Terahertz Response of Bulk and Nanostructured ZnO

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Abstract — We present experimental characterization of far-infrared optical and dielectric properties of single-crystal ZnO and nanostructured ZnO of different morphologies by terahertz time-domain spectroscopy. Frequency dependent complex dielectric function, power absorption, and refractive index of single-crystal, nanowire, tetrapod, tubular, and prismlike ZnO structures are experimentally measured in the terahertz regime, respectively. The experimental results are analyzed and well fit with dielectric theories and effective medium models.

1. INTRODUCTION

As an II-VI semiconductor, Zinc oxide (ZnO) with a room-temperature wide band gap 3.37 eV, has attracted much attention because of their unique properties and large span of promising applications in electro-optic, acousto-optic, optoelectronic devices, ultraviolet (UV) light emitters, chemical sensors, and piezoelectric materials [1–4]. The increasing interest not only focus on bulk crystal, but also much more on the nanocrystalline ZnO. ZnO nanostructures have potential applications for piezoelectric transduction, optical emission, catalysis, actuation, drug delivery, and optical storage with promising photoelectronic, photochemical, and catalytic properties [4]. In the terahertz regime, ZnO possesses a number of advantages in terms of device applications, such as ease in fabrication, wide band gap, rather high mobility and resistivity, and transparent in a broad terahertz frequency range [5–7]. It thus is essential to explore the detailed optical and dielectric properties of ZnO in the broad terahertz frequency region. Here, we present far-infrared optical properties and the complex dielectric function of high-resistivity bulk crystal and nanostructured ZnO, including wire, tetrapod, tubular, and prismlike structures characterized by terahertz time-domain spectroscopy (THz-TDS). The measured refractive index, power absorption, and complex dielectric function are well fit by appropriate theoretical models.

2. SAMPLE PREPARATION AND THZ-TDS EXPERIMENTS

The single-crystal ZnO is an undoped, 5 mm\texttimes 5 mm\texttimes 0.5-mm-thick, \textless 0001\textgreater-oriented slab with c-axis perpendicular to the surface (MTI Corporation, USA). Hydrothermal growth method was used to fabricate the wurtzite, high-resistivity ZnO with purity higher than 99.99%. The detailed fabrication processes of the nanostructured ZnO as shown in Fig. 1 were described elsewhere [8–11]. The ZnO samples are characterized by use of a photoconductive switch-based THz-TDS system with a useful bandwidth of 0.1–4.5 THz and a signal to noise ratio (S/N) of $>1.5\times10^4$ : 1 [11].

![Figure 1: Scanning electron microscopic images of (a) nanowire, (b) tetrapod, (c) tubular, and (d) prismlike ZnO structures.](image-url)
3. RESULTS AND DISCUSSIONS

3.1. Single-crystal ZnO

The measured power absorption \( \alpha(\omega) \) and the refractive index \( n(\omega) \) of single-crystal ZnO are shown in Figs. 2(a) and 2(b). The power absorption increases with increasing frequency and no prominent absorption peaks are observed below 3.5 THz. This can be verified by the refractive index which shows no remarkable features as well. Employing the measured data of power absorption and refractive index, we obtain the frequency-dependent complex dielectric function through the relation:

\[
\epsilon(\omega) = (n_r + in_i)^2,
\]

where the imaginary part of the refractive index \( n_i \) is related to the power absorption as:

\[
n_i = \alpha \lambda / 4\pi.
\]

The filled circles shown in Figs. 2(c) and 2(d) represent the recorded data of complex dielectric constant. Generally, optical absorption of ionic crystals in the terahertz region originates from lattice vibrations. The interaction of a radiation field with the fundamental lattice vibration results in absorption of electromagnetic wave due to creation or annihilation of lattice vibration. In the frame of the classical theory of independent pseudo-harmonic approximation, such process can be described below, considering the phonon contribution to dielectric function [12]:

\[
\epsilon_m(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\omega_{TO}^2 / (\omega_{TO}^2 - \omega^2 - i\gamma\omega),
\]

where \( \epsilon_\infty \) is the high-frequency dielectric constant, \( \epsilon_0 \) is the low frequency dielectric constant, \( \omega_{TO} \) is the frequency of the transverse optical (TO) phonon mode, and \( \gamma \) is the damping constant. Three parameters are used to fit the experimental data: \( \epsilon_0 = 7.77, \omega_{TO}/2\pi = 12.42 \) THz and \( \gamma/2\pi = 0.82 \) THz. Given the high-frequency dielectric constant \( \epsilon_\infty = 3.705 \), the frequency-dependent complex dielectric constant is obtained. This theoretical calculation gives well fit on the data measured by THz-TDS, as shown by solid curves in Fig. 2.

![Figure 2: Comparison of THz-TDS data (filled circles) with theoretical fitting (solid curves) for (a) power absorption, (b) refractive index, (c) real part of dielectric constant \( \epsilon_{mr} \), and (d) imaginary dielectric constant \( \epsilon_{mi} \).](image)

3.2. ZnO Nanowires and Tetrapods

In Fig. 3, we present THz-TDS results on ZnO nanowires and tetrapods. The measured absorption coefficients are represented by filled circles in Figs. 3(a) and 3(b), and the index of refraction is shown in Figs. 3(c) and 3(d), respectively, for nanowires and tetrapods. These two nanostructures exhibit a similar absorption behavior, which increases steadily with increasing frequency. The extracted real and imaginary parts of complex dielectric function are depicted by the filled circles in Figs. 3(e)–3(h). Because the measured samples are composites of nanostructures and air, the given complex dielectric constant is called effective dielectric constant that consists of contributions from both pure ZnO nanostructures and air. The effective dielectric function can be treated by simple effective medium theory, \( \epsilon_{\text{eff}}(\omega) = f \epsilon_m(\omega) + (1 - f)\epsilon_h \), where the dielectric function of pure ZnO nanostructures \( \epsilon_m \) is calculated based on the pseudo-harmonic model. The filling factor \( f \) defines the volume fraction of pure nanostructures and was measured directly in the experiment; \( \epsilon_h \) is dielectric constant of the host medium, giving \( \epsilon_h = \epsilon_{air} = 1.0 \) for air. The absorption responses of pure ZnO nanowires and tetrapods are mainly attributed to lattice vibration, which is well described theoretically by the classical pseudo-harmonic phonon model. The good agreement between the experimental data and theoretical fitting, as shown by the solid curves in Fig. 3, implies that the
absorption of both nanowires and tetrapods are dominated by the transverse optical mode localized at \( \omega_{TO}/2\pi = 12.41 \pm 0.2 \) THz, with linewidths \( \gamma/2\pi = 12.5 \pm 0.2 \) THz and \( \gamma/2\pi = 21.0 \pm 0.2 \) THz, respectively. This feature is quite consistent with what has been observed in bulk single-crystal ZnO. This indicates that ZnO nanowires and tetrapods exhibit similar dielectric properties as those for bulk ZnO.

3.3. Tubular and Prismatic ZnO

The filled circles in Fig. 4 illustrate the measured data for tubular and prism-like ZnO structures. The absorption behavior shown in Figs. 4(a) and 4(b) appears very similar to those observed in nanowires and tetrapods and it steadily increases with frequency. However, it can be seen clearly that both the tubular and prism-like structures have significant higher absorption than those of nanowires or tetrapods. At 1.0 THz, the power absorptions for both samples are higher than 200 cm\(^{-1}\). The refractive index, as shown in Figs. 4(c) and 4(d), exhibits a monotonic decrease with increasing frequency. These prominent distinctions than those for nanowires and tetrapods due to morphology implicate that different response mechanism is involved in the absorption process in tubular and prism-like ZnO samples. The real and imaginary parts of complex dielectric constants, as shown in Figs. 4(e)–4(h), further indicate that diverse mechanisms are responsible for the dielectric properties of tubular and prism-like structures.
It is well known that for most metals and semiconductors, optical absorption is caused by the interaction of incident light with free carriers. The most commonly used model to describe such dielectric response process is the Drude model,

$$\varepsilon_m(\omega) = \varepsilon_m + \frac{i\varepsilon_m}{\varepsilon_m + 2\varepsilon_{eff}} + \frac{1}{\varepsilon_{h} + 2\varepsilon_{eff}} = 0$$

Taking the contribution of free electrons through the Drude model and the contribution of air from Bruggeman effective medium theory [11, 13]:

$$f[(\varepsilon_m - \varepsilon_{eff})/(\varepsilon_m + 2\varepsilon_{eff})] + (1 - f)[(\varepsilon_{h} - \varepsilon_{eff})/(\varepsilon_{h} + 2\varepsilon_{eff})]$$

into account, we obtain good fits to the THz-TDS data of tubular and prismlike ZnO samples. As shown by solid curves in Fig. 4, the measured power absorption, index of refraction, and the corresponding complex dielectric constant are well reproduced. From our results, we clearly see that ZnO nanostructures exhibit quite different characteristics due to various morphologies. In fact, besides morphologies, many factors have influences on the optical and dielectric properties of ZnO nanostructures as well, such as growth conditions, environment, impurities, defects, and so on. Therefore, it is not surprising that the mechanism for terahertz absorption response of ZnO nanowires and tetrapods, similar to that in single-crystal ZnO, is mainly dominated by the interaction of incident light with lattice vibrations, while it is ascribed to the contributions from free electrons for tubular and prismlike structures.

4. CONCLUSION

We have studied the far-infrared dielectric and optical properties of bulk and nanostructured ZnO. The THz-TDS data for power absorption, refractive index, and complex dielectric function of these samples are well fit by dielectric models combined with the effective medium theories. Our THz-TDS characterization implicates that the dielectric function of ZnO nanowires and tetrapods, similar to those in bulk ZnO, is related to the $E_1$(TO) phonon mode at 12.41 THz. However, the tubular and prismlike structures exhibit the Drude behavior due to the dominant role of free electrons in terahertz dielectric response. The dissimilar and similar properties of different ZnO nanostructures are related to morphologies, growth processes, defects, and impurities.

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REFERENCES

