

# Single-Wall Carbon Nanotubes Oriented by Gas Flow at Synthesis by Aerosol CVD Method as Terahertz Polarizers

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**Abstract**—Single-wall carbon nanotubes were synthesized by aerosol CVD method. Simplified technique for obtaining oriented carbon nanotubes was used. The technique is based on carbon nanotubes orientation by gas flow directly after the synthesis process. Terahertz dielectric properties of the nanotube films were measured. Pronounced polarizing effect in terahertz range was found.

## I. INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) exhibit outstanding physical and chemical characteristics that define the broad spectrum of their possible use. One of potential applications of carbon nanotubes is connected with designing of polarizers for terahertz frequency range.<sup>1</sup> Currently, great interest is shown in the creation of effective THz optical components such as phase shifters, modulators, filters, polarizers and waveguides. Relevant elements are essential components of the analytical spectroscopic systems. Compared to common metal wire-grid polarizers CNT-based polarizers can work in a broader frequency range and have superior mechanical properties. The problem is to find efficient and not too expensive technology for obtaining oriented nanotubes. In the present work thin films of SWCNTs with anisotropic structure were produced using single stage aerosol CVD method. Their terahertz dielectric susceptibility spectra were measured using THz-TDS. The clear polarization effect was found.

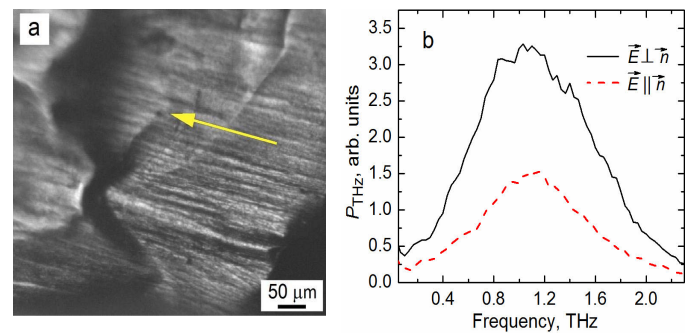
## II. EXPERIMENTAL DETAILS AND RESULTS

Carbon nanotubes were grown by thermal decomposition of ethanol<sup>2,3</sup> at a temperature of 825–900°C. Ferrocene with a mass fraction in ethanol of 0.08% (1 iron atom per 10<sup>4</sup> carbon atoms) was employed as a catalyst precursor. The components (ferrocene solution in ethanol) in the form of aerosol particles with diameters of 0.5–5 μm were fed into the reaction zone through a cooled nozzle in an argon flow (99.996%) with a rate of 0.5 l/min. Aerosol particles at the outlet of the nozzle were mixed with the additional argon flow bypassing the nozzle. It was previously shown that this method allows to obtain isotropic layers of randomly oriented SWCNTs with typical diameters of 0.7–1.4 nm.<sup>2</sup> The advantages of the aerosol method include high purity and quality of the synthesis products, which eliminates time-consuming steps of CNT purification.<sup>4,5</sup> To produce films with anisotropic structure, the SWCNTs were deposited onto a cooled cylindrical tip placed along the axis of quartz tube with diameter of 22 mm at the output of the CVD reactor hot zone. The modified scheme of

the CVD reactor allows SWCNTs to be oriented by gas flow during deposition and does not require additional processing steps.

The dielectric properties of SWCNT films were studied using conventional THz-TDS setup. The terahertz pulses were produced by generation from InAs surface under excitation by femtosecond pulses from MaiTai SP (Spectra-Physics, USA) laser ( $\tau \approx 100$  fs,  $\lambda = 780$  nm). After the emitter a wire grid polarizer was placed to ensure the horizontal polarization of the generated terahertz radiation. The terahertz pulses were electro-optically detected in 1 mm thick ZnTe crystal. The sample of SWCNT thin film was placed onto a rotation stage so that could be rotated around the propagation direction of the incident terahertz pulses. During the measurements the azimuth angles providing minimum and maximum of terahertz transmission were determined. These angles differed by 90° and corresponded to the orientations of the nanotubes along the polarization of terahertz radiation and perpendicular to it.

The photograph of the sample surface is given in Fig. 1a, where the direction of a fiber orientation is clearly seen. The material has the ability to endure without destroying the numerous bends and its structure resembles a piece of fabric. As can be seen from Fig. 1a, despite some bending of surface layer, there is a certain regularity in the arrangement of the fibers, each consisting of CNT bundles (parallel lines with a sufficiently uniform distribution on the layer).

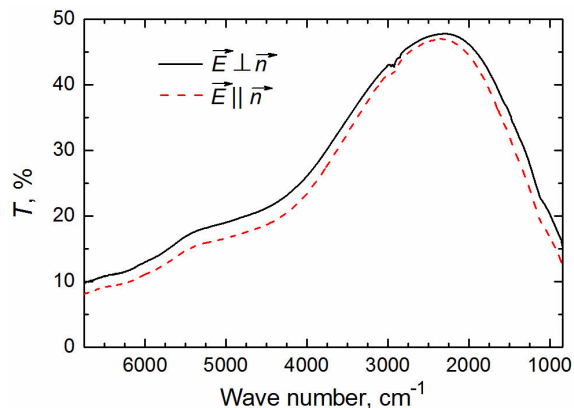


**Fig. 1.** (a) Photograph of the surface of the SWCNT film. The arrow shows the direction of a predominant orientation  $\vec{n}$  of the fibers. (b) Spectra of terahertz radiation transmitted through the SWCNT film at  $\vec{n} \parallel \vec{E}$  and  $\vec{n} \perp \vec{E}$ .

The results obtained by THz-TDS are shown in Fig. 1b, which shows the frequency dependence of the power of THz radiation transmitted through the sample. SWCNT film was irradiated with linearly polarized radiation incident at normal angle. The orientation of polarization with respect to the direction along and perpendicular to preferential orientation of

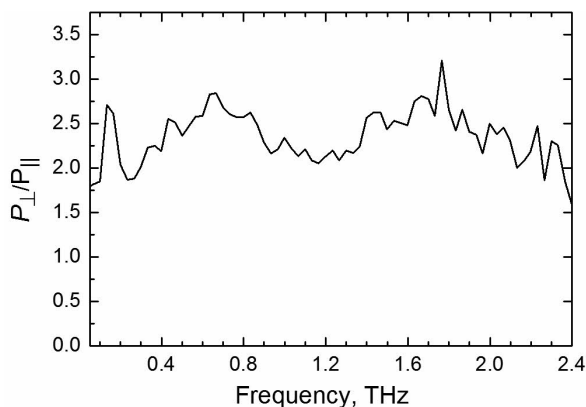
the fibers could be arbitrarily changed by rotating the sample to a desired angle around the electromagnetic wave propagation direction. The solid curve in Fig. 1b corresponds to the maximum power  $P_{\max}$  of terahertz radiation (at a given frequency) transmitted through the sample in the experimental geometry corresponding to  $E \perp n$  condition, where  $E$  is the electric field vector. The dashed curve was obtained by rotating the plane of polarization by  $90^\circ$  and corresponds to the minimum level  $P_{\min}$  of the registered signal. Comparison with the data of transmission electron microscopy showed that in the second case SWCNTs were oriented predominantly parallel to the plane of polarization of the incident light, which explains the anisotropic nature of the transmission spectrum.

For the obtained anisotropic films we also carried out measurements of the transmission spectra in the range from about 7000 to 1000  $\text{cm}^{-1}$ . The typical result of the measurements is shown in Fig. 2. As can be seen from Fig. 2, a film transmittance spectrum in the infrared range has a broad peak with maximum at 2400  $\text{cm}^{-1}$ , and shows a clear polarization dependence with the degree of polarization of 10%.



**Fig. 2.** IR transmission spectra of the SWCNT film for light polarized along and perpendicular to the direction  $\vec{n}$  of the fibers.

A comparison of Fig. 1b and Fig. 2 leads to conclusion that anisotropic characteristics of the obtained samples in the THz frequency range are much more pronounced. Indeed, as shown in Fig. 3, the ratio  $P_{\max}/P_{\min}$  reaches 2–3 in the frequency range 0.1–2.3 THz.



**Fig. 3.** Power ratio of THz radiation passed through the SWCNT film at two polarization directions.

It follows from the measured data that polarization degree for the pulses in the range 0.1–2.3 THz is about 40% (on the average) after passing through the sample. In some narrow spectral regions ( $\sim 0.6$ – $0.8$  THz and  $\sim 1.7$ – $1.9$  THz), the degree of polarization is greater than 46%. These results are of interest in terms of possibilities of using films based on SWCNTs in the terahertz optoelectronics.

It should be noted that the reached polarizing efficiency is considerably lower than in some other works,<sup>6</sup> where much more complex technology of fabrication of oriented carbon nanotube films was used. Nevertheless there is a potential to improve our technology. It is well known that the arrays of thin metal strips attached to the metal framework or uniformly arranged on the polymer membrane are presently widely used as terahertz polarizers. Among their disadvantages are high cost, fragility, risk of degradation with time as a result of the gradual oxidation of the metal layers (usually, aluminum or copper) in the air and subsequent deterioration of conductivity. Unlike standard wire grid polarizers, CNTs, which are quasi-one-dimensional objects, are able to work in a much wider range, which determines their advantage for practical use. Improving the technology of producing the CNT films with an ordered structure will improve the quality of film polarizers, which are potentially capable of operating in the spectral range up to the mid-IR wavelength.

### III. SUMMARY

Possibility of obtaining terahertz polarization effect using thin films of SWCNTs oriented in gas flow during synthesis by aerosol CVD method was verified. Pronounced anisotropic properties of the samples in THz range were found. It is required to improve the deposition technology to get higher degrees of orientation and polarizing efficiency.

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