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Optical modulation of low-energy-electron transmission: ZnO

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When low-energy (0–100 eV) electrons are incident on a solid surface, some are transmitted into the bulk of the solid where they can be readily measured. This paper reports measurements made on ZnO of both this transmitted current and the optically modulated component of this transmitted current which arises when chopped light is incident on the surface. Both of these experimental quantities have a pronounced dependence on incident electron energy. At lower incident electron energies (1–21 eV), this dependence is related to the conduction-band density of states for ZnO. The cause of the electron energy dependence at higher incident electron energies (22–91 eV) is not yet understood, but several possibilities are suggested.

INTRODUCTION

This paper is part of a series which reports the experimental results of a new experimental probe, optical modulation of the transmission of incident low-energy electrons, for a range of semiconductor materials.[1-4] The data presented here were obtained for etched single-crystal ZnO. In agreement with the work on other semiconductors, the ZnO results indicate that the optical modulation of the low-energy electron transmission originates in the photovoltaic change in the work function of the semiconductor. In contrast to previous work, however, the optically modulated current measured for ZnO depends on incident electron energy in a complicated fashion. In this paper, this structure in the optically modulated current is examined in detail.

EXPERIMENTAL

The ZnO single crystal (supplier: Materials Research Corporation) was oriented with the *c* axis perpendicular to the front face. The sample was nominally undoped and was etched for 1 h in 85% H_3PO_4 before In contact was made to the rear face. The crystal was then immediately mounted on a Mo plate and placed in the vacuum system, where it was heated during the bakeout necessary

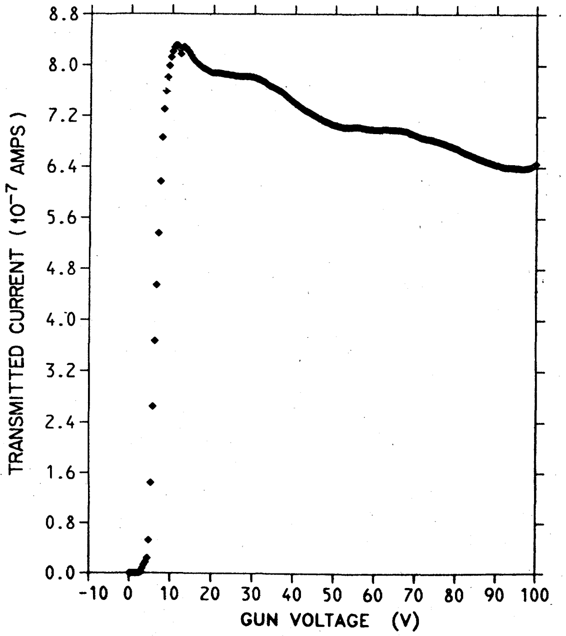

FIG. 1. Total transmitted current as a function of electron gun voltage for unilluminated ZnO.

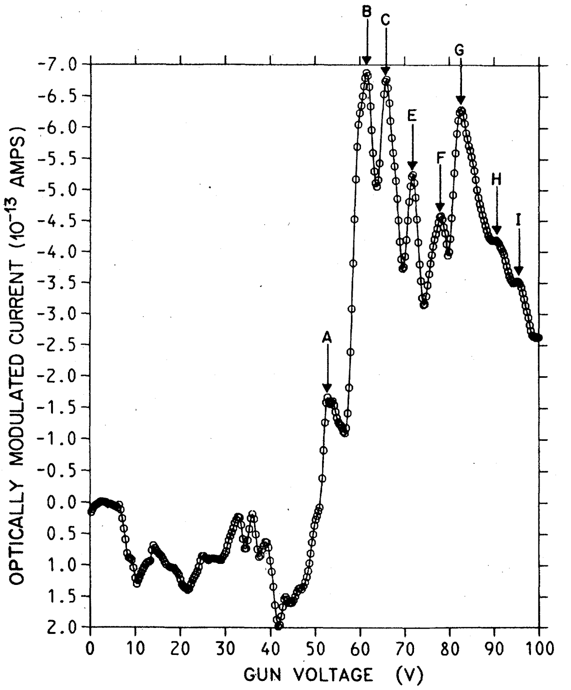

FIG. 2. Optically modulated component of transmitted current as a function of electron gun voltage for photon energy = 4.1 eV and a chopping frequency of 42 Hz.

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to obtain ultrahigh vacuum (500 K, 12 h). The base pressure in the vacuum system after this bakeout was $\leq 2\times 10^{-10}$ Torr. In order to remove possible carbon contamination, the sample was chemically cleaned by backfilling the vacuum system with 10^{-3}-Torr oxygen and illuminating the surface with a photon flux of $\sim 10^{14}$ photons cm^{-2} sec^{-1} for several hours. This has been reported to be an effective cleaning technique, as determined by Auger spectroscopy,[5] and it was determined that this procedure produced a ZnO surface which gave reproducible experimental results. The experimental apparatus used for measuring the optically modulated transmitted current has been described in detail in the literature.[1,2]

RESULTS AND DISCUSSION

Figure 1 shows the transmitted fraction of the electrons incident on an unilluminated ZnO surface as a function of the biasing potential of the electron gun. As expected, this transmitted current increases sharply at electron energies which correspond to the vacuum level of the semiconductor.[2] When chopped light is incident on the ZnO surface, the small fraction of the transmitted current which is optically modulated can be readily measured with lock-in detection. Figure 2 shows this optically modulated current and it is evident that it depends on the electron gun voltage and the associated incident electron energy in a complicated fashion. The sign of the optically modulated current in Fig. 2 was determined from the time dependence using the standard sign convention, i.e., a positive signal corresponds to an increase in transmitted current due to the incident light. The pronounced multiplet structure labeled with arrows

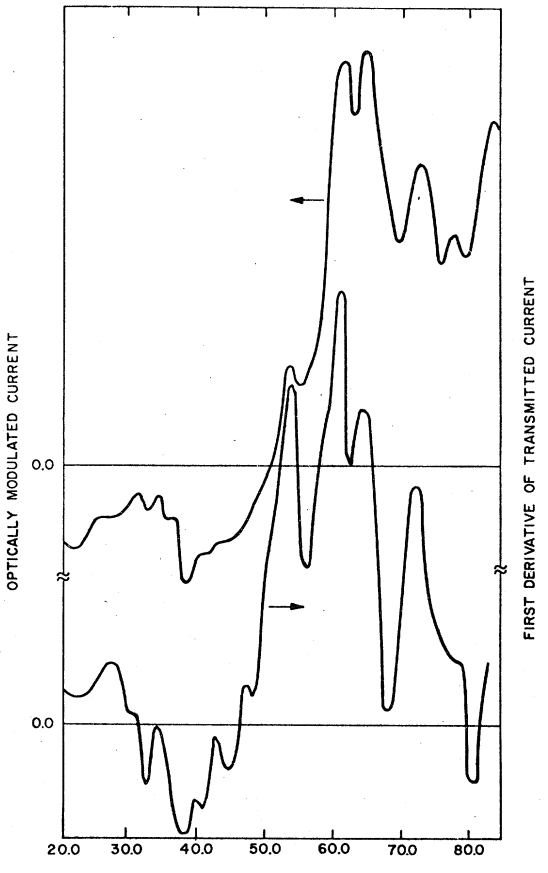

FIG. 3. Weighted first derivative of total transmitted current compared to optically modulated component of transmitted current. (Weighting function is broad Gaussian centered at 70 V with a full width at half maximum of 20 V.) These data have been both normalized and inverted in sign for ease in presentation.

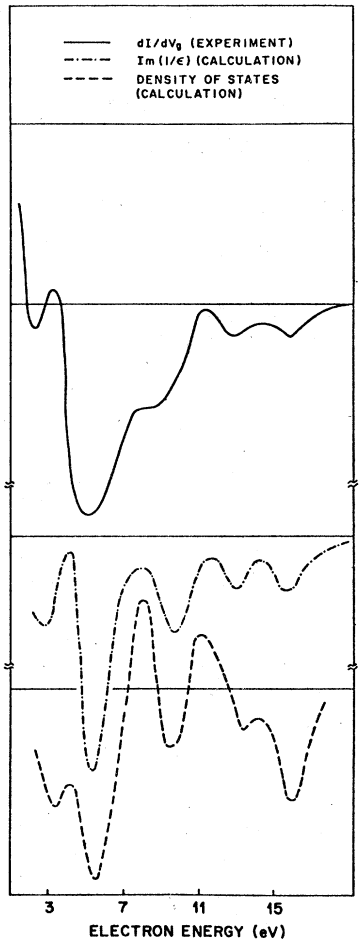

FIG. 4. Top curve shows the first derivative of the transmitted current with respect to the incident electron energy which is obtained by numerically differentiating Fig. 1. The second and third curves show the results expected from the dielectric and conduction-band density-of-states models (see text).

in Fig. 2 differs sharply from the relatively broad and featureless dependence on gun voltage which is observed for semiconductors such as Si and GaP, and which has been attributed to the optical modulation of secondary-electron-emission processes.[2,3]

One possible origin for the complicated structure in Fig. 2 is the experimental artifact which can arise if the time dependence of the optically modulated current varies with electron gun voltage. Such effects have previously been observed in ZnSe.[4] To eliminate this possibility, the time dependence of the optically modulated current has been measured at a range of gun voltages. The optically modulated current was observed to have approximately a square-wave time dependence at all gun voltages, and since this time dependence was independent of gun voltage, the complicated structure in Fig. 2 does *not* originate in this kind of experimental artifact.

The optically modulated current from Fig. 2 has been reproduced as the top curve in Fig. 3. The bottom curve in Fig. 3 shows the total transmitted current from Fig. 1, after numerical differentiation to enhance its inherent structure. This bottom curve has also been multiplied by a broad weighting function which was chosen to achieve peak height correlation between the two curves. The resemblance between the two curves in Fig. 3 is fairly good, and in particular, most of the peak positions are replicated. Thus the complicated dependence on gun voltage observed in the optically modulated current appears to be directly correlated with the gun voltage dependence of the total transmitted current.

In discussion of the possible causes of the gun voltage dependence illustrated in Fig. 3, it is useful to separate the results into two regions based on gun voltage and the corresponding incident electron energy. Electron gun voltages from 10 to 30 V will be defined as the low-energy region, and those from 30 to 100 V as the high-energy region.

Low incidence electron energies (V_g=10-30 V)

The top curve in Fig. 4 shows the derivative of the total transmitted current obtained by numerically differentiating the data in Fig. 1. The experimentally measured electron gun voltage has been converted in the standard fashion to the proper value of the incident electron energy by subtracting 9 V, which was the suitable correction determined by the position of the "knee" of the curve in Fig. 1.[2] The bottom two curves in Fig. 4 originate from theoretical calculations which will now be discussed.

Unfortunately, the theoretical efforts in the literature for electron transmission in this energy region has been rather sparse. This ZnO sample probably does not have sufficient crystalline perfection to result in the kind of Bragg interference effects which can occur for low-energy electrons incident on a semiconductor surface.[6] A previous study has separated the problem of electron transmission into two contributing factors. One

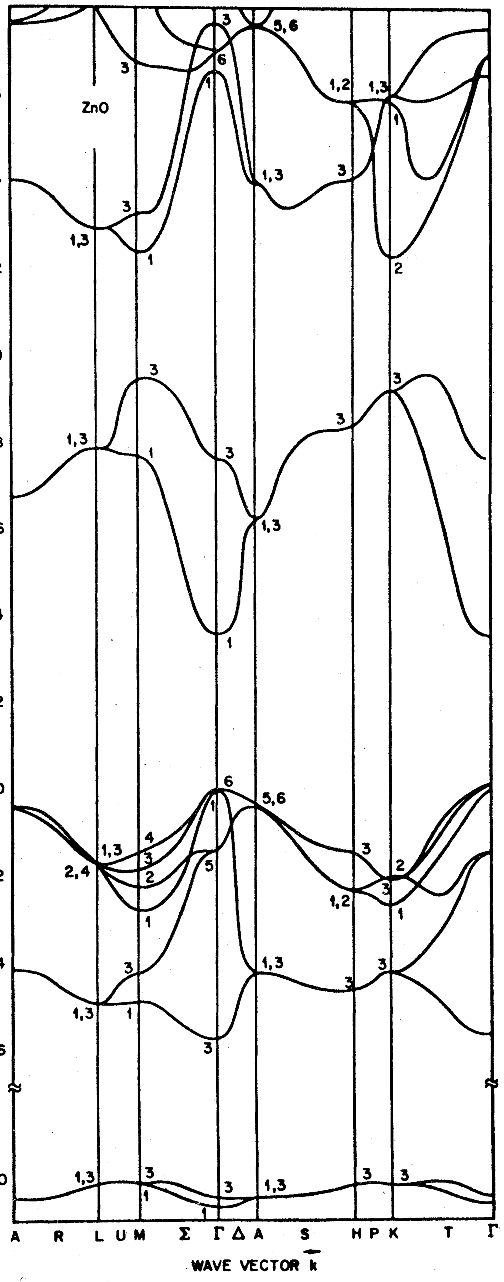

FIG. 5. Theoretical density of states for ZnO (from Ref. 11 by permission).

factor was an elastic scattering term which arises from the matching of the energy and parallel component of the wave vector of an incident electron with a Bloch state in the crystal. The other contributing factor was an inelastic term, which considers the matching process followed by the production of secondary electrons by single-particle excitations initiated by the incident electron. While the previous study is applicable to the problem at hand, it contains flaws which prevent its direct use.[8]

The analysis in this paper differs slightly from the previous theoretical treatment in that the physical process will be separated into two effects. The first will consider the probability of the primary electron being transmitted into the bulk, and will be based on energy matching between the incident electrons and energy levels at the semiconductor surface. This combines the matching condition for both the elastic and inelastic scattering. The second process involves the inelastic scattering and the resultant energy loss from the production of secondary electrons. Both effects would be expected to influence the total amount of current transmitted into the bulk, and the relative contribution would depend somewhat on the surface conditions. With an ideal surface, the matching condition would be expected to play the major role. Conversely, if the surface has many defects such as etch pits or steps, the major contribution to structure would be expected to arise from the production of secondary electrons.

First, the effect on the total transmitted current due to energy matching will be considered. A matching procedure for metals has been considered by other workers.[9,10] Rather than proceed in this fairly complicated fashion, it will be assumed that the total transmitted current resembles the density of states to a first approximation. In other words, if an absolute gap exists for an energy region in the density of states, no current in this energy region would be transmitted. Conversely, if a large density of states exists within a certain energy region, a large current would be transmitted since a large number of states would be available for matching.

The density of states is obtained from a recent self-consistent field calculation for ZnO.[11] The conduction-band density of states was superposed on a background function for the purposes of comparison with experiment. The background current is assumed to be a smoothly decreasing square-root function of the gun voltage away from the low-energy region.[7] The middle curve in Fig. 4 displays the results. Again, a numerical differentiation was performed to enhance the structure. The zero reference in the density-of-states diagram (Fig. 5) is the valence-band maximum, while the zero reference used in this paper is the vacuum level. The difference between the two zero references is related to the work function and the position of the Fermi energy for this material. In this paper, it will be assumed that the vacuum level is approximately 8 eV above the top of the valence band. Even though this choice was slightly arbitrary, it appears reasonable on the basis of electron energy loss spectroscopy measurements for ZnO[12] and it results in excellent agreement between the experimental and theoretical curves shown in Fig. 4.

All of the basic features in the experimental spectrum are reproduced by the density-of-states calculation with the exception of the structure near 7 eV. Here a weak shoulder is found in the experimental spectrum, while a strong peak is observed in the theoretical results. This apparent discrepancy arises from the approximate matching conditions used in this analysis. The origin in the density-of-states structure near 7 eV in Fig. 4 arises from band structure of ZnO in the 14–16-eV region (Fig. 5). Perpendicular to the c axis (e.g., A to H) the conduction bands are fairly dispersionless. Thus these bands contribute to a large peak in the density of states. However, the electron beam is oriented along the surface normal and an incident electron with a small wave vector parallel to the surface cannot be matched to these states. Thus the density of states in this energy region overestimates the transmitted current.

The second process affecting the total transmitted current involves the energy losses of the incident electron. As an electron passes through a solid it will lose energy via the creation of single-particle excitations and collective oscillations (plasmons). The single-particle excitations result in the production of secondary electrons which can contribute to the transmitted current. Plasmons created by an incident electron can in principle also affect changes in the transmitted current by reducing or enhancing the back-scattering processes. These inelastic processes can be understood by an examination of the energy loss spectrum. The energy loss spectrum is determined by the behavior of $-\mathrm{Im}(1/\epsilon)$, where ϵ is the complex dielectric function of the solid.[13] The dielectric function can be obtained experimentally from the optical data or theoretically from a band-structure calculation.

The bottom curve in Fig. 4 displays the calculated derivative of the current using $-\mathrm{Im}(1/\epsilon)$ factor. The dielectric function was obtained from the same band calculation as the conduction-band density of states, and the background function was identical in both cases. As before, the results have been numerically differentiated to enhance the structure. The agreement between the theory and experiment is slightly improved with the $-\mathrm{Im}(1/\epsilon)$ results as compared to the conduction-band density-of-states results. Again, the main discrepancy arises in the 7-eV region.

Unfortunately, in ZnO the conduction-band density of states and $-\mathrm{Im}(1/\epsilon)$ functions quite clearly resemble one another. The reason for this situation can be understood by examination of the band structure of ZnO (Fig. 5). The valence bands in ZnO are fairly narrow. This means the structure in the dielectric function is dominated by conduction-band features. As a consequence, the relative contributions due to the energy matching effect on the transmission of the primary electrons as opposed to the energy loss resulting from secondary-electron production is difficult to determine. Work on semiconductor materials with broader valence bands would be necessary to distinguish between the relative contributions of the two effects.

In summary, the dependence on incident electron energy illustrated in Fig. 3 in this low-energy region appears closely correlated with the conduction-band density of states. Although it is not clear if this is due to energy matching, or to energy loss processes, it does indicate that incident electrons in this energy region are probing the electronic structure of the ZnO semiconductor.

High incident electron energies (V_g=30-100 V)

In Fig. 2, the largest peak in the optically modulated current appears at 64 V. If the gun voltage is set at this value and the photon energy is varied, the optically modulated current has a spectral dependence which is shown in Fig. 6. The raw data have, as usual, been corrected for spectral variations in lamp intensity. As is evident in Fig. 6, the optically modulated current decreases rapidly for photon energies below the band-gap energy of ZnO (3.3 eV), and also shows little spectral structure for photon energies above this band gap. These results are an indication that, as in previous work on other semiconductors,[1-4] the physical mechanism responsible for the optical modulation of the transmitted current involves a photovoltaic modulation of the ZnO work function.

In Fig. 7, the dependence of the optically modulation current on gun voltage is shown for a range of photon energies, and it is evident that this series of curves is relatively insensitive to photon energy. To further demonstrate this point, Table I shows the gun voltage values where experimental maxima in the optically modulated current occurred. These maxima have been labeled alphabetically as in Fig. 2 for ease in tabulating the data. The data in Table I indicate that there is approximate agreement in peak positions for the various photon energies, although there is some variation which appears to lie outside of normal

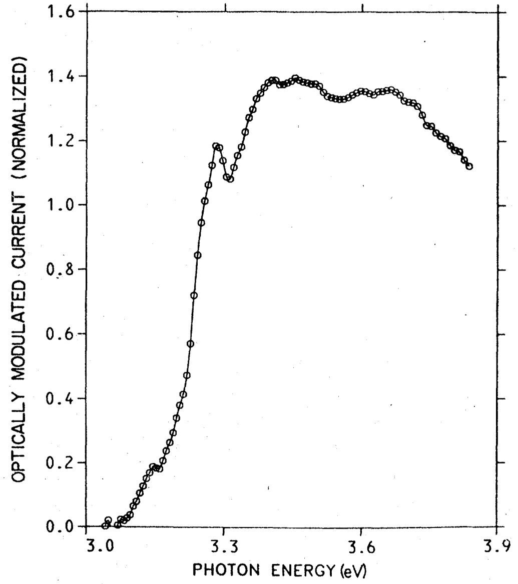

FIG. 6. Optically modulated current as a function of incident photon energy for a fixed electron gun voltage (= 64 V).

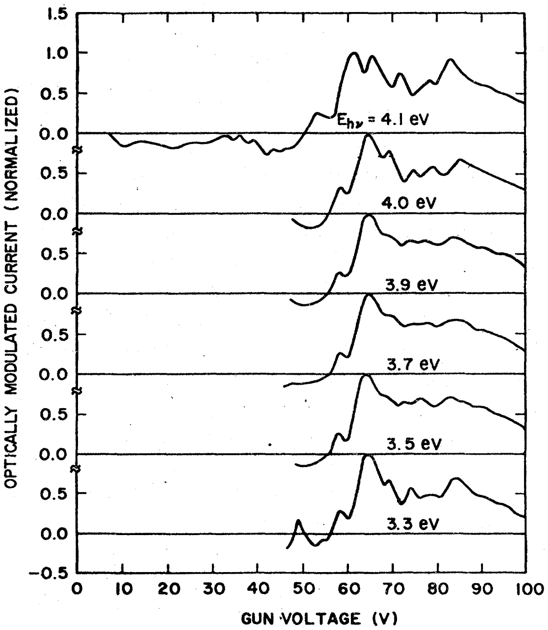

FIG. 7. Optically modulated component of transmitted current as a function of electron gun voltage for a range of incident photon energies.

TABLE I. Gun voltage values for maxima in optically modulated current. Note that electron energies in eV can be obtained from gun voltages by subtracting ~9 V from value shown in this table.

E_h	A	B	C	D	E	F	G	H
3.3	55.6	58.3	64.3	68.7	73.8	84.0	89.7	90.6
3.5		57.6	63.7	67.0	72.6	82.7	89.7	92.6
3.7		58.2	64.1	68.4	73.4	83.5	89.3	
3.9	55.1	58.4	64.0	68.2	73.6	83.8	90.1	94.6
4.0		58.7	64.3	69.2	74.5	84.6		
4.1	52.8	61.4	65.9		71.8	82.5	90.4	93.9

experimental fluctuations.

The origin of the complicated multiplet structure in Fig. 3 at the higher incident electron energies is not yet known. It is not known if the structure in this energy region correlates with the conduction-band density of states as it did at the lower incident electron energies, since the calculations have not been extended into this higher-energy regime. A second possibility is that it originates from one or more electron loss mechanisms which involve the interaction of the incident electrons with the electrons of the solid sample. Structure similar to the incident electron energy dependence of Fig. 3 has been observed using low-energy-loss spectroscopy by a number of workers.[14-16] Recently, a third possibility has been suggested which involves electron stimulated desorption.[17]

CONCLUSION

The transmitted current due to an incident low-energy electron beam, as well as the optically modulation component of this transmitted current, have been reported for ZnO. Both exhibit a qualitatively similar dependence on incident electron energy which is characterized by a complicated multiplet structure. At lower incident electron energies, this structure is closely correlated with the conduction-band density of states in ZnO. This could originate from either energy matching and/or energy loss processes. At higher incident electron energies, however, this correlation no longer applies and several possible physical mechanisms for the observed structure are briefly discussed.

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