Activation energies of purely thermal and photostimulated desorption of oxygen from the surface of CdSe

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The kinetics of purely thermal and photostimulated desorption of oxygen from the surface of CdSe were measured. These measurements of semiconductors are among the first of their kind. The activation energies were determined for the removal of oxygen on the CdSe surface in a charged (0.78 eV) and neutral (0.13 eV) state.

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We shall examine n-type semiconductors with chemisorbed, acceptor-type molecules. The chemisorption was achieved by localizing a carrier in a surface state (SS) of adsorbed particles (charged adsorption). It is easy to see that in the absence of external excitation that can cause a redistribution of carriers in the electron subsystem of a crystal, the energy picture of the desorption of charged particles (E_c) is determined by their thermal ionization energy (E_t) and by the energy (E_n) needed to remove the molecules from the surface, which have entered the state of physical (neutral) adsorption as a result of ionization.

The transition of the system to a nonequilibrium state can destroy the SS by the recombination method, irrespective of the mechanism for generation of electron-hole pairs (Fig. 1a). As a result of nonequilibrium charge transfer of the latter, the energy E_c abruptly decreases by the amount E_t and desorption becomes easier. The energy picture of nonequilibrium desorption is completely determined by the value of E_n.

According to the aforesaid, a study of the thermal (equilibrium) and nonequilibrium desorption will serve as a direct method of determining the heat of different adsorptions and the parameters of the SS. In the available literature, however, there is no information on the kinetics of this type of desorption nor on the surface processes in semiconductors based on these kinetics.

We have performed such measurements using the CdSe + O$_2$ system. Although the electrical measurements[1-5] established that oxygen adsorption is effective, they have not solved the important problem of determining the SS parameters of the CdSe + O$_2$ system. Thus, an investigation of the latter, along with a determination of the adsorption energies, which have not been determined with equal accuracy for other semiconductors, should include an estimate of the SS characteristics.

The CdSe samples, which have a thin-film configuration, were grown on quartz by using the gas-transport-reaction method.[6] After the samples were grown, they were transferred to the working chamber in which they were subjected to a long (2.5 hours), vacuum $(p = 10^{-7}$ mm Hg) annealing $(T \approx 450$ K).
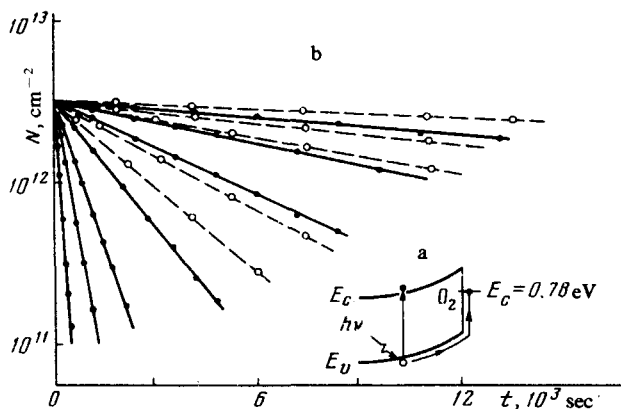
FIG. 1. (a) Energy level diagram of the CdSe + O_2 system. The arrows indicate the electron transitions with participation of surface states under nonequilibrium conditions, (b) kinetics of the high-temperature (350–450 K) dark desorption (solid lines) and of the low-temperature (130–200 K) natural-light-stimulated desorption (dashed lines) of oxygen from the surface of single-crystal CdSe films. The slope of the desorption lines increases regularly with increasing temperature. The equilibrium density of electrons in CdSe at 293 K is $n \approx 5 \times 10^{15}$ cm^{-3} and the mobility is $\mu_n = 200$ cm^2/V·sec. To reduce the influence of surface bending of the bands on the recombination processes, we measured the photodesorption in the region of high photoexcitation, where the value of E_n does not vary appreciably with exposure.

The experimental study of surface effects by using direct methods involves the difficult problem of measuring the density of absorbed particles (N). We have solved this problem, however, by directly estimating the value of N by using the resonant-piezoquartz-balance method.[7] The film substrate was used as the balance pan.
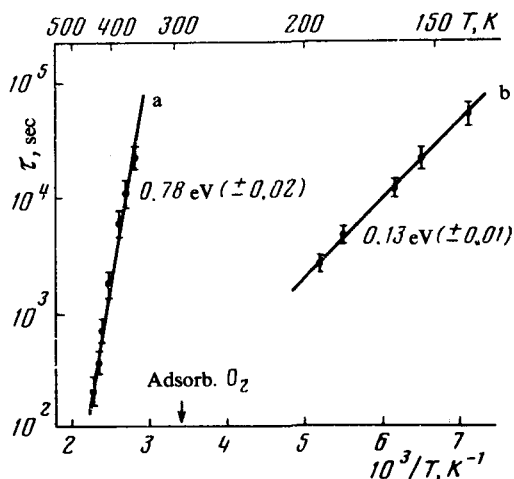

FIG. 2. Temperature dependence of the lifetime of oxygen molecules adsorbed on a CdSe film in the dark (a) and when the light in the intrinsic absorption region acted on the sample (b).

The oxygen adsorption was performed after a heat treatment at 293 K ($p_{O_2} = 10$ mm Hg). After reaching a certain value N, the oxygen was pumped out to $p = 10^{-7}$ mm Hg. The bound fraction is comparatively small ($N < 10^{13}$ cm^{-2}), which indicates that it exists in charged form on the surface.

This experiment was based on the idea that the temperature regions of purely thermal and nonequilibrium desorption can be "separated" because of the difference in the E_c and E_n values. Thus, the first type of desorption can be efficiently performed at high temperatures, whereas the second type, which is not attributable to thermal ionization of the SS, can be realized at low temperatures.

The kinetic curves of the high-temperature, purely thermal desorption and of the low-temperature, photostimulated[1] desorption are shown in Fig. 1b. We can see that the desorptions can be described by the exponential law $n_{c,n} = N_0 \exp(-t/\tau_{c,n})$. The lifetimes of the adsorbed particles under equilibrium and nonequilibrium conditions are $\tau_c = \tau_{c_0}\exp(E_c/kT)$ and $\tau_n = \tau_{n_0}\exp(E_n/kT)$. According to the data for the temperature dependence of the parameters τ_c and τ_n (Fig. 2), $E_c = 0.78$ eV (± 0.02), $\tau_{c_0} = 7\times10^{-8}$ sec, $E_n = 0.13$ eV (± 0.01), and $\tau_{n_0} = 7\times10^{-1}$ sec.

The purely thermal desorption and photodesorption occur in two stages. The non-activiation processes of drift and recombination of holes at the SS are responsible for the first stage of photodesorption (Fig. 1a). Therefore, the photodesorption energy $E_n = 0.13$ eV should be included in the second stage of thermal removal of molecules that have been neutralized as a result of recombination.

Understanding the role of polarization van der Waal interaction shows that the physical-adsorption energies must be in the range $E_n = 0.01$–0.1 eV.[8] The E_n value experimentally measured by us in close to the upper limit of this interval.

Both states of the purely thermal desorption—thermal ionization of the SS and removal of the neutral particles—are activation processes. By extrapolating the straight line $\tau_n = f(1/T)$ to the high-temperature desorption region (Fig. 2), we can easily prove that the contribution of the second state to the value $\tau_c = \tau_t + \tau_n$ is small (τ_t is the lifetime of carriers in the SS) and that the purely thermal desorption rate is limited by the first stage ($\tau_c = \tau_t$). The activation energy measured from the data of the $\tau_c = f(1/T)$ dependence is determined by the quantity $E_t = E_c$. Thus, the depth of the oxygen SS of CdSe with respect to the conduction band is $E_t = 0.78$ eV (± 0.02).

At $\tau_c = \tau_t$ the pre-exponential factor is $\tau_{c_0} = (v_n N_c S_t)^{-1}$, where v_n is the thermal velocity of electrons, N_c is the effective density of states in the conduction band, and S_t is the electron capture cross section of the SS. At $\tau_{c_0} = 7\times10^{-8}$ sec (see above) a calculation gives the value $(1$–$5)\times10^{-19}$ cm^2 for S_t.

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[1]Desorption by the action of light, which we assumed to be the external excitation, is known as "photostimulated" desorption, despite its recombination.[8] This terminology was used in this paper, although the term "recombination-stimulated" describes the process more precisely. This terminology can also be used with a different nonequilibrium factor.

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