

## Detection of Optically Excited States in Wide-Band-Gap Semiconductors with Tunneling Spectroscopy

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Tunneling spectroscopy has been used to detect the photoexcitation of charge carriers in the wide-band-gap semiconductors, ZnO and cubic SiC. Photoexcitation, which increases the charge carrier population and thus reduces the width of the depletion layer at the semiconductor surface, is detected as an enhancement in the tunnel current. Because the process is energy sensitive, valence-to-conduction band or defect charge transfer transitions may be selectively excited and detected by tunneling spectroscopy. Two types of transitions were detected which change the tunneling response; for cubic SiC valence-to-conduction band transitions were excited, while for Co<sup>2+</sup>- and Mn<sup>2+</sup>-doped ZnO electron charge transfer transitions from the dopants to the conduction bands occur. The enhancement of the current was greater in air than under vacuum and more easily detected at small sample-tip separations. [Key words: tunneling, spectroscopy, semiconductors, scanning tunneling microscopy, photoconductivity.]

### I. Introduction

THE value of the scanning tunneling microscope (STM), which has generated a great deal of enthusiasm, lies more in its ability to collect spectroscopic information at high spatial resolution than in its imaging capabilities. In the short time since its invention<sup>1</sup> the technique has been applied to metal,<sup>2</sup> semimetal,<sup>3</sup> and semiconductor<sup>4</sup> surfaces to study such phenomena as surface reconstructions and adsorbate interactions. As such measurements are made on an increasing variety of materials, it is becoming clear that analysis of wide-band-gap materials (ceramics) can be problematic.<sup>5</sup> Two possible situations may exist during STM analysis: either a high density of surface states pin the surface Fermi level or a Schottky barrier forms. In either case, the bulk energy bands are bent and a depletion layer forms under the probe tip which can "pinch" off the tunnel current if wide enough.<sup>6</sup> Because the width of the depletion layer decreases as the carrier concentration increases, it is possible to minimize the depletion layer width and enhance the conductivity by bulk chemical doping. An alternative approach, explored in this paper, is to temporarily increase the free carrier concentration by photoexcitation.

Photoexcitation by monochromatic light sources has been previously used in STM experiments to modulate the sample-

tip separation through local heating,<sup>7</sup> to increase conductance in semi-insulating GaAs,<sup>8</sup> to examine the surface photovoltage effect on the Si (111) (7 × 7) surface,<sup>9</sup> and to selectively image impurities at Si grain boundaries.<sup>10</sup> The primary goal of this work is to demonstrate the feasibility of probing subsurface chemical defects using tunneling spectroscopy (TS) augmented by optical excitation. The absorption of light can temporarily produce free carriers if the energy of the incident light is sufficient to create mobile electrons in the conduction bands or mobile holes in the valence band. A band-to-band excitation will typically create a pair of mobile carriers which will drift in different directions in the depletion layer field gradient, while a charge transfer transition of an electron to the conduction band or a hole to the valence band will create one free carrier which can move in the field. The increased carrier concentration will cause a reduction in band bending, since the depletion layer depth is inversely proportional to the square root of the charge carrier density, and should be detected in the STM as a change in local capaci-

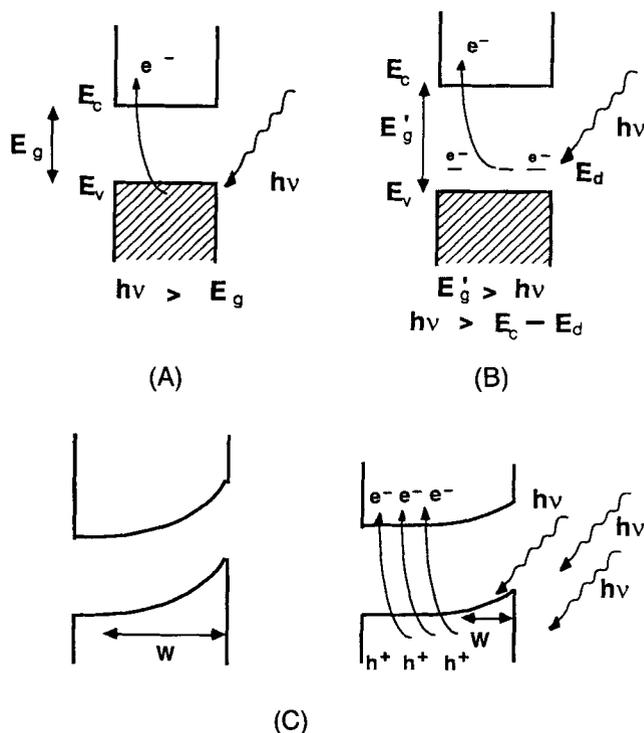


Fig. 1. Schematic energy level diagram illustrating the two methods of photoexcitation, (A) valence-to-conduction band and (B) bound defect state-to-conduction band, and (C) the associated change in the depletion layer width.

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tance, in conductance at constant sample-tip separation or in tunnel barrier height.

The experiments described in this paper were designed to test two possible mechanisms (illustrated in Fig. 1) for enhancing the free charge carrier population by photoexcitation. The first is a valence-to-conduction band transition whereby a free electron is created in the conduction band and a hole in the valence band, and the second is a charge transfer excitation of electrons or holes from donor or acceptor defect states creating single free electrons or holes. To explore the first mechanism, hexagonal SiC, with a band gap of 2.79 eV, and cubic SiC, with a band gap of 2.51 eV, were examined during illumination with 2.81-eV light. Valence-to-conduction band transitions should be allowed for cubic SiC, but only weakly so for the case of hexagonal SiC. To test the second mechanism, pure ZnO, with a band gap of 3.24 eV, and ZnO doped with  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ , which give rise to donor states 1.9 eV<sup>11,12</sup> below the conduction band, were examined under the same 2.81-eV illumination. In this situation, transitions from the  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  levels to the conduction band should be allowed while valence-to-conduction band transitions are forbidden. The results presented in this paper demonstrate that, using TS, it is possible to detect the enhancement of the charge carrier concentration caused by photoexcitation of electrons from either intrinsic valence band states or extrinsic defect states. Although we have not yet determined the spatial dependence of these transitions, our motivation for developing this technique is to eventually utilize the well-known high spatial resolution of the tunneling probe. The results also indicate that photoinduced carriers might permit the STM and TS analysis of samples that normally have insufficient conductivities.

## II. Experimental Procedure

Scanning tunneling microscopy was carried out in an ultra-high-vacuum (UHV) chamber at pressures ranging from  $<5 \times 10^{-10}$  torr ( $\approx 7 \times 10^{-8}$  Pa) to ambient. The microscope used in these experiments was of a standard design, described in detail elsewhere,<sup>5</sup> and the tips were formed mechanically by snipping 0.01-in. Pt wire. Samples were attached to silver or copper plates using silver print after ultrasonic cleaning in acetone and then ethanol. The chamber was configured such that the sample could be illuminated by an external light source while tunneling, as shown schematically in Fig. 2. In the experiments described here, the light source was a He-Cd laser which produces a 7-mW beam of 441.6-nm, 2.81-eV light. Photon flux reaching the sample is estimated at  $1.5 \times 10^{16}/\text{s}$ . Current-voltage ( $I$ - $V$ ) curves were acquired over an energy range of up to 6 eV using the interrupted-feedback method (the feedback circuit was momentarily disabled while the sample bias was ramped) both with and without laser illumination at a variety of sample-tip separations. In this method, the sample-tip separation is adjusted by altering the bias on the tunnel junction while under feedback control. Each  $I$ - $V$  curve presented here represents an average of between 10 and 32 sequentially acquired  $I$ - $V$  curves.

Five samples were examined, a cubic SiC crystal, a hexagonal SiC single crystal, a ZnO single crystal, and two compositions of polycrystalline ZnO. The cubic SiC crystal was grown by chemical vapor deposition methods (CVD) and was a transparent crystal 20 mm thick and had a yellowish color.<sup>13</sup> The green, transparent, hexagonal SiC crystal, grown by the Acheson process, was 450  $\mu\text{m}$  thick and presumably of mixed polytypes. Nearly intrinsic, transparent, colorless, single-crystal ZnO was annealed at 500°C in a zinc overpressure to introduce a population of shallow donors. The electronic conductivity of the crystal increased and it became orange in color as a result of the doping. The polycrystalline ZnO samples were prepared via chemical methods.<sup>14</sup> The first ZnO sample (referred to as ZnO 1) contains 0.1% CoO, 0.1% MnO, 0.1%  $\text{Bi}_2\text{O}_3$ , and 150 ppm  $\text{Al}_2\text{O}_3$ ; the second (referred

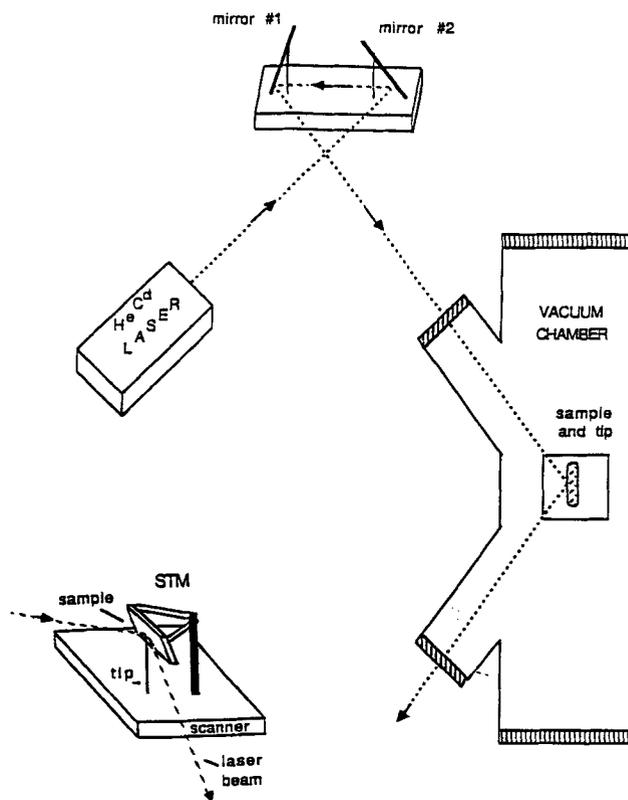


Fig. 2. Schematic illustration of the experimental setup.

to as ZnO 2) contains 0.5% CoO and 0.56%  $\text{Bi}_2\text{O}_3$ . The defect chemistry of these samples, which has been rather well characterized, is summarized in Table I and is discussed in some detail in Section IV.

The electronic structure of these samples will determine their interaction with the 2.81-eV laser illumination, and the method and efficiency of laser-induced charge carrier creation. For intrinsic band-to-band excitations the important consideration will be the band gap energy ( $E_g$ ) and the absorption coefficient of the crystals at the laser photon energy. For electron or hole charge transfer excitations, the donor-to-conduction band or valence band-to-acceptor transition energy and the absorption coefficient of this transition when excited by 2.81-eV photons will dictate the efficiency of charge carrier creation. The band gap energy of a bulk material can be experimentally determined from the bulk absorption coefficient by a fitting procedure where either a direct or indirect band gap model is presumed and the absorption coefficient over some range is fitted. This has been performed for the SiC samples, where transmission and reflectance measurements were performed using a UV-vis spectrophotometer,<sup>†</sup> and the absorption coefficient  $a$  in units of  $\text{cm}^{-1}$ , determined using a 2-D Newtons method which corrects for multiple internal reflectance losses in the sample, is shown in Fig. 3. The range of the absorption coefficient measured and, therefore, fitted determines to a degree the band gap energy reported. If the crystal is thick enough to limit the transmission of light near the fundamental absorption, only small absorption coefficients (say  $1 < a < 100 \text{ cm}^{-1}$ ) are probed and the fit to  $a^2 E^2$  for a direct gap model will produce a smaller reported gap energy than if the fundamental absorption edge is probed at much higher absorption coefficient values. Still, comparisons of band gap energies determined by fitting comparable ranges of the fundamental absorption edge demonstrate the differences in the band energies of the samples. The cubic SiC sample has a direct gap energy of 2.51 eV for

<sup>†</sup>Lambda-9, Perkin-Elmer, Norwalk, CT.

Table I. Summary of Excitations Observed in Tunneling Response

| Sample             | Relevant energies (eV)   | Effect in air                 | Effect under UHV        |
|--------------------|--|-------------------------------|-------------------------|
| ZnO single crystal | 3.24 (band gap)<br>0.32 (O vacancy)<br>0.03 (Zn interstitial)  | No effect                     | No effect               |
| ZnO 1              | 3.24 (band gap)<br>1.92 (tet. $\text{Co}^{2+}$ )<br>1.9 ( $\text{Mn}^{2+}$ )<br>0.32 (O vacancy)<br>0.03 (Zn interstitial) | Large increase in conductance | Not clear               |
| ZnO 2              | 3.24 (band gap)<br>1.92 (tet. $\text{Co}^{2+}$ )<br>0.32 (O vacancy)<br>0.03 (Zn interstitial)                             | Large increase in conductance | Increase in conductance |
| SiC, hexagonal     | 2.79 (band gap)  | No effect                     | Not attempted           |
| SiC, cubic         | 2.51 (band gap)  | Increased conductance         | Increase in conductance |

fitting  $75 < a < 150 \text{ cm}^{-1}$ , while the hexagonal SiC sample has a direct gap energy of 2.79 eV fitted in the same range of  $\alpha$ . The absorption depth ( $d$ ) of the laser's photon flux can be determined from the absorption coefficient by the condition  $ad = 1$  and determines the volume of the sample in which the incident photons will excite charge carriers. For the cubic SiC the absorption coefficient at 2.81 eV is  $410 \text{ cm}^{-1}$  while for the hexagonal SiC it is only  $56 \text{ cm}^{-1}$ . There is roughly a factor of 10 increase in the volume over which the laser excites charge carriers in the hexagonal SiC sample, and therefore a factor of 10 decrease in this sample's depletion layer charge carrier increase under illumination compared to the cubic SiC sample. The hexagonal SiC sample also exhibits a defect absorption at 2.0 eV which is visible in Fig. 3, and must arise from a non-charge-transfer transition.

None of the ZnO samples examined by TS were suitable for optical measurements. However, the band gap energy of a nearly intrinsic ZnO crystal was determined by spectroscopic ellipsometry. The absorption coefficient determined from ellipsometry is not accurately known in regions where the extinction coefficient ( $k$ ) is near zero because of the inherent accuracy of rotating analyzer ellipsometers for small  $k$  values. But the increase of  $k$  and  $a$  at the fundamental absorption edge is well represented and a direct gap fit for this ZnO sample gives a band gap energy of 3.24 eV for  $200000 < a < 300000 \text{ cm}^{-1}$ . Although the band gap energies of the samples studied by TS may differ slightly, they are still much larger than the laser's photon energy and therefore the band-to-band

charge carrier creation mechanism is ruled out for these samples. Only doped samples with charge transfer excitation from defect states exhibited the photoinduced STM effect.

It was difficult, in some cases, to reproducibly observe the photoexcitation effect by TS on the same material on every attempt. However, by slightly adjusting the aim of the laser or sometimes changing the tip, the effect would eventually be observed and continue to be observed reproducibly until the experimental configuration was altered. A plausible explanation for this behavior is that certain asymmetric tip or sample geometries "shadowed" the sample from the primary beam.

When the laser illuminates the sample and tip surfaces, there is always a change in the vertical position of the tip. The change in position, which was found to occur even when the laser is aimed at the tip well away from the sample surface, is the result of a small local temperature increase. The temperature increase, measured to be  $2^\circ$  to  $3^\circ\text{C}$  in air by aiming the laser at a thermocouple, causes the sample and tip to expand and thus the vertical position of the tip is changed in order to maintain a constant tunneling current. This tip extension, which is easily compensated for by the feedback circuit, causes several potential difficulties which must be considered. The first is that the area of the sample into which the electrons are tunneling may change. This is especially important for inhomogeneous samples such as polycrystalline materials, in which experimental reproducibility was verified at several locations on the sample surface. The second is that the current set point of the feedback circuit can be altered by extreme changes in the  $z$  position. In order for the sample-tip separation to be constant, the current must be readjusted to the original value; otherwise the comparison is invalid. The last problem is that the expansion can be so great that the range of the vertical extension is exceeded, in which case the sample must be brought out of tunneling to avoid a "tip crash" while the system comes to thermal equilibrium. It must be assumed that when tunneling is reestablished following thermal equilibrium, a new portion of the sample is being probed. In most cases, however, tunneling is not interrupted by the illumination so that the dark and light spectra can simply be obtained in alternation, the illumination time being only that required to make the measurement, approximately 10 s.

It is well-known that the electronic structure of ZnO surfaces is affected by atmospheric gases which can be adsorbed on the surface.<sup>16</sup> The uncharacterized state of many of the sample surfaces examined in these experiments is one unsatisfactory aspect of this study. In an attempt to identify any possible effects due to photodesorption of contaminants during the experiment, a ZnO 1 sample was cleaned in situ. After this surface was polished with  $0.25\text{-}\mu\text{m}$  diamond paste, the 2-mm-thick wafer was ultrasonically cleaned in acetone and then ethanol. The sample was subsequently heated in air to

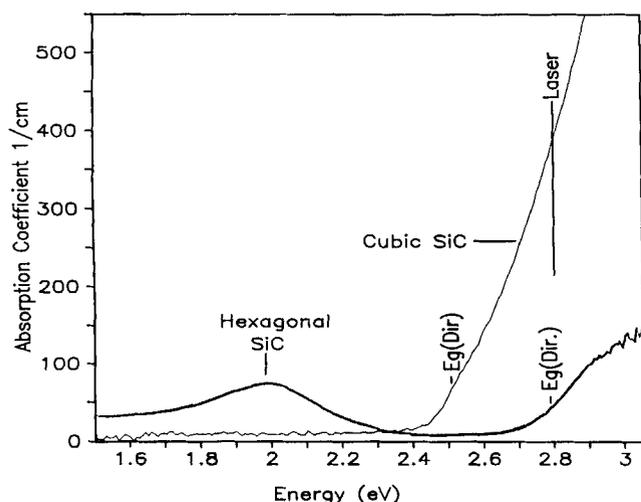


Fig. 3. Optical absorption spectrum of cubic and hexagonal SiC.

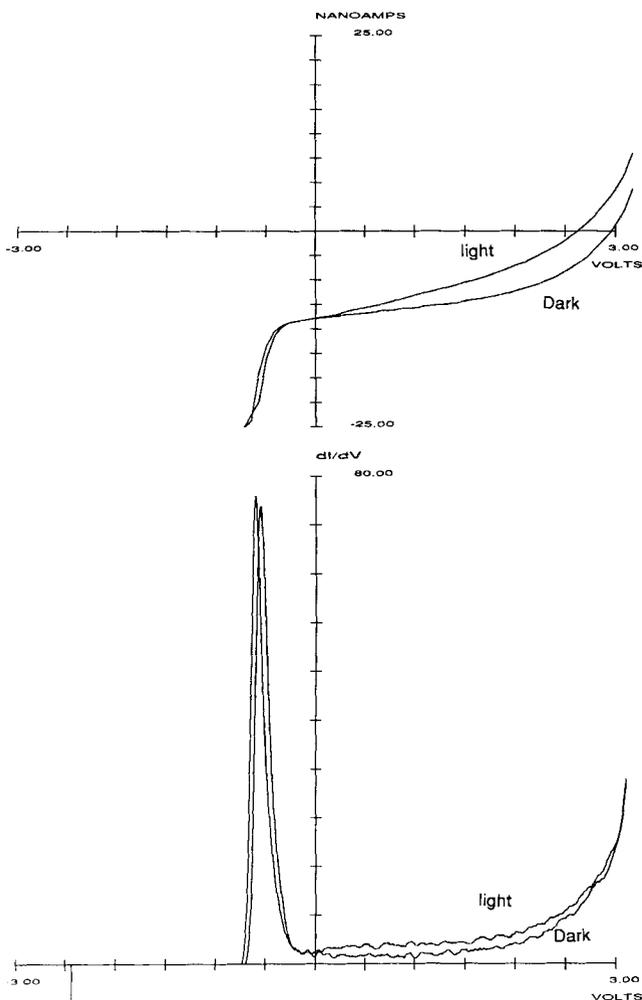
140°C for 30 min and then to 500°C for 30 min. Although the surface conductivity of the sample following this treatment was insufficient for tunneling in air, it increased to acceptable levels after evacuation of the STM chamber. Interestingly, the sample remained conductive for an extended period (at least several days) after subsequently venting the chamber with air so that results could be obtained in ambient atmosphere and compared to those acquired under UHV. The cause of this phenomenon is the absorption and desorption of surface water which changes the depth of the surface space charge layer.<sup>17</sup> After evacuation of the chamber, the sample was heated to 400°C for 10 min to remove any chemisorbed gases. Auger electron spectroscopy analysis of the samples following this treatment (and the transfer of the sample through air to a second chamber) indicated that the surface carbon concentration was less than 18 at.% of a monolayer. Higher-temperature treatments, which were more effective in removing carbon from the surface, could not be used because they also segregated bismuth to the sample surface.<sup>17</sup> The composition of residual gases in the chamber, monitored before, during, and after laser illumination, showed no detectable change.

### III. Results

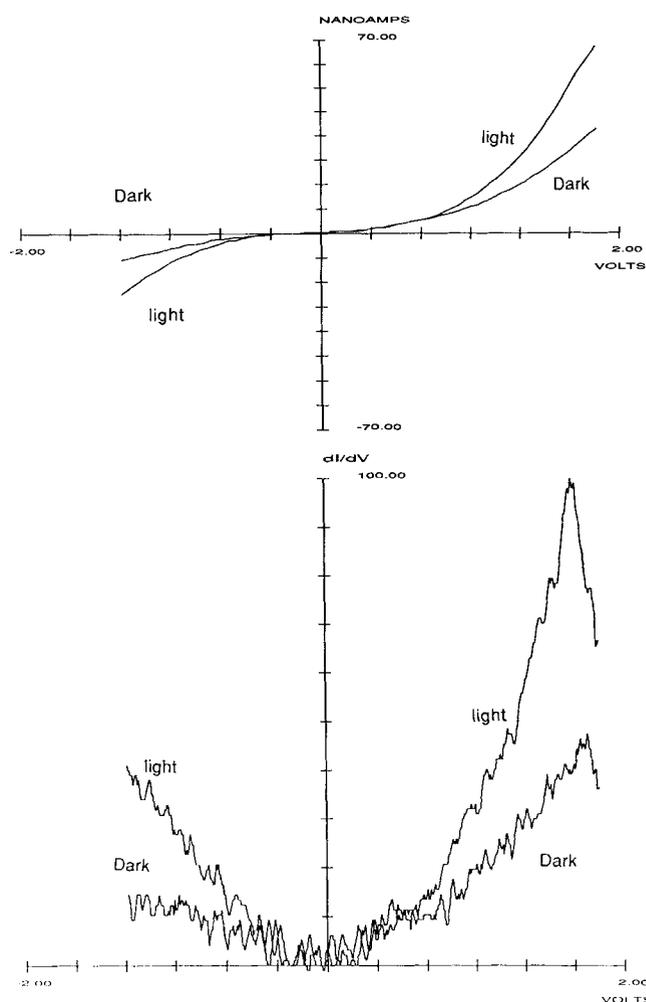
No photoconduction effect was observed in the tunneling spectra or in the current on contact (current measured when the tip was pushed into direct contact with the surface) in the

analysis of the hexagonal SiC crystal in air. Although there was some optical absorption detected at 2.81 eV, the number of free carriers created apparently did not increase the current enough to be detected. Consequently, this sample was not analyzed under UHV. The results of the analysis of cubic SiC, which had an absorption coefficient 10 times greater than that of hexagonal SiC at 2.81 eV, are illustrated in the current-voltage curves and derivative spectra of Fig. 4. Illumination of the junction in air increased the conduction above the Fermi level (which is at 0 V in the spectra). Unfortunately, the limited dynamic range of the current digitizer used for these experiments prevented the accurate measurement of the high current levels detected below the Fermi level. Under vacuum, the increase in conduction (see Fig. 5) is somewhat smaller but is observed both above and below the Fermi level. The photoexcitation effect was detected only at the smallest relative sample-tip separations obtained using sample biases of -1.0 V and below. In this case the increased conductance must result from valence-to-conduction band transitions.

The current-voltage relationship and the derivative spectra calculated from these data for the ZnO single crystal (10 $\bar{1}0$ ) face in air and under UHV are shown in Fig. 6. The spectra acquired in air are extremely rectified in a manner typical of Schottky barrier formation with an *n*-type semiconductor. The spectra acquired under vacuum indicate flat band conditions exist in the sample with the Fermi level pinned about midgap. The severe band bending that occurs in air precludes the possibility of tunneling into the unoccupied conduction band states above the Fermi level and is discussed in some



**Fig. 4.** Dark and light tunneling spectra of cubic SiC in air. The feedback tunneling conditions were sample bias = 3.25 V and current = 3.0 nA. The offset from zero is due to the capacitance of the microscope.



**Fig. 5.** Dark and light tunneling spectra of cubic SiC under vacuum. The feedback tunneling conditions were sample bias = 1.0 V and current = 6.0 nA.

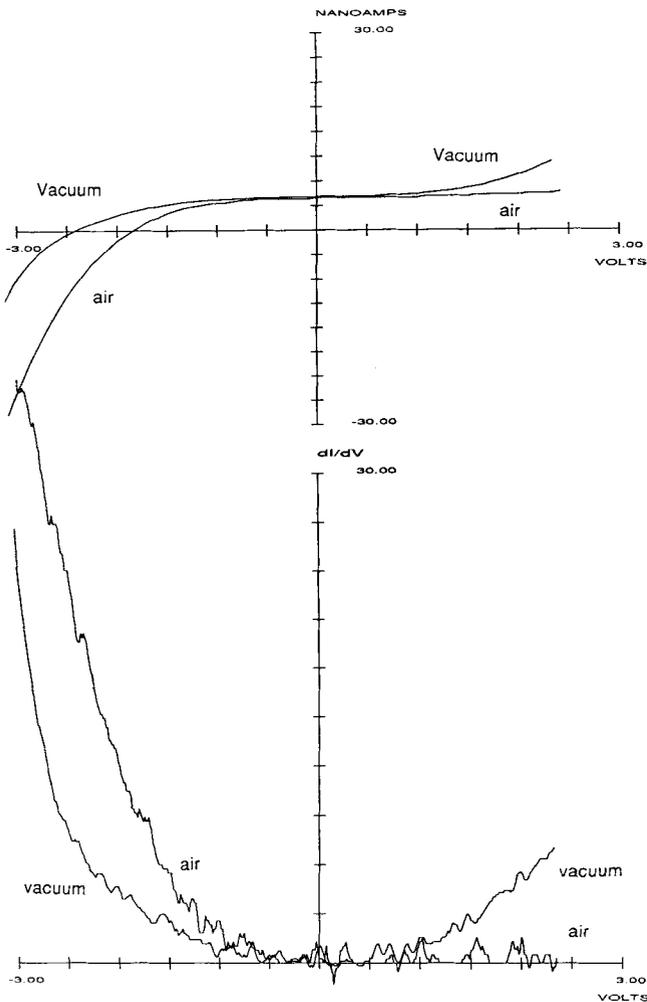


Fig. 6. Comparison of tunneling spectra obtained in air and under vacuum from single-crystal ZnO. The feedback tunneling conditions were sample bias =  $-2.0$  V and current =  $5.0$  nA.

detail in a forthcoming paper.<sup>17</sup> No effect in the tunneling behavior was observed on illumination of the intrinsic sample with  $441.6$ -nm-wavelength light, a reasonable result as a large density of bulk defect states is not present in the forbidden gap and the light has insufficient energy to induce valence-to-conduction band excitations.

In contrast, both of the polycrystalline ZnO samples containing transition-metal ions exhibited an increased conduction below the sample Fermi level when tested in air. The data from ZnO 2 are shown in Fig. 7. The increased conduction is consistent with the increased carrier concentration that would be produced by the elevation of electrons from the  $\text{Co}^{2+}$  or  $\text{Mn}^{2+}$  ground state to the conduction band. Under vacuum, the ZnO 2 sample showed increased conductance both above and below the Fermi level (see Fig. 8). Like the SiC sample, this effect was only detected at the smallest relative sample-tip separations, obtained with a  $-1.0$  V sample bias. Although the ZnO 1 sample showed a similar effect in air, the effect was most reproducibly detected in the ZnO 2 sample, which also had more than twice the total concentration of transition-metal ions. Under vacuum, however, the detection of photoexcitation could not be verified for ZnO 1 because of an abnormally large change in the vertical position of the tip that occurred upon illumination. When the tip was in contact with ZnO 1, a configuration which corresponds to a metal-semiconductor junction, the current increased by 60% upon illumination. The conditions under which excitations were, and were not, observed are summarized in Table I.

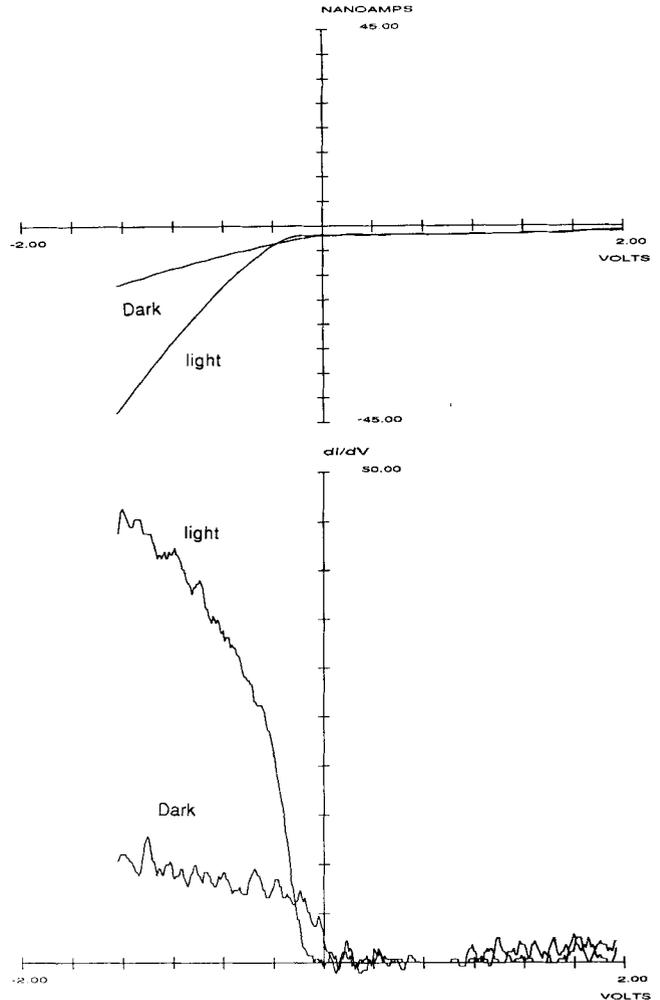


Fig. 7. Dark and light tunneling spectra of polycrystalline ZnO 2 in air. The feedback tunneling conditions were sample bias =  $1.9$  V and current =  $1.0$  nA.

#### IV. Discussion

The absence of a photoexcitation effect in the ZnO single crystal and presence of a photoexcitation effect in the  $\text{Co}^{2+}$ - and  $\text{Mn}^{2+}$ -doped polycrystalline ZnO can be easily explained in terms of electronic structure. Pure ZnO has a band gap of  $3.24$  eV and an intrinsic shallow donor population (oxygen vacancies and/or zinc interstitials) which are ionized at room temperature. In the crystal examined here, the population of these donor defects was enhanced by the high-temperature treatment in zinc vapor. Electrons could not be excited from the valence band to the conduction band because the energy of the incident light ( $2.81$  eV) was well below that of the band gap; hence no photoexcitation effect was observed. If any bound defect states existed within  $2.81$  eV of the conduction band, they were apparently not numerous enough to affect the tunneling current in a significant way.

The polycrystalline samples, on the other hand, had a number of additives and a somewhat different electronic structure. Bismuth, not soluble in ZnO, is known to be concentrated at the grain boundaries and aluminum, which is added as a sintering aid, is also thought to reside at the grain boundaries. Therefore, neither of these additives will be discussed further, since they do not affect the bulk electronic structure of the ZnO grains. However, transition-metal ions such as  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  are soluble in the ZnO matrix and are known to create deep level defect states in the band gap. Because  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  have ground states approximately  $1.9$  eV below the conduction band edge,<sup>11,12</sup> it is possible to excite charge trans-

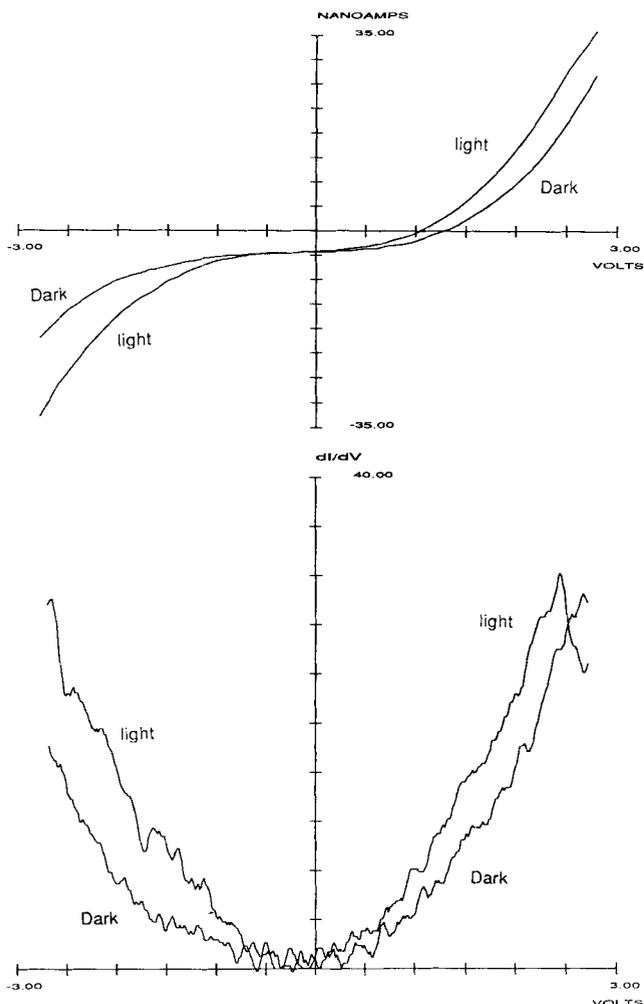


Fig. 8. Dark and light tunneling spectra of polycrystalline ZnO under vacuum. The feedback tunneling conditions were sample bias =  $-1.0$  V and current =  $1.0$  nA.

fer transitions from the donor dopant to the conduction band, increasing charge carrier concentration. It is the excitation of carriers from these states which causes the photoeffect in the polycrystalline ZnO. Previously, Flores and Garcia have demonstrated theoretically that the size of the space-charge region present at semiconductor surfaces during a tunneling experiment decreases with increasing carrier concentration.<sup>18</sup> In this case, the increased carrier concentration created by the illumination causes a temporary reduction in the width of the depletion layer and an increased conductance.

It is well-known that the adsorption of atmospheric gases by ZnO creates a depletion layer at the surface. Therefore, an alternate explanation for the increase in conductance on illumination is that the light stimulates the photodesorption of molecular species from the ZnO surface and causes a reduction in the depletion layer width and increased conductance. There are two reasons why it is unlikely that this process occurs in these experiments. Shapira *et al.* studied photodesorption from ZnO surfaces and found that desorption was stimulated only by photons with energies near or above the band gap.<sup>19</sup> The light used in the current study is in an energy range where almost no detectable desorption occurred in the previous work. This is supported by the fact that there was no detectable change in the residual gas composition of the UHV chamber during the laser illumination of ZnO 1. Also, the same desorption process should have occurred on both the pure and the doped material, yet the photoexcitation effect was detected only in the doped material. Lastly, the effect would not have been reproducible under vacuum since

the prolonged laser irradiations to which the sample was exposed would have degassed the sample surface. It should also be noted that the small increase in sample temperature associated with the illumination is not enough to drastically change the sample conductance and would have had the same effect on all of the samples.

In contrast to the case of ZnO, cubic SiC has an energy gap less than that of the incident light and, therefore, valence-to-conduction band transitions would be expected. In fact, an increase in the conductance was observed when the cubic SiC was illuminated and we attribute this to an increase in the charge carrier density caused by the expected valence-to-conduction band transitions. For hexagonal SiC, on the other hand, no photoexcitation effect was detected. Under 2.81-eV illumination, the increase in the charge carrier concentration arising from valence-to-concentration band transitions is negligible due to the larger band gap energy and the smaller absorption coefficient of this sample.

It is well-known that SiC crystals exposed to ambient conditions are coated with an oxide layer and that tunneling through such layers does not present any difficulty.<sup>20</sup> This is presumably an inert layer which is essentially unaffected by the laser, a reasonable assumption considering the stability of such layers and the difficulties one normally encounters when trying to remove them. The laser, therefore, cannot induce any compositional changes at the SiC/SiO<sub>2</sub> interface which would by themselves change the width of the depletion layer and cause an increase in conductance. It is clear, however, that the presence of surface contamination layers complicates the interpretation of the experimental results and our ongoing studies will address this concern.

## V. Conclusions

The possibility of enhancing the tunneling current during the STM analysis of wide-band-gap materials through photoexcitation has been demonstrated. In the case of doped ZnO, the charge carrier concentration and tunnel current are increased by the excitation charge transfer transitions from bulk donor defect states to the conduction bands, thus allowing the STM to probe subsurface chemical defects for the first time. The energy sensitivity of the process suggests that the tunneling current may be used as a detector for optical spectroscopy with the high spatial resolution of the STM, an exciting development with the potential of identifying microscopic structural and chemical defects. In the case of SiC, the charge carrier concentration and tunnel current are increased by the excitation of valence-to-conduction band transitions. It is hoped that further developments of this technique will extend the range of materials to which STM can be applied, perhaps even to include insulators.

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