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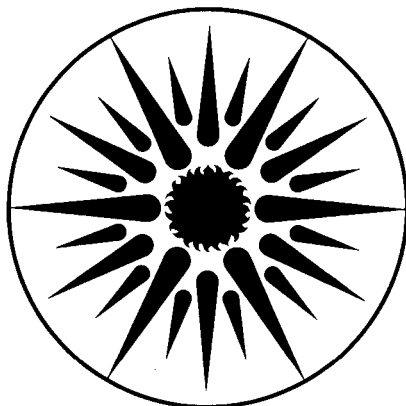
A NEW PROBE OF THE OPTICAL PROPERTIES
OF SURFACES

M.A. Olmstead and N.M. Amer

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A NEW PROBE OF THE OPTICAL PROPERTIES OF SURFACES

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Abstract

We have developed a new technique, photothermal displacement spectroscopy, for studying the optical and thermal properties of surfaces. The ability to distinguish surface and bulk optical absorptions is demonstrated. The signal is directly proportional to the surface absorption coefficient and is insensitive to variations in the real part of the index of refraction.

A NEW PROBE OF THE OPTICAL PROPERTIES OF SURFACES

I. INTRODUCTION

The optical, electronic and chemical properties of the surfaces are primarily determined by the energy and spatial density of the surface electronic states as a function of surface wavevector. As in the study of bulk materials, much can be learned about the physics of semiconductor surfaces through the comparison of optical and electronic experimental data with theoretical band structure calculations. The techniques which are most directly indicative of the surface band structure are angle-resolved photoemission spectroscopy (ARPES) for occupied states, and k-resolved inverse photoemission spectroscopy (KRIPES) for unoccupied states. While these techniques are surface sensitive, like all experiments involving optical transitions photoemission measures a joint density of states. However, the upper state lies above the vacuum level, and is generally assumed to be free-electron like and structureless. Therefore, structure in the kinetic energy and momentum distribution of the electrons relative to the photon energy is assumed to be indicative of the surface density of states near the fermi level.

Currently, there is considerably more photoemission data on the occupied states of semiconductor surfaces [1] than on the unoccupied states [2] as ARPES is an older technique than KRIPES. Even when more KRIPES data are available, it may be difficult to reference an absolute energy difference between the occupied and unoccupied levels. Also, since ARPES leaves a positively charged surface atom and KRIPES a negatively charged atom, these levels may be different than those in the neutral atom which can be probed by optical spectroscopy. Direct

optical transitions from the bands which are well characterized by ARPES into the unoccupied bands can give information about these unoccupied bands when combined with the ARPES data. Visible and infrared optical data on direct transitions into bands characterized by KRIPES from bands studied by ARPES can give information on surface excitonic effects as well as whether the work function and fermi level of the semiconductor are the same for incident and emitted electrons.

A major problem with obtaining optical information about a surface is separating the surface information from the large background due to the bulk contribution. In the visible and infrared portions of the spectrum, photon energies are not sufficient to excite electrons above the vacuum level, so the short mean free path of electrons in solids cannot be exploited for surface sensitivity as in ultraviolet and x-ray photoemission spectroscopies. We have recently developed a new technique, photothermal displacement spectroscopy [3], [4], which can differentiate between optical absorption occurring near the surface and absorption which is uniform throughout the sample. It is also much less sensitive to the non-absorptive dielectric properties of the sample than are traditional reflection spectroscopies. Photothermal displacement spectroscopy yields a signal which is directly proportional to the optical cross section and is easily implemented in ultrahigh vacuum.

II. EXPERIMENTAL CONFIGURATION

Photothermal displacement spectroscopy is based on optical detection of the thermal expansion of a sample as it is heated by absorption of electromagnetic radiation. Details of the experimental configuration are shown in Fig. 1. An optical absorption spectrum is generated as an intensity modulated, tunable light beam (pump beam) is focussed onto the sample, and, depending on the optical cross section, some fraction of the radiation is absorbed. As the excited electrons decay non-radiatively, the sample is heated. The illuminated surface is then displaced as the sample expands. A probe beam reflected from the surface is deflected by the slope of the surface displacement (see Fig. 1b). This deflection is measured by a position sensitive photodiode whose output is then amplified by a phase sensitive lock-in amplifier referenced to the pump beam modulation. Thermal information can be obtained by measuring the shape and phase of the photothermal displacement relative to the illumination as a function of the modulation frequency [4].

The absence of any electrical or mechanical contact with the sample makes this technique especially well suited for ultrahigh vacuum studies, including experiments when a wide temperature variation is necessary. Photothermal displacement spectroscopy can also be performed using interferometry to measure the height of the surface displacement, although long term stability requirements make the beam deflection method more suitable for most experimental situations [4].

III. THE PHYSICS OF PHOTOTHERMAL DISPLACEMENT

The slope of the photothermal surface displacement as a function of time can be calculated from the spatial distribution of the energy deposition through the solution of the thermoelastic equations. A full description of the calculation is found in reference 4. It was also demonstrated in [4] that the experimental measurement of the photothermal surface displacement agrees with the theoretical predictions within experimental error. Two important results of the theory include the different frequency dependences of the surface and bulk contributions to the photothermal signal and the increased sensitivity of the slope of the photothermal displacement to surface absorptions over uniform bulk absorptions. Physical arguments for these differences are given below, although for the exact functional dependences it is necessary to solve the full thermoelastic theory.

A crude expression for the height of the photothermal surface displacement is given by

$$h \sim \alpha_{th} T L_{eff} \quad (1)$$

where α_{th} is the thermal expansion coefficient and T is the temperature rise over an effective expansion length L_{eff} . The temperature rise is proportional to the optical energy absorbed by the sample divided by the heat capacity of the heated volume. When the energy deposition is harmonic in time, the most important length scale is the thermal diffusion length, L_{th} . L_{th} is the distance over which a planar, harmonic, thermal wave decays exponentially to $1/e$ of its initial value and its phase changes by one radian. It is given by:

$$L_{th} = (\lambda / \pi f)^{1/2} \quad (2)$$

where λ is the thermal diffusivity and f is the modulation frequency of the heat source and hence of the thermal wave. The thermal length characterizes the distance in the sample which can contribute to the surface displacement at a given modulation frequency both radially along the surface and vertically into the sample.

The volume which is heated by the absorbed radiation depends both on the absorption length --whether the absorption occurs at the surface (optically thick) or uniformly throughout the sample (optically thin)-- and on the size of the illuminated area. If the optical absorption occurs at the surface of the sample, the heat will diffuse inward to a depth of approximately L_{th} . This entire heated thickness can contribute to the effective length which results in a surface displacement. If the absorption occurs uniformly through the sample, however, thermal diffusion perpendicular to the surface is negligible and the heated thickness remains constant with a variation in frequency. The effective thickness which can contribute to displacement of the surface, however, is still governed by L_{th} , and decays with increasing frequency. If the pump beam waist on the sample, w_0 , is less than L_{th} then the heat will diffuse radially into an area proportional to L_{th} , or inversely proportional to the frequency. If $w_0 \gg L_{th}$, the heated area will be governed by the pump beam and will remain constant with increasing frequency.

There is one further dependence of the displacement of the frequency which is common to both surface and bulk absorptions. The energy which is deposited per cycle is the product of the absorbed power and the time that the beam is incident on the sample. It is thus inversely

proportional to the modulation frequency of the pump beam.

The frequency dependence of the photothermal surface displacement is obtained by combining all of the factors mentioned above. Rewriting equation 1 the height of the displacement is:

$$\text{where } h \sim (\alpha_{th} \beta P / 2 \rho C) [L_{eff} / (f(AL)_{heated})] \quad (3)$$

β = fraction of power absorbed
 P = incident power
 ρ = mass density
 C = heat capacity/gram
 and $(AL)_{heated}$ = the heated volume.

If $L_{th} > w_0$, the heated area is inversely proportional to the frequency and counteracts the frequency dependence due to cyclic heating. In this regime,

$$\begin{aligned} h(f) &\sim L_{eff} / L_{heated} \\ \text{or } h(f)_{\text{surface}} &\sim \text{constant} \\ \text{and } h(f)_{\text{bulk}} &\sim f^{-1/2}. \end{aligned} \quad (4)$$

It is thus possible to enhance to ratio of surface to bulk contributions of the signal by increasing the modulation frequency.

The dependence of the slope of the photothermal surface displacement on frequency differs from that of the height of the displacement, since the shape of the displacement also changes with frequency. A distinction between the surface and bulk signal dependence on frequency is still present, however, in a measurement of the slope. One consequence of the difference between this simple argument for the height of the displacement and the actual solution for the slope is that the regime where $L_{th} < w_0$ cannot be used reliably to separate surface and bulk contributions to the signal by varying the frequency.

The shape of the photothermal surface displacement is different for surface and bulk absorptions. There is also a difference in the behavior of the phase of the displacement relative to the modulation of the pump beam. When the sample is heated via a uniform optical absorption and $w_0 \gg L_{th}$, thermal diffusion is negligible and the displacement lags about 90° behind the pump beam modulation. This is expected as being the time integral ($\sin \omega t$) of the optical heating ($\cos \omega t$). If the sample is heated by a surface absorption, heat diffuses into the sample at a rate proportional to the gradient of the temperature, and the peak surface displacement occurs at a phase lag of about 45° . Near the center of the beam in both the surface and bulk cases there is some structure in the phase due to the Gaussian shape of the laser heating, which causes radial temperature gradients that vary with position.

If $w_0 \ll L_{th}$ and the sample is both optically and thermally thin, thermal diffusion is primarily radial, and the phase of the displacement varies with position along the surface as approximately one radian/ L_{th} . If the sample is optically and thermally thick, the thermal diffusion is primarily hemispherical, and the phase changes at a rate of about $27^\circ/L_{th}$ along the surface. This is approximately half of the value for radial diffusion. Away from these asymptotic limits there is more structure in the phase, but there is always a difference in the behavior of surface and bulk absorptions at any given ratio of w_0 , L_{th} , and the sample thickness. It is necessary to solve the thermoelastic equations using the appropriate experimental conditions to interpret data taken in these intermediate regimes.

The difference between radial and hemispherical heat flow also causes a change in the shape of the photothermal surface displacement. The slope of a displacement caused by surface heating decays more quickly with radial position than that caused by uniform bulk heating. This occurs because the effective expansion length decreases with radial distance from the pump beam when there is hemispherical heat flow, but remains constant with radial heat flow. The slope is also enhanced by this change in shape, and the beam deflection signal is larger for surface absorptions than for an equivalent bulk absorption. This is demonstrated in the following section.

IV. EXPERIMENTAL RESULTS: SURFACE AND BULK INFORMATION

The ability of photothermal displacement spectroscopy to distinguish between surface and bulk absorptions on the same sample is demonstrated in figure 2. A 50 Å gold film was evaporated on didymium glass. In the wavelength region investigated, about 1/4 of the incident light is absorbed by the Au film; didymium glass has a strong absorption band with a peak value of 6.4 cm^{-1} (see Fig. 2b). For the Au coated didymium glass, the photothermal signal is the sum of the structureless surface (thin film) absorption due to the gold and the peaked substrate absorption. As the frequency is increased by a factor of 25, the signal due to the Au (in the region $< 730 \text{ nm}$, e.g., all the signal is due to the Au) is decreased by a factor of about 2; the signal due to the glass (the bump at the center of the spectrum) has decreased by an additional factor of 2 or 3. By examining the change in the spectrum as a function of frequency, it is possible to distinguish absorptions occurring at the surface from the more uniform bulk absorption.

The increased sensitivity of photothermal displacement spectroscopy to surface absorptions over bulk can be seen by noting the relative magnitudes of the two signals. Using published values for the index of refraction of evaporated gold films[5], the percentage of the incident light reflected, transmitted and absorbed at 750 nm can be calculated using the three layer Fresnel equations to be 15%, 59% and 26%, respectively. The 6.4 cm^{-1} peak absorption of the 0.25 cm thick didymium glass absorbs 80% of the light transmitted through the Au film. Thus about twice as much light is absorbed in the glass as on the surface, but the signal due to the didymium at 5.1 Hz is only about 1/7 of the

signal due to the 50 Å film. Even if the effective length of the didymium is taken to be the thermal length, the signal is still heavily weighted by the surface heating. At 5.1 Hz the thermal length of the glass is about 160 microns, so 10% of the transmitted light (6% of the incident light) is absorbed in the first thermal length. Thus the didymium signal would be expected to be about 1/4 that of the Au signal, which is clearly not the case.

The gold layer has a different thermal conductivity than the glass substrate, and the thermal diffusion is modified from a surface absorption on a homogeneous substrate. There is more radial heat diffusion along the surface, and this dominates the phase of the signal a few hundred microns from the pump beam center. Closer to the center of the displacement, however, the phase varies as about $27^\circ/L_{th}$ of the glass; in the same way as, e.g., the phase for silicon when Si is illuminated with above band gap radiation and all of the optical energy is deposited in a thin layer near the surface. This difference in the behavior of the phase between these two cases may prove useful in determining the mode of heat flow from the de-excitation of surface states: whether it is primarily tied to the surface and surface phonons or to the bulk. Any difference in the dependence of the magnitude and phase on the radial coordinate between absorption by surface states and by interband transitions could be attributed to the thermal conductivity of the surface itself.

Didymium glass has a very small diffusivity of 4.2×10^{-3} cm²/sec, making it difficult to focus the pump beam much smaller than the thermal diffusion length at reasonable modulation frequencies. This is not a

problem when studying semiconductors, where the thermal diffusivities are typically higher by a factor of 200. This allows a wider range of frequency over which to separate out the surface and bulk signals. Also, the noise from the intensity and pointing fluctuations of the probe beam, as well as electronic noise, is lower at higher frequencies. These factors and the radial nature of heat flow in the gold film combine to make it more difficult to separate the bulk and surface contributions of the Au/glass system than in a homogeneous, high thermal diffusivity system. Thus the ability to distinguish the surface and bulk contributions in the case we present here assures the ability to distinguish them when studying semiconductor surfaces.

In photothermal displacement spectroscopy, the ability to separate the surface absorption from the background is independent of the two lineshapes, especially if a subtraction is performed as in reflection spectroscopy. We investigated weakly absorbing thin dye films deposited on a variety of glass filters with different absorptive properties. The subtracted spectra of before and after the application of the dye were all similar, independent of the frequency of modulation or whether the signal from the glass substrate was larger or smaller than the signal from the dye.

V. DISCUSSION

The optical cross section of surface state transitions is, through the Fermi golden rule, proportional to the square of the dipole matrix element connecting two states and the joint density of the occupied and unoccupied states. Photothermal displacement spectroscopy is a direct measurement of this quantity, as the signal is directly proportional to the amount of energy deposited in the sample. Luminescence is negligible for these surface states, so all of the absorbed energy is converted into heat and detected. Information about the diffusion of the heat from these surface states is contained in the shape of the displacement as a function of time. This is a separate measurement from that of the maximum slope as a function of wavelength, which maps out the absorption spectrum.

Interpretation of the photothermal displacement signal is not highly sensitive to any model for the dielectric properties of the surface, such as in reflection spectroscopy, or for the surface-bulk recombination processes and band bending, such as in surface photoconductivity (SPC) and surface photovoltage (SPV) spectroscopies. Photothermal displacement spectroscopy should prove very useful in conjunction with SPV and SPC as it can be used to deconvolute the optical cross section from the signal. This will enable a determination of the effect of surface state occupation on the Fermi level, as seen in SPV; and on the near surface free carrier concentration, as seen in SPC.

Photothermal displacement spectroscopy gives very similar information to reflection spectroscopy, but it does so with a simpler experimental configuration and much less complex data reduction. Performance

of reflection spectroscopy on semiconductor surfaces requires taking two spectra: once with a clean surface; and once when the surface has been covered with an adsorbate such as hydrogen or oxygen to remove the surface state from that energy region. These two spectra are subtracted and then the difference, ΔR , is divided by the spectrum from the adsorbate covered surface. This is because structure in the real part of the index of refraction of the surface itself (N_s) or of the bulk material (N_b) can cause changes in the reflectivity comparable to changes in the imaginary part of the surface index of refraction (K_s). It is the imaginary part of the index which gives information on the joint density of states and is thus the most useful parameter to be obtained from the data. In photothermal displacement spectroscopy, the measured beam deflection is directly proportional to the surface absorption, which is in turn proportional to K_s .

The fraction of the incident beam absorbed at the surface layer is much less sensitive to the dielectric properties of the bulk material than the reflected intensity. This can be seen by reference to the calculated reflectance and absorption in the McIntyre and Aspnes model [6] which treats the surface as a thin layer with different real and imaginary parts of the index of refraction from the bulk. The reflectivity, R , is then calculated using the three layer Fresnel equations, and the the absorbed fraction, A , is calculated as

$$\begin{aligned} A &= (1-R)\exp(-4\pi K_s/\lambda) \\ &= (1-R)\exp(-\alpha_s). \end{aligned} \tag{5}$$

where α_s is defined as the surface absorption coefficient. Consider a 5 Å surface layer on Si with $N_s=N_b=3.45$. The percentage reflection of an

incident beam ($\lambda=2.6$ microns) changes by the same amount when the bulk index is changed by 1 1/2% to 3.5 as when the surface absorption coefficient, α_s , changes from zero to 0.014, a value where 1% of the incident beam is absorbed. It is this change in reflectivity which is measured to obtain information on the surface absorption, so care must be taken to separate changes due to structure in the bulk index from surface effects. The absorbed fraction of the incident beam changes only very slightly as the bulk index is varied. This small change arises from the variation of the amount of light actually entering the surface film, proportional to $(1-R)$, as the reflectivity changes. In a photothermal measurement, the entire absorbed fraction is measured, so that this small change in N_b appears only as a very small change in the signal, and not as something equivalent to a surface signal.

The photothermal displacement signal is directly proportional to the surface absorption coefficient. The proportionality constant does not change if the real part of the surface index of refraction is also modified by the band structure which gives rise to the absorption. This can be seen in figure 3 where the absorbed fraction of the incident light and the fractional change in reflectivity from that when there is no surface absorption are plotted as a function of α_s for two values of N_s . The absorption, as measured by photothermal displacement spectroscopy, changes imperceptibly as N_s is changed from 3.45 to 3.0. The fractional change in reflectivity, however, is modified. This means that if the real part of the surface index is modified through the same structure in the surface bands which causes the absorption, the reflectivity signal will not remain strictly proportional to the imaginary

part of the index. The photothermal signal is again changed only by the very small variation in the reflected intensity which is measured in reflection spectroscopy.

The insensitivity of the photothermal signal to structure in the real parts of the indices of refraction of the surface and bulk, as well as the ability demonstrated in Section IV to distinguish surface and bulk contributions to absorption due to the imaginary part of the index of refraction, reduces the need to procure two spectra of the surface, before and after contamination. It would, of course be useful to have both spectra to assure that the phenomena recorded were truly surface states, but in many experiments it would be useful not to have to contaminate the surface after one measurement, such as in studies which vary the temperature of the sample. This feature as well as the simplicity of the technique and the ability to obtain information of the thermal properties of the surface promise to make photothermal displacement spectroscopy an exciting new tool for surface studies.

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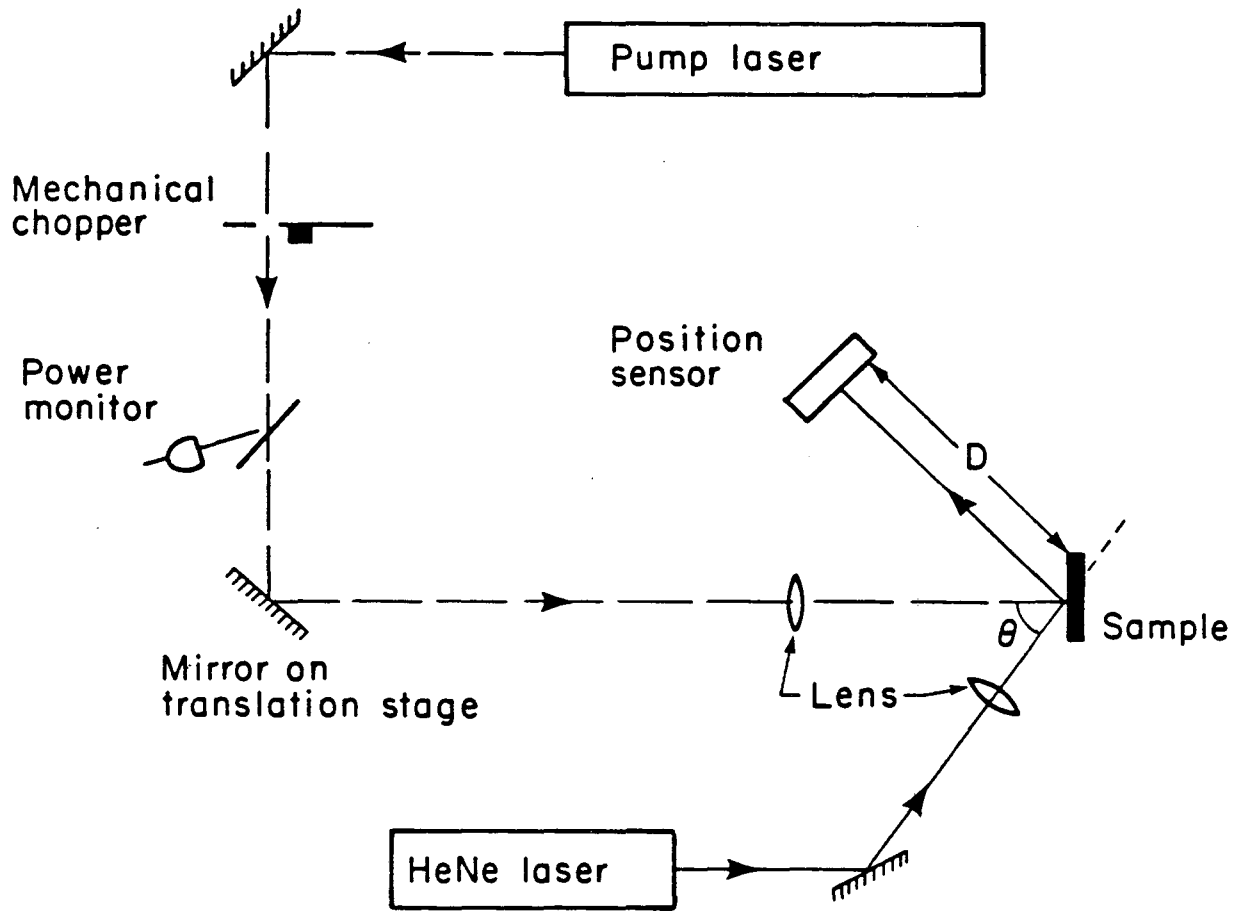
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Figure Captions

Figure 1. a) Experimental Configuration. b) Expanded view of the surface region. Probe beam path alternates between a and b as the surface is photothermally displaced. [figure taken from ref. 4]

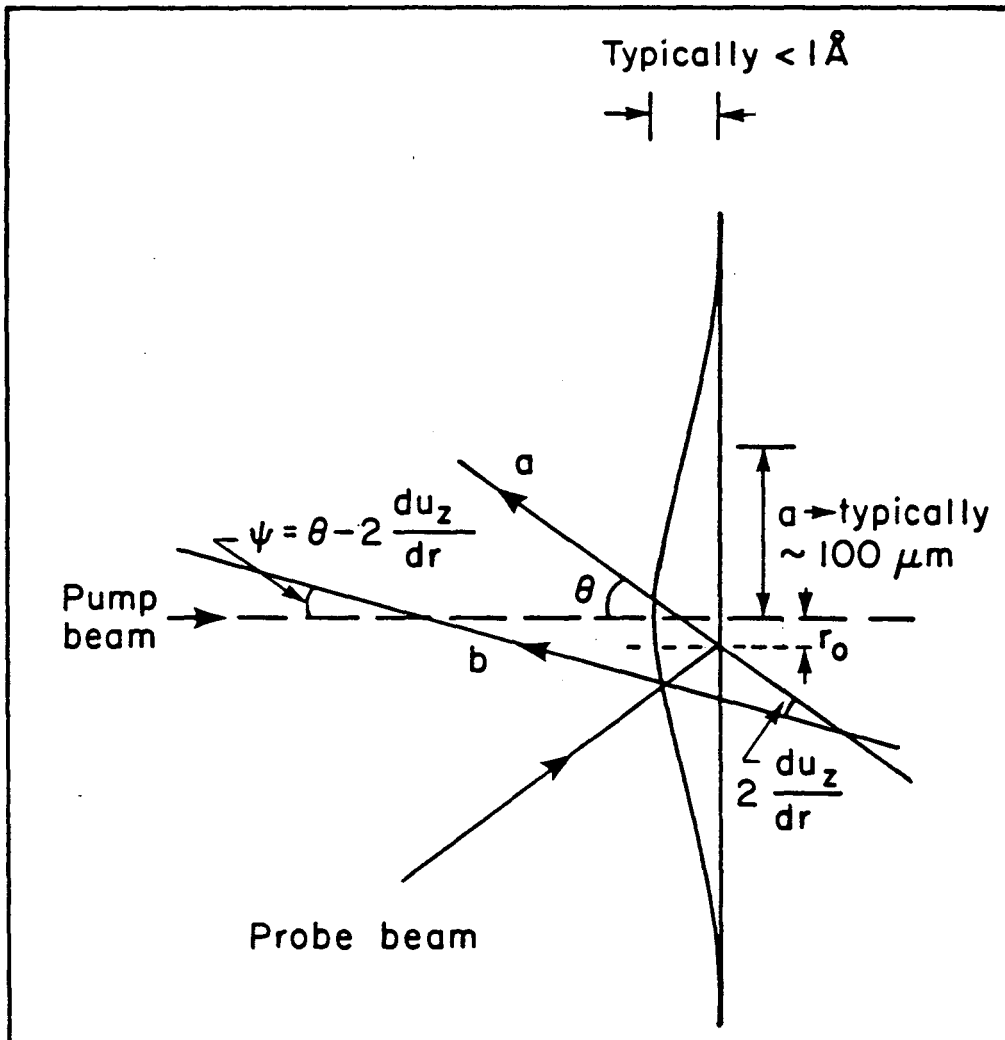
Figure 2. Surface and bulk differentiation. a) Spectra of 50Å gold film on 0.25 cm thick didymium glass at 5.1, 25.4 and 127 Hz. The pump beam was focussed to a waist of about 25 microns. The solid line is the 127 Hz spectrum on an expanded scale, normalized to the signal from the Au. b) Spectra of 50Å film on transparent glass (x) and clean didymium (solid line) (arbitrary units). The Au absorption at 750 nm is 26% and the peak didymium absorption coefficient is 6.4 cm^{-1} .

Figure 3. Theoretical absorption and fractional change in reflectivity vs. surface absorption coefficient using three layer Fresnel equations and equation 5. The parameters used were $\lambda = 2.6 \mu$, and a 5Å surface layer with index $3.45 + iK_s$ on a substrate with index $N_b = 3.45$. $\Delta R/R$ calculated as $(R(\alpha_s) - R(\alpha_s = 0)) / R(\alpha_s = 0)$ where $R(\alpha_s = 0) = 0.3031$.



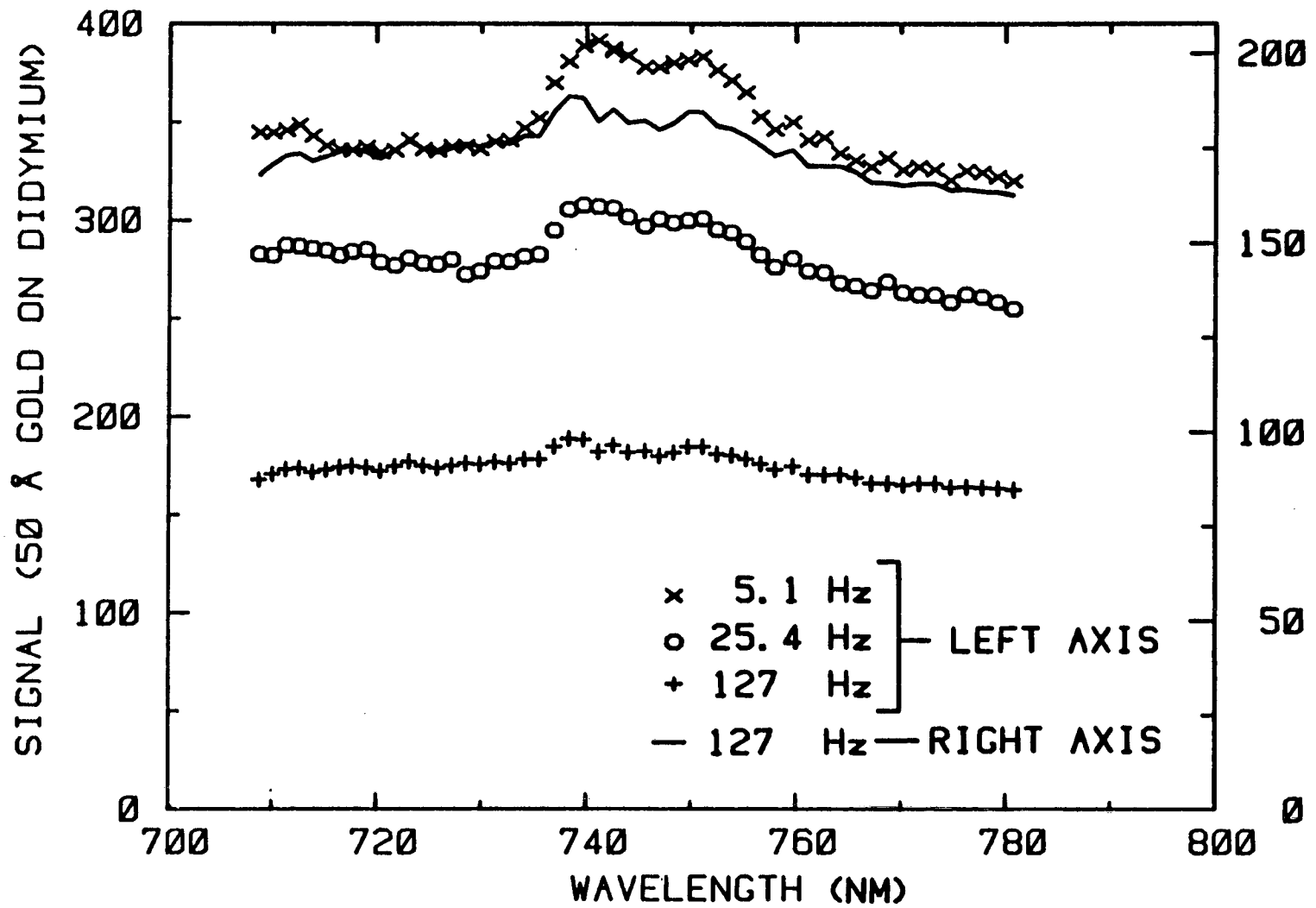
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Fig. (1.a)



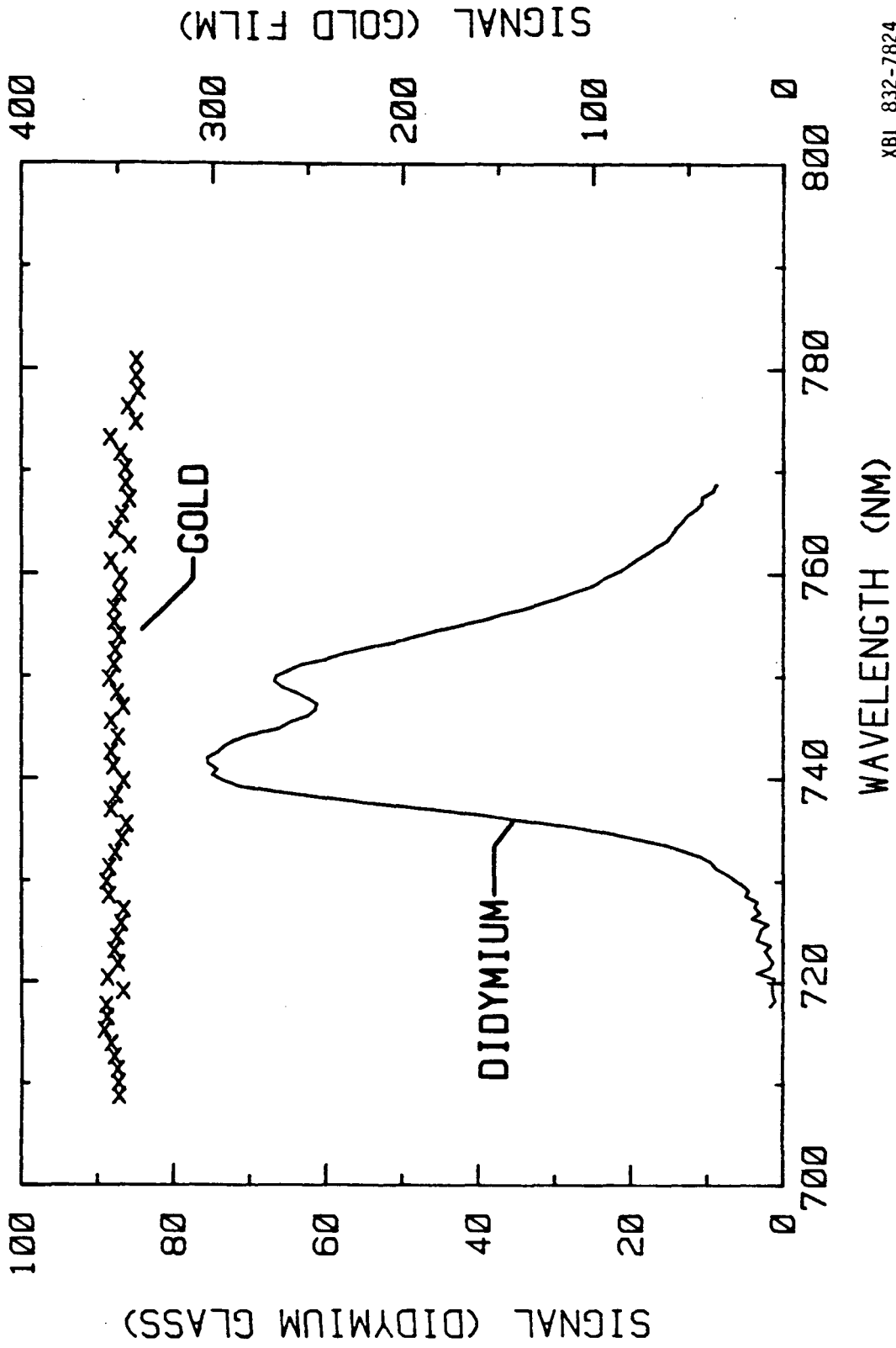
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Fig. (1.b)



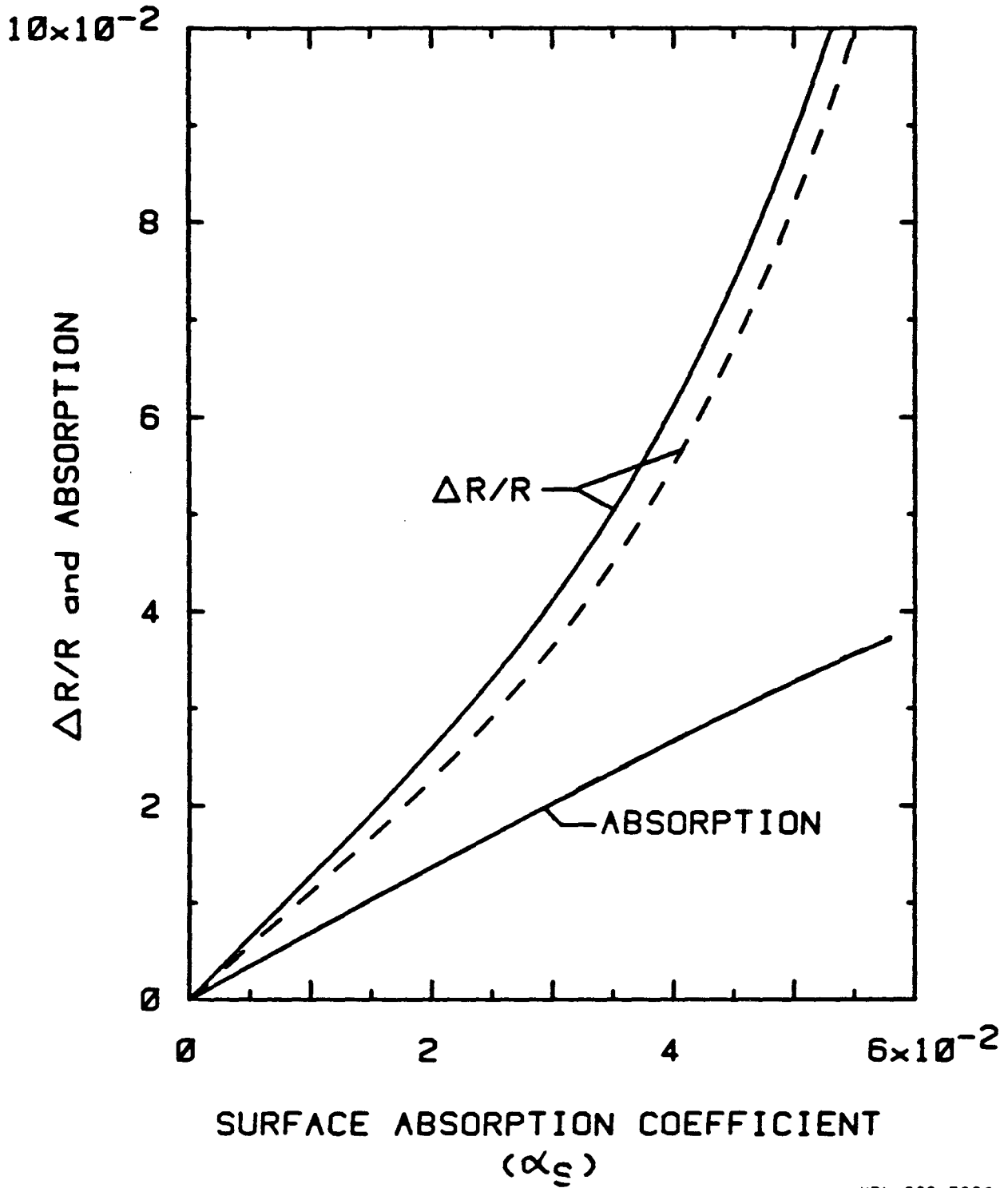
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Fig. (2.a)



XBL 832-7824

Fig. 2.b)



XBL 832-7826

Fig. (3)

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