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Report on the doctoral thesis of Elisseos Verveniotis

E. Verveniotis has presented a doctoral thesis entitled "***Structuring and study of electronic and chemical properties of semiconductor surfaces***" to obtain the PhD title from Charles University in Prague, Faculty of Mathematics and Physics. The goals of this thesis have been to perform the research conducted towards fabrication, characterization and control of local (down to nanoscale) structural, electronic and chemical properties of silicon and nanocrystalline diamond (NCD). The fabrication and characterization of nanostructures is despite long-term development still very challenging problem because of fundamentally new physical phenomena arising at nanoscale. Moreover, combining the NCD with a widely used silicon can bring new properties, higher thermal conductivity and biocompatibility with the utilizing in biosensors. Therefore, I consider this research beneficial and actual.

The manuscript is divided into four chapters.

Chapter 1 introduces the thin films and nanostructures of Si and diamond as well as assembly of nanoparticles on surfaces.

Chapter 2 consists of two parts where the author describes the methods used for material deposition and characterization. There is a description of plasma-enhanced chemical vapor deposition (PE – CVD) used for deposition of nanocrystalline diamond and hydrogenated amorphous silicon (a-Si:H) and thermal evaporation of Ni/Ti bottom electrodes on glass substrate in the first part. The second part summarizes the wide selection of analytical tools from macroscopic electrical current measurement methods over scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), Kelvin probe microscopy (KPM), conductive atomic force microscopy (c-AFM) and Raman spectroscopy (micro-Raman) that were all used in nano- and micro-scale characterization experiments. The special attention is paid to AFM-aided surface modification by control of the voltage or current between the AFM tip and sample resulting in local charging of NCD or nanocrystallization of a-Si:H (field-enhanced metal-induced solid-phase crystallization, FE-MISPC). The large number of techniques capable of analyzing the structures down to a nanoscale has provided robust base for experimental results interpretation.

Chapter 3 represents a key part of the whole thesis. It consists of 8 original papers published in peer-reviewed scientific journals all of which E. Verveniotis is the first author (the total number of his publications is 15 most of which he is the main contributor) and the last subchapter. The papers deal with local diamond charging and nanocrystalization of a-Si:H, the subchapter with selective growth of NCD on a-Si:H. The papers are logically and clearly arranged, accompanied with supporting information and notes in the text. I appreciate highly systematic approach to problem solving where all the new findings are put in the context of the previous experience and the knowledge base of the whole group at IP AS CR that made a pioneering work in this field.

Chapter 4 summarizes the main results and contributions of the work. I consider the following findings and outputs the most significant for the development of the field:

NCD

a) The electronic transport in NCD occurs predominantly due to the presence of grain boundaries and thus sp^2 bonded carbon.
b) The demonstration that the local charge trapped in NCD can electrostaticaly attract or repel the nanoparticles (patterned nanoparticles assembly).
c) The suggestion of a model for description of common current/voltage influence on local charging of the NCD.

silicon

d) The necessity of local dielectric breakdown for the nanoscale crystallization of a-Si:H (FE-MISPC) to take part figured out from current fluctuations mapping.

NCD/silicon system

e) The demonstration of selective growth of diamond nanocrystals on silicon thin film.

The applicant should reply to following questions and comments:

Questions:

1. The silicon surface had to be etched by solution of HF acid to remove the oxide and passivate the surface by hydrogen. What was the concentration of the HF solution? Have you tested the time the H passivated surface is resist against the re-oxidation?
   (page 19, paragraph 2)
2. "The deflection is caused by mechanical, Casimir or Van der Waals forces depending on the mode of operation." Can you specify which forces you mean by mechanical forces?
   (page 25, paragraph 2)
3. How many times were you able to restore the potential back to the potential of unexposed surroundings?
   (page 39-40, figure 4)
4. There is a KFM measurement on locally charged NCD commented and shown on pages 56-57. The detail figures 4 b, e prove the higher potential at grain boundaries. Have you compared this measurement with potential contrast of uncharged (outside) regions?
   (page 56 – column 2 – paragraph 2 and page 57 figure 4)
5. Could you comment the physical reasons for necessity of current spikes for achieving the crystallization of amorphous silicon (FE-MISPC)? Have you tried to use the current pulses intentionally?
   (page 78 – column 1 – paragraph 3, page 89 – column 2 – paragraph 1)

6. The EDX was used for characterization of AFM-tip-apex material. The usual depth of EDX material information is 0.5 – 5 um. How was this problem solved in the case of tip coating up to 100 nm? Was it solved by the orientation of the tip and the SEM beam? (page 77 – column 1 – paragraph 1)

Comments

- the down-arrow in the Stokes Raman scattering should be one phonon longer (page 33 – figure 2.13)
- the comment on the figure (page 74) is one page further
- the values and units should be at the same row (page 26 – paragraph 1)
- 10 nm – 50 pm (page 27 – paragraph 2)
- the caption a), b), c) are missing in the figure 1 (page 63)

In conclusion, this PhD thesis contains a large number of results, with those dealing with the common influence of the electric field and current induced charging of NCD being unique, original and very important for a complete understanding of the local NCD charging principle by AFM tip. In addition to that, E. Verveniotis has also performed a very careful analysis of the physical and chemical properties of the locally charged diamond and nanocrystallized a-Si:H that are of great importance for the applications and development of these nanolithography techniques. The number of techniques that he had to employ and understand is large and their description in the work shows he has well understood them well. The presented work proves researcher’s qualities. For all these reasons, I support his application for defending his thesis without any reservation.

Brno, February 28, 2013

Miroslav Bartošík