

## Contactless microwave study of shallow traps in thin-film CdSe

Serguei Yu. Grabtchak and Michael Cocivera\*

*Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

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The contactless microwave technique was used to measure light-induced transients in the power absorption by thin films of polycrystalline CdSe. Because the rise time of the detector was 500 ns, the analysis was limited 1  $\mu$ sec or longer. Measurement of these transients at a number of fixed frequencies across the "dark" resonance frequency made reconstruction of the difference signal possible. This signal, which represents the difference between the "dark" and "light" Lorentz resonance curves, was determined at various times during the decay. Analysis of these signals provided the changes in the real and imaginary parts of the dielectric constant as a function of time. The decays of these parameters were characterized by the sum of two exponential terms:  $\tau_1 = 16.9 \mu$ sec and  $\tau_2 = 261.5 \mu$ sec for the change in the imaginary part, and  $\tau_1 = 18.5 \mu$ sec and  $\tau_2 = 283 \mu$ sec for the change in the real part. The close agreement of these values indicates the simultaneous presence of both trapped and free electrons having identical decay times. A mechanism consistent with these results involves rapid equilibration between the free electrons and those in the two shallow traps. Decay from each trap is the rate limiting step, and the time to reach thermodynamic equilibrium must be less than 500 ns. The initial electron densities in the two traps were  $2.1 \times 10^{18}$  and  $1.0 \times 10^{18} \text{ cm}^{-3}$ , and the corresponding concentrations of the free electrons were  $3.6 \times 10^{17}$  and  $1.4 \times 10^{17} \text{ cm}^{-3}$ . For the free electrons, the values for the drift mobility were 2.1 and  $1.8 \text{ cm}^2/\text{V s}$ , respectively. Using the harmonic-oscillator model for trapped electrons, the trap energies were 0.096 eV for the fast decay and 0.152 eV for the slower decay. The initial changes in a real part of the dielectric constant were 44.9 and 11.9, respectively. Thus, the photoinduced concentrations of electrons in naturally existing shallow traps are sufficient to effect large changes in the dielectric constant on a short time scale.

### I. INTRODUCTION

Multiple trapping of photoelectrons at shallow centers is believed to have important consequences for photoconductivity in thin-film polycrystalline semiconductors. Trapping by these shallow levels reduces the fraction of time electrons spend in the conduction band and, therefore, slows carrier transport through the lattice. One useful method for monitoring electrons in the conduction band and shallow traps is the contactless microwave technique, which determines changes in the complex dielectric constant of the material resulting from changes induced in the carrier densities. In their seminal papers, Hartwig and Hinds<sup>1-3</sup> demonstrated that excess electrons in the conduction band and traps caused changes in the real and imaginary parts of the dielectric constant at 4.2 K where the decay rates were slow. Extending this type of analysis to systems in which rapid decay occurs requires measurement on a much shorter time scale. Such studies were reported for silver halide powders for which the time domain was extended to transients having lifetimes in the 100-ms (Ref. 4) and 1- $\mu$ s (Ref. 5) ranges. In the second work, the time scale was achieved by scanning only a small portion of the resonance signal (near the peak maximum) after a short pulse of light. Consequently, the entire light-induced signal was not determined, and the change in the imaginary part of the dielectric constant was inferred from the decrease in the peak maximum. In both these studies, the microwave system required equipment such as automatic frequency

control or a rapid frequency scanner, which can limit the time resolution of the measurement.

A more direct method in which the time resolution is limited only by the time constant of the cavity and detector diode, was suggested and tested on silver halide powders and crystals.<sup>6-8</sup> In this approach, light-induced transients were measured at a number of fixed frequencies near the "dark" resonance frequency, and a partial curve representing the difference between the "dark" and "light" Lorentz resonance signals was determined at various times during the decay. From each difference signal, the light-induced frequency shift (related to the change in the real part of the dielectric constant) was calculated using the "zero frequencies" approach,<sup>9</sup> which required a number of assumptions. The change in the imaginary part of the dielectric constant was subsequently calculated from this result. The time resolution was reported to be 50 ns.

The present paper reports an extension of this approach. It involves a fit of the *total* difference signal to the difference between the dark and light Lorentz resonance signals. Because the total rather than the partial difference signal was used, the fit could be accomplished without the simplifying assumptions required for the zero frequencies analysis<sup>6-8</sup> described above. Furthermore, it avoids the limitations inherent in the rapid scan approach<sup>5</sup> discussed above. This initial study involves thin-film CdSe prepared by conversion of CdO thin films.<sup>10</sup> With this approach, we were able to determine the changes in the real and imaginary parts of the dielec-

tric constant unambiguously. As a result, we were able to separate the contributions of the conduction and trapped electrons.

Most of the previous microwave studies of transients in semiconductors have involved either single crystalline or powder materials. A few have involved thin films of semiconductors such as  $\alpha$ -Si:H,<sup>11</sup>  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ,<sup>12</sup> and  $\text{Ga}_{1-x}\text{In}_x\text{As}$ .<sup>13</sup> In these cases, the transient was measured only at the resonance frequency, and the difference signal was not determined. Consequently, it was not possible to separate the relative contributions of conduction and trapped electrons. A similar limitation applied to the photoconductivity studies of polycrystalline Si wafers.<sup>14</sup> Although not directly observed, the presence of trapped electrons was inferred from the temperature dependence of photocurrent transients for thin-film polycrystalline CdTe.<sup>15</sup>

## II. THEORY

When a homogeneous material is isotropic, the dielectric constant can be expressed as a complex function

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \equiv \varepsilon' - j\frac{\sigma}{\omega'\varepsilon_0}, \quad (1)$$

in which  $\varepsilon'$  is a normalized (relative) dielectric constant (real part),  $\varepsilon''$  is the imaginary part,  $\sigma$  is the material conductivity,  $\varepsilon_0$  is the permittivity, and  $\omega'$  is the real angular frequency.<sup>16</sup> Changes in the resonance frequency  $f_0$  and loaded cavity quality factor  $Q_L$  can be related to the changes in the complex angular frequency:

$$\begin{aligned} \frac{\delta\omega}{\omega_2} &= \frac{(\omega_2' - \omega_1') + j(\omega_2'' - \omega_1'')}{\omega_2' + j\omega_2''} \\ &\approx \frac{f_{02} - f_{01}}{f_{02}} - j \left[ \frac{1}{2Q_{L2}} + \frac{1}{2Q_{L1}} \right], \end{aligned} \quad (2)$$

which can be related to the complex dielectric constant by the cavity perturbation formula<sup>16</sup>

$$\frac{\delta\omega}{\omega_2} = \frac{(\mu_2^* - \mu_1^*) \int_{V_s} \bar{H}_1 \bar{H}_2 dV - (\varepsilon_2^* - \varepsilon_1^*) \int_{V_c} \bar{F}_1 \bar{F}_2 dV}{\int_{V_c} (\varepsilon_1^* \bar{F}_1 \bar{F}_2 - \mu_1^* \bar{H}_1 \bar{H}_2) dV}. \quad (3)$$

In these equations, the subscripts 1 and 2 refer to the dark and light parameters,  $V_s$  and  $V_c$  are the sample and cavity volumes,  $\bar{H}$  and  $\bar{F}$  are the magnetic and electric fields, and  $\mu^*$  is the complex magnetic permeability.

When a narrow thin strip of nonmagnetic material is placed in the maximum electric field inside a  $\text{TE}_{101}$  cavity, the photoinduced changes in the resonance frequency  $\delta f_0$  and the cavity quality factor  $\delta(1/2Q_L)$  are

$$\frac{\delta f_0}{f_{02}} \equiv \frac{f_{02} - f_{01}}{f_{02}} = -\frac{\delta\varepsilon'}{\varepsilon'} \frac{2V_s}{V_c}, \quad (4)$$

$$\delta \left[ \frac{1}{2Q_L} \right] \equiv \left[ \frac{1}{2Q_{L1}} - \frac{1}{2Q_{L2}} \right] = \frac{\delta\varepsilon''}{\varepsilon'} \frac{2V_s}{V_c}, \quad (5)$$

in which  $\delta\varepsilon' = \varepsilon_2' - \varepsilon_1'$  and  $\varepsilon_1' = \varepsilon'$ . The only assumptions made in the derivations are that  $Q_L \gg 1$  and that  $\varepsilon' \gg \varepsilon''$ , which are verified experimentally:  $Q_{L1} \approx 2 \times 10^3$  and  $\varepsilon'' = \sigma/\omega'\varepsilon_0 \approx 2 \times 10^{-5}$ , using  $\varepsilon' = 10$  for CdSe in the dark,<sup>17</sup>  $\omega' = 2\pi f \approx 6.3 \times 10^{10}$  Hz,  $\sigma = 10^{-7}$  ( $\Omega \text{ cm}$ )<sup>-1</sup> for undoped thin-film CdSe.<sup>10</sup> As a result, changes in the real and imaginary parts of the dielectric constant can be determined separately from  $\delta f_0$  and  $\delta(1/2Q_L)$ , respectively. It should be noted that the long thin slab geometry of the sample avoids the problem of photoconductive crosstalk that can occur<sup>5</sup> with spherical samples for which  $\delta f_0$  may be dominated by  $(\delta\varepsilon'')^2$ .

When only active losses are associated with the dissipation of energy in the resonance circuit, the resonance profile has a Lorentzian form.<sup>18,19</sup> As a result, the difference signal  $\Delta P(f, t)$  can be expressed as the difference between the dark and light Lorentz signals

$$\Delta P(f, t) = \frac{y_{01}}{1 + \left[ 2 \frac{f - f_{01}}{\Delta f_{1/2}} \right]^2} - \frac{y_{02}}{1 + \left[ 2 \frac{f - f_{02}}{\Delta f'_{1/2}} \right]^2}. \quad (6)$$

In this equation,  $f$  is the microwave frequency,  $y_{0n}$  is the amplitude at the resonance frequency, and  $\Delta f_{1/2}$  is the bandwidth at half maximum amplitude. Because the dark parameters can be measured directly, a fit of Eq. (6) to the difference signal is made with three adjustable parameters  $y_{02}(t)$ ,  $f_{02}(t)$ , and  $\Delta f'_{1/2}(t)$ , which are used to calculate the changes in the real and imaginary parts of the dielectric constant according to Eqs. (4) and (5). The time dependence corresponds to the time dependence of the difference signal.

## III. EXPERIMENT

The sample consisted of a thin strip ( $3 \times 60 \times 1$  mm<sup>3</sup>) of quartz on which a thin film of CdSe (about 1  $\mu\text{m}$ ) was deposited using a conversion process described earlier.<sup>10</sup> Using a specially designed micrometer sample holder, this strip could be carefully positioned in the cavity. The dark resonance and the light-induced transients were measured for this sample using the X-band microwave apparatus shown schematically in Fig. 1. The microwave source was a 1-W klystron (8.2–9.6 GHz), model A7273, controlled by a Narda 438 power supply. A rectangular  $\text{TE}_{101}$  cavity, constructed in our laboratory, had a loaded  $Q_L = 1814$ , which corresponded to a time constant  $\tau = Q_L/\omega' \approx 30$  ns. The cavity, which had a volume  $V_c = 4.89$  cm<sup>3</sup>, had two perpendicular through holes for sample insertion and illumination.

The sample cavity, which was placed in one arm of a hybrid (magic) tee, was mounted on a slide screw tuner used for impedance matching. This tuner and the one in the reference arm were adjusted to assure that the dark resonance profile had the appropriate Lorentz form. All microwave signals were measured using an IN23WE detector diode. The time resolution in these experiments was limited by the rise time of this diode in combination with Narda 510 detector mount (about 500 ns). The signal from the detector diode was recorded by a 20-MHz Nicolet 2090-III digital oscilloscope connected to an

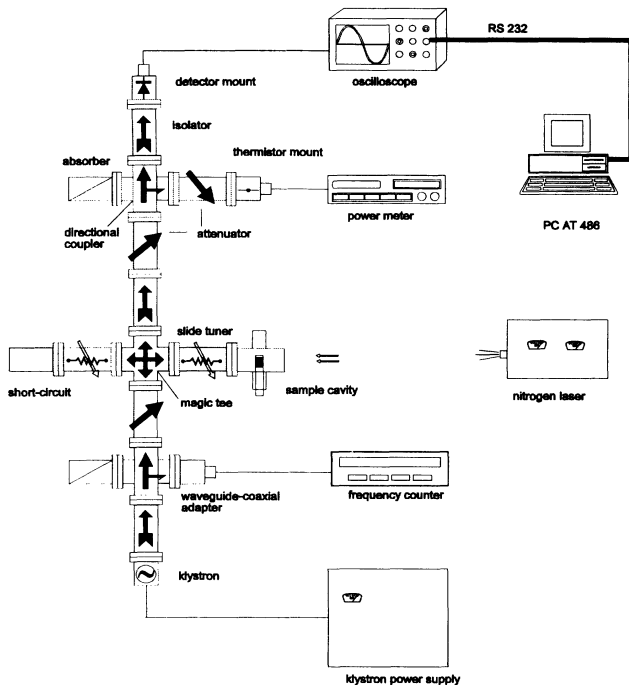


FIG. 1. Schematic diagram of the waveguide arrangement and the equipment used for the contactless microwave measurement of photoinduced changes in the complex dielectric constant.

80486 computer by an RS 232 interface. The oscilloscope was triggered by an electric pulse produced by the laser power supply. A known fraction of the microwave power was diverted from the detector diode to an HP X486A thermistor mount and measured with an HP 431B power meter for calibration of the diode. The microwave frequency was measured by an HP 5340A frequency counter.

The light source used in these experiments was an LN 1000 nitrogen (337 nm) pulsed laser (Photochemical Research Associates, Inc.) with a pulse width of 600 ps. The maximum incident laser power was 0.25 mJ/pulse ( $4 \times 10^{14}$  photons/pulse), which corresponds to  $6 \times 10^{15}$  photons/cm<sup>2</sup> pulse. Laser power was measured using an ED-100A joulemeter (Opticon Corp.).

Calibration of the diode detector indicated that it produced a voltage proportional to the rf power at low levels of incident microwave power (square-law behavior). In the milliwatt range, it produced a voltage proportional to the square root of the microwave power (linear behavior). The microwave power used in our experiments lay in the range at which the transition from square law to linear behavior occurred. A fit to the sum of the linear and square law provided the calibration curve for subsequent data processing.

The dark resonance profile of the cavity containing the unilluminated sample was measured as the power reflected from the cavity using a slow sawtooth modulation of the klystron. The profile was often distorted from the pure Lorentz form because the slide screw tuner was not properly adjusted. Adjustment to the proper setting

required a fitting procedure, which used only about 40 points from the profile in the early stages of the fit, but the final fit was carried out over all 4096 experimental points to determine  $y_0$ ,  $f_0$ , and  $\Delta f_{1/2}$ . The experimental resonance curve and the fitted (smooth) curve are shown on Fig. 2. As a check, the fitting procedure was tested on a simulated Lorentz curve and was found to be unambiguous.

#### IV. RESULTS AND DISCUSSION

Before illumination, the resonance signal parameters of the loaded cavity containing the CdSe sample were  $y_0 = 664.01$  mW,  $f_0 = 9.562108$  GHz, and  $\Delta f_{1/2} = 5.274$  MHz. The frequency resolution was 5 kHz. The light-induced transients, which were measured in the range 9.5580–9.5675 GHz, were determined at 22 frequencies. The sign and intensity of the transient signal depended significantly on the microwave frequency, as might be expected. There was no dependence of the photodecay on the number of laser pulses, indicating that photodecomposition was not important under these conditions.

Figure 3 shows the decay at the dark resonance frequency. This decay was best described by the sum of two exponentials, and the fit is also illustrated as the solid curve. Although such a decay is often considered to be a direct measure of the photoconductivity decay,<sup>11–14</sup> this conclusion can be ambiguous without a complete analysis of the light-induced resonance profile. For this purpose, the transients obtained at various frequencies across the resonance profile were used to reconstruct the difference signal at various instants after the light pulse. Data points at specified instants of time after the light pulse

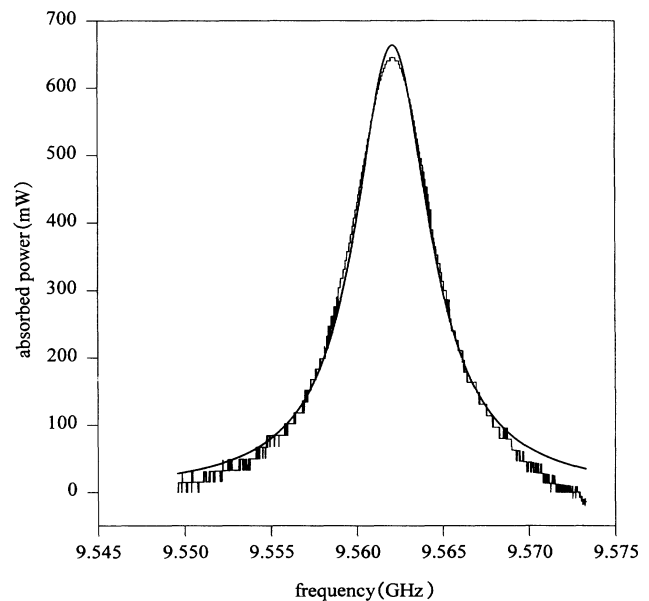


FIG. 2. Measured and simulated Lorentz resonance curve for thin-film CdSe on quartz in the dark at room temperature. The maximum amplitude, resonance frequency, and width at half height are  $y_0 = 664.01$  mW,  $f_0 = 9.562108$  GHz, and  $\Delta f_{1/2} = 5.274$  MHz.

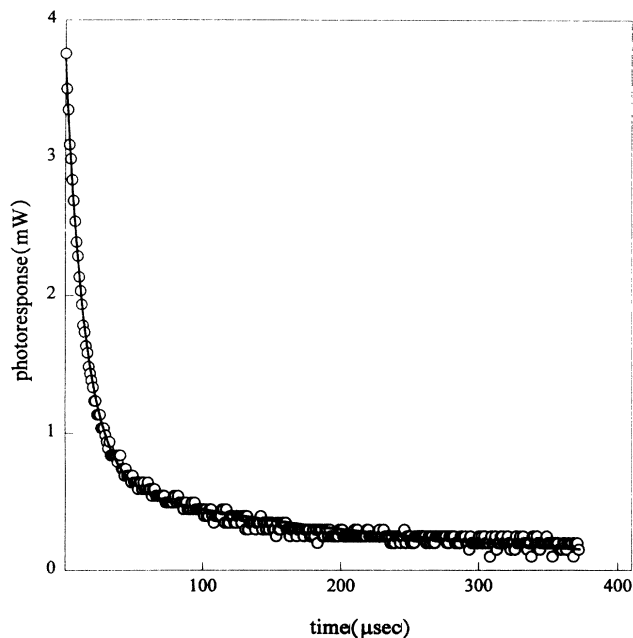


FIG. 3. Light-induced transient at  $f_0=9.562108$  GHz (the dark resonance frequency) for thin-film CdSe on quartz at room temperature. The solid curve is the fit to the sum of two exponential terms. See text for intercepts and lifetimes. The total of 4096 data points were used in the fit, and not all are illustrated in the figure for clarity.

were collected and plotted vs frequency. In this way the difference signal was reconstructed point by point for a fixed instant of time. Figure 4 illustrates three typical plots of the reconstructed difference signals corresponding to various times ranging from 2 to 90  $\mu\text{s}$  after the laser excitation. The full set of such plots were obtained in 100-ns steps over a time range of 100 ns up to approximately 400  $\mu\text{s}$ . However, because the rise time of the detector was 500 ns, only data obtained at 1  $\mu\text{s}$  or longer were used in the fits.

The corresponding fits according to Eq. (6) are illustrated as the solid curves in Fig. 4. The fits provide the light-induced values of  $y_{02}$ ,  $f_{02}$ , and  $\Delta f'_{1/2}$  at each time. The corresponding time dependence of the light-induced shift of resonance frequency ( $\delta f_0$ ) and the bandwidth change  $\delta(\Delta f_{1/2})$  are presented in Figs. 5 and 6, respectively. It was found that the time dependence of both parameters could be fit by the sum of two exponential

terms, and these curves are also illustrated in the figures. For  $\delta(\Delta f_{1/2})$  the fitting parameters were  $\delta(\Delta f_{1/2})_{01}=30$  kHz,  $\tau_1=16.9\pm 0.2$   $\mu\text{s}$  and  $\delta(\Delta f_{1/2})_{02}=10$  kHz,  $\tau_2=262\pm 3$   $\mu\text{s}$ . For  $\delta f_0$ , the values were  $(\delta f_0)_{01}=-30$  kHz,  $\tau_1=18.5\pm 0.2$   $\mu\text{s}$ , and  $(\delta f_0)_{02}=-8$  kHz,  $\tau_2=283\pm 3$   $\mu\text{s}$ . As can be seen, these values are not only close to each other, but also the decay times are close to those of the photoresponse at the dark resonance frequency:  $\tau_1=14.4\pm 0.2$   $\mu\text{s}$  and  $\tau_2=256\pm 3$   $\mu\text{s}$  (Fig. 3).

Experimentally it has been found that excess electrons in the conduction band cause a positive shift in the resonance frequency, while electrons in traps cause a negative shift.<sup>2,3</sup> Accordingly, the negative frequency shift found for both transients in CdSe indicates that electrons were present in two trap states. Consequently, the two lifetimes observed for the frequency shift cannot be ascribed to the initial trapping of free electrons. In fact, it is very likely that the initial decay of free electrons would have a substantially shorter lifetime because photoluminescence decay lifetimes for thin-film CdSe prepared by the same method are in the ps range at room temperature.<sup>20</sup> On the other hand, the change in bandwidth, which is proportional to the change in the cavity quality factor, has been shown to be due mainly to electrons in a conduction band.<sup>3</sup> Trapped electrons can also contribute to the change in this parameter; however, the contribution is expected to be small relative to that of the conduction electrons. In the case of CdSe, using values for the momentum relaxation in the reasonable range of  $10^{-13}$ – $10^{-14}$  s, the contribution of conduction electrons is more than  $10^4$ – $10^2$  larger than that of the trapped electrons. As a result, the density of trapped and free electrons calculated below indicates that the free electrons are at least partially if not wholly responsible for the bandwidth changes associated with both transients. The simultaneous presence of both trapped and excess free electrons having identical decay time constants is consistent with a mechanism involving rapid equilibration between trapped and free electrons, with decay from each trap being the rate limiting step. The time to reach thermodynamic equilibrium must be less than 500 ns (instrumental limitation) because no transients with lifetimes between 500 ns and 18  $\mu\text{s}$  were detected. Assignment of these traps to either surface or bulk states is not possible without additional measurements as a function of temperature and light intensity along with diffusion-limited kinetic measurements.<sup>21</sup>

According to Castellan and Seitz,<sup>22</sup> the concentration

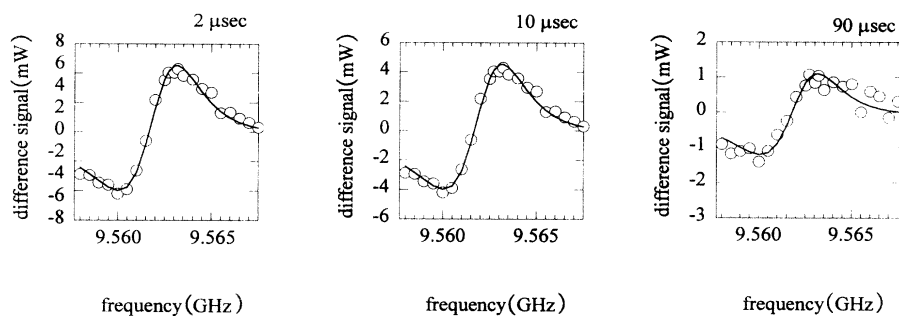


FIG. 4. Difference signals reconstructed from the transients measured at various frequencies across the microwave resonance profile at three instants during the decay of the excess electrons. The solid curves represent the fit as the difference between the dark and light Lorentz curves using adjustable light parameters.

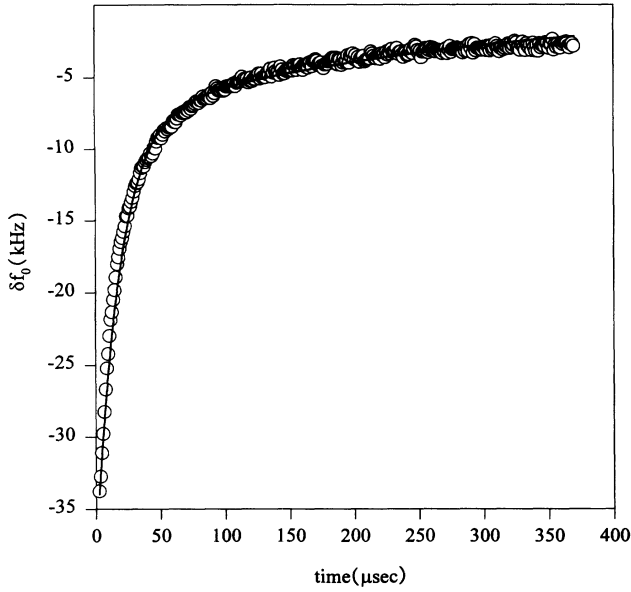


FIG. 5. The time dependence of the light-induced change in the resonance frequency for CdSe at room temperature. The data were obtained from the fit of each difference signal measured at 100 ns intervals between 1 and 400  $\mu$ s.

of shallow centers is given by

$$N_t = \frac{1}{4\pi\alpha \left[ \frac{1}{\delta\epsilon'} + \frac{1}{3\epsilon'} \right]} \quad (7)$$

Using  $\delta\epsilon'$  equal to the change of the real part of the dielectric constant for each transient at  $t=0$  after the

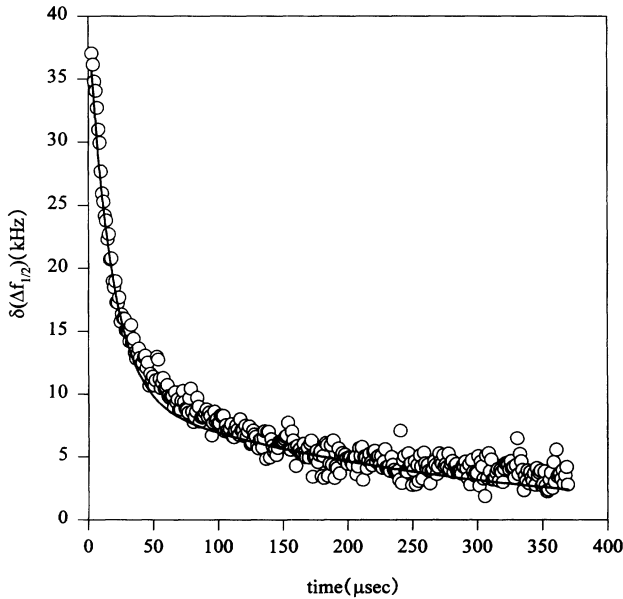


FIG. 6. The time dependence of the light-induced change in the linewidth at half height for CdSe at room temperature. The data were obtained from the fit of each difference signal measured at 100-ns intervals between 1 and 400  $\mu$ s.

laser pulse, this equation was used to estimate the electron densities in the two shallow traps. For this calculation,  $\delta\epsilon'$  was calculated using Eq. (4) in which  $V_s = \pi d^2 h / 4$ , and  $d = 0.33$  cm is the diameter of the laser spot at the sample surface. The thickness  $h$  of the active volume was chosen to be  $0.2 \mu\text{m}$  (the reciprocal of the absorption coefficient of CdSe at 337 nm). The polarizability of both traps was taken to be  $\alpha_{\text{EMA}} \approx 6.8 \times 10^5 \text{ \AA}^3$ . This value is similar to the corresponding polarizability values of shallow centers in Si ( $6.42 \times 10^5$ ) (Ref. 23) and AgCl ( $2 \times 10^5$ ).<sup>5</sup> It was calculated for CdSe using the effective-mass approximation (EMA) developed by Castellani and Seitz,<sup>22</sup> and validated experimentally by Bethin, Castner, and Lee:<sup>23</sup>

$$\alpha_{\text{EMA}} = \alpha_H \epsilon'^4 \left[ \frac{m}{m^*} \right]^3 \quad (8)$$

In this equation,  $\alpha_H$  is the polarizability of atomic hydrogen,  $\epsilon' = 10$  is the real part of dielectric constant, and the effective electron mass  $m^* = 0.13m$  for CdSe.<sup>17</sup>

Based on the initial values of the shift in the resonance frequency found for the two decay components ( $-30.0$  and  $-8.0$  kHz), the changes in a real part of the dielectric constant were  $\approx 44.9$  and  $\approx 11.9$ , respectively. Although these values are large, they are not unprecedented. For example, the static dielectric constant of single-crystal germanium increased from 16 to 107 when shallow ionized donor states were filled at liquid-helium temperatures.<sup>24</sup> The impurity concentration was  $10^{17} - 10^{18} \text{ cm}^{-3}$ . Values as high as 35–40 were found for antimony- and arsenic-doped single-crystal silicon at low temperatures.<sup>25</sup> The impurity densities were  $(2-3) \times 10^{18} \text{ cm}^{-3}$ . These results were supported by similar low-temperature behavior observed for Si by other workers,<sup>23</sup> and by the metal-insulator transition photoinduced in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>26</sup> Also, they are consistent with Mott transition theory for heavily doped semiconductor.<sup>27-29</sup>

The transient microwave results for CdSe at room temperature demonstrate that the detection of large changes in the dielectric constant is not restricted to steady-state conditions at low temperatures, and that it is not necessary to dope the sample heavily. Thus the photoinduced concentrations of electrons in naturally existing shallow traps are sufficient to effect large changes in the dielectric constant on a short-time scale. Based on the changes in the real part of the dielectric constant and Eq. (7), the electron densities in the two traps were  $2.1 \times 10^{18}$  and  $1.0 \times 10^{18} \text{ cm}^{-3}$ , which are in the region of the asymptotic value ( $\approx 3.5 \times 10^{18} \text{ cm}^{-3}$ ) where large changes in the dielectric constant occur.

Using Eq. (5) and the change in the cavity quality factor, the changes in the imaginary part of the dielectric constant were 22.5 and 7.5 for the fast and slow components of the decay, respectively. These values and Eq. (1) were used to calculate the conductivity associated with the excess free electrons in equilibrium with the traps ( $12.0$  and  $4.0 \Omega \text{ m}^{-1}$ ). With these data and the values for the density of trapped electrons  $N_t$ , the drift mobility  $\mu_d$  and density of electrons in the conduction band  $n$  were calculated using  $\sigma = ne\mu_d$  and  $(n + N_t)\mu_d$

$=n\mu$  with the Hall mobility<sup>30</sup>  $\mu=14$  cm<sup>2</sup>/V s. For the two components of the decay the values for the drift mobility were 2.1 and 1.8 cm<sup>2</sup>/V s. These values are very similar, as might be expected since they refer to the mobility of the free electrons. The concentrations of the free electrons in equilibrium with the traps were  $3.6 \times 10^{17}$  and  $1.4 \times 10^{17}$  cm<sup>-3</sup>.

Using the harmonic-oscillator model for trapped electrons, the changes in the real and imaginary parts of the dielectric constant can be related to the trap energies.<sup>1-3</sup> When  $n_i$  carriers are redistributed among subband-gap states, changes in the real and imaginary parts of the complex dielectric constant of a semiconductor can be written as

$$\delta\epsilon' = \frac{e^2}{m^* \epsilon_0} \sum_i \frac{\omega_{0i}^2 - \omega'^2}{(\omega_{0i}^2 - \omega'^2)^2 + (\omega'/\tau)^2} n_i, \quad (9)$$

$$\delta\epsilon'' = \frac{e^2}{m^* \epsilon_0} \sum_i \frac{\omega'/\tau}{(\omega_{0i}^2 - \omega'^2)^2 + (\omega'/\tau)^2} n_i, \quad (10)$$

in which  $\omega_{0i}$  is the characteristic frequency of the oscillator  $i$ ,  $e$  is the electronic charge,  $m^*$  is the electron effective mass,  $\tau$  is the momentum relaxation time ( $\tau = m^* \mu / e$ ), and  $\omega'$  is the angular frequency of the applied field. The oscillating frequency of the electron is related to its binding energy  $E_i$  by the equation

$$\omega_{0i}^2 = \frac{2}{m^*} \frac{(4\pi\epsilon_0)^2}{e^4} E_i^3. \quad (11)$$

Two regions can be considered: one corresponding to trapped carriers ( $\omega_{0i} \gg \omega'$ , large binding energy) and the other, to free carriers ( $\omega' \gg \omega_{0i}$ , low binding energy). According to Eqs. (9) and (11), the change in dielectric constant is positive and proportional to  $E^{-3}$  for trapped electrons. Consequently, only electrons in shallow traps can affect the real part of the dielectric constant, and deep traps cannot be detected. Using  $\omega_{0i} = \omega'$ , the energy for a crossover from free to trapped carrier behavior is estimated to be 3 meV for CdSe at the frequency used. On the basis of Eq. (4), electrons in traps having a smaller energy cause a positive shift in the resonance frequency (free-carrier behavior), and larger energies cause a nega-

tive shift in the resonance frequency (trapped electron behavior).

Equation (11) was used to calculate the binding energy  $E_i$  of the traps associated with the two decays. The fast decay has a shallower trap (0.096 eV) than the slower decay (0.152 eV). For this calculation,  $\omega_{0i}$  was calculated according to Eqs. (9) and (10). The plasma resonance frequency of the free electrons<sup>2,3</sup> was not included because it occurs in the infrared to visible region for the free-carrier densities obtained in the present experiments. With the present data, it is not possible to identify these traps as either bulk or surface states. In addition, clarification of the decay mechanisms for these traps will require detailed variable temperature studies, which are planned.

In summary, the detailed studies of trapped and excess free electrons using the contactless microwave technique has been extended from low-temperature, steady-state conditions<sup>1-3</sup> to room-temperature and transient conditions in an unambiguous manner. This analysis was made possible by development of a methodology to reconstruct the difference signals at various times using data from transients measured at various frequencies across the microwave resonance profile. A complete fit of these difference signals provided the time dependence for the changes in the real and imaginary parts of the complex dielectric constant. Having demonstrated this procedure at room temperature for thin-film semiconductors, extending it to variable temperature studies will not be difficult. Systematic studies of the effects of dopants on the energy and density of shallow traps are planned. Because the technique does not require contacts, it has a very general application to a wide variety of materials including single-crystal semiconductors and insulators as well as powders, surface films, and photoactive polymers.

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\*Author to whom all correspondence should be addressed.

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