# Thermal characterization of thin carbon nanotubes films

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**Résumé**

Carbon nanotubes (CNTs) are grown with a three steps process combining pulsed laser deposition and radio frequency plasma enhanced chemical vapor deposition techniques. The result is a dense thin film made of vertically aligned and multi-walled CNTs. To characterize the thermal properties of the film by pulsed photothermal method, it is necessary to deposit on the top a metallic thin layer of 600 nm acting as a photothermal transducer. The thermal conductivity and volumetric heat capacity of the CNTs film are identified. They are found to be respectively 180 $\mathrm{Wm^{-1}K^{-1}}$ and $5\times10^4$ $\mathrm{JK^{-1}m^{-3}}$. The thermal resistance between the CNTs film and the metallic transducer is identified as well : $1\times10^{-7}$ $\mathrm{Km^2W^{-1}}$.

## Introduction

One of the great challenge for futur microelectronics components is to manage the heat within circuits. This point is of special concern, because of the continuous components size decrease. This trend leads to a continuous current density increase through connexions between components and between external circuit and components [1, 2]. It becomes then crucial to efficiently evacuate the heat to avoid the damages due to either electromigration or thermomigration within the electrical connectors. For this reason, new materials are looking for since some years by microelectronic industries. Among the possible ways, carbon nanotubes (CNTs) are seen as potential substitutes thanks to their unusual thermal properties along with their electrical ones [3]. To answer the question "Can carbon nanotubes be used as heat sink ?" their thermal properties must be measured. For this goal, we prepared vertically aligned carbon nanotubes films [4] and characterized their structure by electronic microscopy and their thermal properties by pulsed photothermal method.

## Growth of CNTs films

The growth of the CNTs films is a three-step process which takes place in the same reactor without venting the chamber between steps. First, the catalyst thin film (less than 10 nm) is deposited at room temperature by pulsed laser deposition (PLD). We first optimized the catalyst film thickness in order to obtain sufficiently high and dense CNTs films [5].

In the second step, the catalyst film is annealed to the CNTs growth process temperature (550-700°C) in order to get nanoparticles which will catalyze the CNTs growth. Then, the temperature is kept constant under a pressure of 1 Pa for 15 min.

Finally, the carbon-containing gas mixture is introduced for the growth of the CNTs by plasma enhanced chemical vapor deposition (PECVD) technique at a pressure of 150 Pa. The mixture is composed of ethylene ($C_2H_4$)/hydrogen ($H_2$) in the ratio of 1 :2. A RF plasma is created, its power is kept at 25 W.

The CNTs obtained with this technique are vertically aligned perpendicular to the substrate surface, with a diameter distribution between 5 and 20 nm and form a porous film of few to several tens of $\mu$m in height (see Fig. 1) and whose porosity has been evaluated to 70% (Fig. 1(right)). Moreover, catalyst can be found within the body of the CNTs, especially at the top.

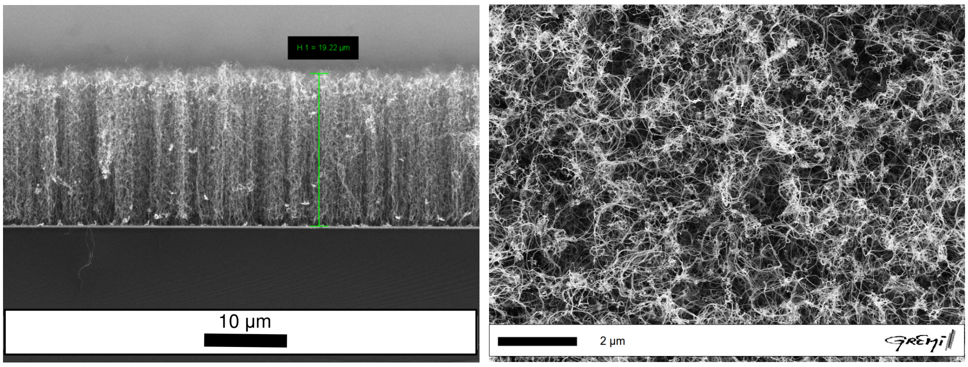

FIGURE 1 – SEM images of CNTs film obtained by PLD-PECVD groth process. Cross-sectional view (left) and top view (right).

## Thermal characterization setup

The thermal characterization is done with the pulsed photothermal method (PPT) : the sample surface is heated up with an UV KrF laser. This allows to heat only the extreme surface of the sample (several tens of nanometers) which is really suitable for the thermal characterization of thin films [6]. The only stringent condition is that of a homogeneous absorption of the laser beam energy.

Thermal properties of thin films are determined from the time relaxation of the surface temperature after one laser pulse. In order to deduce the surface temperature from the electrical signal of the IR detector, a calibration process is necessary for each sample. In fact, the emissivity of each surface depends on the nature of the material, its surface state and its thickness. For the calibration, a resistive heater and a K-type thermocouple are in contact with the back side of the sample. The sample is heated by this resistance, and once the thermal steady state is reached, the thermal radiations emitted from its front surface are measured by the IR detector and can be plotted versus thermocouple temperature values [7].

## Deposition of a metallic transducer : a metallic thin layer on the top of CNTs films

The use of the pulsed-photothermal method is possible only if the laser beam energy is homogeneously absorbed by the sample surface. For porous and complex surface as is the top of the CNTs films, this condition is not met. When the laser beam heats the surface, it interacts with carbon material and air between CNTs. To force the homogeneous heat transfer from laser beam to CNTs, the deposition of a metallic thin film, which acts as a transducer, on the CNTs surface is required : this metallic thin layer absorbs the UV beam energy, becomes a uniform heat source, and transmits the photon energy toward the substrate by phonon vibrations [6]. The transducer must thus be chosen according to following requirements : non-transparent medium at 248 nm, good and thermally stable emissivity in IR and chemically and mechanically stable when irradiated.

Furthermore, CNTs emit non-thermal IR photoluminescence signal under UV excitation [8, 9] which is added with the thermal one and lead to wrong properties identification. The metallic transducer then prevents the photoluminescent signal by blocking the direct UV excitation of CNTs.

According to previous conditions, titanium, tungstene or nickel layers can be used. They can be deposited by magnetron sputtering technique [10]. As seen on the Fig. 2 for the Ti example, the metallic thin layer does wrap around the upper part of the CNTs ; with the proper deposition conditions it is seen as a homogeneous film by the laser beam and can be used as a transducer.

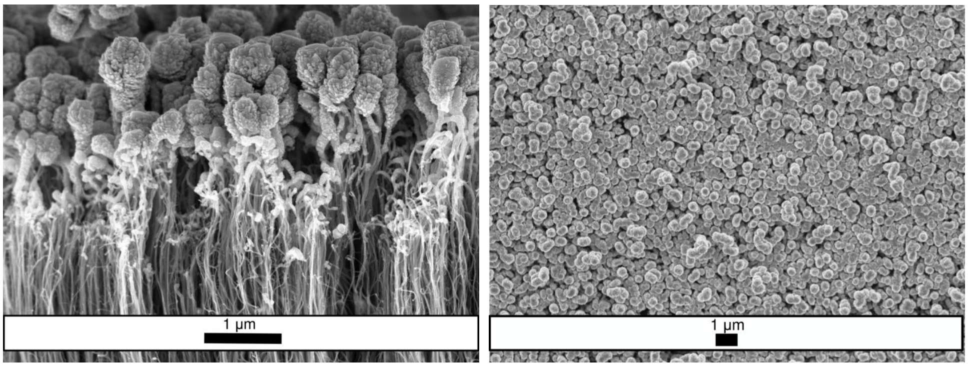

FIGURE 2 – SEM images of CNTs + 600 nm Ti film : cross-section of the upper part (left) and top view (right).

## Thermal Properties

After a calibration step (thermal properties of metals onto silicon substrate), the thermal properties are determined for a sample composed of a 600 nm thick film of metal deposited on a CNTs film of 20 $\mu$m in height. Typical surface temperature evolution of transducer/CNTs sample is given in Fig. 3, normalised to the relaxation temperature. The transducer temperature rises up to about 250°C. When using log-log scale, it appears that the temperature relaxation occurs with two different slopes. The first slope (first tens of ns) corresponds to the transducer relaxation and the second slope to the CNTs film relaxation. The thermophysical properties of the CNTs carpet as well as of the thermal transducer obtained from these curves are listed in Table 1. The values of the thermal contact resistance, $R_{th}$, and the volumetric heat capacity, $\rho c_p$, explain well the slow temperature relaxation.

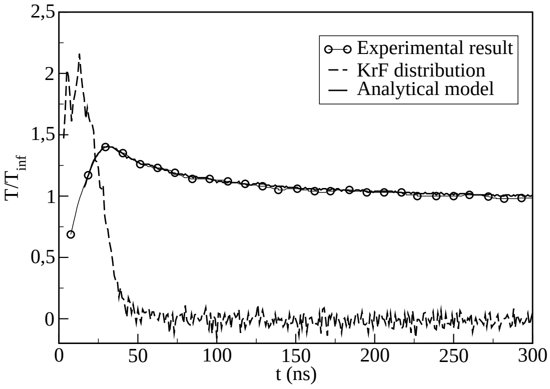

FIGURE 3 – Experimental (point) and analytical (line) curves of the normalised temperature temporal relaxation $T/T_{inf}$ in semi-log scale. Real laser beam shape (dotted line) used during experiments. See text for $T_{inf}$ definition.

## Conclusion

Vertically aligned multi-walled CNTs are grown thanks to PLD catalyst deposition and then RF PECVD growth process. The SEM images show that the films obtained are composed of vertically aligned CNTs of several $\mu$m in height. Actually, the films are porous media as the typical porosity is estimated around

| | Ti | CNT |
|---|---|---|
| $\kappa$ ($\mathrm{Wm^{-1}K^{-1}}$) | $22 \pm 2.2$ | $180 \pm 5$ |
| $\rho c_p$ ($\mathrm{JK^{-1}m^{-3}}$) | $(1.4 \pm 0.14)\times10^6$ | $(5 \pm 0.5)\times10^4$ |
| $R_{th}$ ($\mathrm{Km^2W^{-1}}$) | $(1 \pm 0.5)\times10^{-7}$ | |

TABLE 1 – Thermophysical properties of Ti transducer and CNTs carpet : thermal conductivity, $\kappa$, and volumetric heat capacity, $\rho c_p$ as well as thermal contact resistance, $R_{th}$, between these two medias, determined by the model.

70% at least and can be considered as composite films made of multi-walled CNTs of various diameter with catalyst particles inside.

These porous media is characterized with the PPT method in order to estimate its thermal properties as conductivity and volumetric heat capacity. To apply this technique with porous objects, it is necessary to deposit a thin metallic layer on the top of the CNTs film. Then, it is possible to obtain the thermal contact resistance between the CNTs film and this metallic layer.

These porous nanomaterials are found to be good thermal conductors, compare to known and used connectors. Moreover, their properties are independant of the location at which the thermal properties are evaluated (the probed depth within the CNTs film) wich means that the entangled shape of the top of CNTs film does not influence their thermal properties. This confims that they can be used where thermal conductivity and heat sink effect are requested.

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