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THz SPECTROSCOPY AND NANOSTRUCTURES: A SHORT INTERESTING REVIEW

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Abstract

I present a short detailed interesting review regarding importance and results of THz spectroscopy in studying nanostructures, in particular in relation to the most studied materials at today.

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Introduction

The frequency-dependent complex photoconductivity and charge transport properties of semiconductor nanomaterials are very important in relation to their use in the world of nanodevices, in particular at electro-optic level [1]; so the understanding of the microscopic details of carrier transport in nanocrystalline thin films is required in a great variety of photochemical and photo-electro-chemical cells based on interpenetrating networks. However the photoconductivity measures in these materials are a serious problem for various difficulties, in particular in relation to wires connections to objects at nanoscale; moreover there is the fact that picosecond (ps) carrier dynamics plays a very important role in transport and efficient charge separation, but the low temporal resolution of experimental traditional methods, used to determine the photoconductivity, precludes their use if it is studied sub-ps to ps dynamics. The time-resolved THz spectroscopy (TRTS) is a non-contact electrical probe technique, able to offer photoconductivity measures from sub-ps to nanosecond (ns) timescale [2,3]. The main goal of THz spectroscopy is to allow measures of the complete frequency-dependent complex-valued conductivity (real and imaginary parts), therefore not only the average time-dependent conductivity properties, working on sub-ps timescales, and without ohmic contacts with the sample. For these important peculiarities TRTS has assumed an interesting role in studying the transient complex photoconductivity in the actual most utilized nanostructured materials, as TiO_2, ZnO, and GaAs nanostructures.

THz Spectroscopy and ZnO Nanostructures

The optical and dielectric far-infrared properties of the nanostructured zinc oxide of different morphologies are experimentally studied with good results through the THz spectroscopy; it is possible to measure the frequency dependent dielectric conductibility $\sigma(\omega)$, the absorption coefficient and the refraction index. The results can be analyzed and well fitted with theories on dielectrics combined to effective medium models. Different morphologies of ZnO nanostructures reveal different characteristics; this is due to the different resonance mechanisms dominated by free electrons or phonons. The dielectric conductivity of ZnO structures of prism or tube form exhibits a Drude behaviour, while for nanowires it results dominated by the phonon

resonances to low frequency. Nanostructured and crystalline ZnO is of great interest for its peculiar properties and the great window of applications going from the opto-electronic, electro-optic, acoustic-optic devices to the ultraviolet-light emitters, the chemical sensors, and the piezoelectric materials [4,5,6]. Doped ZnO can be made electrically conductive and transparent in the visible-light spectrum, therefore it can be used as transparent conductive electrode in the solar cells and in the flat screens. In the THz regime, ZnO presents many advantages in terms of device applications, i.e. not complex manufacture, transparency and high mobility in an great interval of THz frequencies [7]. Particular attention has recently been done to ZnO nanostructures, both as fundamental research on their THz regime properties, and in relation to the promising practical applications. Various chemically sinterized ZnO nanostructures have experimentally been studied at level of dielectric infrared distant properties and low frequency phononic resonances through THz "time-domain" (THz-TDS) spectroscopy combined with high-resolution Raman spectroscopy. The experimental results are analyzed through phononic and dielectric dispersion theories and effective medium models and then compared with those of ZnO tetrapods and wurtzite single crystals. The performances of devices based on semiconductor materials can sensitively depend from the nanostructures morphology. The thickness of nanocrystalline semiconductor films is typically of the order of 10 μm and consists of ZnO nanoparticles with diameter of around 10 nm. With respect to TiO_2, ZnO has the advantage to have a crystalline structure which can be grown anisotropically, so that it is possible to realize dye sensitized solar cells (DSSC) based on nanowire arrays. Recent efforts have suggested that dense ZnO nanowire arrays could improve the electronic transport, offering direct conduction paths toward the substrate and maintaining a great surface area [8]. The hybrid solar cells which use nanowire arrays with nanoparticles in the interstitial spaces, are promising in relation to the combination among great nanoparticles surface area and direct transport through nanowires [9]. The "modulated intensity" photocurrent spectroscopy (IMPS) and the "transient photocurrent time-of-flight" (TOF) are "pump/electrical probe" optical techniques, which are utilized as principal methods to study the macroscopic electronic transport in mesoporous semiconductors. The two above cited techniques are however not able to reveal informations on very small length and time scales. The THz "time resolved" spectroscopy (TRTS) is an excellent complement to the measures through IMPS and TOF techniques, since it measures the far infrared frequency dependent complex photoconductivity on temporal nano-, pico- and sub-pico-second scales using an optic pumping and a THz probe. TRTS is an ideal technique for the study of conductivity since it scans the spectrum region of the far infrared (0.2-2 THz or 6-66 cm^{-1}), which corresponds to the typical charge scattering times from 10^{12} s^{-1} to 10^{14} s^{-1} [10]. THz "THz-TDS" spectroscopy and TRTS spectroscopy can offer detailed informations about the conductivity with respect to other optical techniques as "Fourier transform infrared spectroscopy" (FTIR) also for two important reasons:

1) TRTS and THz-TDS measure both the amplitude and the phase of the single-cycle oscillations of the THz electric field and do not ask for a Kramers-Kroenig analysis to extract the absorption coefficient and the refraction index;

2) the THz frequency range is of order of the charge scattering time, allowing so a more accurate data modelling. Moreover, since TRTS is a "non-contact optical probe" technique, it eliminates the need and the complications of ohmic contacts, making it ideal for the semiconductor nanomaterials. Such technique has also recently been used in the study of nanomaterials photoconductivity for Si microcrystalline thin films, TiO_2 nanoparticles films, CdSe quantum dots, InP arrays and quantum dots [11].

THz spectroscopy combined with the effective medium theories can be used for determining the permittivity of a nanostructured semiconductor inserted in a host matrix through measures of permittivity of the composite. With such procedure it is possible to extract the absorption coefficient of the semiconductor, the refraction index and both native and photoinduced conductivity. Annealed thin films, nanowires and nanoparticles have absorption coefficients near to zero and refraction indexes of order of 3, with good

correspondence with the high resistivity values of ZnO bulk. The electronic concentrations are of order of 10^{18} cm^{-3} in the grown samples and 10^{16} cm^{-3} in those annealed.

The frequency dependent photoconductivity of the ZnO morphologies are enough well fitted with the Drude-Smith model. The model points out that the annealed samples and those with great grains tend to be ideal conductors, while the samples to smaller grains and those grown only (not annealed) have higher scattering rates and great persistence of negative velocity, although the different samples are enough comparable. The morphology plays also an important role in relation to the electronic lifetime. The photoconductivity remains approximately constant for at least 1 ns in continuous films, but for nanowires and nanoparticles it decreases to 78% and 55% of its maximum value, respectively, after 800 ps. The frequency dependent photoconductivity shows an increased electronic mobility in films and nanowires in comparison to the nanoparticles and the pumping scans show that the inherent disorder and the high quantity of interfaces in the nanoparticle films bring to shorter electronic lifetimes.

In tables 1, 2 and 3 below we consider important parameters, determined through the theories used in this sector, for various typologies of ZnO nanostructures.

Table 1: *Theoretical parameters calculated through the pseudo-harmonic phonon model and EMT model for ZnO nanowires and tetrapods [12].*

Sample	ε_∞	ε_{st}	$\omega_{TO}/2\pi$ (THz)	$\gamma/2\pi$ (THz)	f
Nanowires	1.75	1.42	12.41±0.2	12.50±0.2	0.082
Tetrapods	1.50	3.40	12.41±0.2	21.00±0.2	0.017

(ε_{st}: oscillator strenght; ε_∞: high frequency dielectric constant; $\varepsilon(0)$: low frequency or background dielectric constant. It holds: $\varepsilon_{st} = \varepsilon(0) - \varepsilon_\infty$; ω_{TO}: transvers optical frequency; γ: charge damping constant; f: filling factor (volume rapport among pure structures and composites))

Table 2: *Theoretical parameters calculated through the Bruggeman model for ZnO prism and tubular type [12].*

Sample	ε_∞	$\omega_p/2\pi$ (THz)	$\gamma/2\pi$ (THz)	f
Tubes	3.7	37.5±0.2	6.7±0.2	0.33
Prisms	3.7	22.5±0.2	9.8±0.2	0.27

(ω_p: plasma frequency)

Table 3: *Parameters of electronic density and scattering times from photoconductivity fits (Drude-Smith model) for ZnO samples in the indicated typology [7].*

Sample	N_e (10^{16} cm^{-3})	τ (fs)
Annealed films	2.3	101
Films	1.1	93
Annealed NWs	6.6	88
Nanowires	2.0	84
Nanoparticles	2.0	77

THz Spectroscopy and TiO_2 Nanostructures

TiO_2 nanostructures are very promising in the global field of nanotechnology, as alternative energy sources, efficient and low cost, with established efficiencies of solar energy conversion in electric energy (up to 10.4%), constituting the heart of the dye sensitized solar cells (DSSC). TiO_2 nanoparticles in such cells are sensitized to allow a suitable interparticle charge transport in devices [13,14]; however at today the details of this transport have not been completely characterized and comprehended, also in relation to the most utilized theoretical models of the sector (Drude, Drude-Lorentz, Smith, EMT´s models). At this proposal a recent theoretical analytical formulation [15,16,17] seems to be able to fit very well the experimental data and to offer interesting predictions of various peculiarities in nanostructures.

TRTS spectroscopy is utilized with good results also in the study of such oxide. Such technique results however not so good sensitive to dye molecules absorbed to solar cells DSSC, since it measures only mobile carriers in the conduction band of TiO_2. DSSC cells have been studied previously using ultrafast pumping techniques “UV-pump/mid-infrared”, which are sensitive to TiO_2 carriers, as TRTS [18]. The conductivity “time-resolved” microwaves measures (TRMC) have shown to be a non-contact modality probe very useful for the porous TiO_2, but with temporal resolution of only nanoseconds. Studying the

far-infrared conductivity of porous dye sensitized TiO_2 films on a temporal picoseconds scale, the Drude model, the simplest conductivity model, does not offer an appropriate description. The models including the disorder induced from charge location or backscattering describe experimental data with greater accuracy. TRTS results of these years seem to show that the charges inside TiO_2 nanoparticles deviate from their Drude-like bulk behaviour. Nevertheless, at short length scales, the charges are still rather mobile, with transport hindered by disorder. Such conclusions have been obtained in particular from measures of TRMC of various different TiO_2 morphologies. In these last years the experimental techniques have done an amazing detail level about the microscopic nature of charge transport in TiO_2 nanocrystalline films. Through measures of the frequency dependent complex conductibility $\sigma(\omega)$ on sub-picosecond temporal scale, it has been shown that the charge cooling in the conduction band happens in around 300 fs. These observations are consistent with the present understanding of dc transport in the actual DSSC solar cells, and give new ideas for the understanding of the nature of conduction mechanisms. The microscopic interpretation of the transport processes, increased by trapping/detrapping inside nanoparticles, seems nevertheless to be inconsistent with new acquired observations. It appears clear that the electrons inside nanoparticles are enough mobile, even if disorder hinders their bulk transport.

THz Spectroscopy and GaAs Nanostructures

GaAs is with ZnO and TiO_2 one of the most used and promising material at nanometric level, particularly in the sector of single photon detection, electric guide lasers, nanoscale transistors, dye sensitized solar cells [19,20]. As for ZnO and TiO_2, the conductivity of photoexcited GaAs nanowires has been determined at temporal scales from the sub-ps to ns using the THz "time-domain" (THz-TDS) spectroscopy. For analyzing the carrier dynamics in semiconductors, the excited kinds can be photoinjected in a sample using an impulse from a femtosecond laser; the complex conductivity can be revealed with a delayed "single-cycle" pulse of THz radiation. The great bandwidth of THz pulses allows the characterization of the complex conductivity of a sample in a frequency range to the typical plasma frequencies and to the scattering moment rates in semiconductors. Recent studies on nanomaterials with the use of THz-TDS technique have examined micro- and nanocrystals of Si, InP and CdSe nanoparticles, and nanostructured ZnO [7,21,22]. The mean advantage of THz-TDS approach is based on non-contact modality and therefore it avoids situations that can modify the electric measures because of ohmic contacts at nanometric level. The measures of THz transient conductivity of GaAs nanostructures on temporal scales from sub-ps to ns reveal conductivity dynamics differing from those of GaAs bulk, and indicating ultrashort lifetimes (~1 ps). Such results open the possibility to use these nanowires in ultrafast switch devices, whose properties can be optimized through a great variety of mechanisms, as the covering of nanowires with a high bandgap material or the chemical passivation of surface defects [23]. The electronic mobility of the nanowires at environment temperature is extracted by modelling data of plasmonic resonance forming in the first 300 fs after the excitement. The resultant value of 2600 $cm^2/(Vs)$ is lower than a 3 factor with respect to the typical one of GaAs bulk, and this fact seems to show the possibility to produce nanowires with excellent electronic properties. Besides the conductivity, it results essential the determination of the carrier mobility and of the lifetime at environment temperature, for utilizing such materials in the sectors of nano- and optoelectronics. The growth at two temperatures and the encapsulation of GaAs nanowires with materials at higher bandgap bring to meaningful increases of the carrier lifetime. The transition from the growth procedure at one temperature to that at two temperatures allows the growth of the intrinsic carrier mobility in nanowires, from 1200 $cm^2/(Vs)$ to 2250 $cm^2/(Vs)$. This change of growth procedure of wires has the highest effect on the charge mobility and it seems to derive from the improvement of the growth techniques. Increases in the

mobility growth through the mentioned technique had already been postulated for GaN nanowires of diameter of more than 100 nm [24]. Further investigations are requested for the complete understanding of the microscopic origin of the mobility changes through overcoating.

Conclusions

THz "time-resolved" spectroscopy is therefore an interesting and viable possibility for obtaining carrier mobilities both in bulk and in nanostructured samples; in particular in the second case it is of great importance because of the big difficulties to attach wires to nanoscale particles. If coupled with an ultrafast photoexcitation laser, i.e. performing TRTS, it is possible to monitor the carrier mobility as it evolves as a function of time after photoexcitation. Such technique is demonstrating very interesting in studying the most important materials used today at nanoscale, i.e. Si, TiO_2, ZnO, and GaAs [25].

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