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Size and surface effects on transient photoconductivity in CdS nanobelts probed by time-resolved terahertz spectroscopy

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Ultrafast optical-pump terahertz probe spectroscopy was performed over a graduated size distribution of CdS nanobelts to investigate the size and surface effects on the transient photoconductivity. It was found that the nanobelt size has a profound influence on the carrier localization and photoconductivity dynamics, brought about by the carrier trapping at surface defects. The strong carrier localization in the nanobelt is ascribed to the internal surface boundaries arising from the surface depletion layer. The increased thickness of surface depletion layer due to a continuous trapping of photocarriers at surface defects results in more pronounced carrier localization after photoexcitation. © 2012 American Institute of Physics [http://dx.doi.org/10.1063/1.4748300]

One-dimensional (1D) and quasi 1D semiconductor nanostructures have attracted much attention in recent years. In particular, CdS nanowires (NWs) and nanobelts (NBs) have received much attention and are considered as promising materials for applications in the area of photonics, photodetectors, photovoltaics, and photocatalysis. To optimize the performance of these electronic and optoelectronic devices, a comprehensive understanding of the transient electrical and optical response, carrier relaxation and diffusion as well as the size- or surface-dependent effect on the carrier dynamics is essential. However, there are few investigations on the transient terahertz (THz) photoconductivity of 1D CdS nanostructures or any other nanobelt materials. It is extremely challenging to measure the static conductivity of semiconductor nanostructures due to the inherent difficulties with the fabrication of Ohmic contacts on nanostructures with the traditional technique (i.e., four-electrode probe method). However, the transient complex-valued and frequency-dependent photoconductivity of nanostructures can be easily probed by the time-resolved THz spectroscopy (TRTS). In this technique, the photoinduced carriers in a sample are probed contact-free with a time-delayed picosecond THz pulse following the photoexcitation. In this case, the photoconductivity of a material can be probed using the transient electric field of the THz pulse rather than a static one as in conventional transient photoconductivity measurements.

In this letter, the ultrafast THz complex photoconductivity of CdS NBs with varying sizes is investigated by means of the optical-pump THz-probe (OPTP) technique. We seek to obtain a clear understanding of size- and surface-dependent effects of NBs on photoconductivity dynamics. The carrier scattering, carrier trapping, and the variation of the surface depletion layer following photoexcitation are systematically investigated in this work.

In this study, the CdS NBs were synthesized using a vapor-transport method as discussed in earlier reports. Briefly, CdS powder (99.995%, Sigma Aldrich) contained in a quartz boat was placed at the center of the quartz tube in a furnace. Muscovite mica is used as the substrate because it is colorless transparent and is thus suitable for transmission spectroscopy directly on the as-synthesized samples. The central temperature of the furnace was elevated to 750 °C with the carrying gas of 30 sccm Ar with 5% H₂ for half an hour. CdS NBs of different sizes were grown at different locations on one mica substrate placed downstream as shown in Fig. 1, ranging from 6 to 12 cm from the center of the furnace. The closer the mica substrate to the CdS powder source (i.e., the higher the local temperature of the substrate) the larger the size of NBs. The morphology of the samples was characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). For the OPTP measurements, the 35 fs optical pulses centered at 800 nm with the repetition rate of 1 kHz from a regenerative Ti:sapphire amplifier are focused through a β-barium borate (BBO) crystal to generate THz wave through air-plasma technique. The transmitted THz probe pulse wave through the sample is detected with the THz air-biased-coherent-detection (THz-ABCD) method. The 400 nm (3.1 eV) laser pulse, obtained by frequency-doubling the 800 nm laser with BBO crystal, is used to pump the sample. The entire OPTP setup is enclosed in a chamber purged with dry nitrogen to reduce water vapor absorption. All the measurements were performed at room temperature.

Low and high magnification SEM images of CdS NBs showed a uniform distribution of randomly oriented NBs across the substrate (Fig. 1). The average length, width, and thickness of the NBs are about 100–150 μm, ~5 μm, and ~200 nm for large NBs, 50–100 μm, ~2 μm, and 150 nm for the medium NBs, and 10–50 μm, ~1 μm, and 50 nm for small NBs, respectively.
The transient photoconductivity ($\Delta \sigma(\sigma, t)$) of the NBs induced by the photoexcited charge carrier is determined by monitoring the changes of the main peak amplitude of transmitted THz probe pulse ($\Delta E(\sigma, t)$) as a function of pump-probe delay time. The THz wave forms transmitted though the photoexcited nanobelts at different delay times were measured and no significant delay time-dependent phase shift of the THz pulses was measured. Therefore, the peak of THz pulse was recorded to get the differential transmission of THz probe in our experiment. Figure 2(a) shows the normalized pump-induced change in the peak of transmitted THz probe pulse for the three different sized CdS NBs and for a 0.5 mm thick CdS bulk wafer. Each of the probe trace exhibits a fast resolution-limited rise in the photoconductivity and followed by a biexponential decay. The fast decay component ($\tau_{fast}$) is dominated by the dynamics of the carrier trapping at the surface defects. Thus, the faster decay of $\tau_{fast}$ for smaller sized NBs is due to the higher concentration of surface defects because of the larger surface-to-volume ratio. Figure 2(b) summarizes the pump fluence dependent time constant of $\tau_{fast}$ for CdS NB samples. As shown for all three NB samples, $\tau_{fast}$ increases with the pump fluence, suggesting that the trapping of the photocarriers by the surface defects begins to saturate at higher pump fluence. As larger NBs have fewer amounts of surface defects, the saturation is more pronounced. Similar phenomenon was also observed in other semiconductor nanostructures.\(^{10}\) In comparison, the photoconductivity of bulk CdS decays slowly with monoexponential behavior and a carrier lifetime of ~8 ns at the same pump fluence. Accordingly, the fast decay of the photoconductivity of NBs is therefore attributed to the carrier trapping by surface defect states (i.e., sulfur vacancies), while the slow decay originates from the...
In order to obtain the transient photoconductivity spectrum of $\Delta \sigma(\sigma)$, the entire transmitted THz probe pulse through the unexcited sample ($E_0(\sigma)$) and the pump-induced change of the entire THz probe pulse transmitted through the excited sample ($\Delta E(\sigma)$) were recorded by the probe scans at a given pump-probe delay. The $\Delta \sigma(\sigma)$ of NBs can be obtained by using equation (1),

$$\Delta E(\sigma) = \frac{1}{E_0(\sigma)} - 1,$$

where $Z_0 = 377 \, \Omega$ is the impedance of free space, $f_a$ is the filling factor of NBs in photoexcited region of NBs network film, $d$ is the optical penetration depth of 400 nm excitation wavelength in CdS, which is taken as the inverse of absorption coefficient ($1/\alpha \approx 60 \, \text{nm}$) in our measurement.\(^1\)\(^5\) Due to such a short excitation depth, the pump photon will be mainly absorbed by the top-most NBs. Therefore, the filling factor $f_a$ in the photoexcited region is taken as the area fraction of NBs in the low magnification SEM images (as shown in Fig. 1), which is 0.51, 0.46, and 0.29 for large, medium, and short NBs, respectively as analyzed by IMAGEJ software.\(^1\)\(^4\) $N(\sigma) \approx 2.15$ is the refractive index at terahertz frequencies of the mica substrate and measured by THz-time domain spectroscopy (THz-TDs).

The transient $\Delta \sigma(\sigma)$ spectra of four CdS samples measured at 5 ps after photoexcitation are shown in Figs. 2(c) and 2(d). The photoconductivity of bulk CdS is well fitted by the Drude model with photoexcited carrier density of $9.1 \times 10^{17} \, \text{cm}^{-3}$ and scattering time of 67 fs. For CdS NBs, the value of the real component of the photoconductivity is larger for the larger sized CdS NBs, and the photoconductivity spectra for three NBs share the similar features: the real component of photoconductivity increases with the increasing THz frequency, and the imaginary components are negative at low frequency. These two features together indicate a high degree of carrier localization in NBs, which can be explained by Drude-Smith model: 15

$$\sigma(\omega) = \frac{\varepsilon_0 \varepsilon_r \tau_i}{1 - i \omega \tau_s} \left(1 + \frac{c}{1 - i \omega \tau_s}\right),$$

where $\tau_s$ is the scattering time, and $\sigma_p^2 = n e^2 / \varepsilon_0 m^*$ is the plasma frequency, $n$ is concentration of mobile charge carriers induced by the photoexcitation, $m^*$ is the carrier effective mass. This model was used previously to explain the unusual phenomenon of THz frequency dependent conductivities of nanostructured materials (e.g., InP nanoparticles, ZnO nanoparticles and NWs, Si nanocrystal films) exhibiting strong carrier localization over nanometer length scales.

Hereinto, the parameter $c (-1 < c < 0)$ is associated with the degree of backscattering or carrier localization, and is proportional to the probability of carrier reflection at the NB surfaces, where $c = -1$ corresponds to fully carrier localization, $c = 0$ to the absence of carrier localization. The real and imaginary components of the THz photoconductivities of the CdS NBs samples can be well fitted using Drude-Smith model as shown by the solid lines in Figs. 2(c) and 2(d).

Figure 3 shows the fitted parameters as a function of delay time following photoexcitation for three NB samples. The error bars of the three fitted parameters ($\tau_s$, $\tau_i$, $n$) with Drude-Smith model arise from the estimation that there is a maximum uncertainty of 10% in photoconductivities introduced by the estimation of area fraction and/or thickness of CdS NB deposits. Nonetheless, the general trend for the three different-sized samples is clearly seen in the best-fit parameters. The concentration of photoinduced mobile carriers $n$ decreases with delay time, as shown in Fig. 3(a), which can be easily understood in terms of carrier trapping by surface states and carrier recombination at longer delay times.

**FIG. 3.** Time dependence of the best-fit parameters with Drude-Smith model: (a) carrier density $n$, (b) parameter $c$, and (c) $\tau_s$ from 5 to 500 ps for the transient complex photoconductivities of large (black square), medium (red circle), and small (blue triangle) sized NBs after photoexcitation with the pump fluence of 20 $\mu$J/cm$^2$. (d) The extracted time dependent percentage of depletion layer in NBs. Inset is the schematic picture of the time evolution of depletion layer.
The carrier concentration of larger NBs is higher, which should be due to the fewer defects concentrations. Besides, another reason is that the re-absorption of the emitted photons is stronger in bigger NBs. Recent work by Li et al. has shown that, when the thickness of the CdS NBs (synthesized with some methods as used in the present study) is larger than half of the wavelength of the emitted light in the NBs, the emitted light could be reabsorbed due to the internal reflection. When the refractive index of CdS is taken as 2.5 at the emission peak of 500 nm, the wavelength of the emitted light in the CdS NBs is around 200 nm at room temperature. For large NBs, the thickness is about 200 nm and photoreabsorption is expected to be stronger. So the carrier density is larger for the larger NBs.

For nanostructures, the carrier localization is mainly determined by the ratio $a$ of the nanostructure size to the carrier mean free path $l_{\text{free}}$. When $a$ is small (e.g., for $a < 10$ in semiconductor nanoparticles), the photoconductivity can be explained by the Drude-Smith model. In the CdS NBs, the main boundary scattering is the surface scattering, so the ratio of the thickness of NB ($d_{\text{NB}}$) to the carrier mean free path, $a = d_{\text{NB}}/l_{\text{free}}$, is considered, where $l_{\text{free}} = v_{\text{therm}}t_{\text{bulk}}$ $\approx 7$ nm and $v_{\text{therm}}$ is the thermal velocity ($\sim 10^7$ cm/s). $a$ is calculated to be as large as 7, 22, 29 for small, medium, and large sized NBs, respectively. Therefore, the photoconductivity spectra of NBs should exhibit Drude-like behavior, especially for medium or large sized NBs, rather than the Drude-Smith like behavior as shown in Fig. 2(d). Besides, the fitted parameter $c$ in Fig. 3(b), which represents the carrier localization due to NB size, is not expected to change with delay time. These unexpected results can be accounted for by the occurrence of carrier trapping by the surface states as described below.

The as-grown CdS NBs are usually n-type due to the sulfur vacancies. Sulphur vacancies on the surfaces can serve as active sites for adsorption of oxygen and/or water molecules, thereby creating two depletion layers near both surfaces of the nanobelt (as shown in Fig. 3(d)) by capturing the intrinsic free electrons as well as the photoexcited electrons. The surface become negatively charged, which results in an electric potential at the surface of the NB. Therefore, there will be internal surface boundaries which confine the carriers within the core of NBs. As a consequence, the effective thickness of conductive layer of NB will be decreased from $d_{\text{NB}}$ to $d_{\text{NB}} - L$ ($L$ is the total thickness of depletion layer). It should be noted that this $L$ includes the thickness of the original surface depletion layer (i.e., usually with a thickness of about tens to hundreds of nm) in the NB before photoexcitation and also the depletion layer generated by surface trapped photocarriers. After photoexcitation, more and more photoexcited carriers will be trapped at surface within several tens of ps as represented by $\tau_{\text{fast}}$. As a result, the carriers will have increased backscattering probability and have increased probability of localization in the NB. Hence, the parameter $c$ approaches $-1$ with increasing delay time, as shown in Fig. 3(b). Similar phenomenon has also been recently observed in Si nanocrystal films

If we assume that the carriers follow the Drude model (i.e., $c = 0$) when $L = 0$, according to Matthiessen’s rule, the carrier mobility is determined by the fitted scattering time $\tau_s$, bulk scattering time $\tau_{\text{bulk}}$ and boundary scattering time $\tau_{\text{bdry}}$ through the equation $\mu = e \tau_s/m^*$. Therefore, the effective dc carrier mobility $\mu_{\text{eff}}$ in the $d_{\text{NB}} - L$ region will be reduced to $(1 + c)\mu_s$. So,

$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_{\text{bulk}}} + \frac{1}{\mu_{\text{bdry}}}.$$  

Where the $\mu_{\text{bdry}}$ is the carrier mobility associated with boundary scattering time $\tau'_{\text{bdry}}$ after the considering the surface depletion layer.

In addition, the $\mu_{\text{bdry}}$ is a function of the thickness of conductive semiconductor layer $d_{\text{time}}$ and has an empirical relation of $\mu_{\text{bdry}} = d_{\text{time}}/4\tau_s v_F$, where $v_F$ is the Fermi velocity. Accordingly, $\mu_{\text{bdry}}/\mu_{\text{bdry}} = (d_{\text{time}} - L)/d_{\text{bulk}}$. Combining with Eqs. (3) and (4), we can obtain the percentage of depletion layer in NB by $L/d_{\text{NB}}$

$$\frac{L}{d_{\text{NB}}} = \frac{\tau_{\text{bulk}}}{\tau_{\text{fast}} - (1 + c)\tau_s}.$$  

The calculated $L/d_{\text{NB}}$ as a function of delay time is shown in Fig. 3(d). The initial value of $L/d_{\text{NB}}$ mainly represents the relative volume of intrinsic depletion layer in NBs. As illustrated, it is obvious that the depletion layer occupies a major region of the NB, which is consistent with previous report in Si nanowires. Consistently, the smaller sized NB has higher $L/d_{\text{NB}}$, which is due to the higher concentration of surface defects because of the larger surface-to-volume ratio. The increase in the $L/d_{\text{NB}}$ value after photoexcitation arises from an increase in the population of trapped carriers at the surface defects. Finally, these trapped-carrier-induced depletion layers in NBs will vanish when these trapped carriers undergo nonradiative recombination after long time (i.e., in ns or $\mu$s range).

In conclusion, we have investigated the transient photoconductivity of CdS NBs using optical-pump THz-probe spectroscopy. The photoconductivity of NBs is strongly influenced by the surface effect of nanostructures, the smaller the size of NBs, the stronger the carrier localization. The increased thickness of the surface depletion layer due to the continuous trapping of photocarriers at surface defects results in more pronounced carrier localization after photoexcitation. These findings provide valuable information about the size- and surface-dependent effects of CdS NBs on photoconductivity dynamics for potential applications in ultrafast nanoscale optoelectronic devices.

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