Far-infrared conductivity of CuS nanoparticles measured by terahertz time-domain spectroscopy*

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This paper reports that terahertz time-domain spectroscopy is used to measure the optical properties of CuS nanoparticles in composite samples. The complex conductivity of pure CuS nanoparticles is extracted by applying the Bruggeman effective medium theory. The experimental data are consistent with the Drude–Smith model of conductivity in the range of 0.2–1.5 THz. The results demonstrate that carriers become localized with a backscattering behaviour in small-size nanostructures. In addition, the time constant for the carrier scattering is obtained and is only 64.3 fs due to increased electron interaction with interfaces and grain boundaries.

Keywords: terahertz time-domain spectroscopy, conductivity, effective medium theory, Drude–Smith model

PACC: 3320E, 7820D

1. Introduction

Copper sulfides are IB-VIA compounds. In the copper sulfide system, there are several known solid phases: Cu_2S (chalcocite), $Cu_{1.96}S$ (djurleite), $Cu_{1.8}S$ (digenite), and CuS (covellite). All of these phases have recently received considerable attention due to their potential applications in numerous fields, such as in photothermal conversion of solar energy,[1] as coatings for microwave shields in the form of thin films,[2] as solar cell devices,[3] as selective radiation filters on architectural windows,[4] and as room temperature ammonia gas sensors. Among them, covellite copper sulfide (CuS) has attracted increasing attention in recent years due to its application as a cathode material in lithium rechargeable batteries[5] and its unique property showing metallic conductivity and transforming into a superconductor at 1.6 K.[6]

In the past few years, various attempts have been focused on the synthesis of CuS in the form of nanoparticles (NPs),[7] nanorods,[8] nanotubes,[9] nanowires,[10] nanodiscs,[11] etc., because of their special optical, electronic, and magnetic properties and wide applications in nanodevices. However, measuring the conductivity of semiconductor nanostructures is a challenge. Traditional conductivity measurement relies on measurement of current as a function of applied voltage between two electrodes and the sample. Poor electrical connection between the tiny sample and electrodes and the difficulty of characterizing a large number of NPs require an alternative technique for conductivity measurement. Terahertz time-domain spectroscopy (THz-TDS) has been proven to be a very useful noncontact technique for conductivity measurement of semiconductor NPs.[12−15] The complex dielectric constant, which is directly related to the complex conductivity of the sample, can be obtained from the THz response. The conductivity measurement by THz-TDS yields the AC conductivity of the system, rather than the DC conductivity obtained by traditional conductivity measurements.

In this article, we demonstrate a simple wet-chemical method for preparing CuS NPs in the presence of a nonionic surfactant, cetyltriethyl ammonium bromide (CTAB). This method requires neither complex apparatus nor long synthesis times in comparison with other methods including reverse micelles,[16] the hydrothermal method,[17] the solvothermal process,[18] and microwave irradiation.[19] Meanwhile, the optical properties of the composite samples are measured by using the THz-TDS technique and the

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complex conductivity of pure CuS NPs is calculated by the Bruggeman effective medium theory. The Drude–Smith model of conductivity provides a good fit on the measured data. The results demonstrate that carriers become confined with a complete backscattering behaviour in small-size NPs.

2. Materials and sample preparation

The CuS nanostructures were synthesized by the wet-chemical method at room temperature. All chemical reagents used in our experiment are of analytical grade. The CuS NPs were synthesized as follows: 200-mg CTAB and 171-mg $CuCl_2.2\ H_2O$ were dissolved in 100-ml H_2O, which was stirred with a magnetic stirrer. Meanwhile, 140-mg $Na_2S{\cdot}9H_2O$ was dissolved in 100-ml H_2O, which was stirred with a glass rod for 15 min to ensure that the Na_2S was dissolved completely. Then, Na_2S solution was added drop-wise into the $CuCl_2$ and CTAB solution under constant stirring. A black CuS precipitate was soon produced. After stirring for 10 min, the CuS precipitate was washed with distilled water for several times to remove the surfactant CTAB, NaCl and unreacted precursors. Finally, the product was dried in air.

The identity, crystal structure, and size of the products were examined by powder x-ray diffraction (XRD) and transmission electron microscopy (TEM). As shown in Fig. 1, all diffraction peaks can be perfectly indexed to hexagonal CuS with cell constants $a = 0.59362$ nm and $c = 1.634$ nm (JCPDS file No. 06-0464). The d values of the three main peaks with 2θ of 27.68°, 29.27° and 47.78° are 0.322 nm, 0.305 nm and 0.190 nm, respectively, which are in good agreement with the values of P63/mm-CuS. No characteristic XRD peaks arising from impurities such as CTAB, NaCl are detected, indicating that the product is composed of pure CuS phase. In addition, the broad XRD lines are indicative of the small size of CuS nanoparticles. From the Dedye–Scherrer equation, the average size of CuS NPs is estimated to be around 13 nm. Furthermore, the TEM image (not shown) of CuS NPs shows that the nanocrystals are not perfectly spherical and the particles tend to agglomerate to some extent. This is probably due to the high surface-to-volume ratio and surface energy in nanostructures.

As is known, CuS NPs have a high absorption in the THz range due to their metallic conductivity. Therefore, in order to improve the signal-to-noise ratio (SNR) of the measured data, we mixed the CuS NPs with polyethylene (PE) powders as a filling material, which has a low absorption in the THz range. The mixture of CuS NPs and PE powders (CuS–PE) was pressed into a 1.46-mm-thick pellet to ensure physical stability and planar interfaces. The THz beam waist in the layer plane was ∼2 mm while the radii of the particles were in the nanometre region. Therefore, we can consider that the THz beam is uniform.

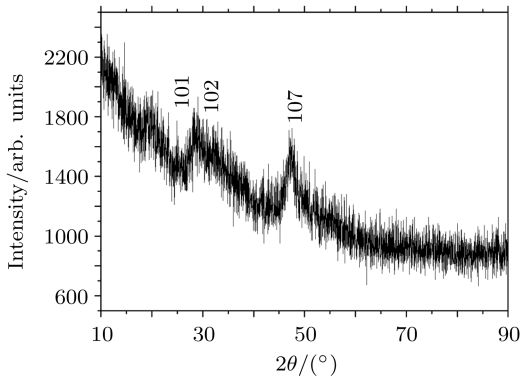


Fig. 1. The XRD pattern of the as-prepared CuS nanopatricles.

3. Experimental methods

In our experiment, the THz spectrometer in the transmission mode was used to investigate the optical properties of CuS NPs. A Ti:sapphire regenerative amplifier produces ultrashort optical pulses with a pulse duration of 100 fs and a central wavelength of 800 nm at a repetition rate of 1 KHz. The source beam is split into two portions, corresponding to terahertz generation and probe beams, respectively. The THz wave generation is assigned to four-wave mixing in the air plasma produced by a β-BaB_2O_4 (BBO) crystal.[20] The THz radiation is detected by free-space electro-optic sampling in a ⟨110⟩ ZnTe crystals. Then, the signal is collected by a lock-in amplifier with phase locked to an optical chopper. The path with THz radiation is enclosed and purged with dry nitrogen.

4. Effective medium model

When a composite medium of CuS nanostructures and PE is investigated by using THz spectroscopy, the optical constants of the pure CuS NPs can be obtained by using effective-medium theory (EMT) because the wavelength of the THz radiation (150 μm–1.5 mm) is much larger than the characteristic particle

dimensions.[21] The EMT is most often used to calculate the permittivity of a composite material given the permittivity and volume fraction of each of the individual components. However, it can also be used reversely to calculate the permittivity of one component when the permittivities of the other component and the composite are known. This "reverse EMT" approach is employed in this work.

The Bruggeman effective medium approximation (EMA)[22] and Maxwell–Garnett theory (MGT)[23] are two of the most commonly used EMTs. They are both based on the Clausius–Mossotti equation but with slightly different assumptions, and each has its advantages and limitations. For example, the MGT describes a system with small inclusions of one component embedded in a matrix of the other, which limits its use to small filling factors. Instead, the Bruggeman EMT can satisfactorily describe the system whose fraction of each component is not small. In this theory, two elements are treated equally and their properties are determined self-consistently. Here, we employ the Bruggeman theory to obtain the optical constants of the pure CuS NPs. The Bruggeman EMA is given by

$$f\frac{\varepsilon_{\rm CuS}-\varepsilon_{\rm eff}}{\varepsilon_{\rm CuS}+g\varepsilon_{\rm eff}}+(1-f)\frac{\varepsilon_{\rm PE}-\varepsilon_{\rm eff}}{\varepsilon_{\rm PE}+g\varepsilon_{\rm eff}}=0, \qquad (1)$$

where f is the filling fraction of the CuS NPs, being 1/5 in our sample. Furthermore, g is a geometric factor characterizing the shape of the inclusions. Theoretically, g is 1 for an array of cylinders with its axis collinear with the incident radiation and 2 for spherical NPs.[24] The $\varepsilon_{\rm eff}$, $\varepsilon_{\rm CuS}$ and $\varepsilon_{\rm PE}$ are the complex dielectric functions related to CuS–PE, CuS, and PE, respectively. It is clear that the complex dielectric function of pure CuS NPs can be calculated if we know $\varepsilon_{\rm eff}$ and $\varepsilon_{\rm PE}$. Rearranging Eq. (1) to solve for the particle permittivity, $\varepsilon_{\rm CuS}$ gives

$$\varepsilon_{\rm CuS}=\frac{\varepsilon_{\rm eff}[f(\varepsilon_{\rm PE}+2\varepsilon_{\rm eff})+2(1-f)(\varepsilon_{\rm PE}-\varepsilon_{\rm eff})]}{\varepsilon_{\rm PE}+(1+f)\varepsilon_{\rm eff}}. \qquad (2)$$

The complex permittivity and complex conductivity are related by

$$\hat{\sigma}=\sigma_{\rm r}+{\rm i}\sigma_{\rm i},\ \sigma_{\rm r}=\varepsilon_0\omega\varepsilon_{\rm i},\ \sigma_{\rm i}=\varepsilon_0\omega(1-\varepsilon_{\rm r}). \qquad (3)$$

5. Results and discussion

In order to obtain $\varepsilon_{\rm eff}$ and $\varepsilon_{\rm PE}$, we utilize the reference signal of free space and the propagated THz pulses through the PE and CuS–PE samples. Figure 2 shows the time-domain waveforms of the reference and sample signals. Compared with the reference pulse, the propagated THz pulses through samples exhibit a drop in amplitude and a delay in time. However, the THz pulse transmitted through the CuS–PE mixture shows an obvious broadening in pulse duration and a sharp decrease in amplitude relative to the PE sample, indicating that the absorption and the loss of the high-frequency components are stronger in the CuS–PE mixture.

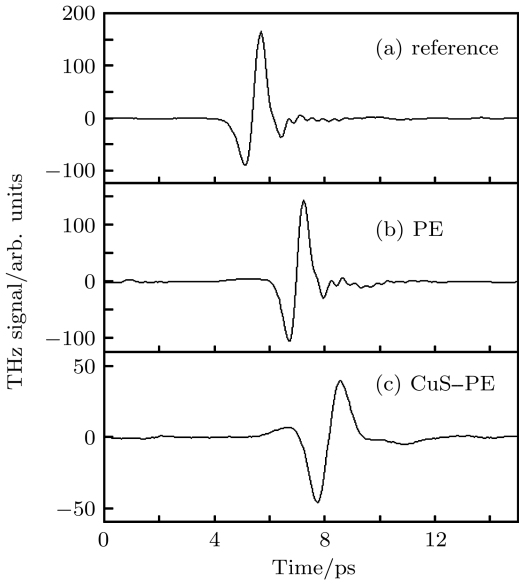


Fig. 2. The reference signal of free space (a) and the propagated THz pulses through PE sample (b) and the CuS–PE mixture (c).

From the transmitted THz waveforms, the complex permittivities of the two samples are calculated with real part $\varepsilon_{\rm r}$ and imaginary part $\varepsilon_{\rm i}$ in the 0.2–1.5 THz region, respectively. As shown in Fig. 3, the complex permittivity of the CuS–PE mixture ($\varepsilon_{\rm eff}$) is higher than that of the PE sample ($\varepsilon_{\rm PE}$). The average values of $\varepsilon_{\rm r}$ are about 2.5 and 2.0 for the effective medium and PE sample, respectively. Moreover, $\varepsilon_{\rm i-eff}$ is rather high and frequency-dependent whereas $\varepsilon_{\rm i-PE}$ is nearly unchanged with the value of zero in the 0.6–1.5 THz region, indicating the strong absorption and dispersion of the CuS NPs.

Then, by using Eq. (2), the complex dielectric function of pure CuS NPs ($\varepsilon_{\rm CuS}$) is easily calculated, as presented in Fig. 4. It is clear that $\varepsilon_{\rm CuS}$ is much higher than $\varepsilon_{\rm eff}$ and $\varepsilon_{\rm PE}$. In addition, the average values for the real and imaginary parts of $\varepsilon_{\rm CuS}$ are about 6.5 and 2.5, respectively.

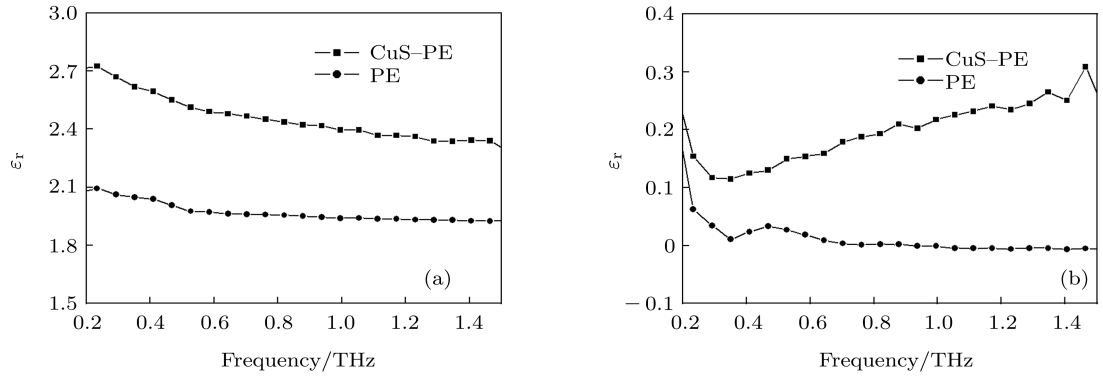


Fig. 3. Complex dielectric constant of the CuS–PE system (solid squares) and PE sample (solid circles).

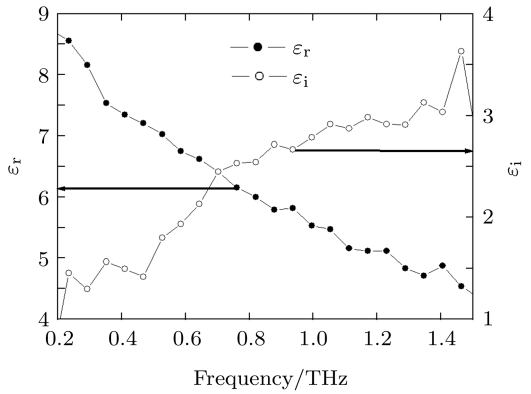


Fig. 4. Complex dielectric constant of the pure CuS nanoparticles with the real part ε_r (solid circles) and the imaginary part ε_i (open circles).

Figure 5 shows the calculated conductivity of pure CuS NPs with the real part σ_r and the imaginary part σ_i. The real part of the conductivity is positive and increasing with increasing frequency, while the imaginary component is negative and decreasing with increasing frequency. Furthermore, we find that the calculated conductivity is deviated from the Drude model, which dictates maximum value at zero frequency in the real part and positive minimum value

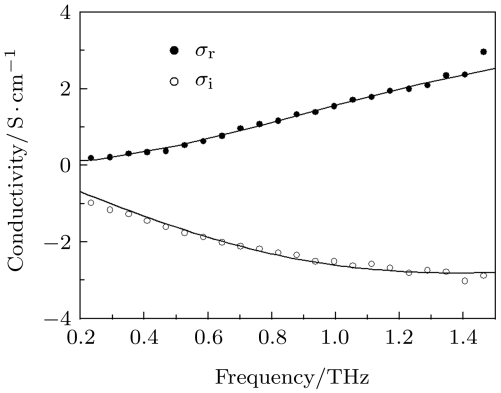


Fig. 5. Complex conductivity of the pure CuS nanoparticles with the real part σ_r (solid circles) and the imaginary part σ_i (open circles). The solid lines are the corresponding theoretical fit for the data.

in the imaginary part. In our case, the real conductivity has a maximum at nonzero frequency and all imaginary parts have negative values.

We attribute the negative imaginary conductivity to preferential backward scattering of electrons after collisions. A fraction, but not all, of the backward scattering is a result of the electron reflecting from surfaces or grain boundaries. It can also result from a Coulombic restoring force from positively charged holes. This restoring force or backward scattering can be modelled by modifying the Drude model according to Smith who induced a persistence of velocity parameter to describe the scattering event. The Drude–Smith model is given by[25]

$$\tilde{\sigma}(\omega) = \frac{n^* e^2 \tau / m^*}{(1 - \mathrm{i}\omega\tau)} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - \mathrm{i}\omega\tau)^n}\right]. \quad (4)$$

The summation in Eq. (4) is often truncated after the first term, where the parameter c_1 is a measure of persistence of velocity and its negative value implies a predominance of backscattering. The parameter c_1 can vary between 0 and –1 corresponding to the Drude conductivity for $c_1 = 0$ and complete carrier of backscattering or localization for $c_1 = -1$. Additionally, n^* is the electron density, e is the elementary charge, m^* is the electron effective mass, and τ is the characteristic scattering time.

Separating the real and imaginary parts, we obtain the conductivity

$$\sigma_r(\omega) = \frac{n^* e^2 \tau / m^*}{(1 + \omega^2\tau^2)} \left[1 + \frac{c_1(1 - \omega^2\tau^2)}{(1 + \omega^2\tau^2)}\right], \quad (5a)$$

and

$$\sigma_i(\omega) = \frac{\omega\tau \cdot n^* e^2 \tau / m^*}{(1 + \omega^2\tau^2)} \left[1 + \frac{2c_1}{(1 + \omega^2\tau^2)}\right]. \quad (5b)$$

The Drude–Smith model fits the conductivity quite well for the real and imaginary parts, as shown

by the solid lines in Fig. 5. The parameters of the fitting curves are $c_1 = -0.996$ and $\tau = 64.3$ fs. Generally, NPs with smaller grains tend to have higher scattering rates and more negative persistence of velocity while larger NPs have longer scattering time.[12] The value of c_1 in our fitting, close to –1, implies a complete carrier of backscattering or localization because of the strong confinement effects in nano-structured materials. Additionally, because the average size of our samples is only several nanometres the scattering time is as short as 64.3 fs, which cannot be measured directly by other techniques.

6. Conclusion

In summary, we have investigated the native THz conductivity of CuS NPs. A Drude–Smith model provides an excellent fit to the observed conductivity in our work, revealing a localized behaviour with high electron backscatter in the nano-structured materials. The scattering time is characterized by an average value of 64.3 fs, which is dependent on the size of NPs. Our investigation suggests that the THz-TDS technique is a powerful method for detecting the complex conductivity in semiconductor nanostructures, and could help us to reveal the material properties in the THz range and to find out the promising physical effect for application.

References

[1] Nair P K and Nair M T S 1991 *J. Phys.* D: *Appl. Phys.* **24** 83

[2] Yamamoto T, Kubota E, Taniguchi A, Dev S, Tanaka K and Osakada K 1992 *Chem. Mater.* **4** 570

[3] Sukarova B M, Najdoski M, Grozdanov L and Chunnilall C J 1997 *J. Mol. Struct.* **410** 267

[4] Nair P K, Garcia V M, Fernandez A M, Ruiz H S and Nair M T S 1991 *J. Phys.* D: *Appl. Phys.* **24** 441

[5] Chung J and Sohgn H 2002 *J. Power Source* **108** 226

[6] Zhang W, Wen X and Yang S 2003 *Langmuir* **19** 4420

[7] Chen X Y, Wang Z H, Wang X, Zhang R, Liu X Y, Lin W J and Qian Y T 2004 *J. Cryst. Growth* **263** 570

[8] Wang W Z and Ao L 2008 *Mater. Chem. Phys.* **109** 77

[9] Lu Q, Gao F and Zhao D 2002 *Nano. Lett.* **2** 725

[10] Roy P and Srivastava K 2006 *Cryst. Growth Deg.* **6** 1921

[11] Zhang P and Gao L 2003 *J. Mater. Chem.* **13** 2007

[12] Baxter J B and Schmuttenmaer C A 2006 *J. Phys. Chem.* B **110** 25229

[13] Murphy J E, Beard M C and Nozik A J 2006 *J. Phys. Chem.* B **110** 25455

[14] Chen H and Wang L 2009 *Chin. Phys.* B **18** 2785

[15] He X J, Wang Y, Wu Q, Zhang S Q and Zhuang L L 2009 *Chin. Phys.* B **18** 1801

[16] Pilenti M P 2003 *Nat. Mater.* **2** 145

[17] Lu Q, Gao F and Zhao D 2003 *Nanotechnology* **13** 741

[18] Qu S M, Xie Q, Ma D K, Liang J B, Hu X K, Yu W C and Qian Y T 2005 *Mater. Chem. Phys.* **94** 460

[19] Liao X, Chen N Y, Xu S, Yang S B and Zhu J J 2003 *J. Cryst. Growth* **252** 593

[20] Xie X, Dai J and Zhang X C 2006 *Phys. Rev. Lett.* **96** 075005

[21] Fujii M, Wada M, Kayashi S and Yamamoto K 1992 *Phys. Rev.* B **46** 15930

[22] Bruggeman D A G 1935 *Ann. Phys.* **24** 636

[23] MaxwellGarnett J C 1904 *Philos. Trans. R. Soc. London* Ser. A **203** 385

[24] Black M R, Lin Y M, Cronin S B, Rabin O and Dresselhaus M S 2002 *Phys. Rev.* B **65** 195417

[25] Smith N V 2001 *Phys. Rev.* B **64** 155106