Writing simple RF electronic devices on paper with carbon nanotube ink

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Abstract
This paper shows that we can print on paper simple high-frequency electronic devices such as resistances, capacitances or inductances, with values that can be changed in a controllable manner by an applied dc voltage. This tunability is achieved with the help of an ink containing functionalized carbon nanotubes and water. After the water is evaporated from the paper, the nanotubes remain steadily imprinted on paper, showing a semiconducting behavior and tunable electrical properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Paper is the most encountered and cheapest flexible organic material. Moreover, paper is a dielectric up to 3 GHz, with an electric permittivity of \( \varepsilon_r \approx 3.3 \) and losses expressed by \( \tan \delta \approx 0.08 \). Using inkjet printing technology and silver nanoparticle inks, some basic radio-frequency (RF) circuits, such as antennas, resonators and wireless identification tags (RFID), were implemented and tested [1]. Also, paper was used as the substrate in various devices including thin-film FET transistors, simple logic circuits, displays or batteries [2].

We have to point out that, due to the low mobility of carriers in organic materials (1–2 cm² V⁻¹ s⁻¹), these devices listed in [2], including the FET on cellulose fiber paper, cannot be used at high frequencies and neither in RF applications or in computers where the clock rate is actually 4 GHz. To overcome this serious drawback, we study in this paper some simple RF electronic devices printed on paper with the help of an ink based on carbon nanotubes (CNTs), because single CNTs display very high mobilities (\( 7 \times 10^4 \) cm² V⁻¹ s⁻¹) [3]. Although the CNT ink is a random network of CNTs and not a single CNT, it still has a high mobility. For example, when CNT ink is used to produce FETs, the mobility of these transistors is greater by at least two orders of magnitude than in any FET based on organic materials. Moreover, the FETs printed with CNT ink display a huge \( 10^7 \) on-off ratio [4] and have a cutoff frequency of a few GHz [5].

Printing of CNT inks on various substrates is an extensively used method to fabricate various patterns or devices. In this respect, multi-walled carbon nanotube (MWCNT) inks were used to print various patterns on plastic and paper. After tens of times repetitive printing with a common printer with the cartridge loaded with the MWCNT ink, in the dried ink the random network of MWCNTs attached on the substrate displayed an impedance with the real part of a few MΩ up to 1 MHz. However, no impedance tuning with the applied voltage was observed [6]. CNT transistors based on various ink solutions were also printed on various organic substrates or semiconducting doped-Si substrates used as a back gate using inkjet techniques [7]. Moreover, single-walled carbon nanotube (SWCNT) conductive lines up to 75 mm in length were fabricated using inkjet printing on glass substrates; their real part of the impedance decreases from 517 to 7.4 kΩ at 100 kHz as the number of overwriting increases from one to eight [8].

Also, various devices based on CNT inks were printed on PMMA, PET, glass or silicon [9], and alumina [10]. So,
the CNT print is a very versatile technique for printing thin films on various substrates and used further for optical devices, sensors and high-frequency devices. The print of CNT is done with simple printers found on a desk where the CNT ink is loaded in the cartridge or with advanced inkjet equipment. Various CNT inks based either on SWCNTs or MWCNTs are now commercially available and inexpensive.

Taking into account all the above results the role of this paper is to merge the research and technologies on paper used as a dielectric substrate up to a few GHz with the CNT ink technology to implement simple tunable high-frequency RF devices.

2. CNT Ink Preparation and Characterization

A prerequisite of almost any RF device is to be tunable, i.e. the real part \( R \) or the imaginary part \( X \) of the impedance \( Z \), or both, must be tunable when a dc bias voltage \( V_b \) is applied. This is a feature never met up to now in RF devices on paper or on any kind of flexible substrate, although encountered in previous studies on random MWCNTs placed between nanogaps [11].

The characteristic \( Z(V_b) = R(V_b) + iX(V_b) \) is crucial for the implementation of high-frequency devices on paper substrates, since the \( R = (V_b) \) and \( X(V_b) \) dependences are unavoidable features for matching of RF networks, for bandwidth tuning of filters and RF signal detection. In principle, no radio or sensor in the RF spectrum is possible without having in its configuration tunable components such as resistors, capacitors or inductances. When these dependences are nonlinear, RF detection or mixing is possible. So, the quest of a CNT ink deposited on paper, which could produce conductive lines or patterns with a tunable impedance opens the possibility to build tags, sensors and even a radio on paper. This would be a significant advance of wireless technology based on nanotechnologies.

The search for a CNT ink printable on normal paper, with printed patterns that display a tunable impedance, started with the choice of the CNT type to be used in the ink. We have known from previous studies that double-walled carbon nanotube (DWCNT) mixtures, i.e. randomly oriented DWCNTs and SWCNTs as in the case of the CNT inks, have a dielectric behavior up to 65 GHz [12]. Up to 3 GHz the electric permittivity of DWCNTs is about 4 and \( \tan \delta \approx 0.7 \). The further step was then to functionalize the DWCNTs (shown in figure 1(a) before oxidation) to display a semiconducting behavior and to be hydrophilic in water.

The DWCNTs were prepared by CCVD synthesis as described earlier [13]. We obtained samples that contain typically ca. 80% of DWCNT, together with 15% of SWCNT and 5% triple-walled CNT [7]. A stable suspension of DWCNTs without the need of the addition of a surfactant was prepared by rendering the surface of the DWCNT hydrophilic via an oxidation treatment. More precisely, 50 mg of DWCNT were oxidized by heating for 3 h in 35 ml of 0.38 M solution of \( \text{K}_{2}\text{Cr}_{2}\text{O}_{7} \) in \( \text{H}_{2}\text{SO}_{4} \) 8.2 M. The set-up was equipped with a condenser to avoid the evaporation of the liquid during the operation. After oxidation, the sample was first filtered on a polypropylene membrane (with a pore size of 0.45 mm) and then washed with deionized water until neutrality. Afterward, the sample was dried in air at 80 °C in an oven. To prepare a suspension in water, 3 mg of oxidized DWCNT were mixed together with 5 ml of deionized water and dispersed by sonication (bath) for 10 min. After a 12 h sedimentation, the supernatant was separated.

The TEM (JEOL 1011 operated at 100 kV) observation of the oxidized DWCNT, represented in figure 1(b), revealed that some of the CNTs have probably been cut. The presence of an amorphous-like deposit on the DWCNT is obvious and possibly corresponds to hydrolyzed oxygenated functions or graphene-like carbon debris.

The oxidized DWCNTs were characterized by Raman spectroscopy (see figure 2). The non-oxidized CNTs have a Raman spectrum which is reported by one of the authors in [14]. Five spectra were recorded in different places of the sample with \( \lambda = 632 \) nm. The mean ratio intensity between the D and G bands was close to 30%, which suggests the presence of structural defects in the CNT due to the oxidizing treatment. The presence of RBM peaks confirms that, in spite of the strong oxidizing conditions, DWCNTs are still present in the sample. Further, as illustrated in figure 3, we have prepared different CNT inks denoted A to F in which the DWCNTs were introduced to water in different concentrations, and an
additional ink G in which the DWCNTs were introduced in NMP (N-methyl-2-pyrrolidone). Ink A has the highest concentration of CNTs, of 1 mg l⁻¹, the CNT concentrations decreasing progressively up to F, the CNT concentration in ink G is 10 mg l⁻¹. Then, with a pipette we have added the same number of CNT ink drops on normal paper of 80 g cm⁻³ (cellulose-fiber-based) used for usual laser printers in any office, forming a disc with a diameter of 7 mm. We have measured the impedance of all CNT ink discs after the water was evaporated, and we repeated the measurements after several hours, and then days. After two months the discs formed by the CNT ink deposited on paper were not dispersed and the impedance measurements were only slightly different from those presented below.

3. Measurements and discussion of the results

The impedance was measured with the impedance analyzer HP 4294 A connected to a probe station, which has two sharp needles located at the margins of the CNT discs. The impedance analyzer was calibrated with a calibration test set before the measurements. The CNT discs are denoted with the same letters as the ink from which they have originated. Since the diameters of the discs are much longer than the length of the CNTs, the measured current is due to the formation of a random network of semiconducting CNTs. Measurements showed that CNT discs A to E have an impedance tunable with the applied voltage, while disc G has displayed a very small resistance and no tunability. In all cases the CNT concentration is higher than the threshold needed for the formation of a percolation path for conduction through carrier hopping between the semiconducting CNTs. In figure 4 we present the results on CNT disc A, figures 4(a) and (b) displaying, respectively, the dependence of $R$ and $X$ on frequency at various applied voltages. These figures show that the resistance decreases as a function of the applied voltage, being almost constant at an applied bias of 10 V (with a value of 30 kΩ) as a function of frequency up to a few MHz, while the reactance has the behavior of a tunable capacitance, i.e. a varactor, beyond 1 MHz. Lower values of the resistances could be obtained by increasing the number of imprints, as also indicated in [8]. The voltage dependence of the resistance is a clear indication of the semiconductor nature of the random networks. The increase of the capacitance at high frequencies could be related to the mechanism reported in [12], which involves a capacitive coupling between CNTs at high frequencies. The instabilities observed in both the resistance and (especially) the reactance....
dependence on frequency above 10 MHz are consistent with a similar behavior reported in [8], due to insufficient network formation in the sample.

As the concentration of CNTs in the discs decrease, the resistance should increase. The dependence on the applied voltage of the resistance and the reactance of disc E at 1 MHz is represented in figure 5. The resistance is higher than that of disc A at higher voltages, and its dependence on the applied dc bias is less pronounced. From figure 5 it follows also that the reactance of the disk E behaves as a tunable inductance. This behavior is consistent with that described in [6], where it is shown that the inductive behavior can be justified by regarding the curved nanotubes as tiny coils. This behavior is stronger for low CNT densities, since at higher CNT concentrations the local magnetic fields in the coils affect each other and the total inductance decreases.

How will an RF radio look on paper? Any direct receiver should have an antenna which could be a folded dipole or another antenna configuration, a tunable filter and a nonlinear element for detection and batteries. In principle, except for the battery which must be mounted separately on paper, the entire radio could be printed on paper using a normal printer since the antenna [1], the tunable filter and the detector can be printed on paper using the techniques described above. The radio on paper will consist of an antenna (which will be the subject of further research, but which could be printed on paper using silver nanoparticles), and a couple of discs containing CNT ink with various concentrations. The connections between various variable devices could be made with CNT ink of concentration $G$ which has an impedance mostly resistive of around 600 $\Omega$ which does not depend strongly on the applied voltage. This concept of a radio on paper is illustrated in figure 6 where, in the case of the antenna E, playing the role of detector and filter, respectively, we have introduced their photos. In conclusion, the paper demonstrated that quite inexpensive tags, sensors or even a rudimentary radio could be fabricated using a CNT ink printed on normal papers.

4. Conclusions

We have demonstrated that elementary electronic devices such as resistances, capacitances or inductances can be fabricated on normal paper used nowadays in any office. These devices are tunable with the applied voltage. We will extend this research to print the electronic circuit of a simple radio on normal paper to be used in various areas as a wireless tag. A miniaturized loudspeaker and battery will then be sold on this printed circuit, the cost of the entire device being less than a few dollars.

References