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Characterization of the electron interaction with ZnSe surface states by the photovoltaic modulation of low-energy-electron transmission

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When low-energy electrons are incident on a solid surface, some are reflected and some are transmitted. In the case of semiconductors, the number that are transmitted can be photovoltaically modulated with incident light. The time dependence of this modulated transmitted current has been examined for undoped, single-crystal ZnSe, and is found to consist of two components, the relative size of which depends on the light intensity, electron flux, and electron energy. A theoretical model that satisfactorily accounts for the observed phenomena involves an accumulation space-charge region at the ZnSe surface and a surface state whose electronic population can change due to its interaction with low-energy electrons that are incident on the surface.

I. INTRODUCTION

The elctronic population of the surface states of a solid can be affected by an incident electron current. This physical process is the first step in electron-induced gas desorption from solids[1] and also affects the reduction in the performance of electron multipliers operated for prolonged periods in ultrahigh vacuum.[2] In addition, the electronic population of surface states can also be changed by the optical excitations caused by absorbed light. The coupling of these two effects at the surface or interface is of critical importance to a variety of semiconductor optoelectronic devices. In this paper, this phenomenon is measured for single-crystal ZnSe by optically modulating the transmission of incident low-energy electrons. This experimental approach has been used previously to measure the photovoltaic changes in work function of a wide variety of semiconductors.[3,4] This is, however, the first time that the incident low-energy electrons have been observed to affect these surface photovoltaic properties by interacting with the ZnSe surface states. Such electron–surface-state interactions have previously been observed for ZnSe, however, using low-energy-electron loss spectroscopy.[5]

II. EXPERIMENTAL

The experimental apparatus has been described in detail in previous publications.[3,4] Briefly, it consisted of low-energy-electron gun and sample holder in an ultrahigh vacuum system. The electron gun filament was floated at a variable negative bias defined as V_g, the gun voltage. The sample was grounded through one of several high-impedance detection circuits. The total current transmitted through the semiconductor sample was measured with a micro-ammeter and was assumed to be linearly related to the current incident on the sample. The optically modulated ac component of this transmitted current was measured after suitable amplification with a nicolet signal averager. The total transmitted current was on the order of 2×10^{-7} A and the optically modulated component of this current was approximately 5×10^{-11} A. A xenon lamp provided the incident light which was mechanically modulated with a programmable shutter. The absolute light intensity was measured with a calibrated photodiode and the approximate light intensity at the ZnSe surface was 10^{12} photons $cm^{-2}\,sec^{-1}$. This could be reduced with the appropriate neutral density filters.

Both single-crystal (Atomergic) and polycrystalline (Eagle Picher) ZnSe were examined. Both were nominally undoped and were approximately $1\times1\times0.25$ cm. The samples were not etched before an indium electrical contact was made to the rear surface and this contact was heated to 500 K during the bakeout necessary to achieve ultrahigh vacuum. Although white light was used in all the results reported here, the spectral dependence of the optically modulated current was also examined and there was a sharp decrease in the optically modulated current at the band edge of ZnSe (~2.6 eV). There was little or no below band-gap signal for the single-crystal ZnSe at either 300 or 77 K. This was in contrast to the polycrystalline ZnSe where large amounts of below band-gap signal at 77 K was observed. On the basis of earlier photoconducitvity measurements,[6] this difference was attributed to residual copper impurities in the polycrystalline material. For this reason, as well as possible anomalous photovoltaic effects at the grain boundaries of the polycrystalline material,[7] only the results for the Cu-free single-crystal ZnSe are reported.

The experimental results are reported as a function of electron-gun voltage that is correlated

to the incident electron energy in the following way. If the total transmitted current is measured as a function of the externally applied voltage between the electron gun and the sample, at a given voltage there is a sharp rise in the transmitted current. If the voltage difference across the electron-gun filament can be neglected, the break in the slope of this curve corresponds to the contact potential difference between the electron-gun filament and the sample.[8] At this externally applied voltage the energy of the incident electrons corresponds approximately to the vacuum level of the semiconductor. The externally applied voltage is equal to the electron-gun voltage plus the other voltages in the electronic circuit. The voltage difference arising in the detection circuit is negligible and the voltage arising from the voltage drop across the filament is also fairly small.[4] In the present case of undoped ZnSe, however, the voltage difference caused by sample charging is appreciable. This charging by the incident electrons can be qualitatively monitored by measuring the hysteresis in the transmitted current as a function of electron-gun voltage when the electron gun is first turned on. The ZnSe sample appears to charge rapidly (<1 min) when the gun is turned on and to discharge slowly (>15 min) when the gun is turned off. Fortunately, this time scale is such that it is possible to perform the experiments with a constant correction term due to the sample charging and therefore it is possible to relate the measured gun voltage to an incident electron energy.

III. RESULTS AND DISCUSSION

Figure 1 shows the total transmitted current as a function of the electron-gun voltage. This paper follows the standard procedure of measuring the total transmitted current when the sample is unilluminated, even though in this case the change in the total transmitted current due to illumination is negligibly small. The current increases sharply at 20 V, and is approximately constant from 25 to 65 V. At 65 V there is another slight increase in the transmitted current that is characteristic of this single-crystal ZnSe sample. The exact cause for this increase at 65 V is not known but it is thought to be due to patches on the ZnSe surface that are more highly charged by the incident electrons. In this paper, the reported measurements will be limited to gun voltages below 60 V to avoid possible complications from this extraneous effect. The transmitted current as a function of gun voltage has been measured at a range of incident currents and the shape of Fig. 1 is unchanged. The break in the slope of the curve can be extrapolated and the "knee" in Fig. 1 appears at a gun voltage of 23 V. As noted above, the energy of the incident electrons is approximately equal to the vacuum level of the ZnSe sample at this gun voltage.

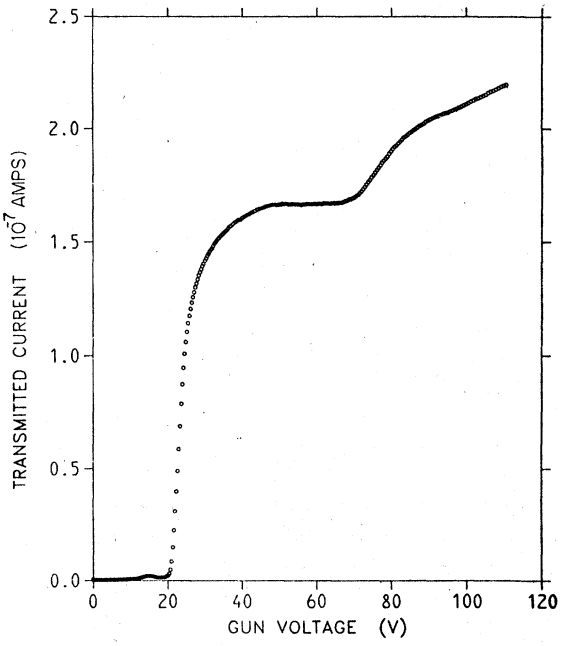

FIG. 1. Transmitted current as a function of gun voltage.

As shown in Fig. 1 the total transmitted current is fairly independent of electron energy in the gun-voltage region 23.4–60 V. Also, the total transmitted current is to a good approximation unchanged by incident light and is assumed to depend linearly on incident current. In contrast to this simple behavior the optically modulated component of this transmitted current is found to depend on these experimental parameters in a complicated fashion. Before discussing the experimental results in detail, the theoretical model that will be used to correlate the data will be described.

When light is incident on a semiconductor surface, the separation of the electron-hole pairs which are generated in the surface-space charge region changes the energy-band bending at the surface. This photovoltaic modulation of the energy-band bending affects the transmission probability for incoming primary electrons.[3,4,9,10] The measured time dependence of the optically modulated current is therefore determined by the time dependence of this photovoltaic modulation of the energy-band bending. For all of the moderately doped semiconductors which have been examined previously, the time dependence of the optically modulated current is unaffected by changes in the

incident electron current and energy.[4,9,10] This implies that the incident electrons are not perturbing the photovoltaic change in the band bending. With undoped ZnSe, however, this is not the case and the time dependence of the optically modulated current depends strongly on both the incident electron current and energy.

One theoretical model that can account for this experimental dependence postulates that the electrons which are incident on the semiconductor surface can interact with surface states and the changed electron population of these surface states then affects the photovoltaic modulation of the energy-band bending. The effect of this electron capture on the photovoltaic time dependence can readily be calculated. This model is analogous to one in the literature for electron capture from the bulk of the semiconductor.[9,10] Of course, electron capture from both the bulk and from incident electrons could be present on a real surface. In the present derivation it will be assumed that the number of captured electrons is negligibly small compared to the size of the optically modulated current and therefore, the time dependence of the optical modulation of the current is still approximately equal to the time dependence of the photovoltaic modulation of the energy-band bending.

For the sake of both simplicity and specificity in the derivation a number of additional assumptions are made. It is assumed that the semiconductor has a surface depletion layer and a surface state of uniform energy distribution located at the Fermi energy. It is also assumed that the energy distribution of this surface state is broad compared to the photovoltaic changes in band bending. In addition this surface state is assumed to be in poor electrical contact with the bulk so that the recombination between electrons captured in the surface state and photogenerated holes in the bulk can be neglected. Any or all of these assumptions could be discarded with a resultant increase in the mathematical complexity of the problem.

Qualitatively, the physical model is fairly simple to understand. As light is incident on the semiconductor surface electron-hole pairs are generated at a rate g. Since a depletion layer is present at the surface, the photogenerated holes are rapidly swept to the surface. These holes of surface concentration n_h are able to recombine with electrons that are present in the surface region at a rate τ_1^{-1}. The rate of formation of these photogenerated holes at the surface is therefore

$$\frac{dn_h}{dt} = g - \frac{n_h}{\tau_1} . \tag{1}$$

These holes result in a lowering of the energy-band bending and this in turn, results in a lowering of the surface state with respect to the Fermi energy. As a result the newly emptied levels in the surface state can capture electrons from the incident primary electron beam and the rate for this electron capture could depend on the incident electron energy. The rate of this electron capture is proportional to the population of empty energy levels below the Fermi energy created by the band bending multiplied by the rate of electron capture by a single energy level. The number of empty energy levels is equal to $\rho\Delta\phi$, where ρ is the uniform density distribution of the surface state and $\Delta\phi$ is the photovoltaic change in the band bending. The rate of electron capture at a single level is equal to N_0/τ_2, where N_0 is the incident flux of electrons and $(\tau_2)^{-1}$ is the capture rate for a single electron. The rate equation for electron capture is therefore

$$\frac{dn_e}{dt} = (\rho\Delta\phi)\frac{N_0}{\tau_2} , \tag{2}$$

where n_e is the number of captured electrons. This expression involves the photovoltaic change in the band bending, $\Delta\phi$. In the actual experiments the light intensity employed was well below the photovoltaic saturation intensity and thus the photovoltaic change in the band bending is small compared to the total amount of band bending. Therefore, it is assumed that $\Delta\phi$ is simply proportional to the difference between the photogenerated holes at the surface and the electrons captured by the surface state as a result of the incident light at any moment in time. We have

$$\Delta\phi = \alpha(n_e - n_h) . \tag{3}$$

Equations (1)–(3) form a system of differential equations which can readily be solved in closed form for the time dependence of the photovoltaic change in the band bending. Then noting that the time dependence of the optically modulated transmitted current is related to the time dependence of the photovoltage by

$$\Delta I(t) = -\beta N_0 \Delta\phi(t) , \tag{4}$$

where β is the appropriate proportionality constant that depends on incident electron energy.[4] Substituting the solution for the time dependence of the photovoltage in Eq. (4) and considering light modulation intervals that are long compared to the recombination times yields

$$\Delta I(t) = \begin{cases} A\left[\exp\left(\frac{-t}{\tau_2'}\right) - \exp\left(\frac{-t}{\tau_1}\right)\right], & t < t_{\text{off}} , \\ -A\left[\exp\left(\frac{-t'}{\tau_2'}\right) - \exp\left(\frac{-t'}{\tau_1}\right)\right], & t > t_{\text{off}} , \end{cases} \tag{5}$$

where

$$A=\frac{\beta N_0 \alpha g \tau_1 \tau_2'}{\tau_1-\tau_2'}\,,\quad \tau_2'=\frac{\tau_2}{\rho\alpha N_0}\,,\quad t'=t-t_{\text{off}}\,.$$

The qualitative form of Eq. (5) is fairly simple to understand. When light is first incident on the semiconductor depletion layer, holes drift to the surface and the resulting decrease in the band bending causes an increase in the transmitted current. Because of this decrease in the band bending, there are empty levels in the surface state below the Fermi energy which capture electrons from the incident electron beam. This electron capture increases the band bending and decreases the transmitted current. If the light is incident on the surface for a sufficiently long time, the photogenerated holes at the surface are balanced by the electrons in the surface state and no steady change in the transmitted current results. Thus the optically modulated current should increase and then decrease back to its zero value during the interval of light exposure. Conversely, the photogenerated holes recombine and the captured electrons are freed from the surface state when the light is turned off and the resulting transmitted current decreases then increases back to its zero value during the unilluminated interval.

The simple time dependence in Eq. (5) originates in two assumptions made in the derivation. The first was that the direct recombination between the captured electrons in the surface state and the holes at the surface was negligible. This is inherent in assuming that the surface state is in poor electrical contact with the bulk of the semiconductor. As a result of this assumption, Eq. (5) predicts that an incident light pulse produces only a transient change in the transmitted current. The second simplification was the assumption that τ_1 and τ_2' were independent of the incident light intensity. This results in the symmetry of Eq. (5): The time dependence of the illuminated interval is equal and opposite to the time dependence of the unilluminated interval.

For other semiconductor materials the time dependence of optically modulated current is both asymmetric and has a steady-state value for long light exposures.[9,10] Unfortunately, if the two assumptions described are discarded, the resulting system of differential equations is no longer soluable in closed form. This paper will therefore follow the previous practice of numerically fitting the experimental data to a functional form with two components similar to Eq. (5) (Ref. 10). Again considering light modulation intervals that are long compared to the recombination time the specific formula which will be used is

$$\Delta I(t)=\begin{cases} B[1-\exp(-t/\tau_B^{\text{on}})] \\ -A[1-\exp(-t/\tau_A^{\text{on}})], & t<t_{\text{off}}\,, \\ (B-A)-B[1-\exp(-t'/\tau_B^{\text{off}})] \\ -A[1-\exp(-t'/\tau_A^{\text{off}})], & t>t_{\text{off}}\,. \end{cases}$$

Equation (6) is written to be consistent with the experimental practice of defining the zero of the optically modulated current as its value at the end of the unilluminated interval. Equation (6) predicts a steady-state change in the optically modulated current equal to $(B-A)$. Also, since the recombination times in Eq. (6) can depend on the illumination conditions, the time dependence of the optically modulated current can be asymmetric.

The experimentally measured time dependence of the optically modulated current can be fairly accurately described by the functional form of Eq. (6). To demonstrate this, the points of Fig. 2(a) show the experimental time dependence of the optically modulated current for a given set of experimental conditions.[11] The curve in Fig. 2(a) was obtained from a nonlinear least-squares fit of Eq. (6) to the experimental data: $A=2.67\times10^{-11}$ A, $B=3.82\times10^{-11}$ A, $\tau_B^{\text{on}}=0.0202$ sec, τ_A^{on}

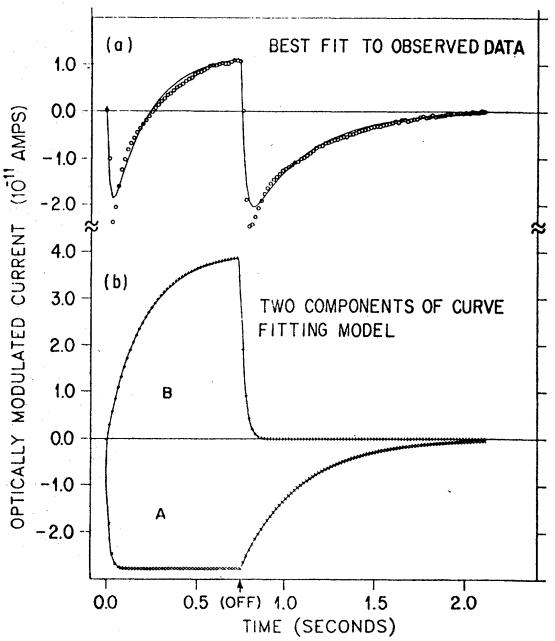

FIG. 2. (a) Points show the experimental time dependence of the optically modulated component of the transmitted current for a total transmitted current of 1.5×10^{-7} A, gun voltage 50 V, and 21.5% of full light intensity. The curve is a nonlinear least-squares fit of Eq. (6) to these data ($A=2.67\times10^{-11}$ A, $B=3.82\times10^{-11}$ A, $\tau_B^{\text{on}}=0.202$ sec, $\tau_A^{\text{on}}=0.015$ sec, $\tau_B^{\text{off}}=0.022$ sec, and $\tau_A^{\text{off}}=0.318$ sec). (b) A and B components of curve shown in part (a).

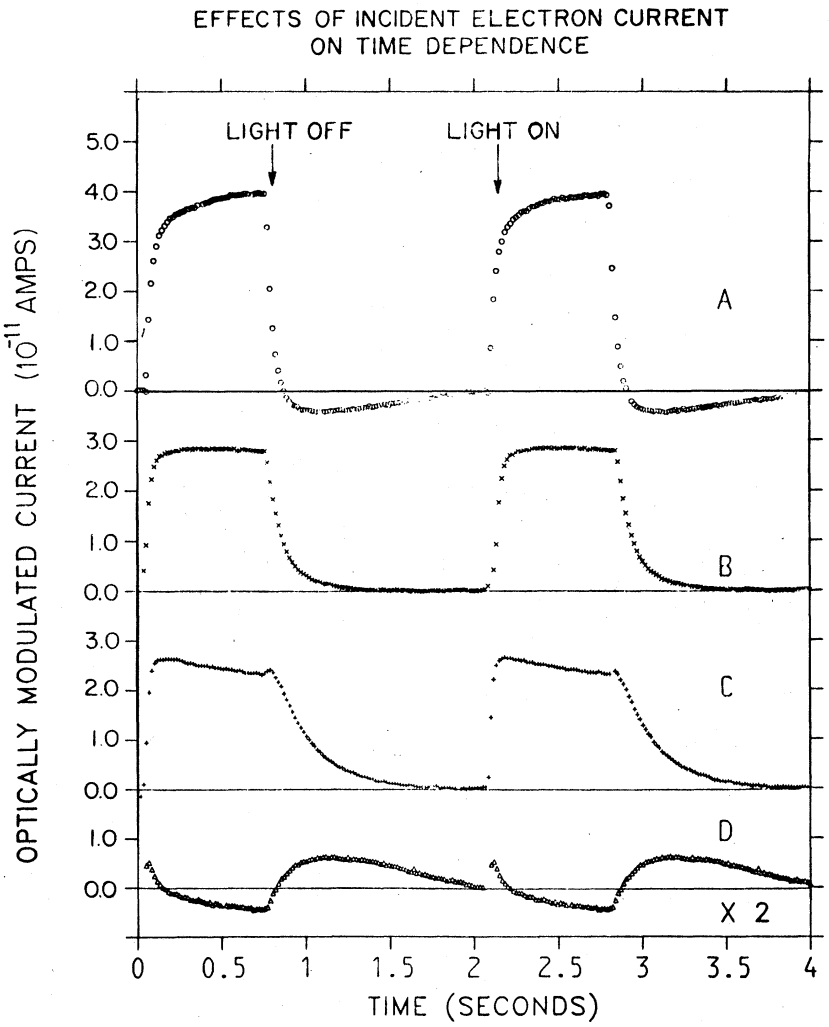

FIG. 3. Effect of total incident current on time dependence of optically modulated component of the transmitted current. These results are for gun voltage 50 V, 31.5% of full light intensity, and a range of incident currents, 7×10^{-8} A (A), 5×10^{-8} A (B), 3×10^{-8} A (C), and 1×10^{-8} A (D).

$= 0.015$ sec, $\tau_B^{\text{off}} = 0.022$ sec, and $\tau_A^{\text{off}} = 0.318$ sec. The fit to the experimental data is poorest immediately after the light pulse is turned on and immediately after it is turned off. As a result, the faster recombination times derived from fitting the data with Eq. (6) are probably not as accurate as the values obtained for the slower recombination times and for A and B. Figure 2(b) shows the A and B components of the curve in Fig. 2(a). Equation (6) is applicable only when the duration of the light exposure is long compared to the recombination times involved. The lower half of Fig. 2 indicates that this was indeed the case, since both components reach a saturation value before the light exposure was terminated. It is also evident that there is an experimentally observed steady-state change in the optically modulated current. The recombination times depend markedly on incident light intensity: τ_B^{off} is much faster than τ_B^{on} and τ_A^{on} is much faster than τ_A^{off}. This results in the asymmetry of the experimental results: The time dependence during illumination is clearly not equal and opposite to the time dependence during the unilluminated interval.

Figure 2 demonstrates the Eq. (6) can be used to describe the time dependence of the optically modulated current for a particular set of experimental conditions. In fact the time dependence of the optically modulated current has been measured for a wide range of incident light intensities, electron energies, and currents and in all cases the parameters in Eq. (6) could be adjusted to give a fairly good fit to the experimental data. This is useful in itself simply as means of characterizing the results. In addition, however, it is possible to correlate changes in the parameters obtained from the curve-fitting procedure with the changes in the experimental variables and this approach

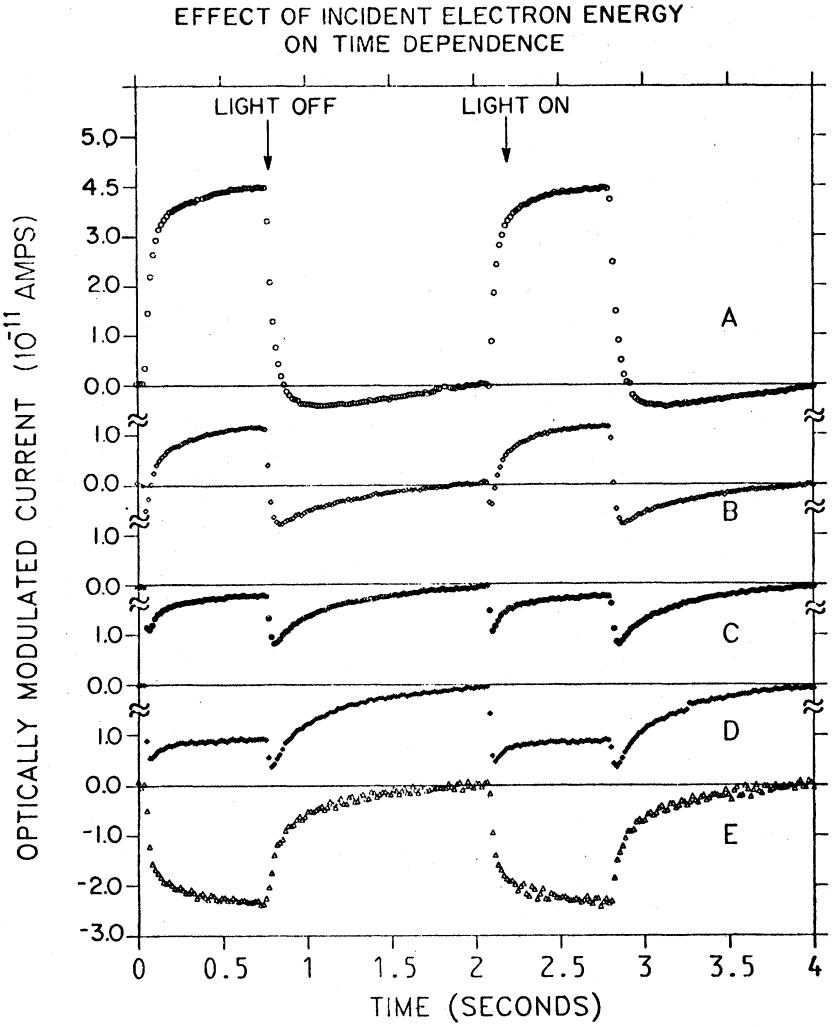

FIG. 4. Effect of incident electron energy on time dependence of optically modulated current. These results are for an incident current of 7 $\times 10^{-8}$ A, 31.5% of full light intensity, and a range of gun voltages, 50 V (A), 39.0 V (B), 33.0 V (C), 30.1 V (D), and 20.3 V (E).

gives additional insight into the ZnSe surface.

Consider first the dependence on N_0, the incident electron current. The preexponential term depends both directly and indirectly on N_0. This fairly complicated dependence on incident current is simplified when the incident current is very small. In this limiting case τ_2' becomes much longer than the light modulation interval and therefore Eq. (5) reduces to a simple expression in which the time dependence depends only on τ_1, the recombination time for carriers in the surface space-charge layer. Equation (6) would be expected to depend on the incident current in a way analogous to Eq. (5). In other words, at low incident currents the time dependence should be dominated by the component associated with recombination in the surface space-charge layer.

Figure 3 shows the experimental time dependence of the optically modulated current at a range of incident currents. These curves have been broken into the A and B components of Eq. (6) by the curve-fitting procedure described previously and the relative size of these two components clearly depends strongly on incident current. At very low incident currents [curve D, Fig. 3] the time dependence is dominated by the A component in Eq. (6). On the basis of the preceeding arguments this component is attributed to recombination in the space-charge layer. Since the transmitted current decreases with incident light, this is associated with an accumulation space-charge layer and therefore labelled the "accumulation" component. By elimination, the effect of the interaction of incident electrons with surface states is the B com-

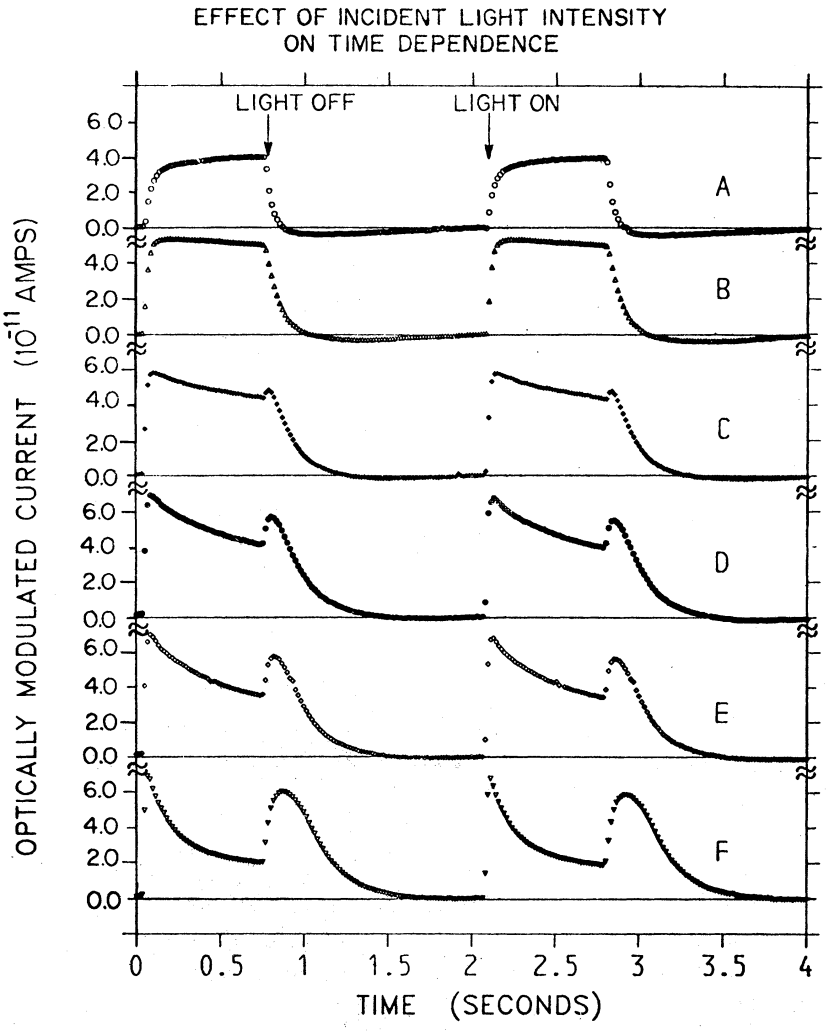

FIG. 5. Effect of incident light intensity on time dependence of optically modulated current. These results are for an incident current of 7×10^{-8} A, a gun voltage of 50 V, and a range of relative light intensities, 31.5% (A, 39.7% (B), 50.1% (C), 63.0% (D), 79.4% (E), and 100% (F).

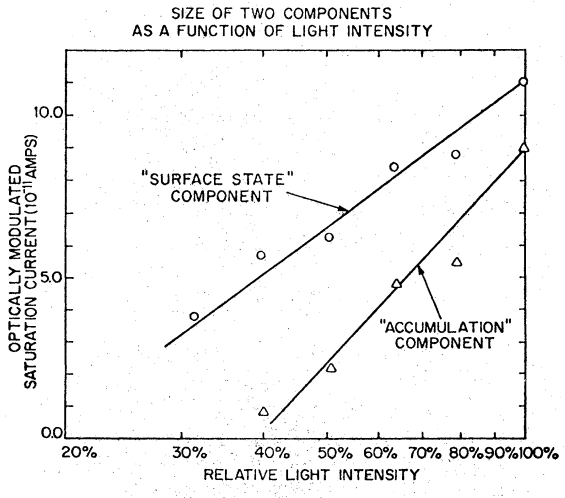

FIG. 6. Data in Fig. 5 were fit by a nonlinear least-squares procedure and this shows the saturation current for each component in Eq. (6) as a function of light intensity.

ponent of Eq. (6) that will therefore be labelled the "surface-state" component. Figure 3 demonstrates that increasing the incident current increases the size of this "surface-state" component over the size of the "accumulation" component in curve D, while it is dominated by the "surface state" component in curve A.

Equation (6) can also be used to qualitatively correlate the experimental results when the incident electron energy is varied. Figure 4 shows the time dependence of the optically modulated current for a range of gun voltage settings, which determine the incident electron energy. Curve A in Figs. 3 and 4 are identical and as previously noted, are dominated by the "surface-state" component of Eq. (6). There is not *a priori* way of predicting how a decrease in incident electron energy will affect the interaction of the incident electrons with the surface states of the ZnSe, and therefore the relative size of the "surface state" and "accumulation" components. The experimen-

tal results illustrated in Fig. 4 indicate that the "surface-state" component decreases with increasing electron energy, while the "accumulation" component reaches a maximum at the gun voltage corresponding to the sharp increase in the transmitted current observed in Fig. 1. The behavior of this "accumulation" component originates in the dependence of β on electron energy in Eq. (4) and is consistent with the behavior of a wide range of other semiconductor materials where incident electron "surface-state" interaction is not observed.[3,4]

Figure 5 shows the effect of varying light intensity on the time dependence of the optically modulated current. Curve A in Figs. 3–5 are identical. The "accumulation" and "surface-state" components of these curves have again been separated with the curve-fitting procedure and Fig. 6 shows the resulting saturation currents in Eq. (6) as a function of relative light intensity. Figure 6 demonstrates that these saturation currents decrease with decreasing light intensity and the resultant decreasing photovoltaic change in the band bending as expected. The data in Fig. 5 and 6 also show that the "accumulation" component of the time dependence falls off much more rapidly as a function of light intensity than the "surface state" component. This changes the relative ratio between the two components as a function of light intensity and accounts for the complicated time dependence illustrated in Fig. 5.

IV. SUMMARY

In contrast to the results for other semiconductors, the time dependence of the optically modulated current measured for ZnSe was observed to have a complicated dependence on the incident electron current and energy. This complicated time dependence can be greatly simplified by separating it into two components which differ in sign. The experimental results are consistent with a ZnSe surface accumulation space-change layer and a surface state whose population can change due to the incident electron current.

ACKNOWLEDGMENT

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