PHOTOACOUSTIC MEASUREMENT OF NONLINEAR ABSORPTION IN SOLIDS

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The photoacoustic technique, using a piezoelectric transducer to detect acoustic signals induced in semiconductors by the absorption of light, has been used to measure twophoton absorption. The transducer signal amplitude is directly proportional to the absorbed energy from all absorption processes, nonlinear as well as linear. This signal was monitored as a function of the intensity of single, picosecond, 1.06 µm, pulses. At high intensities, beam depletion was observed, and a direct comparison was made with the sample transmission. The sensitivity of this technique allows nonlinear absorption to be measured at intensities significantly lower than when using transmission. In addition, the advantage of the nonlinear photoacoustic technique over the recently described calorimetric technique is that powerful signal averaging techniques can be used. This is because the absorption at a given intensity can be determined by a single pulse in a few microseconds while calorimetry requires at the least several seconds.

We describe the use of the photoacoustic absorption measurement technique for the determination of nonlinear absorption in solids. Advantages and disadvantages of this method (using a piezoelectric transducer to detect acoustic signals induced in solids by the absorption of light) are discussed, as well as suggestions for future uses where the particular advantages of the nonlinear photoacoustic technique should prove valuable [1,2]. The photoacoustic signals, using a piezoelectric transducer to detect the acoustic signals induced in CdTe and CdSe by two-photon absorption of light, are directly compared to transmission measurements made simultaneously on the samples.

We show that the photoacoustic measurement of two-photon absorption on samples whose linear absorptivity is small offers significant increases in sensitivity over conventional measurements such as transmission. Similar advantages occur for higher order nonlinearities. The increased sensitivity is directly related to the increased sensitivity of the recently developed nonlinear laser calorimetric method while offering the additional advantage that an absorption measurement can be made rapidly (μ sec) [3]. Calorimetry measures a rate of change in sample temperature as determined by a thermocouple output and thus requires considerably longer experimental times. On the other hand calorimetry absolutely calibrates the measured absorption coefficient while the photoacoustic signals need to be calibrated.

Figure 1 shows the photoacoustic experiment modified to observe nonlinear absorption. The usual chopped cw laser is replaced by a pulsed laser anticipating the need for higher intensities. If the laser is repetitively pulsed the acoustic signals can be signal averaged using lock-in amplifiers or box-car integrators. The sample cell shown is a liquid filled cell where the acoustic wave is coupled to the piezo-electric via the liquid as was done in the experiments presented here [4]. Alternatively the transducer can be directly attached to the sample [1].

The increased sensitivity of photoacoustic spectroscopy (PAS) over transmission experiments for observing two photon absorption in transparent materials (i.e. small linear absorption) is shown by the following analysis. Two photon absorption (2PA) is proportional to the square of the intensity, I, such that

$$\frac{dI}{dT} = -(\alpha + I) I \qquad (Eq. 1)$$

where α is the linear absorption coefficient and β is the 2PA coefficient. For a sample of length L with a surface reflectivity r this equation can be solved yielding for the inverse of the transmission T, a linear function of the incident intensity I_{0} , given by

$$\frac{1}{T} = \frac{e^{\alpha L}}{(1 - r)^2} + \frac{\beta I_0}{(1 - r)} \frac{(1 - e^{-\alpha L})}{\alpha}$$
(Eq. 2)

where the effects of light reflected into the sample at the rear surface are ignored. If the index mismatch is large this approximation can lead to significant errors as discussed in Ref. 3. Using liquid filled samples cells reduces this index mismatch. Within this approximation the ratio of absorbed energy, E_a , to incident energy, E_i , is given by

$$\frac{E_a}{E_4} = 1 - r - \frac{T}{1 - r}$$
 (Eq. 3)

We are now in a position to compare the two methods of PAS and transmission. Assume that the total absorption is small i.e., $(\alpha + \beta I)L << 1$, then eq. 2 reduces to

$$\frac{1}{f} = \frac{1}{(1 - r)^2} \left[1 + \alpha L + \beta I_0 L(1 - r) \right]$$
(Eq. 4)

and eq. 3 reduces to

$$\frac{E_a}{E_1} = (1 - r) [\alpha L + \beta I_0 L(1 - r)]$$
(Eq. 5)

In order to get the same percentage change in the transmission experiment due to 2PA, as in the photoacoustic experiment, we compare the 2PA term (third term in eq. 4, second term in eq. 5) to the other terms. For transmission we find that to observe a 10% change in the signal

$$\beta I_{\alpha} L(1 - r) \cong (.10) (1 + \alpha L) \cong (.10)$$
 (Eq. 6)

while for PAS we find

$$I_0 L(1 - r) \cong (.10) \alpha L$$
 (Eq. 7)

Using samples of low linear loss the PAS method has a clear advantage. For example, using a sample of 1 cm length having a linear absorption coefficient of 10^{-3} cm⁻¹ would allow the 2PA term using PAS to be 10^{-3} as large as when using transmission. Thus, to measure the same 2PA coefficient, intensities using PAS can be 10^{-3} as large as intensities using transmission; or 2PA coefficients 10^{-3} as large can be measured using the same intensity. Clearly to take advantage of the PAS method samples having small linear absorption must be used. In addition, in eq. 7 for PAS, the length L cancels. The fractional change in the PAS due to 2PA is independent of the sample length. It may, therefore, be possible to use the PAS technique to observe nonlinear absorption in optical coatings.

The experiments presented here directly compare the PAS signal to the transmission on a single shot basis. Signal averaging is not used nor do the samples have particularly low linear absorptivities. Thus, these experiments do not demonstrate the ultimate sensitivity of nonlinear PAS but do show the feasability of the technique for observing nonlinear absorption and how the PAS signals compare to the standard nonlinear transmission measurements. Similar work to that presented here using a tunable repetitively pulsed nanosecond dye laser is being performed in Austria [5].

The laser source for the studies was a passively mode-locked microprocessor-controlled, Nd:YAG system operating at 1.06 μ m. A single pulse of measured Gaussian spatial and temporal intensity distribution was switched from the mode-locked train and amplified. The temporal pulsewidth was approximately 40 picoseconds. The width of each pulse was monitored by measuring the ratio, R, of the square of the energy in the fundamental (1.06 μ m) to the energy in the second harmonic, produced in a LiIO₃ crystal. This ratio is directly proportional to the laser pulsewidth as long as the spatial profile remains unchanged. The ratio was calibrated by measuring the pulsewidth using Type I second harmonic autocorrelation scans.

The spatial beam distribution was determined by pinhole beam scans and by vidicon scans of single laser shots. The beam was thus determined to be Gaussian and stable from pulse to pulse. The energy on target was varied by changing the angle between a calibrated pair of Glan polarizers that were arranged to keep the direction of polarization at the sample surface constant. The output energy of the laser and the energy transmitted through the sample were continuously monitored by sensitive photodiode peak-and-hold detectors. These detectors were determined to be linear over their range of use and were absolutely calibrated with respect to a pyroelectric energy monitor. The pyroelectric detector was in turn checked with a thermopile calorimeter.

The samples were placed in a water filled photoacoustic cell similar in design to that of Patel and Tam [4]. The acoustic signal generated in the solid travels through the solid, is transmitted through the liquid and then to a stainless steel plug in contact with the piezoelectric transducer. Since the acoustic wave travels fastest in the solid it is detected before the signal produced by the linear absorption in water [6]. Using the liquid filled cell has the advantage that the Fresnel reflections are reduced, and samples are readily interchanged. The amplitudes of the first acoustic spike for both samples as read directly off an oscilloscope constituted the PAS signal. This signal has been shown to be directly proportional to the total absorbed energy [4]. By monitoring this signal as a function of intensity, the contributions from nonlinear as well as linear absorption are determined.

If the solid sample is placed at one extreme end of the sample cell it is observed that the first spike in the acoustic signal varies linearly with intensity. Many microseconds later a spike that grows nonlinearly with intensity is observed that is due to absorption in the sample. The delay is the time it takes sound to travel the extra distance through the liquid. Thus, the response of the system is shown to be linear.

Figures 2 and 3 show inverse transmission as a function of intensity of picosecond pulses for CdSe and CdTe respectively. The intensity distribution of the pulses incident on the sample was

$$I(r,t) = I_0 e^{-\left(\frac{r}{W_0}\right)^2} e^{-\left(\frac{t}{\tau}\right)^2}$$

after taking into account reflections from the windows in the sample cell and the absorption in water. Here τ was 25 ± 5 psec and w was .17 cm for CdSe and .15 cm for CdTe. Thus, rather than using eq. 2, eq. 1 was integrated over space and time to yield

(Eq. 8)

$$T = \frac{2\alpha e^{-\alpha L}(1-r)}{\sqrt{\pi}\beta I_{0}(1-e^{-\alpha L})} \int_{0}^{\infty} dx \ell n [1 + \frac{\beta}{\alpha} I_{0}(1-r) (1-e^{-\alpha L}) e^{-x^{2}}]$$
(Eq. 9)

Using for CdSe $\alpha = 1.01 \text{ cm}^{-1}$ and $\beta = 0.035 \text{ cm/MM}$ and for CdTe $\alpha = 0.45 \text{ cm}^{-1}$ and $\beta = 0.050 \text{ cm/MM}$ gave the fits shown in Figs. 2 and 3. The CdSe sample was 2 mm thick and the CdTe was 2.13 mm thick. The deviation at high intensities has been observed previously and has been explained as being due to the linear absorption of free carriers created by 2PA [7]. The value of β for CdSe is consistent with Ref. 7 while β for CdTe is a factor of two larger. By using the values for T obtained from Figs. 2 and 3 we calculate what the expected PAS signal divided by incident energy should be from eq. 3. These are plotted in Figs. 4a and 5a. Figure 4b and 5b show the actual PAS signal divided by incident energy. Since the PAS signal voltage is not absolutely calibrated the vertical axis was scaled to coincide with the low intensity data of Fig. 4a and 5a. For CdSe there is a 1 to 1 correspondence of the data from the transmission and PAS experiments. The apparent deviation at the very lowest intensities is not understood but may be an electronic noise problem and is not considered significant. For CdTe at very high intensities (greater than 500 MW/cm²) there is a clear deviation of the PAS signal below what is expected from the transmission data. At these high intensities it is possible that stimulated emission processes become appreciable. CdTe has been made to lase at .79 µm. Energy reemitted at another wavelength does not increase the PAS signal but it does lower the transmission at 1.06 µm. A 1.06 µm filter was used in front of the detectors. In order to account for the observed difference between Fig. 5a and 5b the fraction of energy absorbed that contributed to reradiation at .79 µm would need to be nearly 20%. This appears somewhat unlikely in which case we may be seeing a saturation the acoustic signal. The voltages obtained from the piezoelectric at these intensities were millivolts. However, the voltages using the CdSe sample were comparable and no such deviation was observed. Th

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Figure 1. Nonlinear photoacoustic experiment.



Figure 2. Inverse transmission as a function of the intensity of picosecond pulses in CdSe. The line is a fit for low intensities using $\alpha = 1.1 \text{ cm}^{-1}$ and $\beta = 0.35 \text{ cm/MW}$.



Figure 3. Inverse transmission as a function of the intensity of picosecond pulses in CdTe. The line is a fit for low intensities using $\alpha = 0.45 \text{ cm}^{-1}$ and $\beta = 0.51 \text{ cm/MW}$.

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Figure 4(b). The observed PAS signal divided by incident energy as a function of incident intensity for CdSe.



Figure 5(a). The expected PAS signal divided by incident energy as a function of incident intensity as calculated from the observed transmission of CdTe.



Figure 5(b). The observed PAS signal divided by incident energy as a function of incident intensity for CdTe.

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It was pointed out that saturation effects are sometimes seen in PAS for strongly absorbing liquids. Nonlinear affects in liquids as well as solids can thus be seen using PAS. Surface and bulk absorption can also be separated using PAS, as has been demonstrated at the University of California, Berkeley, and also at the University of Michigan. Transient absorption can also be studied using PAS up to the 100 MHz limit of the detector.