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Review

Tunable inkjet printed hybrid carbon nanotubes/nanocrystals light sensor

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ABSTRACT

In recent years carbon based devices are exploited for a wide range of applications related to electronics and optoelectronics, due to their unique electrical, optical and mechanical properties. Many sensors, emitters, transistors and logic devices use carbon nanotubes as their major building block. Here we present a technology for inkjet printing of a hybrid tunable detector composed of carbon nanotubes and nanocrystals. The printing can be performed on flexible elastic transparent substrates, as well as on a rigid semiconductor or dielectric substrates. The presented detector is low cost, operates at room temperature and can be printed easily in a large format. We show that these types of sensor function with high quantum efficiency due to a gating effect induced by the light excitation.

Contents

1. Introduction

Carbon nanotube (CNT) based devices are an emerging field in electronics and optoelectronics, due to their wide range of unique electrical, optical and mechanical properties [1]. CNT and specially hybrid NCs–CNTs systems were used in a wide variety of electronic and optoelectronic devices, such as CNTs thin film transistors [2–8] and field effect diodes [9,10]. Recently several works presented the use of carbon based detectors [11]. In this work we present a simple wet chemistry technology for inkjet printing flexible detectors based on carbon nanotubes and nanocrystals (NCs). The exact wavelength of the detector is tunable and can be optimized to the required wavelength by changing the adsorbed nanocrystals size and material.

Theoretical and experimental reports indicated that CNT has a characteristic electronic structure due to a low dimensionality. For example the density of states of the CNT has one dimensional features and the van-Hove singularity is predicted in such a system [12]. In the approximation of the zone folding scheme one third of all the single wall CNTs are metallic and always have a wider energy gap than the semi conducting ones with almost the same diameter. In contrast, studies of defect-free single wall nanotubes have shown that the electronic properties of nanotubes depend not only on radius and chirality but also on their detailed curvature and local environment [13]. The authors claimed that previously predicted "metallic" zigzag tubes are actually narrow gap semiconductors, whereas isolated armchair nanotubes do not have energy gaps and are truly metallic. This says that taking a simple and low cost dispersion of CNT will results in a mixture of both metallic and semiconductor material. Any device fabricated from this mixture should consider both types of CNT. In addition, multi walled carbon nanotubes (MWCNT) can be obtained by stacking several (single walled) tubes into each other in a coaxial method. The electrical properties can be varied and determined by the chirality and diameter of the tube [14,15]. In all cases due to the large surface area of the CNT the conductivity

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is very sensitive to surface changes. In this case surface charge trapping, influence strongly the properties of optoelectric devices [16].

These rich electrical features together with the large surface of the nanotubes are readily used to achieve ultrasensitive CNT based transistors. The CNT active surface is being exposed to the environment and changes the conductivity of the tube [16]. Using the same properties, CNT based systems can provide a platform for new types of sensors and optoelectronic devices. For example, Liu et al. described a method to produce stimuli-responsive optoelectronic CNT transistor functionalized by photoactive quantum dots [11]. It is important to note that most of these devices are fabricated through a complex ordering and contact scheme, where the single or multiple CNT are connected directly to the metallic contacts. Usually e-beam writing or SEM is used to connect the tubes which make the process complicated and expensive. Furthermore, the use of organic molecules to attach NC's to the CNT surface is done by modifying the surface, thus creating long charge trap times, and therefore slow response [17–19].

Semiconductor nanoparticles are used as a building blocks for electro-optical devices, that take advantage of their photoluminescence and absorption spectra that can be tuned by varying their size, composition and shape [20,21]. The chemical accessibility of the colloidal nanocrystals also enables linking them to different surfaces [22]. For example, efficient emission was reported for CdTe dots deposited on quantum wells surfaces, introducing an additional appealing method for electrical activation of their fluorescence [23]. This approach is used mainly in the photovoltaic cells [4,10,24–27]. Recently, it has been demonstrated that the electronic properties of semiconductor-based devices can be modified by nanocrystals adsorbed to their surfaces due to gating effects [28]. Therefore, it is expected that the combination of nanocrystals with CNT can further enhance the ability to control properties of a light detector.

Most of the infrared and visible detectors used today are solid state detectors. These are grown by epitaxial MBE or MOCVD machines on a solid state substrate. Therefore they are expensive, not transparent and rigid. The detectors fabrication requires lithography and clean rooms based processes [29,30]. These light detectors are of high quality but do not bring a simple low cost solution for large arrays. On the other hand, inkjet printing brings an easy solution for array fabrication, for both flexible and rigid substrates, and can be performed in large format and roll to roll printing.

In the present research we developed a technology for inkjet printing multi walled carbon nanotubes–nanocrystals (MWCNTs–NCs) hybrid detectors on a variety of substrates for electronic and optoelectronic applications. Under illumination charge dipoles are created on the surface CNT–NCs gating the semi-conducting CNT. The exact action spectrum of the device is controlled by the nanocrystals. Accordingly, the research provides the platform for fabricating large-scale low cost photo sensors. We believe that this device will supply simple domestic use of flexible nanodetectors. Such sensors could be printed on stickers, vehicles, furniture, food packaging material and more.

2. Methods

The fabrication process includes three stages: (a) first, gold metal contacts were evaporated using lithography on 0.5 mm thermal silicon oxide, a technique that was developed in previous studies [31]. The contacts were evaporated to mimic array fabrication technology and to help measure the contact and channel resistance. Arrays were printed with 100 μm × 100 μm contact size and 100 μm spacing between neighbor contacts. The same results could be achieved by contacts printing [32]. The substrate with the contacts is sonicated and cleaned, in acetone and methanol. Then, MWCNT ink is printed forming continuous line on the metal contacts. (c) Lastly, the NCs are adsorbed onto the printed MWCNT lines by dipping the printed substrates in diluted 1 × 10 aqueous dispersion of CdTe for 30 s, provided by MKnano.

For the 2nd stage a highly concentrated MWCNT inks were prepared using a short type of carbon nanotubes (CheapTubes Inc., USA) characterized by a purity of >95%, an outer diameter a polymeric dispersant SOLSPERSE® 46000 (1 wt%) (Lubrizol, USA), a wetting agent (0.2 wt%) (Byk 348; Byk-Chemie GmbH, Germany), in de-ionized water. The ink was prepared using a horn sonicator (model Vibra-Cell, Sonics & Materials Inc., USA) for 15 min at 750 W. The samples were cooled in an ice water bath during the sonication process. The viscosity of the inks was 1.89 cp, measured at 100 rpm, $T = 25\,^{\circ}C$, with a spindle S-18 using the Brookfield Viscometer (model DVII + viscometer, Brookfield, USA). The surface tension of the inks is 30.0 ± 0.4 mN/m, measured at $T = 25\,^{\circ}C$ using a ring tensiometer (model TE2, Lauda, Germany).

Subsequently a line with a width between 100 and 1300 μm (with 10 layers) was printed using the MWCNT ink. The printing was performed with a Microfab JetDrive III inkjet printer with a 60 μm diameter single nozzle (see Fig. 1a). The applied waveform was 70 V; rise time 3 μs; echo time 30 μs; dwell time 30 μs; and fall time 3 μs, while printing at 40 Hz. The movement of the substrate was controlled by a DMC-21 × 3 XY table (Galil motion control). The substrate temperature was set to 60 °C with a Peltier heater/cooler, and the humidity within the printing chamber was 35–45% RH during the printing experiments. The above procedure was performed for various substrates. The optical results presented here were taken using detectors that were printed on a solid Si substrate.

The CdTe NCs (MKnano, emission at 550 nm, average sizes of 2.55 nm) were adsorbed onto the CNT of the device by contacting the printed CNT with the colloidal dispersion. The samples were dipped in the nanocrystals aqueous dispersion (diluted 10×) for 30 s and dried at room temperature. When the device is illuminated by light with different wavelength both NCs and the MWCNT can absorb the light depending on their energy band gap. When the NCs absorb the light, the photo-excited holes are transferred to the surface states of the printed CNT, change the surface potential, bend the conduction band, and enhance the conductivity.

Fig. 1a is a schematic drawing of the fabrication process for MWCNT–NC's assembly. In the process the MWCNTs lines are printed between a net of metal contacts and the CdTe NCs are adsorbed on top of the CNT lines. Fig. 1b presents a typical high resolution SEM view of the printed CNT line with the adsorbed NCs (white dots). In Fig. 1c the full device on a chip is displayed. The measurements are performed on devices which were printed on grown 0.5 μm thermal oxide layer of intrinsic silicon wafer.

3. Results and discussion

In order to examine whether the device can serve as a tunable detector responding both to the NCs absorption spectrum as well as to the MWCNT spectrum, a device was printed on 0.5 μm grown thermal silicon oxide. On top of the detector line CdTe NCs were adsorbed (see Fig. 1c). The absorption spectrum and photoluminescence spectrum of the MWCNT and NCs in the dispersions are presented in Fig. 2 and its inset respectively. Note that the energy band gap of the NCs is around 530 nm.

Fig. 3 shows the DC response of the device with and without NCs as a function of laser illumination at various wavelengths. We measured the voltage across the device for a fixed current of 1 mA, before and after NP's adsorption. The response was measured for different illumination wavelengths at different frequencies. We used four types of lasers, two above and two below the NCs band