Contactless THz-based bulk semiconductor mobility measurements using two-photon excitation

J. K. WAHLSTRAND and E. J. HEILWEIL*
Engineering Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Abstract

We perform contactless bulk mobility measurements for ZnSe, ZnTe, GaP, CdS, and GaSe in an optical pump THz probe experiment. As opposed to above-gap excitation or contact methods, two-photon absorption excites the entire sample thickness producing measurable signals with $10^{13}$ carriers/cm$^3$ and higher density. For ZnTe and GaSe samples, the measured mobility using two-photon excitation is higher than that measured with one-photon excitation.

Carrier mobility is an important quantity to measure when evaluating electronic materials. Highly dependent on impurities and defects, it can vary widely depending on a variety of factors including doping levels and growth method and so it is beneficial to develop rapid characterization techniques capable of measuring mobility. Standard mobility measurements require ohmic contact with samples (e.g. Hall van der Pauw technique [1]). Time domain THz techniques [2,3] offer a contact-free way to quickly evaluate the conductivity of a sample. When used in an optical pump, THz probe scheme, the change in THz conductivity due to photoexcited carriers allows separation of the carrier density and mobility contributions to the conductivity, enabling estimation of mobility parameters. Mobilities extracted using this technique were recently shown to agree well with Hall van der Pauw values in pure and doped silicon samples [4].

One issue with this method, particularly in direct bandgap semiconductors, is that the small penetration depth (~10 nm to 1 µm) results in high photoexcited carrier density, which may affect the measured mobility. Also, photogenerated carriers are close to the surface, leading to additional sources of scattering. To alleviate these issues, here we perform mobility measurements using two-photon absorption. By exciting at below bandgap wavelengths with sufficient intensity to produce two-photon absorption, a pulsed laser can excite the interior of a sample [5]. By exciting the entire depth of the sample, we can produce a measurable change in conductivity at much lower carrier density than is possible with one-photon excitation. The majority of the photoexcited carriers are thus far from the crystal surfaces.

The time-resolved THz spectroscopy (TRTS) apparatus used has been described previously [4,6]. It is based on a 1 kHz repetition rate Ti:sapphire amplifier producing 50 fs, 800 nm pulses. THz radiation is generated by optical rectification in a 1 mm thick ZnTe (110) crystal
and collimated and focused by off axis parabolic mirrors onto the sample. The THz radiation is then collected and refocused by off axis parabolic mirrors onto another 1 mm thick, ZnTe (110) crystal for electro-optic sampling detection.

The ZnSe, ZnTe, GaP, CdS, and GaSe samples studied all have bandgaps in the 2–3 eV range. We photoexcited with 800 nm (1.55 eV) pulses for two-photon excitation and 400 nm (3.1 eV) by doubling in β-barium borate (BBO) for one-photon excitation. By measuring the amplitude change of the THz waveform, the full complex differential conductivity spectrum may be found as a function of pump-THz delay. Here, as in most of the measurements in [4], we measure the pump-induced change in THz amplitude averaged over all frequencies, which can be found by measuring the change in peak THz field due to the pump pulse using an optical chopper and lock-in amplifier. Crystalline samples were obtained from commercial sources as previously described [4] except a pristine ZnTe crystal is different than the one used in [4] to eliminate the possibility of poor sample composition and quality. Ultrahigh purity CdS flakes were available in house.

Data showing the normalized peak THz field $\Delta E/E_0$ as a function of time and pump power are shown in Fig. 1. Each row of plots corresponds to one sample. Typical time traces are shown in the leftmost plots for 400 nm (blue) and 800 nm (red) pump pulses. Photoexcitation of carriers reduces the THz pulse transmission resulting from interaction of the THz with the free carriers. In a few samples, the transmission partially recovers on the tens of picoseconds timescale. We use this equilibrated value to calculate THz conductivity. Oscillations near zero time delay are attributed to THz generated by the pump pulse.

The power dependence of the recovered peak THz transmission for 400 nm (above gap) excitation is shown in the middle plots. Each point corresponds to a particular pump beam average power ($P$). The dependence is linear for relatively low power but saturates for ZnSe and CdS. We attribute this to reduced mobility at high carrier densities [4]. A fit of the low power data points to $\Delta E/E_0 = aP$ is shown as a solid blue line.

The power dependence of the peak THz transmission for 800 nm pump pulses is shown in the rightmost plots. A fit of the low power data points to $\Delta E/E_0 = aP + bP^2$ is shown as a solid red line. Just the quadratic component $bP^2$ is shown as a dashed red line. The small linear component present for some samples is attributed to linear absorption by impurities.

For a layer of conductivity $\sigma$ of thickness $d$, thin (<10 µm) compared to THz wavelengths, located on the surface of a substrate of THz refractive index $n$ [2],

$$\frac{\Delta E}{E_0} = \frac{Z_0 d}{1 + n \sigma}$$

($Z_0$ is the vacuum impedance). This expression holds for both a homogeneous thin film of thickness $d$ and for a photoexcited surface where the conductivity as a function of depth $z$ is $\sigma \exp(-z/d)$, as for above bandgap excitation. The equation above is easily inverted to find $\sigma$ from the normalized field transmission coefficient [4].
The conductivity change due to photoexcitation is given as:

$$\Delta \sigma = e N_p (\mu_e + \mu_h),$$  \hspace{1cm} (2)

where $e$ is the electron charge, $N_p$ is the photoexcited carrier density, and $\mu_e$ and $\mu_h$ are the electron and hole mobilities, respectively. For one-photon excitation [4], the photoexcited carrier density $N_p$ is estimated by calculating the number of pump photons absorbed in the excitation volume (accounting for front surface Fresnel loss), since each absorbed photon results in one electron and one hole. Knowledge of $N_p$ enables a measurement of the total mobility $\mu_e + \mu_h$ from the measured change in conductivity.

The mobility measured for each sample with 400 nm pump wavelength is given in Table 1. Measurements were taken over a range of fluences, each yielding a mobility value. The numbers given in the table for each sample are for a data point near the high end of the fluence range over which the peak THz change was linear. The carrier density was estimated from the penetration depth based on previously measured optical constants [7–11]. Owing to relatively small mobility, the carrier densities required to produce measurable signals are high, $>7 \times 10^{17}$ cm$^{-3}$. The last column in Table 1 shows the average mobility value found from the linear fit of the power dependence shown in the middle plots in Fig. 1.

In the case of two-photon excitation the entire sample thickness $L$ is excited and Eq. (1) does not apply. However, for a uniform change in conductivity $\sigma$ one obtains,

$$\frac{\Delta E}{E_0} = \frac{Z_0 L}{2n \sigma}. \hspace{1cm} (3)$$

In the experiment, the pump intensity drops as the pulse propagates through the sample and the precise carrier distribution depends on the pulse intensity. We therefore used a numerical calculation to convert the THz pulse transmission to obtain the total change in conductivity.

One must also apply the two-photon absorption coefficient $\beta$ for each material to find $N_p$. For all samples studied, the value of $\beta$ reported in the literature is widely scattered, so we performed our own measurements on each sample. First, we performed the established Z-scan technique [12]. The 800 nm pump beam employed in the THz experiment is unfocused and not Gaussian which is unacceptable for making accurate Z-scan measurements. Instead a Gaussian beam profile Ti:sapphire oscillator with repetition rate of 81 MHz and 800 nm central wavelength was used. A beam sampler was used to monitor the input laser power while the remaining laser power was focused with a 5 cm focal length lens onto the sample. The pulse duration at the sample location was measured to be 60 fs and the transmitted beam was collected by another lens and onto a large area silicon photodiode. A chopper and lock-in amplifiers were used to measure the transmitted and reference beam signals and the power transmission coefficient $T$ was calculated by dividing them. The sample was scanned through the focus and $T$ was measured as a function of $z$. Typical data is shown in Fig. 2(a).
For a thin sample compared to the Rayleigh length of the beam, and assuming the laser pulse is Gaussian in space and time, the theoretical change in transmission is [12]

$$\frac{\Delta T}{T} = 1 - \frac{q_0}{2\sqrt{2}1 + \left(z - z_c\right)^2/z_0^2} \quad (4)$$

where $q_0 = \beta I_0 L$, $z_c$, and $z_0$ are found from the fit. Fits to Eq. (4) are shown in Fig. 2(a) as solid lines. The Rayleigh range found from the fit roughly agreed with the experimentally determined parameter found by imaging the focus. In calculating the two-photon absorption coefficient for optically flat and clean crystal surfaces, we found $I_0$ using the pulse duration and beam waist and corrected for Fresnel losses at the first crystal surface.

For further comparison, we measured the transmitted power as a function of input power with the same pump beam used in the THz measurement. The 800 nm pulse energy directly after the sample position was measured with and without the sample in place using a pyroelectric energy probe. The laser spot image and measurement of the pulse width were used to find the peak intensity for each incident pulse energy. For $T^{-1}$ plotted as a function of peak irradiance, the slope is proportional to $\beta$ and the intercept gives the Fresnel losses and linear absorption coefficient [13]. Two example plots are shown in Fig. 2(b).

The $\beta$ measurement results are summarized and compared with literature values in Table 2. The largest source of uncertainty in either measurement technique is in the peak intensity, which is calculated from the spot size, pulse duration, and laser power. We estimate uncertainties of about ± 25% in our measurement of $\beta$. The two techniques agreed within this level of uncertainty except for GaP. This could have been caused by the long carrier lifetime, which may have resulted in cumulative effects in the Z-scan measurement since the 81 MHz repetition rate of the laser may not permit all carriers to recombine between pulses.

The averaged two-photon absorption coefficients determined above were used to find $N_p$ as a function of input pump power in Eq. (2) to extract mobility from the THz signal measured with 800 nm pump wavelength. Results of these analyses are given in Table 3. As in the $\beta$ measurements, the largest source of uncertainty arises from the peak intensity. The mobilities we find using two-photon excitation are significantly higher than with one-photon excitation (see Table 1), except for CdS.

As an aside, if we assume the mobility measured by two-photon excitation is the same as measured by one-photon absorption, we can also use the TRTS measurements to find $\beta$ rather than the mobility. With this assumption, we find $\beta = 4.7$ cm/GW for ZnSe, 119 cm/GW for ZnTe, 3.66 cm/Gw for GaP, 2.3 cm/GW for CdS, and 0.84 cm/GW for GaSe (see Table 2). Note that these values are different from our measured values of $\beta$ by factors of 2 to 50. The largest discrepancy by far is for ZnTe, which reflects the much higher mobility measured by two-photon excitation. The mobility measured by one-photon absorption in this ZnTe sample is much smaller than was reported in [4].
In conclusion, we applied THz photoconductivity measurements using two-photon excitation to extract low photodope density (ca. $10^{14}$ cm$^{-3}$) mobility values for various bulk semiconductor crystals. If the two-photon absorption coefficient $\beta$ is well known (from independent z-scan, below gap absorption or indirect one-photon normalized TRTS absorption), it can be used to extract the average carrier mobility in a bulk sample. With one-photon excitation [4], the excited layer thickness is typically microns or much less, so the photocarrier density is typically relatively high (ca. $>10^{17}$ cm$^{-1}$) and the photoexcited mobility can be affected by impurities and carrier interactions. With two-photon excitation, the entire sample thickness is excited and for the same THz absorption change, the carrier density is much lower and limiting mobility values are measured. We will soon report a parallel study of previously examined pure and doped “standard” Si samples using two-photon excitation to directly compare to above gap excitation measurements [4].

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Fig. 1.
THz measurement results: Each row shows data for a different sample. In the left column, typical THz traces are shown for 400 nm pump wavelength (blue) and 800 nm pump wavelength (red). In the middle and right columns, the peak change in peak THz field amplitude is shown as a function of input power for 400 nm pump wavelength (middle column) and 800 nm pump wavelength (right column).
Fig. 2.
Measurements of two-photon absorption coefficient $\beta$. (a) Z-scan measurements using 81 MHz laser system. Typical experimental data (dots) and fits to Eq. (4) (lines) are shown for ZnSe (red), GaP (blue), and CdS (green). (b) Power-dependent transmission measurements using the same laser used in THz measurements. Experimental data (dots) and fits (lines) are shown for GaP (red) and GaSe (blue).
Table 1.

One-photon (400 nm) measurements of mobility

| Sample | Power (mW) | Fluence (μJ/cm²) | ΔE/E₀ | N₀ (cm⁻³) | μ (cm²/V·s) | μ.avg (cm²/V·s) |
|--------|------------|------------------|-------|-----------|-------------|----------------|
| ZnSe   | 0.45       | 2.85             | 0.016 | 7.1 × 10¹⁷| 226         | 238            |
| ZnTe   | 2.3        | 14.5             | 0.017 | 3.2 × 10¹⁸| 52          | 51             |
| GaP    | 2.5        | 15.8             | 0.0952| 2.66 × 10¹⁸| 214         | 223            |
| CdS    | 0.94       | 5.9              | 0.058 | 1.06 × 10¹⁸| 382         | 424            |
| GaSe   | 1          | 6.3              | 0.007 | 2.9 × 10¹⁷| 51          | 49             |
Table 2.
Sample lengths and measured two-photon (800 nm) absorption coefficients

| Sample | \( L \) (cm) | \( \beta \) (cm/GW) Z-scan | \( \beta \) (cm/GW) Power-dependent transmission | \( \beta \) (cm/GW) Literature |
|--------|-------------|-----------------|---------------------------------|-------------------------------|
| ZnSe   | 0.2         | 2.1             | 1.8                             | 3.4\(^a\), 3.5\(^b\)         |
| ZnTe   | 0.05        | 5.2             | 6.5                             | 7.0\(^a\), 7.3\(^c\)         |
| GaP    | 0.01        | 0.73            | 2.0                             | 1.0\(^d\)                    |
| CdS    | 0.013       | 4.6             | 6.5                             | 6.4\(^a\), 6.4\(^b\)         |
| GaSe   | 0.055       | 0.3             | 0.4                             | 0.56\(^e\)                   |

\(^a\) Value of \( \beta \) calculated using the parabolic band model given in [14], Eq. (22)

\(^b\) [15], measured at 780 nm

\(^c\) [16], measured at 790 nm on a (110) crystal

\(^d\) [17], measured at 800 nm on a (100) crystal

\(^e\) [18], measured at 800 nm
Table 3.

Mobilities measured using two-photon (800 nm) excitation

| Sample | Power (mW) | Fluence (µJ/cm²) | $\Delta E/E_0$ | $N_p$ (cm⁻³) | $\mu$ (cm²/Vs) | $\mu_{avg}$ (cm²/Vs) |
|--------|------------|------------------|----------------|--------------|----------------|---------------------|
| ZnSe   | 5          | 31.6             | 0.066          | $4 \times 10^{13}$ | 740            | 572                 |
| ZnTe   | 3.5        | 22.1             | 0.02           | $6 \times 10^{13}$ | 695            | 532                 |
| GaP    | 20         | 126              | 0.05           | $7.7 \times 10^{14}$ | 687            | 598                 |
| CdS    | 10.4       | 66               | 0.02           | $6 \times 10^{14}$ | 258            | 212                 |
| GaSe   | 45         | 285              | 0.43           | $6 \times 10^{14}$ | 143            | 118                 |