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The Effect of Bulk Compensation on the Sorption-Dependent Semiconductivity of Thin Evaporated CdS Films*

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The effect of compensation on the chemisorption-dependent semiconductivity of thin evaporated CdS films is described. An exponential surface state distribution is associated with the chemisorption.

Introduction

There have been numerous studies eliciting the effects of oxygen chemisorption on the conductivity of both single crystals (*1*) and thin films (*2–5*) of the *n*-type materials CdS and CdSe. Most of these efforts interpret the chemisorption mechanism and the observed reduction in the conductivity by treating the chemisorbed oxygen as an acceptor-like surface state derived from the electron affinity of the oxygen. Considerable effort has been expended to determine the surface state density associated with the adsorbate (*1, 6*). Examination of disordered single crystal surfaces (*1, 7*) and of evaporated thin films (*1, 8*), has revealed that an exponential distribution $D_s(E) = N_s \exp(E - E_c)/kT_c$ with $E < E_c$, where E_c is the conduction band edge and T_c is a spread parameter, gives the best fit with experimental data. Observations with single crystals have further revealed that ordering the surface so as to give a good LEED pattern causes the adsorbent to become inert to chemisorption (*7, 9*). Chemisorptive activity has thus been associated with surface disorder and the observed exponential distribution has been interpreted accordingly (*7*).

Unrecrystallized thin films are inherently disordered; hence, the observed exponential chemisorption state distribution is not surprising. In addition to being sensitive to the degree of surface order, the ability of an electron transfer adsorption to influence the adsorbent semiconductivity should also depend on the bulk semiconductor parameters. Specifically, the degree of compensation should exert a strong influence on the magnitude and adsorbate pressure dependence of the adsorbate-sensitive semiconductivity (*1*). The purpose of this study was to investigate these relationships with the aid of evaporated CdS films. The principal conclusion is that it appears to be possible to control the ambient-sensitive semiconductivity by bulk compensation in a predictable way.

Description of Samples

The evaporated films were supplied by the Bell and Howell Research Laboratories, Pasadena, CA. They were prepared by evaporating CdS onto a heated (225°C) glass substrate in a vacuum of 10^{-5} Torr. All the films were *n*-type. Prior to CdS evaporation, the substrates were cleaned by an argon glow discharge. Some of the films were subsequently compensated with gold by diffusion from an evaporated underlayer while others were doped with copper by spraying $CuCl_2$ onto the top surface and subsequently diffusing the copper into the lattice. The films are therefore divided into three types: I, with no compensation; II, with only gold compensation; III, with only copper compensation. Specimens of area 1/2 × 1/2 in. were used for the electrical measurements. Film thicknesses ranged from 5 to 10 μm. Ohmic indium contacts were applied in a nitrogen atmosphere so that the current flowed parallel to

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the substrate. The sample chamber and dc measuring circuit have been described elsewhere (*6*).

Experimental Procedure

The following sequence was adopted to record the data: (1) The sample was mounted in the vacuum system which was subsequently pumped to its lowest pressure (~10^{-8} Torr). (2) The samples were heated to 140°C (less than the melting point of indium) and simultaneously illuminated with light of energy exceeding the bandgap. The combination of thermal-and photodesorption (*10*) required about 24 hr to achieve the "desorbed state" for a virgin sample. The desorbed state was defined at that giving the maximum steady state photocurrent (*5*, *6*). (3) The illumination was removed and the photocurrent was allowed to decay to the equilibrium semiconductivity. This also required about 24 hr. (4) The sample (still at 140°C) was cooled by contacting the thermal finger with liquid nitrogen. The current was recorded simultaneously during the cooling period. When the temperature reached its minimum (−163°C), the sample was slowly heated (20°C/hr) during which the sample current was again monitored. (5) When the maximum temperature (140°C) was again reached, the oxygen pressure in the system was raised to the next highest value. Both temperature and pressure were then held constant for 24 hr to allow for the establishment of a new equilibrium. (6) Steps 4 and 5 were then repeated and a set of current-temperature curves with oxygen pressure as parameter was obtained.

Data and Interpretation

The dominant influence of adsorbed oxygen on the conductivity of CdS evaporated thin films cannot be overstated. In the absence of oxygen or of other compensating acceptor-like adsorbates (*11*), the equilibrium conductivity of the type I (no deliberate bulk compensation) is so high that they manifest a rather small incremental photoconductivity. This is illustrated by curve (a) of Fig. 1 which was recorded at 140°C, 2×10^{-8} Torr and 680 μW/cm^2 sec illumination at 0.4 μm (*10*). In contrast, curve (b) was recorded at the same temperature and illumination but at 1 atm. The data were recorded with 1 V applied to the sample. There is almost a five decade change in the equilibrium current and a three decade incremental photoconductivity at 1 atm.

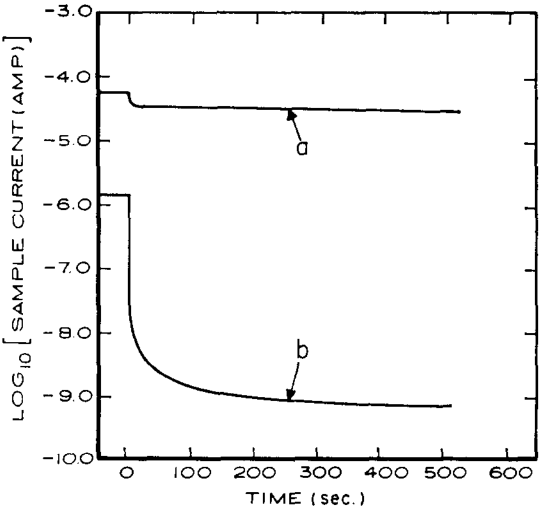

FIG. 1. Photocurrent decay in type I film at 140°C: (a) 2×10^{-8} Torr, (b) 1 atm oxygen.

Figure 2 shows the semiconductivity (log sample current vs $1/T$), also recorded with 1 V applied to the sample, with oxygen pressure as parameter of a representative type I film. These data were recorded during the fast cooling of the

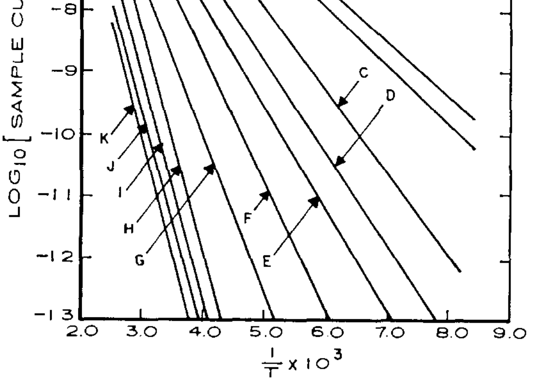

FIG. 2. Semiconductivity in type I film. Oxygen pressure (Torr): (A) 4×10^{-8}; (B) 6×10^{-7}; (C) 5×10^{-6}; (D) 5×10^{-5}; (E) 5×10^{-4}; (F) 5×10^{-3}; (G) 5×10^{-2}; (H) 5×10^{-1}; (I) 5; (J) 50; (K) 760.

sample. The slow heating curves are essentially the same.

By comparing the experimental data of Fig. 2 with similar data generated by a modeling calculation based on several assumed adsorption state densities the exponential distribution mentioned in the introduction is most suitable for achieving agreement. Two examples of such a computation for different sets of parameters are given in Figs. 3 and 4. These were obtained by computing the average conduction band electron concentration $\langle n\rangle$ from

$$\langle n\rangle = \frac{N_c}{W}\left[\exp\left(\frac{-[E_c(0)-E_f]}{kT}\right)\right]\int_0^W e^{-V(z)/kT}\,dz, \tag{1}$$

where N_c is the conduction band effective density of states and where the remaining notation is given in Fig. 5. The parameters $[E_c(0) - E_f]$ and $V(z)$ are obtained from a simultaneous solution of the charge neutrality equation and the Poisson equation [Eqs. (2) and (3) of Ref. (*1*)], where the surface state density in the charge neutrality equation has been equated to an exponential distribution (*1*). Other analytically simple and physically plausible distributions give a poorer accounting of the experimental data. Such distributions include discrete (*1*) $[N_s\delta(E - E_s)]$, uniform (*1*) [N_s constant over ΔE_s] and gaussian (*8*) $[N_s\exp - (E_s - E)^2/(kT_c)^2]$. Physical plausibility for the exponential distribution rests on the association of adsorption sites with surface disorder (*7*).

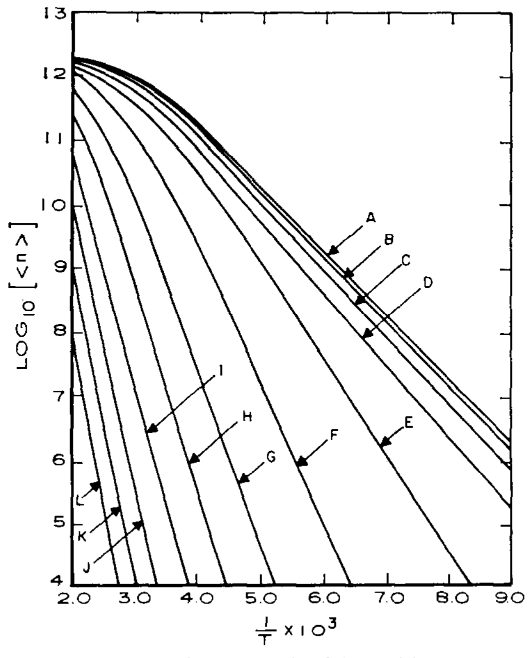

FIG. 3. Computed semiconductivity with the exponential surface state distribution. $T_c = 1000°K$, $N_d = 10^{16}$ cm^{-3}, $N_d - N_a = 2 \times 10^{12}$ cm^{-3}, $E_{cd} = 0.2$ eV, $W = 0.001$ cm. Parameter N_s cm^{-2} eV^{-1}: (A) $\leq 10^{11}$; (B) 3×10^{11}; (C) 10^{12}; (D) 3×10^{12}; (E) 10^{13}; (F) 3×10^{13}; (G) 10^{14}; (H) 3×10^{14}; (I) 10^{15}; (J) 3×10^{15}; (K) 10^{16}; (L) 3×10^{16}.

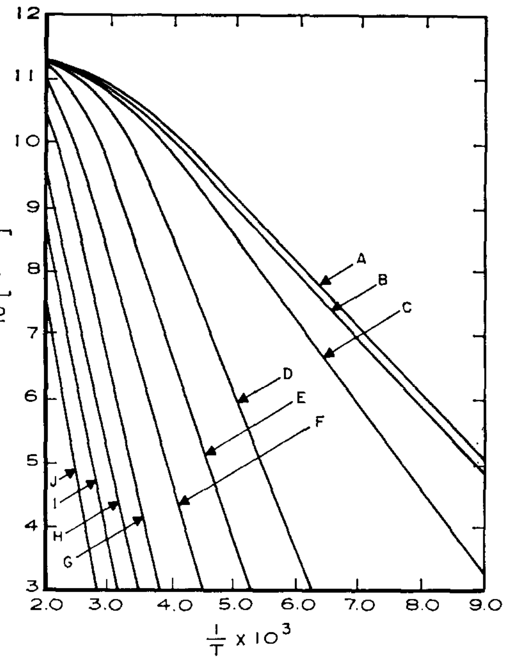

FIG. 4. Computed semiconductivity with the exponential surface state distribution. Materials parameters the same as in Fig. 3 *except* $N_d - N_a = 2 \times 10^{11}$ cm^{-3}. Parameter N_s cm^{-2} eV^{-1}: (A) $\leq 3 \times 10^{10}$; (B) 10^{11}; (C) 3×10^{11}; (D) 10^{12}; (E) 3×10^{12}; (F) 10^{13}; (G) 3×10^{13}; (H) 10^{14}; (I) 3×10^{14}; (J) 10^{15}.

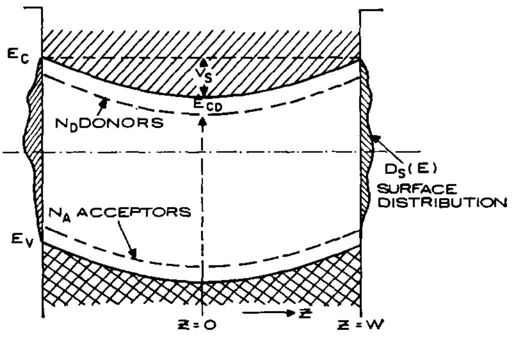

FIG. 5. Schematic energy band diagram: $E_c(E_v)$, conduction (valence) band edge; E_f, Fermi level.

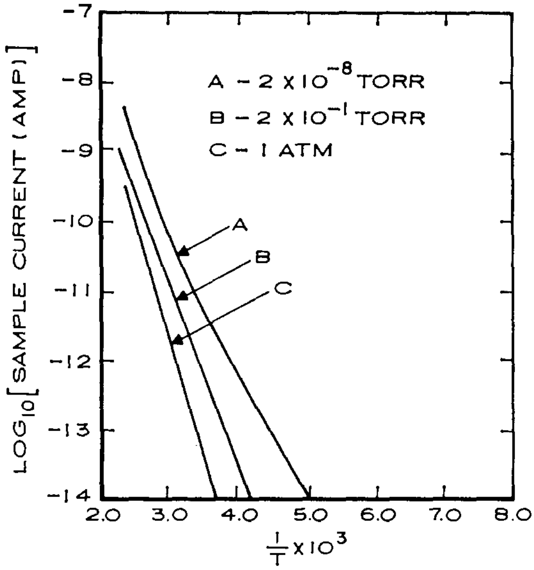

FIG. 6. Semiconductivity in type II (gold compensated) film.

The ambient-sensitive semiconductivity of the type II (gold compensated) and type III (copper compensated) films is illustrated by Figs. 6 and 7, respectively. These differ from the uncompensated type I films in the following ways: (1) At low oxygen pressures, the semiconductivity activation energy is higher. (2) At any given oxygen pressure, the corresponding semiconductivity is lower. (3) At any given temperature, the decrease in the current with a given pressure increment is substantially reduced.

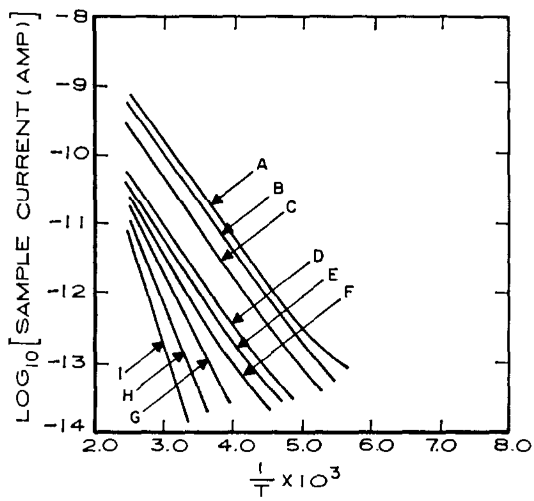

FIG. 7. Semiconductivity in type III (copper compensated) film. Oxygen pressure (Torr): (A) 3×10^{-8}; (B) 3×10^{-7}; (C) 3×10^{-6}; (D) 3×10^{-5}; (E) 10^{-4}; (F) 10^{-3}; (G) 3×10^{-2}; (H) 10; (I) 760 (1 atm).

A qualitative understanding of the first two characteristics, particularly the second, follows from the fact that both gold and copper are acceptors in CdS (they are monovalent cations incorporated substitutionally for Cd). An analytic understanding is achieved using the case of a discrete chemisorption state as an example. For the δ-function distribution, it has been shown (*6*) that $\langle n\rangle$ is given by

$$\langle n\rangle = \left[\frac{N_c N_d}{(N_s/W)}\right]\left[\frac{\sqrt{\pi}\,\mathrm{erf}(V_s/kT)^{1/2}}{2(V_s/kT)^{1/2}}\right] \times \exp\left[-\left(\frac{E_{cs}-V_s}{kT}\right)\right]; \quad N_s > W(N_d - N_a) \qquad (2)$$

where V_s is the surface potential for complete depletion of the semiconductor:

$$V_s = eW^2(N_d - N_a)/2\kappa\epsilon_0, \qquad (3)$$

and E_{cs} is the depth of the surface state relative to the conduction band edge. It has also been shown (*6*) that

$$\langle n\rangle = \frac{N_c}{N_d}[N_d - N_a - (N_s/W)]\,e^{-E_{cd}/kT}; \quad N_s < W(N_d - N_a). \qquad (4)$$

Because the low surface coverage case Eq. (4) contains no surface parameter in the exponent, it can conveniently be referred to as a bulk-controlled regime. By parallel reasoning, the high coverage case Eq. (2) can be considered a surface-controlled regime. It is thus clear from these two equations that to observe the bulk-controlled regime it is necessary that $N_s < W(N_d - N_a)$. It must also be noted in passing that $E_{cs} - V_s$ must always be greater than E_{cd}; otherwise one would have an energetically unfavorable condition for electron transfer into the surface states. This condition has two consequences (*6*). First, the slope of the bulk-controlled semiconductivity is always less than that of the surface-controlled semiconductivity. Second, by combining the above condition with Eq. (3), one obtains

$$(N_d - N_a)\,W^2 < 2\kappa\epsilon_0 E_{cs}/e, \qquad (5)$$

which is a necessary condition involving semiconductor bulk, surface and geometric parameters for observing a surface-controlled regime.

The foregoing stipulates that to observe a bulk-controlled regime with a sample compensated to reduce $N_d - N_a$, a corresponding reduction in surface state concentration and hence in adsorbate pressure would be required. As the uncompensated type I films exhibit a transition between a bulk-controlled and a surface-controlled regime (the semiconductivity curves show a larger change in activation energy with increasing adsorbate pressure than the compensated films), it is reasonable to suggest that the compensated type II and type III films are always in the surface-controlled regime, even at the lowest adsorbate pressures (smallest N_s), as there is a much smaller change in the activation energy with pressure here, especially with the type II film, than there is with the uncompensated type I film. If the adsorption surface state were discrete, the ratio $R =$ (slope at 1 atm)/(slope at $\sim 10^{-8}$ Torr) should approach unity when compensation moves the bulk-controlled regime below 10^{-8} Torr. However, the semiconductivity curves are better interpreted with an exponential adsorption state distribution. The data from Figs. 2, 6 and 7 reveal that R(type I) = 3.7, R(type II) = 1.75 and R(type III) = 2.25, respectively. We may use the computed curves of Figs. 3 and 4, which may be taken to represent the uncompensated (better, *less* compensated) and compensated cases, respectively, to compute similar ratios for a qualitative comparison. If we take $N_s = 10^{12}$ cm^{-2} (curve C of Fig. 3 and curve D of Fig. 4) to represent the high vacuum case, and $N_s = 10^{15}$ cm^{-2} (curve I of Fig. 3 and curve J of Fig. 4) to represent the 1 atm case, we obtain R (Fig. 3) = 3.25 and R (Fig. 4) = 2. That is, we obtain values similar to the experimental ones and only a reduction in R with compensation (as observed) rather than an approach to unity as the discrete surface state model would require. Our interpretation is strengthened further by Fig. 8, which depicts the photoconductivity decay of a type I film (a) and that of a type II film (b), both at 2×10^{-8} Torr. Comparison of curve (b) for the type II film with curve (b) of Fig. 1, which shows the decay of a type I film at 1 atm, that is, in the surface-controlled regime, indicates that the type II film is in the surface-controlled regime even at 2×10^{-8} Torr.

A qualitative understanding of the strong reduction in the current level in the surface-controlled regime with increasing compensation, that is with decreasing $N_d - N_a$, can also be obtained from the analysis of the δ-function model (*6*). It follows from Eqs. (2) and (3) that $N_d - N_a$ occurs in the exponent of $\langle n \rangle$ in the surface-controlled regime.

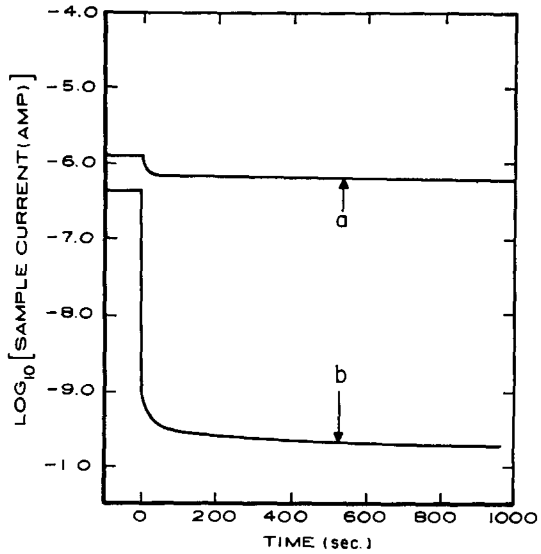

FIG. 8. Photocurrent decay at 140°C and 2×10^{-8} Torr: (a) type I film; (b) type II film.

More quantitatively, computer solutions for the exponential distribution show a similar phenomenon, as can be seen from Figs. 3 and 4 which are computed semiconductivity curves for identical parameters except $N_d - N_a$. For Fig. 3, $N_d - N_a = 2 \times 10^{12}$ cm^{-3} while for Fig. 4, $N_d - N_a = 2 \times 10^{11}$ cm^{-3}. In the former case, for example, taking $N_s = 10^{14}$ cm^{-2} eV^{-1} and $1/T = 3 \times 10^{-3}$ (°K)$^{-1}$, $\langle n \rangle = 10^{10}$ cm^{-3}, while in the latter case, for the same choice of parameters, $\langle n \rangle = 10^5$ cm^{-3}. Thus a one decade improvement in compensation (i.e., reduction in $N_d - N_a$) causes a five decade reduction in $\langle n \rangle$. This phenomenon is quite general and is independent of the specific choice of surface state distribution. Hence its experimental observation with a specimen whose surface state distribution is only approximated with an analytical distribution is not surprising. The physical explanation of the strong reduction of $\langle n \rangle$ with decreasing $N_d - N_a$ is as follows. A smaller $N_d - N_a$ is associated with a smaller surface potential V_s [Eq. (3)] in the surface-controlled regime. Therefore, the transfer of electrons from the conduction band to the surface is less retarded than for the case where V_s is larger, corresponding to a higher $N_d - N_a$.

The third characteristic of the type II and type III films cannot as yet be accounted for on the basis of the physical models under discussion here because these contain N_s as a parameter while in the measurements, the adsorbate pressure is the parameter. The N_s (pressure) dependence is required to clarify this point and it is known from measurements with single crystals that N_s (pressure) depends on surface treatment in a complicated way (*7*, *9*). As instrumentation limitations made it impossible to investigate N_s (pressure), nothing further of substance on this point can be said at this time.

Conclusions

We have observed large changes in the electrical conductivity of evaporated CdS thin films brought on by exposure to oxygen and particularly that this ambient-sensitive conductivity can be strongly influenced by semiconductor doping. These results have been interpreted with a chemisorption model in which the adsorbate surface state distribution is best approximated by an exponential density of states function.

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