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Analysis of scanning tunneling optical spectroscopy applied to narrow gap semiconductors

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ABSTRACT

Homogeneous II-VI narrow gap semiconducting alloys are of interest because of their use in infrared detectors. These compound semiconductor materials are inherently difficult to grow in bulk due to gravity induced convective flows. A microgravity growth environment has therefore been considered. In order to evaluate the quality of crystals grown in space compared to those grown on the ground, it is necessary to characterize both. One important aspect of this characterization is the study of stoichiometry, x. A characterization scheme using scanning tunneling optical spectroscopy (STOS) involves determining the spectral response of the photoexcited tunneling current for a semiconductor. By measuring the photoenhanced tunneling current versus photon energy, the band gap E_g of the semiconductor material can be determined. Such measurements determine $E_g = E_g(x)$ locally, and thus x can be determined as a function of position provided $E_g(x)$ is known. We consider a one dimensional model, involving a simple analysis of absorption of photons, production of photoelectrons, diffusion of photoelectrons to the surface, and tunneling of these electrons to the STM probe. Our results of photoenhanced tunneling current versus photon energy are qualitatively similar to experiment. After our results are presented, we list questions that need to be considered for an improved version of our analysis which is planned.

Keywords: semiconductors, characterization, stoichiometry, tunneling, photoenhanced, microscopy, spectroscopy, alloys, infrared, microgravity,

1. INTRODUCTION

Narrow gap semiconductors have been of interest for many years because of their use in infrared detectors.[1] Because of gravity induced convective flows, homogeneous II-VI narrow gap semiconducting alloys seem to be inherently difficult to grow in bulk, and therefore a microgravity growth environment has been considered. The crystal growth of Mercury Cadmium Telluride, $Hg_{1-x}Cd_xTe$ (MCT), Mercury Zinc Telluride, $Hg_{1-x}Zn_xTe$ (MZT), and Mercury Zinc Selenide, $Hg_{1-x}Zn_xSe$ (MZS), both on earth and in microgravity have been investigated by Lechoczky[2] and others. The x values of particular interest were for energy gaps appropriate for infrared sensor materials (E_g of order 0.1eV). Bulk $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Zn_xTe$ have been grown successfully in microgravity on the Space Shuttle by NASA. It is desirable for crystals to be as uniform as possible with regard to stoichiometry because of the dependence of band gap on x. Microgravity should facilitate the growth of uniform crystals as it may reduce fluid flow.

To evaluate the quality of the crystals grown in space compared to those grown on the ground, it is necessary to characterize both. One important aspect of this characterization is the study of stoichiometry. For many years, a standard method of obtaining compositional distributions, or local stoichiometry, of narrow gap compound semiconductors has been by the use of infrared transmission edge measurements.[3] The idea is that such measurements determine $E_g = E_g(x)$ locally, and thus x can be determined as a function of local position. For degenerate semiconductors, this interpretation is made more complicated by the shift in absorption edge due to

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band filling (Burstein-Moss Effect)[4], but the determination of the stoichiometry as a function of position x(r) can still be made in principle.

An alternative technique for determining local stoichiometry is the one considered in this paper, which is called scanning tunneling optical spectroscopy STOS.[5] This involves studying the spectral response of the photoexcited tunneling current from semiconductors using the scanning tunneling microscope. By measuring photoenhanced tunneling current versus photon energy of a semiconductor illuminated with monochromatic light using a scanning tunneling microscope, the band gap of the semiconductor material can be determined locally.

As far as the applicability of the STM method is concerned, one might wonder if the stoichiometry could vary so rapidly that the resolution of the STM would be required. Perhaps using near-field small-aperture infrared transmission, scanned across the surface, could provide sufficient spatial resolution. Besides the possibility that the tunneling current may allow us to see things we hadn't anticipated, other reasons for considering the STM method include:

(i.) If it works, it will yield very accurate results because it probes a small area of the surface. We do not need to scan the surface with the STM with nanometer resolution, however. For stoichiometry determination, taking measurements every 100,000 atoms (or more) would be sufficient.

(ii.) For infrared transmission measurements, the infrared radiation needs to be directed through the sample, which must be sliced fairly thinly. Otherwise, this technique will be averaging over the diameter of the beam, as well as over the volume of the sample through which the beam passes. Although corrections can be made for measurements on thick samples, such corrections are to be avoided if possible. The STM technique probably averages over a very small area of the surface, and only to a small degree into the volume of the sample.

(iii.) The real question is: over what "volume" of a sample do we want to define stoichiometry? The larger the volume, the greater the chance that defects and non-uniform composition will be included in the determination of the stoichiometry.

2. PHOTOEXCITATION OF ELECTRON-HOLE PAIRS

To analyze STOS, we will consider a one-dimensional model, and will consider electrons only, ignoring holes. We will construct the simplest model that seems to us to contain the essential physics. At the end of this paper, we discuss general corrections which are necessary and also corrections which are necessary so that the technique will be applicable to our narrow gap semiconductor materials.

To consider STOS, we want to consider the effects due to additional electrons which are photo-excited. We assume there is a diffusion region near the surface of the semiconductor where we can neglect drift currents and we assume the depletion region near the surface is thin enough to neglect. In the diffusion region we write:[6]

$$D_n \frac{d^2 \Delta n}{dx^2} - \frac{\Delta n}{\tau_n} + g_E = 0, \quad (1)$$

where g_E is the number of electrons generated per unit volume per unit time by the incident light, and $\Delta n = n - n_0$.

Let $F = F_0 \exp(-\alpha x)$ be the number of photons crossing unit area in unit time, for $x > 0$, where α is the absorption coefficient. If each photon which is absorbed creates an electron-hole pair then,

$$g_E \Delta A \, \Delta x = [F(x) - F(x + \Delta x)] \Delta A, \quad (2)$$

and so we find that

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$$g_E = -\frac{dF}{dx} = \alpha F_0 \exp(-\alpha x). \tag{3}$$

This in effect assumes a quantum efficiency of unity. However, since there are constants in α which may not be precisely known, we will ignore this approximation.

One boundary condition is the fact that the number of photoexcited carriers must vanish as they penetrate deep inside the semiconductor and far from the surface. Therefore, $\Delta_n = n - n_0 = 0$ as x becomes very large.

The properties of the surface are always complex and hard to characterize.[7] We choose to bury our ignorance in a quantity called the surface recombination velocity S_n, defined by [8]

$$D_n \left[\frac{d\Delta n}{dx} \right]_{x=0} = S_n (\Delta n)_{x=0}. \tag{4}$$

Let us define $y = \Delta n$, $a = \tau_n D_n$, and $b = \alpha F_0/D_n$. Then the differential equation becomes

$$\frac{d^2 y}{dx^2} - \frac{y}{a} = -b \exp(-\alpha x). \tag{5}$$

The general solution of the inhomogeneous equation is the sum of the general solution of the homogeneous equation plus a special solution of the inhomogeneous differential equation. Applying the first and the second boundary conditions, and defining $I_n = b/\alpha$, $D = D_n/S_n$, $p^2 = 1/a$, and $B = (\alpha I_n)(1 + \alpha D) / [(\alpha^2 - p^2)(1 + pD)]$, we can write the solution as

$$y = \left[B \exp(-xp) - \frac{b}{\alpha^2 - p^2} \exp(-\alpha x) \right], \tag{6}$$

where B is determined by the second boundary condition. The quantity that we actually need is $y(x{=}0) = (\Delta n)_{x=0}$, which we find can be written:

$$[\Delta n]_{x=0} = \frac{\alpha I_n D}{(\alpha + p)(1 + pD)}. \tag{7}$$

3. TUNNELING AND RESULTS

We now turn to the discussion of tunneling from the semiconductor, to the STM probe.[9-11] For simplicity, we continue to limit ourselves to a one dimensional treatment (see Figure 1). At finite temperatures, the current obtained in transitions from state 1 to state 2 is given by

$$I_{1\to 2} = -A \int |B|^2 N_1(E) f(E) N_2(E - eV) [1 - f(E - eV)] dE \tag{8}$$

where V is the applied voltage, N(E) is the appropriate density of states, and B is the tunneling matrix element. The negative sign indicates that current flows in the opposite direction to the negative electron flow. We obtain the total current by adding the forward current, and subtracting the reverse current:

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$$I_{Total} = -A\int |B|^2 N_1(E)\, N_2(E-eV)\left[f(E)-f(E-eV)\right] dE. \tag{9}$$

Noting that

$$f(E)-f(E-eV) = -eV\left(-\frac{df}{dE}\right) = -eV\,\delta(E-eV), \tag{10}$$

we find at low temperature the total current becomes

$$I_{Total} = eVA|B|^2 N_1(E_F)\, N_2(E_F-eV). \tag{11}$$

We have neglected the tunneling of holes. However, including holes should only affect the value of the unknown constant A. Hence, it does not seem worthwhile to address this problem here.

As a further approximation, we assume that the Fermi energy E_F in the semiconductor equals E at the bottom of the semiconductor conduction band (before irradiation). From now on, we treat the tunneling situation as occurring at a temperature of absolute zero.

Now assume that the surface of the semiconductor is illuminated with monochromatic electromagnetic radiation at the junction of the surface and the STM probe tip. This will produce Δn electrons per unit volume at the surface, and change the Fermi energy E_F to $E_F + \Delta E_F$. If we use the free-electron approximation, then

$$\Delta E_F = \frac{1}{2m}\left(\frac{3h^3}{8\pi}\right)^{\frac{2}{3}} (\Delta n)^{\frac{2}{3}}. \tag{12}$$

Equation (12) assumes a parabolic band, which is not the case for MCT and related crystals, except for very low excitation energies in the conduction band. As far as the current is concerned, ΔE_F acts similar to a driving voltage. We fix the applied voltage at some value, so that the quantity

$$K = A|B|^2 N_1(E_F)\, N_2(E_F-eV) \tag{13}$$

is a constant, where we assume that the density of states are weak functions of the energy. Then the total current can be written as

$$I_{Total} = K\left[eV - \Delta E_F\, \Theta(hf - E_g)\right] , \tag{14}$$

where Θ is the unit step function.

For parabolic bands (again not exactly our case), we can assume the absorption coefficient is given by

$$\alpha = \frac{C}{hf}(hf - E_g)^{\frac{1}{2}}\, \Theta(hf - E_g). \tag{15}$$

Equations (7), (12), (14), and (15) determine the tunneling current. The contribution to the total current as a result of the electromagnetic radiation alone is obtained by subtracting the quantity (K e V) from Equation (14). Our results are presented in Figure 2. Qualitatively, these results compare well to experiment.[5] Experimentally, we would also expect a low frequency tail due to impurity states in the band gap.

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4. APPROXIMATIONS

The actual nature of the processes involved is considerably more complicated. To illustrate this, we list some questions that need to be considered for an improved version of our analysis.

1. What is the nature of the surface?
   a) Can surface states be characterized sufficiently well by a surface recombination velocity?
   b) Is there a diffusion region near the surface where most of the photoelectrons are produced, and is the depletion region thin enough to neglect electric field effects, as well as recombination and generation?
   c) Is surface reconstruction a significant factor for our predictions?
2. Surface states and other causes of electric fields lead to band bending, which can trigger surface photovoltage (SPV). SPV may reduce or change the barrier -- so what is the true nature of band bending near the surface? How serious an error do we make by simply neglecting band bending near the surface?
3. What is the nature of the barrier? Of the following, which ones need to be included?
   a) Vacuum Barrier?
   b) Schottky Barrier?
   c) Image Potential Contribution?
   d) All of the above?
4. How accurate is our treatment of the effect of photoelectrons which are assumed to produce an effective voltage due to producing a ΔE_F?
5. What are the effects due to defect energy levels in the band gap? If they produce a tail, does this disguise the sharp rise in the current sufficiently enough so as to make the determination of the band gap difficult?
6. Is it better to consider the three dimensional nature of the tunneling and put in the transverse momentum, while conserving transverse momentum at the interface? This problem can be readily addressed by using known techniques.[12]
7. The narrow gap semiconductors are non parabolic. How important is this for the effects on the density of states and the absorption coefficient? A theory of absorption coefficients for MCT is available.[13]
8. What is the effect on the tunneling current for the density of states to vary with energy?
9. Do we need to consider the possibility of our semiconductor being degenerate before photoexcitation, and what effects does this have?
10. What is the quantum efficiency for forming electron hole pairs, and what effects are there due to the tunneling of both electrons and holes?
11. This calculation has in effect been done for the temperature approaching absolute zero. What are the effects of temperature?
12. We are also neglecting Franz-Keldish like effects. [14]

The next phase of this research will be to address the above deficiencies and to produce a calculation specific to the materials of interest.

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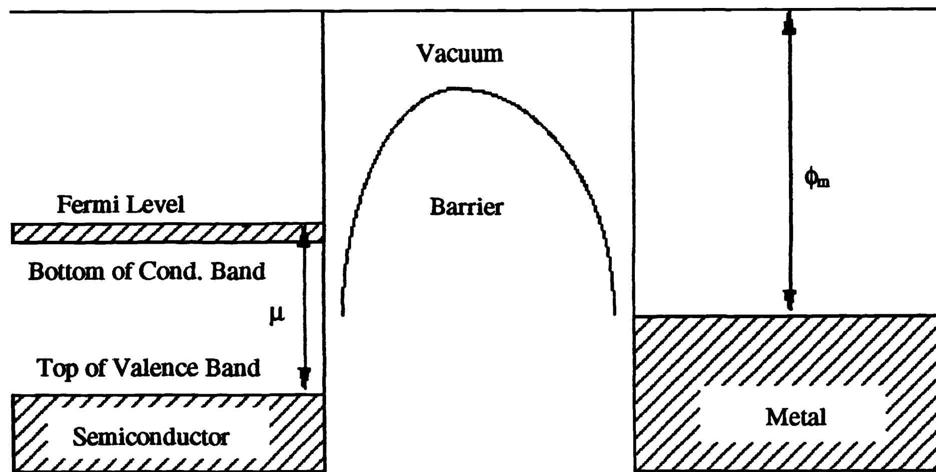
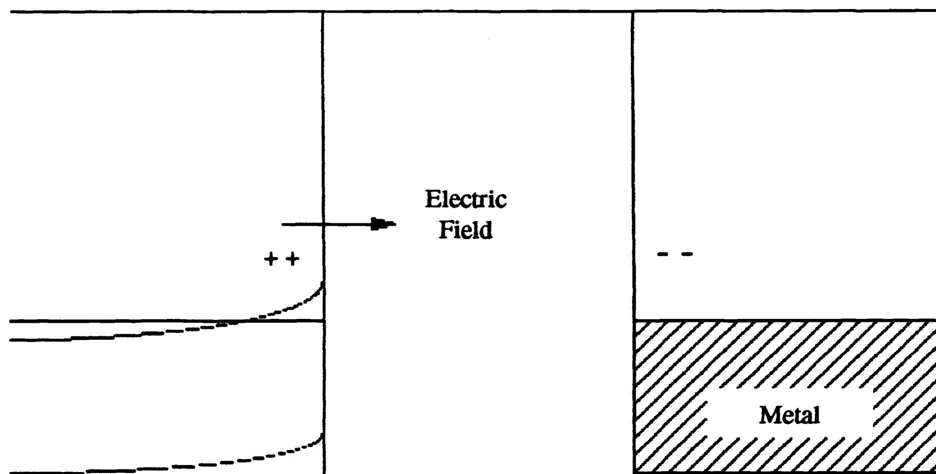


(a) Before Contact



(b) After Contact

Figure 1 (a) and (b). Semiconductor-Metal Tunneling. The Fermi energy in the semiconductor is at μ in the conduction band relative to the top of the valence band. The work function in the metal is at ϕ_m. The actual barrier between the probe and the semiconductor may arise from a variety of causes. The distance from the semiconductor to the probe is typically of order five Angstroms. The figures are to be regarded as schematic only. In Fig. 1 (a), there is no band-bending in the semiconductor since no surface states on the semiconductor have been considered. In Fig. 1 (b), charge flow which equalizes the Fermi levels causes band-bending. The top of the valence band and bottom of the conduction band in the semiconductor are sketched.

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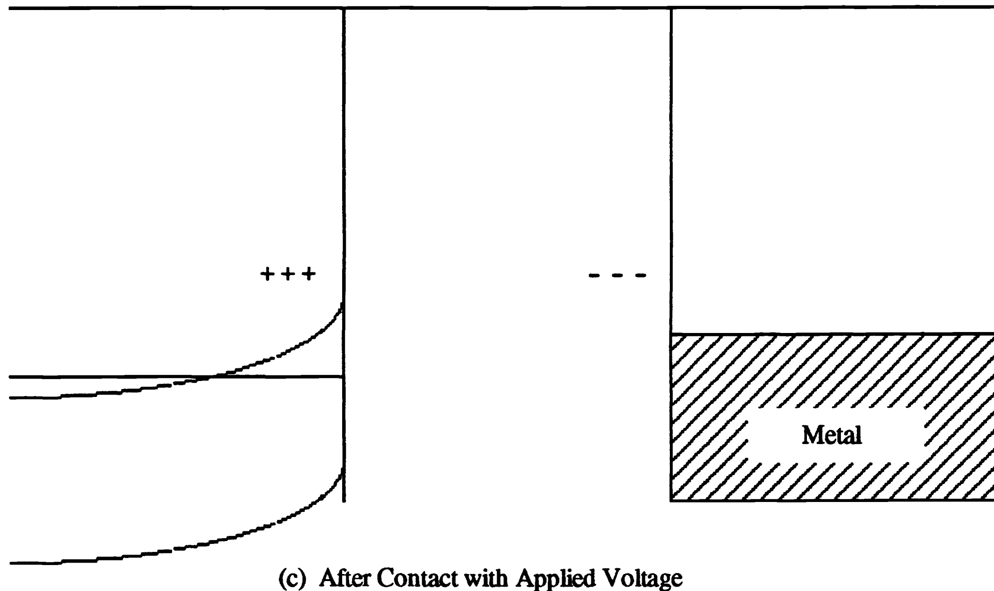
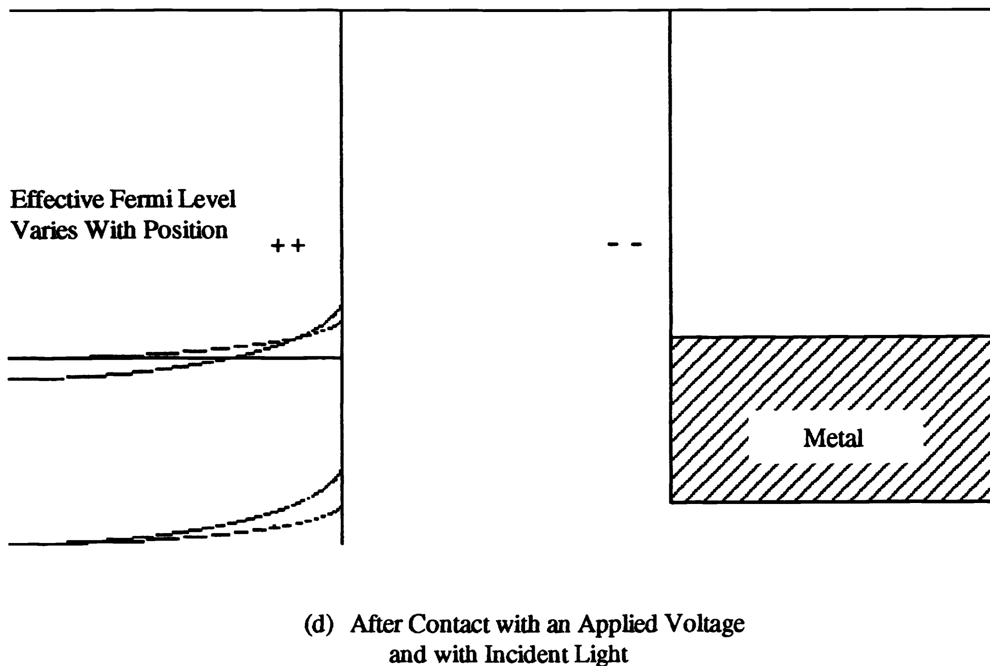


(c) After Contact with Applied Voltage



(d) After Contact with an Applied Voltage
and with Incident Light

Figure 1 (c) and (d). Semiconductor-Metal Tunneling (continued). In Fig 1 (c), the quasi, or effective, Fermi energy is constant, whereas in Fig. 1 (d), the effective Fermi level varies near the surface. In Figures 1 (c) and (d) we have sketched the band-bending of the top of the valence band and the bottom of the conduction band in the semiconductor.

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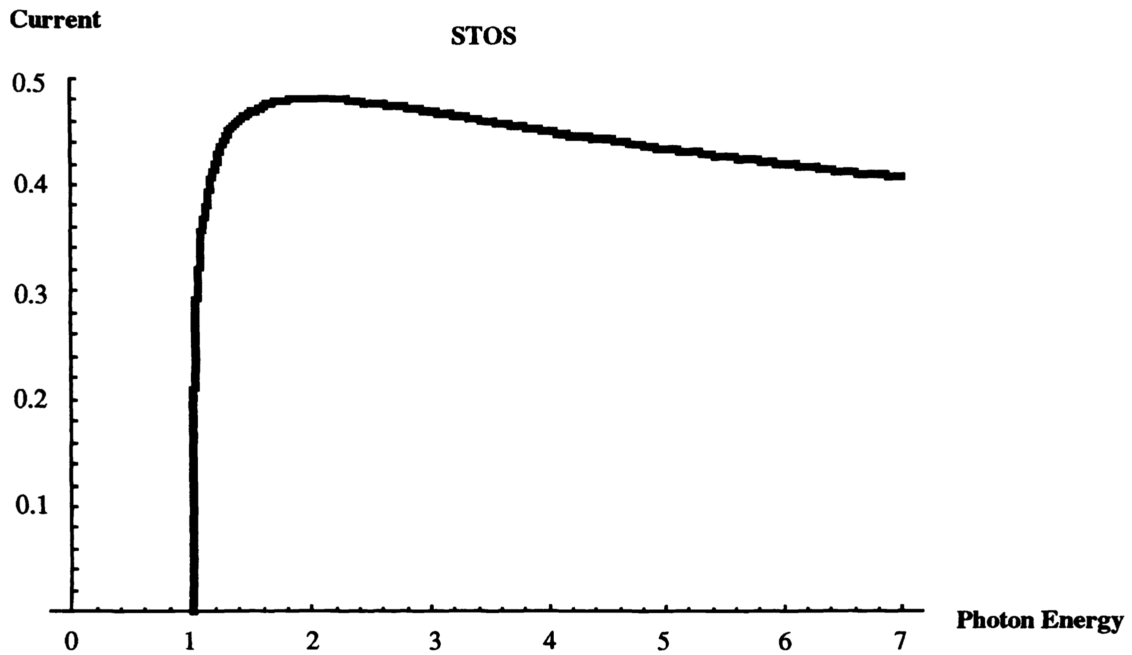

Figure 2. Calculated Results. The magnitude of the increase in current due to optical excitation is plotted in dimensionless units, as is the photon energy (in units of the band gap).

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