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Report on the PhD manuscript of Ms. Ewa ZBYDNIEWSKA entitled: "Electronic Properties of Coupled Semiconductor Nanocrystals and Carbon Nanotubes"

In her PhD manuscript, Ms. Ewa Zbydniewska presents an experimental study entitled *"Electronic Properties of Coupled Semiconductor Nanocrystals and Carbon Nanotubes"*. The manuscript is divided into an introduction, four chapters of similar length detailing and discussing her work, a conclusion and perspectives part, and two annexes. It is globally well-written in English, with very few errors, and rather clearly presented in a valuable synthetic way (79 pages without the annexes).

In the **introduction** part, Ms. Ewa Zbydniewska presents briefly within one page the subject of her PhD work, and introduces the different parts of the manuscript. I would have expected further details on the motivation of this study as well as a more extended state of the art of the subject to be exposed in the introduction part, even if some of these aspects are addressed further on.

The **first chapter** (20 pages) deals with field-effect transistors using carbon nanotubes (CNTs). After a clear presentation of CNTs regarding their definition, history, and electronic properties described from those of graphene, preparation methods are reviewed with their characteristics. Among these methods, Chemical Vapor Deposition (CVD) was chosen in this work since it presents the advantage to define the position the CNT on the substrate. As a main drawback of CVD, the CNT electronic nature (metal, semiconducting, chiral) is poorly controlled. Separation of CNTs to purify and isolate them is addressed. Two methods are described: sonication which may induce unwanted interaction between CNTs and organic solvent, and density gradient ultracentrifugation developed by the group of M. Hersam. The latter consists in surfactant attachment to the CNTs followed by centrifugation, and separation following the densities that are different for semiconducting and metallic CNTs.

Afterwards, CNT field-effect transistors (CNTFETs) are reviewed according to their different geometries. Two possible electrical switching mechanisms of CNTFETs are presented: the MOSFET model, and the Schottky barrier field-effect transistor model. Presentation of electronic properties of CNTs within field-effect transistors (scattering, phonons, contact resistance) could have been better used to determine which kind of CNT is suitable for this PhD study. It is importantly underlined that CNTFETs exhibit interesting performance that can compete with those of silicon MOSFETs: although CNTFETs usually have thicker gate oxide they possess higher ON current, and higher transconductance that leads to higher cut-off frequencies.

In the second part, non-volatile memories based on CNTs (flash memories) are addressed. Three examples are presented form the literature: cell with semiconducting SWCNT operating by threshold shift, CNT as floating gate (capacitance-voltage hysteresis), metal nanoparticles as a floating gate of a CNTFET (I_{SD}-V_G shift versus single electron trapping).

This chapter presents clearly the CNTs and their electronic properties. Concerning their method of preparation, focus has been naturally brought on CVD that was used for the synthesis but the principle and the main parameters involved in this technique and the growth process (specially what happens to the catalyst) should have been detailed since it determines the characteristics of the obtained CNTs. CNTFETs preparation, architecture and operation are presented giving the necessary elements in order to explain the operation of the prepared CNTFET in chapter 3. If the bibliography is rather complete, pioneering work from C. Dekker (*e.g. Science* in 2001) should have been cited for SRAM and logic circuits with CNTs.

In the **second chapter** (19 pages), Ms. E. Zbydniewska presents first the semiconductor nanocrystals. Quantum confinement features (2D, 1D, 0D) is explained based on examples from literature. Origin and synthesis of semiconductor nanocrystals are then addressed. They could be prepared by epitaxy or by colloidal suspension which was preferred in this study due to high control and low price. In this work were used commercial CdSe colloidal nanocrystals rightly coated by a ZnS layer in order to avoid trapping and recombination at surface defects. Blinking phenomenon in semiconductor NCs is detailed from the literature with ON state fluorescence coming from radiative recombination from neutral exciton whereas OFF state should be due to faster non radiative recombination from charged exciton. The dynamics of the phenomenon follows an exponential decay law analog to that of current fluctuations through a single quantum dot (QD) connected within a junction. In CNTFET devices coupled with QDs, random fluctuation noise occurs coming from single-charge trapping/detrapping and is characterized by a Lorentzian power spectrum. Interestingly it is shown from some examples associating Au nanoparticles and CNTs that such effects can be used in CNTFETs to detect single charge modification. Such effects are reviewed being documented using various examples from the literature with Au nanocrystals, top gate CNTFETs giving the best results.

It is also shown that CNT single electron transistor device can also be used to detect a single electron transfer to the Au nanoparticle contacted between the gate and the CNT. The phenomenon can be described through the energy brought by the gate voltage multiplied by the lever arm coefficient enabling to overcome the addition energy of the coupled particle. In this approach V_G values associated to a jump in conductance correspond to single electron transfers. At last, it is mentioned such approach was also developed by M. Zdrojek *et al.* using CdSe nanocrystals, which is actually the subject of this PhD study. It is not mentioned whether it is the unique one in using semiconducting nanoparticles in such devices or not in order to address an extensive state of the art. Moreover, since main results reported from the literature deal with metallic nanoparticles, it seems important to precise the difference with semiconducting nanoparticles, why the latter have been chosen, and what kind of application may motivate their study.

The **third chapter** (16 pages) is dedicated to the fabrication of nanodevices based on back gate CNTFETs and QDs studied in this work. Since top gate seems to bring high control as revealed by the previous bibliography review, one could expect some justification of the choice of a back gate, although it is obviously quite understandable that it is more simple to implement, which should be of course an excellent reason to begin with it! Fabrication of markers, preparation of CNTs on the Si/SiO_2 surface, as well as contact deposition are well-documented, enabling perfect reproduction of the experiments. For the fabrication of CNTFETs, two types of semiconducting CNTs devices were prepared on p-type silicon coated with thermal silicon oxide: "Devices A" with CVD-grown CNTs on 1μm thick oxide, and "Devices B" with commercially purchased CNTs deposited from a suspension on 0.3 μm thick oxide. E-beam lithography was used for markers and contact fabrication. CNTs in solution are commercially purchased and present the advantage of being more surely semiconducting contrary to CVD CNTs grown on drop-casted catalyst. However the latter show high-purity contrary to solution-deposited CNTs on the surface that exhibited a coating with extraneous material that revealed hard to be removed. Contact deposition was then prepared on clean and straight parts of deposited CNTs.

Then is detailed the procedure of electrical characterization of as-prepared CNTFETs that aimed at determining semiconducting CNTs as well as assessing the quality of the metallic contacts. Semiconducting CNTs reveal to be either ambipolar or p-type. CdSe/ZnS nanocrystals in colloidal suspension were commercially purchased with diameters of 4 and 6 nm and drop-casted at the surface of CNFETs devices. Apparently, it seems that most of NCs are deposited without aggregation and some of them could be hopefully in close vicinity to CNT channel, but no details are given on the success of this operation, and on possible effect of the NCs concentration on aggregate formation at the surface. Procedure of blinking experiments conducted on NCs deposited on SiO_2 surface and CNTs carpet is detailed. However it would have been useful to have some results of experiments presented depending on the two diameters of NCs and type of CNTFETs substrate. Several problems were revealed: purity of samples that could be cleverly reduced by suitable UV ozone cleaning, defects in contacts due to inappropriate lift-off procedure, and number of contacted nanotubes different than one, *i.e.*, either zero or several ones. Details on the contact between NCs and CNTs, *e.g.* which distance and if there is a distance influence on the results, and positioning of nanocrystals are not addressed as well as statistics analysis of usable samples.

Results and discussion of charge transfer detection in semiconductor NCs using CNTFETs devices prepared is exposed in **chapter four** (22 pages) which constitutes the ultimate part of this PhD work. CNTFET devices with the two types of CNTs are used in order to eliminate the influence of the type of CNTs in the effect. However the layouts of CNTFETs and NCs with the two kinds of CNTs are different (*i.e.*, oxide thickness and NCs diameters) and this may also affect the results so that it is hard to compare. Reasons of having chosen different parameters (NCs diameters, oxide thickness) between the two types CNTFETs devices need to be explained. Surprisingly, after NCs deposition it appears in Figure 4.1 a rougher surface with grains around CNTs grown by CVD compared to the case of CNTs from the suspension. Nature and influence of these grains on the measurements need to be specified. Charging and discharging of NCs are evidenced at room temperature through the existence of two current levels, high and low, within the time evolution of source-drain current at fixed gate voltage. Interestingly, NCs blinking statistics follows the afore-mentioned power law consistent with single charge transfer as explained in chapter two, and a Lorentzian shape of the Random Telegraph Signal (RTS) power spectrum. If it is underlined such power law is consistent with NCs optical blinking observed in the literature, but also checked in this work, the strength of this PhD study is to deal with electrostatic charge state thus being capable to find out for the first time that blinking statistics of their single charge state follows a power law.

As central and remarkable results of this study, by using both a simple statistics model of a trap center in equilibrium with the Fermi energy applied to RTS time values and the gate voltage variation enabling to switch between high and low current values, it is noteworthy that a single mean value of charging energy around 200 meV at room temperature could be experimentally determined for the two kinds of NCs used in separate CNTSFETs devices (A: CNTs grown by CVD, and B: commercial ones from solution). Although higher than values previously reported in the literature on similar NCs, it is in reasonable agreement with charging of trap states in the NCs band gap. However a difference between the two kinds of devices was highlighted: in CNTFETs-NCs "devices B" with commercial CNTs deposited from suspension the trap charging is activated by the source-drain voltage whereas by the gate voltage for "devices A" prepared with CVD-grown CNTs. In the former case, it was suggested the involvement of out-of-equilibrium trap state population although it is not tentatively justified neither treated by a model.

The last part, after presentation and interpretation of the main experimental results on NCs charging/discharging measurements, is interestingly devoted to a more general discussion from these results. It is noticed that for "devices A", the whole RTS spectrum is probed within a gate voltage range in close agreement with the band gap of the NCs (~2.4 eV) thus making likely the traps should be energetically spread all over the band gap. On the contrary, for "devices B" the gate voltage range is smaller than the band gap indicating a reduced energy range (~1 eV) for the trap states within the gap.

At this stage, a number of future investigation works is proposed. First, positioning the charging energy states relatively to the valence and conduction bands, which requires measurements at low temperature in order to reduce the thermal agitation energy well below the range of the charging energy (20-40 meV). Second, determining the donor or acceptor nature of the traps, which cannot be achieved by the technique used in this PhD study. For this purpose, interesting experiments using Kelvin Probe or Electrostatic Force Microscopy are proposed to be coupled with CNTFETs devices to probe the potential or charge state with respect to the CNTFET channel potential. If one can wonder why such scanning probe microscopy (SPM) techniques have not been tentatively used in this work, an element of answer is given: SPM bandwith is limited, especially in high charge sensitivity measurements.

It seems that a possible way to overcome this problem would be to use SPM under vacuum at low temperature. At last, another further study that this work is suggesting is rightly considered: coupling of electrostatic measurements at the nanoscale and optical experiments such as fluorescence dynamics of individual NCs, as a powerful procedure to further investigate the role of multiple trap states with the time fluctuation of trapping centers or of transfer rate towards them. Measurements could be profitably performed at low temperature.

At the end, before providing two annexes with additional results that give further useful details on CNTs (thermal analysis) and RTS analysis of CNTFETs without NCs, Ms. E. Zbydniewska presents a synthetic one-page **conclusion**. It reminds the main elements of her work, highlights the crucial points her PhD study could reveal on NCs charging/discharging phenomena within a very smart experimental approach, and gives a selected perspective with coupling nanoscale detection of NC trap charge and fluorescence dynamics, to which could be added SPM charge/potential measurements.

This PhD manuscript presented by Ms. Ewa Zbydniewska demonstrates her high expertise in fine preparation of ultimate nanoelectronic devices that are able to detect single charge transfer, which is not trivial, and her ability to propose sharp fundamental models to interpret her results from a good knowledge of the existing literature on the subject. On the basis of the clear presentation given in this manuscript, the innovative development of suitable smart devices and procedures to carry out measurements and analysis of charge dynamics in NCs, and the convincing and high-impact new fundamental results Ms. Ewa Zbydniewska has presented, and that were recently published in a very high-impact journal, I strongly recommend this PhD thesis for being defended orally by Ms. Ewa Zbydniewska in order to obtain her PhD degree jointly from the Warsaw University of Technology and from the University of Lille 1.

Dr. Lionel Patrone.