1/b)\Delta\sigma$ (l is the sample length, and b is its width).

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