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Relationship between photodesorption and surface conductivity in ZnO

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We report measurements of CO_2 photodesorption and associated surface-conductivity changes in ZnO. The measurements show a one-to-one correspondence between the rates of those two quantities. The rates of both CO_2 photodesorption and surface-conductivity changes are initially fast, becoming much slower with illumination time. A calculation, based on the assumption that this time rate of change is related to a change in the degree of band bending during photodesorption, shows excellent agreement with the experimental results. This model is further supported by Auger-electron-spectroscopy measurements. The cross section for photodesorption is estimated to be $\sim 10^{-17}$ cm^2.

I. INTRODUCTION

During the last 20 years chemisorption on and photodesorption from semiconductor surfaces have been investigated both theoretically and experimentally. The relationship between the surface conductivity and the density of the chemisorbed species has been firmly established, particularly in such materials as ZnO. Although the concept of a charge-transfer phenomenon involving the adsorbed species and the semiconductor has been mentioned in the literature since the turn of the century, it was Morrison[1] who in 1955 proposed the currently accepted model of chemisorption on a semiconductor surface. In this model of oxygen chemisorption, the oxygen atoms, or molecules, capture conduction electrons from the adsorbent and are held as negative ions on the surface. As a consequence the process of creating chemisorption bonds causes a decrease in the surface conductivity of the semiconductor.

The details of the chemisorption kinetics were later investigated by Medved.[2] He observed an Elovich-type chemisorption which is characterized by the fact that surface conductance depends on the logarithm of the duration of oxygen exposure. This type of time dependence was also observed by Van Hove and Luyckx[3] who attributed the rate limiting step in the adsorption process to the rate of capture of electrons which must migrate through the created depletion layer. Another study by Arijs *et al.*[4] done under weak accumulation conditions, shows that the surface resistivity depends linearly on the duration of oxygen exposure.

Recent oxygen chemisorption studies by Eger *et al.*[5] established that a change in the initial conditions from weak accumulation to very strong accumulation can cause a change in the dependence of the chemisorption rate from a power of ΔN_e, the excess electron density, to an exponential dependence on ΔN_e.

The chemisorption bond can be broken by photogenerated holes that migrate to the surface where they can neutralize the chemisorbed species. The neutralization of the chemisorbed ion marks the transition of the adsorbed species from the chemisorbed state to a physisorbed state which can then thermally desorb at relatively low temperatures. This model of photodesorption was proposed by Melnick[6] and subsequently utilized by Medved[7] to explain his observation on powdered ZnO; and by Collins and Thomas[8] in their study of ZnO single crystals.

Recently[9] photodesorption measurements by Shapira *et al.*, utilizing mass-spectrometer detection, indicate that CO_2 is the only species desorbed from ZnO. The CO_2 is assumed to have been created by the prior oxidation of surface carbon impurities during the period the surface was exposed to oxygen. By observing the correlation between the conductance change and the simultaneous decay in the rate of CO_2 photodesorption, it has been established[10] that it is indeed CO_2 photodesorption which is responsible for the observed persistent conductivity changes caused by irradiation. Thus, in principle, these measurements confirm the substrate-dependent mechanism suggested by Melnick and provide the first quantitative data on the relationship between the photodesorption and accompanying conductivity changes.

The existence of such data lead us to attempt to formulate a suitable quantitative framework which is based on the accepted model.

In the present paper we develop the rate equations for the surface density of the charged chemisorbed species, of the neutralized species, and of the free holes and electrons. These equations are solved analytically utilizing experimentally supported approximations to yield the illumination time dependence of the surface concentrations of free carriers. In these equations we do not take into account the photocarrier contribution to the conductivity, i.e., the current through the sample is measured *after* the completion of the light pulse so that the only observable effect is due to the *change* in the surface density of adsorbed carbon dioxide ions. In Sec. III the theoretical predictions are compared with experimental results.

II. THEORY

In the model of chemisorption and photodesorption as proposed by Morrison[1] and Melnick[6] it had been assumed that O_2^- is the species which is adsorbed, photodesorbed and which simultaneously causes changes in the conductivity of ZnO. As recent mass-spectrometer measurements[9] have indicated, however, it is CO_2 which is photodesorbed causing changes in the conductivity. On the basis of this observation, we present a modification of the model previously proposed by Morrison and Melnick:

Oxygen molecules approach the ZnO surface and are physically adsorbed at or near surface impurity carbon atoms. The carbon impurities are oxidized in a process that includes the capture of electrons from the ZnO conduction band to form CO_2^- species which are thus chemisorbed to the surface. The removal of electrons from the conduction band manifests itself in a decrease in surface conductivity.

In the photodesorption process, it is suggested that the free holes photogenerated near the surface migrate to the surface where they can recombine with and neutralize carbon dioxide ions which are then desorbed.

An accumulation layer is built up at the surface due to the removal of the negatively charged ions and an increase in the surface conductivity results. As the process continues the CO_2^- concentration decreases, which causes a change in the degree of bending of the energy bands. Thus as the photodesorption process continues it is increasingly difficult for the photogenerated holes to get to the surface, with the result that the rate of photodesorption decreases with continued exposure to band-gap radiation.

In the following calculation we consider continuity equations for the four species of interest. In so doing we assume that only those holes generated within a small distance δ from the surface take part in the photodesorption process and that the remaining photogenerated holes recombine with electrons.

N^-, the surface density of adsorbed CO_2^-, N, the surface density of neutral carbon dioxide molecules, n_s, the volume density of free electrons within δ, and p_s, the volume density of free holes within δ are related by the following four equations:

$$\frac{dN^-}{dt} = An_sN - Bp_sN^-, \tag{1}$$

$$\frac{dN}{dt} = Bp_sN^- - An_sN - \beta N, \tag{2}$$

$$\frac{dn_s}{dt} = \alpha f_0 - An_sN + \frac{n_s\mu_nE_s}{\delta} - \frac{n_s}{\tau_n}, \tag{3}$$

$$\frac{dp_s}{dt} = \alpha f_0 - Bp_sN^- - \frac{p_s\mu_pE_s}{\delta} - \frac{p_s}{\tau_p}, \tag{4}$$

The first term on the right-hand side of Eq. (1) represents the generation of ionized carbon dioxide from neutral molecules on the surface, i.e., the reaction between electrons and neutral molecules to form ions. A is a constant cross section of this reaction. The second term reflects the annihilation of ionized carbon dioxide due to recombination collisions with photogenerated holes. B is a constant cross section of this reaction. In Eq. (2) the last term on the right-hand side indicates the removal of neutral CO_2 due to thermal desorption. β is a constant. The first term in the right-hand side of Eqs. (3) and (4) is the optical generation rate of electrons and holes, respectively. α is the light penetration constant and f_0 is the incident flux. The next to the last term in Eq. (3) and Eq. (4) represent the current of electrons and holes into and out of the small region δ, caused by the internal electric field E_s at the surface. μ_n and μ_p are the electron and hole surface mobilities, respectively. The last terms in Eqs. (3) and (4) yield the direct recombination rate of holes and electrons. The internal field E_s is given by

$$E_s = (e/\epsilon)[(N_0^- - N^-) + (\Delta N)_0],$$

where e is the electronic charge and ϵ the dielectric constant. At $t=0$, $N^- = N_0^-$ and $E_s = (e/\epsilon)(\Delta N)_0$; thus $(\Delta N)_0$ is the surface charge density at $t=0$.

After a very short time (of the order of $\tau_p + \delta/\mu_pE_s$) the hole concentration will be essentially constant, i.e., $dp_s/dt = 0$ and the hole concentration at the surface is given by

$$p_s = \alpha f_0/(C + DN^-), \tag{5}$$

where

$$C \equiv (\mu_p e/\delta\epsilon)[N_0^- + (\Delta N)_0] + 1/\tau_p, \tag{6}$$

and

$$D \equiv B - \mu_p e/\delta\epsilon. \tag{7}$$

We assume further that under high-vacuum conditions, the hole–CO_2^--molecule recombination rate is much higher than the rate of electron capture to form chemisorption bonds, i.e., $Bp_sN^- \gg An_sN$ so that the substitution of Eq. (5) into Eq. (1) yields

$$\frac{dN^-}{dt} = -\frac{B\alpha f_0 N^-}{C + DN^-}, \tag{8}$$

which integrates to

$$C\ln(1 + \Delta N/N_0^-) - D\Delta N = -B\alpha f_0 t, \tag{9}$$

where $\Delta N \equiv N_0^- - N^-$ is the change in the surface density of ionized CO_2 and is therefore directly related to the excess electron concentration ΔN_e.

If the change in the surface density of CO_2 ions is small compared to the initial concentration, i.e., if $\Delta N/N_0^- < 1$, then Eq. (9) becomes

$$C[(\Delta N/N_0^-) + \tfrac{1}{2}(\Delta N/N_0^-)^2] + DN_0^-(\Delta N/N_0^-) = B\alpha f_0 t. \tag{10}$$

From the magnitudes of the constraints involved it is reasonable to assume that

$$(C + DN_0^-)(\Delta N/N_0^-) \ll \tfrac{1}{2}C(\Delta N/N_0^-)^2. \tag{11}$$

The physical interpretation of the assumption contained in Eq. (11) is that there is a large density of photogenerated holes during the period when the light pulse is incident on the sample.

Then Eq. (10) can be solved for ΔN:

$$\Delta N = \left(\frac{2B\delta_\epsilon f_0 \alpha N_0^-}{\mu_p e}\right)^{1/2} t^{1/2}, \tag{12}$$

so that

$$\frac{d\Delta N}{dt} = \left(\frac{B\delta_\epsilon \alpha f_0 N_0}{2\mu_p e}\right)^{1/2} t^{-1/2}. \tag{13}$$

Thus it is predicted that the rate of change of the surface conductivity, which is proportional to ΔN, will decrease reciprocally with the square root of the time of exposure to band-gap radiation.

III. EXPERIMENTAL RESULTS

Experiments were carried out on ZnO powder samples and single crystals. Sample preparation for photodesorption and surface conductivity measurements, as well as the ultrahigh-vacuum system in which those measurements were done, have been described earlier.[10] The light source consisted of a high-pressure mercury lamp equipped with a filter for transmission of its 365-nm line and a shutter for controlled duration and repetition rate of the illumination flashes. Measurement of the changes in surface conductivity were done by observing changes in the current through a powder sample while a constant voltage was maintained across it, or by monitoring the change in voltage across voltage probes of a single crystal while a constant current was maintained through it.

Figure 1 is a semilog plot of the photodesorption and conductivity change rates as a function of time as obtained from a ZnO powder sample at 300 K. The illuminated area of the sample, between the current leads is 2.4×0.8 cm. It was illuminated in the ultrahigh-vacuum system with $\frac{1}{4}$-sec flashes of flux density of 3.3×10^{16} photons $sec^{-1}\,cm^{-2}$, using the 365-nm line of our Hg lamp. Each flash produced a fast-rise-time pulse in the residual-gas-analyzer output which was tuned to the mass-44 (CO_2) peak. Simultaneously a rapid increase in the current i through the sample was monitored. The increase reached a certain maximum and quickly decayed to a constant value, higher than the current initially measured. The transient part is associated with photoconductivity processes and is of no concern to our work. The recorder registered only the steady-state change reached a few seconds after the termination of the short light flash. The difference between consecutive steady-state current before and after each illumination flash Δi was attributed to the net change in surface conductivity. The total change in surface conductivity $\Delta\sigma$ at any time t is given by

$$\Delta\sigma = (l/wV)i(t). \tag{14}$$

Here l is the distance between the current leads on both sides of the illuminated surface, V is the constant voltage across them, w is the width of the sample. The current before the experiment

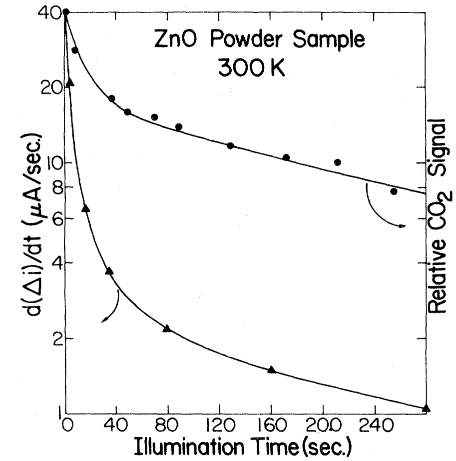

FIG. 1. Semilog plot of the rate of change of steady-state current increments of $(\Delta i)/dt$ as a function of illumination time combined with a relative CO_2 photodesorption signal curve at the same conditions for a ZnO powder sample at 300 K.

started (i.e., after a long exposure to atmospheric pressure of oxygen in the dark) is negligibly small and was taken as zero. The measured differences in steady-state current Δi are actually proportional to the time derivative of the expression in Eq. (14), namely

$$\frac{d(\Delta\sigma)}{dt}=\frac{l}{wV}\,\frac{\Delta i}{\Delta t}\,, \tag{15}$$

where Δt is the duration of the illumination flash. The relation between $\Delta\sigma$ and the excess electron concentration in the accumulation layer ΔN is

$$\Delta\sigma=\mu_n e\Delta N_e=\mu_n e\Delta N. \tag{16}$$

Therefore the measured increments of steady-state current, which are plotted by the triangles in Fig. 1 as a function of total net illumination time, are proportional to the rate of change of excess electron concentration on the surface. This rate should be reflected in the photodesorption rate from ZnO powder, which is shown in the same figure by the full circles. The correspondence between the two curves can be readily seen.

In order to facilitate the correlation of the experimental data with the theoretical analysis, the experimental values of $d(\Delta i)/dt$ of Fig. 1 were converted into $[d(\Delta i)/dt]^{-2}$ and were plotted in Fig. 2 again as a function of illumination time. It should be noted that the relation of this square reciprocal is indeed linear with time as predicted in Eq. (13).

Quantitatively, the slope of the line turns out to be 3×10^{9} sec.A^{-2}. (The ordinate should be multiplied by 10^{12} to be in units of sec^{2}A^{-2}.) From Eqs. (15) and (16) it is clear that

$$\left(\frac{d(\Delta N)}{dt}\right)^{-2}=\left(\frac{wVe\mu_n}{l}\right)^{2}\left(\frac{d(\Delta i)}{dt}\right)^{-2}. \tag{17}$$

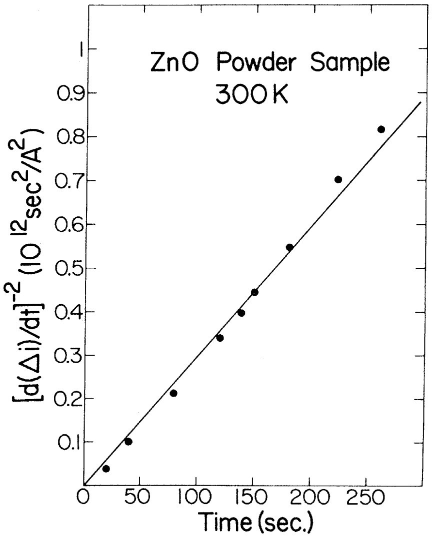

FIG. 2. Linear plot of $[d(\Delta i)/dt]^{-2}$, from Fig. 1, as a function of illumination.

If we insert the numerical values in this expression: $l/w=3$, $V=1$ V, $e=1.6\times10^{-19}$ C and assume a value of 5×10^{-3} m^2 V^{-1}sec^{-1} (50 cm^{2}V^{-1}sec^{-1}) for the surface electronic mobility[11] we get

$$\left(\frac{d(\Delta N)}{dt}\right)^{-2}=\frac{1}{1.6\times10^{43}}\left(\frac{d(\Delta i)}{dt}\right)^{-2}\simeq 2\times10^{-32}t.$$

In order to compare this experimentally derived quantity to our model we have to insert reasonable values for the parameters in Eq. (13). We use the known values of $\epsilon=\epsilon_0\epsilon_r=8\times10^{-11}$ F m^{-1}, $\alpha=2\times10^{7}$ m^{-1}, and $f_0=3\times10^{20}$ photons m^{-2}sec^{-1}. We then take $N_0^-=3\times10^{17}$ m^{-2}, which corresponds to a few percent of a monolayer coverage. This leaves us with the unknown term of $\beta\delta/\mu_p$. We are however in a position to estimate roughly two of these parameters. We designate by δ the depth from which photogenerated holes have a chance of getting to the surface proper. A measure of that distance can be obtained by equating the internal sweeping force eE_s times δ to the thermal energy kT. For ΔN values of 10^{11}–10^{13} cm^{-2}, δ assumes values of 50–0.5 Å, respectively. If we consider a moderate accumulation layer, a value of 5 Å for δ seems reasonable. To the best of our knowledge, the surface hole mobility has not been measured for ZnO, because p-type crystals are not available. Since hole mobility is expected to be much smaller than the electron mobility, a value of 5×10^{-4} m^{2}V^{-1}sec^{-1} (one order of magnitude smaller than the electron mobility) is estimated.

Inserting these values in Eq. (13), we obtain for B a value of 10^{-16} m^{3}sec^{-1}. Since B is actually the cross section for photodesorption times the thermal velocity of the holes (~10^{7} cm sec^{-1}), we obtain a value of ~10^{-17} cm^2 for the cross section for photodesorption.

Figure 3 shows the conductivity and photodesorption data for the oxygen face of a ZnO single crystal. In this case the conductivity changes, which are indicated by triangles in Fig. 3, were obtained by the more accurate four-point measurement. A constant current i was maintained through the sample while it was illuminated with $\frac{1}{4}$-sec flashes of 365-nm light from the Hg lamp. The voltage drop across a pair of probes along the surface was monitored. This voltage $V(t)$ decreases during each illumination flash, quickly decaying to a constant level, lower than before the flash. The steady-state voltages before and after each flash differed by an increment ΔV

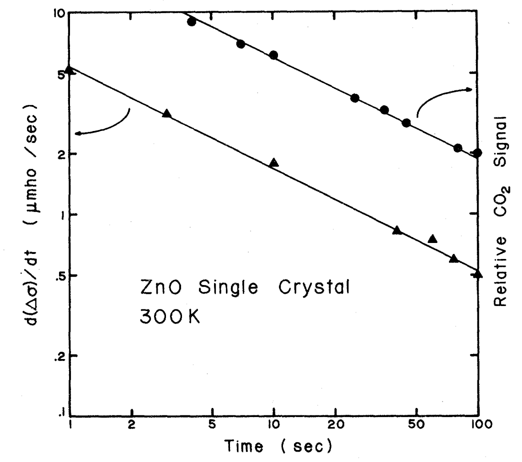

FIG. 3. Log-log plot of the rate of surface conductivity changes (triangles) and of relative CO_2 photodesorption signals (circles) as a function of net illumination time for a ZnO single crystal at 300 K. Note the exact $-\frac{1}{2}$ slope of both lines.

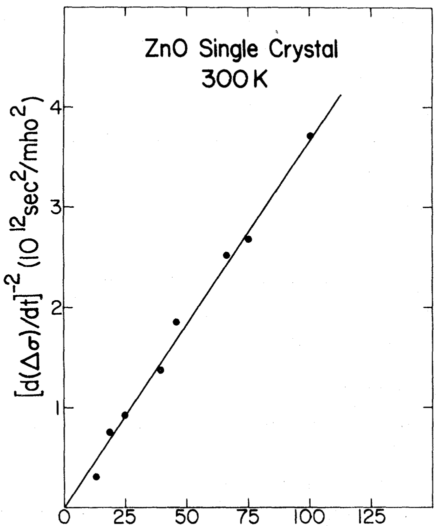

FIG. 4. Linear plot of $[d(\Delta\sigma)/dt]^{-2}$ from Fig. 3 as a function of illumination time.

which was attributed to the net increase in the surface conductivity.

The relation between the time rate of change of those two quantities is given by[10]

$$\frac{d(\Delta\sigma)}{dt}=\frac{l}{w}\,i\,\frac{1}{V^2(t)}\,\frac{\Delta V}{\Delta t}\,. \tag{18}$$

The rate of change of the surface conductivity as calculated by Eq. (18), indicated by triangles in Fig. 3, is given as a function of net illumination time. Unlike the case of Fig. 1, it is presented on a log-log scale, together with the rate of CO_2 photodesorption (full circles). The more accurate nature of the surface conductivity measurements on the single crystal allows for a more quantitative analysis. Indeed the one-to-one correspondence of the two rates is very clearly seen by this presentation. Furthermore, the experimental points lie on lines with a slope of $-\frac{1}{2}$, corresponding to Eq. (13).

The squared reciprocal of the rate of conductivity changes is plotted in Fig. 4 as a function of illumination time. The slope of the line yields the expression

$$\left(\frac{d(\Delta\sigma)}{dt}\right)^{-2}=4\times10^{10}t\,,$$

corresponding to

$$\left(\frac{d(\Delta N)}{dt}\right)^{-2}=2\times10^{-32}t$$

if we assume the same value of μ_n as in the powder case. Again the correspondence with the calculated value is very good, assuming the same numerical values.

Another set of experiments was carried out in that context with the purpose of checking the fundamental claim of the proposed model, namely the nature of the decrease of the photodesorption rate with time. The question is whether this behavior stems from the potential barrier buildup that sweeps holes away from the surface and decreases their recombination rate with the chemisorbed species or from the depletion of chemisorbed species on the surface. For that purpose six ZnO powder samples were prepared and analyzed by Auger-electron spectroscopy (AES). Each sample was partly covered from exposure to light or to the electron beam. The analysis showed a typical spectrum containing mainly Zn, oxygen and carbon peaks. The samples were scanned by the electron beam over most of the exposed area to obtain average values for the quantities: (i) the ratio of the carbon (272 eV) peak-to-peak height to the oxygen (510 eV) peak-to-peak height; and (ii) the ratio of the carbon peak-to-peak height to zinc (994 eV) peak-to-peak height. We shall denote those quantities by h_C/h_O and h_C/h_{Zn}, respectively. A typical spectrum showing these initial conditions is given in Fig. 5 by the solid line. The samples were then exposed to 365-nm illumination continuously for 20 min in air and the exposed areas were analyzed again by AES. The same quantities h_C/h_O and h_C/h_{Zn} were measured again. Both of them were reduced to (20–40)% of their original respective value. It should be noted that for each sample, there was excellent agreement between the ratios of the reductions of h_C/h_O and h_C/h_{Zn}. A typical

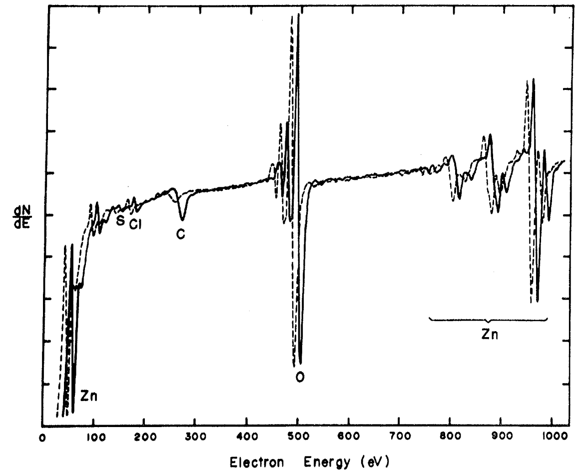

FIG. 5. Auger electron spectrum of a ZnO powder sample as a function of electron energy before (solid curve) and after (dashed curve) a 20-min exposure to uv light in air.

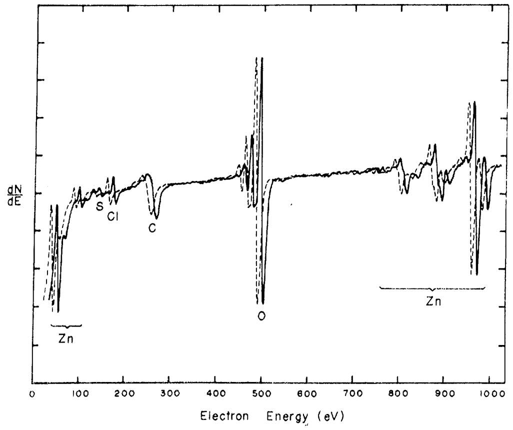

FIG. 6. Auger-electron spectrum of a ZnO powder sample as a function of electron energy before (solid curve) and after (dashed curve) a 20-min exposure to uv light *in vacuo*.

AES spectrum after illumination in air is given by the dashed curve in Fig. 5. The curve was slightly shifted relative to the energy axis for reasons of clarity. The significant decrease in the carbon peak relative to the other peaks can be clearly seen. The same samples were then moved in their holders so as to expose the parts which were not illuminated or analyzed. Those areas were then analyzed to obtain their reference values of h_C/h_O and h_C/h_{Zn}. Those values were very similar individually to the values obtained on the other parts of the same samples prior to illumination. The samples were then continuously illuminated under the same conditions as before, but *in vacuo*, and then analyzed and averaged again. A typical energy spectrum obtained by AES from one of the samples before illumination is given in Fig. 6 (solid line). The dashed curve (shifted in the same way as in Fig. 5) is a spectrum obtained after the sample was exposed to uv illumination *in vacuo*. It is clearly seen that under these conditions the decrease in the carbon peak was only slight. In this case the quantities h_C/h_O and h_C/h_{Zn} decreased to (88–95)% of their initial values before illumination. This is in marked difference from the case where they were illuminated in air. The explanation for the different behavior of the two types of results is discussed below.

IV. DISCUSSION

The data presented here, as obtained by photodesorption, condutivity and AES measurements of powder samples and oxygen faces of ZnO single crystal provide strong support for the proposed model of CO_2 photodesorption and the accompanying electronic processes described in Sec. I.

The AES measurements show that if ZnO samples are illuminated in air, where a continuous supply of oxygen is present to capture electrons from the surface and prevent an accumulation layer buildup, the holes have continuous access to the chemisorbed CO_2 ions and carbon depletion on the surface results. However, if similar samples are illuminated *in vacuo* under the same conditions, photodesorption takes place during the first seconds only and the potential barrier buildup will prevent further desorption even if the light is continuously on. Therefore in the latter case, the AES experiment shows only a negligible depletion of carbon on the surfaces and the assumption leading to Eq. (10), namely that the change in the surface density of CO_2 ions is small compared to the initial concentration, is justified.

The photodesorption and surface conductivity measurements strongly support the predicted evolvement of the band bending and the buildup of the accumulation layer. They show that the squared reciprocal of the conductivity time derivative is indeed linear with time to a very good approximation. Furthermore, the absolute magnitude of the conductivity changes agrees with the calculated value.

It is to be noted that the theoretical prediction concerning the rate of change of the surface conductivity shows a time dependence that agrees with that experimentally observed. The conclusions from the comparison of the theoretical with the experimental results yield estimations for the numerical values of the cross sections for the photodesorption and chemisorption[5] processes, namely $B/\mu_p \sim 3\times10^{-13}$ V m while the value of A/μ_n is 15–20 orders of magnitude lower than that. Even though the values for the charge carriers' surface mobilities could not be measured, it is obvious that those numbers indicate a cross section for photodesorption which is very much larger than that for chemisorption.

On the basis of our results we can therefore conclude that the following conditions exist during the process described: After a long exposure to oxygen in the dark, the excess charge concentration near the surface is very close to zero. Under ultrahigh-vacuum conditions and illumination, the hole concentration quickly reaches a steady state ($dp_s/dt = 0$) and the holes—CO_2^- recombination rate is much higher than the rate of electron capture to form chemisorption bonds (i.e., $Bp_sN^- \gg An_sN$). Upon continued illumination, there is a decrease in the probability that the holes will reach the surface where they can neutralize the carbon dioxide ion. Only after several experimental runs was the surface carbon concentration appreciably reduced. During each individual run, the rate of change of the surface conductivity does indeed behave as predicted by Eq. (13).

V. SUMMARY

Photodesorption and surface conductivity measurements on ZnO are reported which strongly suggest that the long-term decrease in the surface conductivity rate, caused by irradiation with band-gap radiation, can be attributed to band bending and the buildup of an accumulation layer associated with the photodesorption of CO_2.

A calculation, relating the decrease in surface conductivity with illumination time agrees with experimental results and permits an estimation of the cross sections for the photodesorption process.

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