'Anomalous Electron Transport' with "Giant Current Density" at Room Temperature Observed with Nanogranular Materials

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***Abstract* — Focused electron beam induced deposition is a novel bottom up nano-structurization technology. An electron beam of high power density is used to generate nano- structures with dimensions > 20 nm, but being composed from amorphous or nanogranular materials with crystals of 2 to 5 nm diameter embedded in a Fullerene matrix. Those compounds are generated in general by secondary or low energy electrons in layers of inorganic, organic, organometallic compounds absorbed to the sample. Those are converted into nanogranular materials by the electron beam following chemical and physical laws, as given by "Mother Nature". Metals and amorphous mixtures of chemical compounds from metals are normal resistors, which can carry a current density J < 250kA/cm². Nanogranular composites like Au/C or Pt/C with metal nanocrystals embedded in a Fullerene matrix have hopping conduction with 0-dimensional Eigen-value characteristics and show 'anomalous electron transport' and can carry "Giant Current Densities" with values from > 1 MA/cm² to 0.1 GA/cm² without destruction of the materials. However the area connecting the nanogranular material with a metal with a 3-dimensional electron gas needs to be designed, that the flowing current is reduced to the current density values which the 3-D metal can support without segregation. The basis for a theoretical explanation of the phenomenon can be geometry quantization for Coulomb blockade, of electron surface orbitals around the nanocrystals, hopping conduction, and the limitation of the density of states for phonons in geometry confined non percolated granular materials with strong difference in mass and orientation. Several applications in electronics, signal generators, light sources, detectors, and solar energy harvesting are suggested.**

I. INTRODUCTION

EBIP emerged from electron beam contamination lithography for fine electronic or physical structures [1]. The use of organo-metallic precursors and of inorganic precursors opened the field for nano-structured conducting structures and for modification of structures by etching and the deposition of insulators. Figure 1 shows the principle of FEBIP Focused Electron Beam Induced Processing, which is till today the process used in photo-mask repair in the semiconductor industry.

From FEBIP diode experiments it was discovered, that miniaturized electron sources have very superior characteristics if compared to conventional electron emitters [2], like carbon nano-tubes, or Molybdenum tips. In figure 2 high resolution TEM images are shown, from deposited tips fabricated from three precursors using a JEOL 840F SEM with Cold W <311>-FE source at 20 kV and 3 nA. Molybdenum-Hexa-Carbonyle gives an amorphous deposit composed from Mo, MoO, MoC. The material can sustain like similar W compounds a current density J < 167 kA/cm² only. Bottom images show nanogranular tips, left, deposited from Dimethyl-Gold-Trifluoro-Acetyl-Acetonate, and right from Cyclo-Pentadienyl-Platinum-Trimethyl.

TEM images by R. Scholz MPI Halle. Such Materials deliver in field emission currents up to 1.3 mA per emitter tip and sustain in the emitter wire a current density of J > 2 MA/cm², and at the tip >0.1 GA/cm² [3].

II. THE PROBLEM: CONDUCTIVITY IN NANOGRANULAR MATERIALS

The materials characteristics is the behavior of a nanogranular metal /C compound material, which has due to geometry quantization surface plasmon Eigenstates in the crystals, which have energy levels with a separation as small as 60 meV (Au/C) or 120 meV (Pt/C)[4], see figure 3. Like on a multi atom compound, e.g. a benzene ring, also in a nanocrystals the surface atoms contribute charges, which can occupy surface orbital modes. Due to Bohr's law for stable Eigenstates in a central potential such orbits can have energy levels with a level distance of 120 meV for Pt crystals and 60 meV for gold crystals[5]. The Fullerene matrix around the crystals possibly supports such thoughts. Due to the small distances between metal crystals a hopping of electrons along several orbits is possible, and a high, fast current conduction is a result of such a structure [6]. This is also supported by the measurement of the hopping activation energy of the two nanocrystals systems, which gave very similar energies . In a further experiment a photon induced current has been measured with white light [7], and lately with red light, indicating a multi-electron per photo quantum harvesting capability[8] Such energy packages can lift electrons to higher levels, from where they tunnel to the next nanocrystal. Since the nanocrystals, which are produced from Au or Pt precursors have a diameter < 5 nm, all quantum processes are performed with a full charge, according to [9], see figure 4. Typically current flow through such not percolated metal islands is called coulomb blockade, with a resistivity of h/2e² = 12,9 KΩ [10]. Since all experimentally measured current densities surmount the HTc Superconductors capability, see Figure 5 [11], it is assumed that a Bose-Einstein-Condensation possibly takes place in the NG materials. This is to be shown.

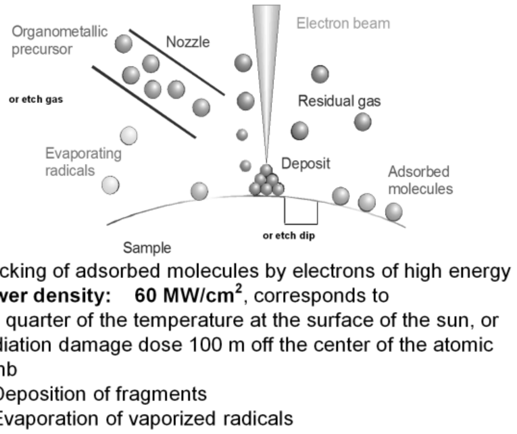
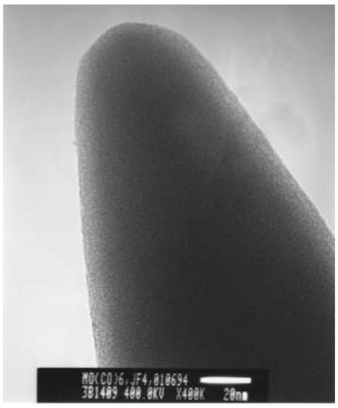


Fig. 1 Principle of focused electron beam induced processing



Mo C, Mo O, Mo amorphous (J < 165 KA/cm²)

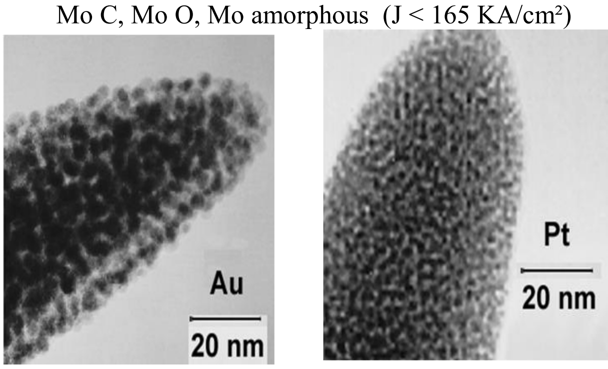


Fig. 2: Deposited tips from three precursors using JEOL 840F Cold W <311>-FE source 20 kV 3 nA Top: Molybdenum-Hexa-Carbonyle. Amorphous deposit : Mo, MoO, MoC. Bottom: J > 2 MA/cm²
Left: Dimethyl-Gold-Trifluoro-Acetyl-Acetonate,
Right: Cyclo-Pentadienyl-Platinum-Trimethyl.
TEM images by R. Scholz MPI Halle.

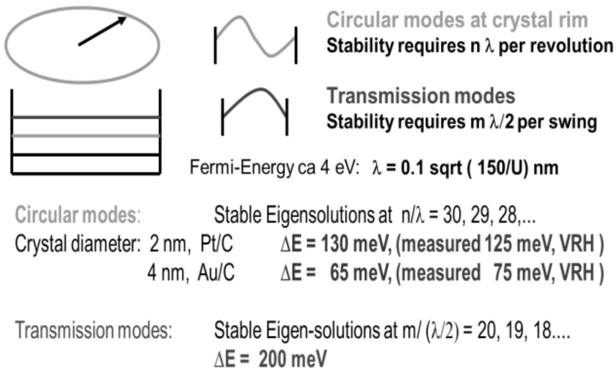


Fig 3: Schematic representation of surface orbital modes in nanocrystals with circular and through the crystal modes.

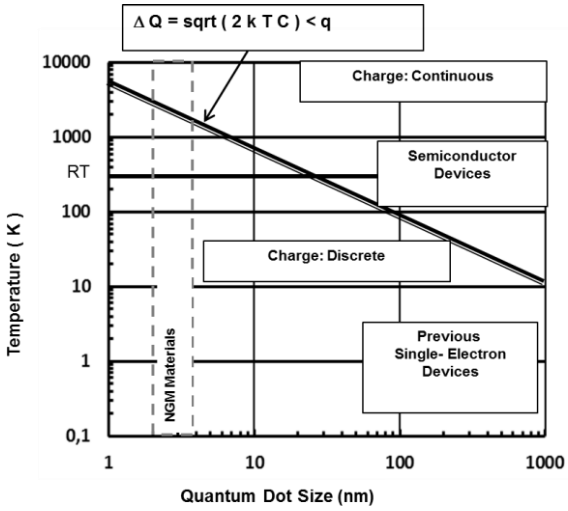


Fig. 4: Discrete or continuous charge in quantum dots versus temperature and region for NGM –nano-granular materials

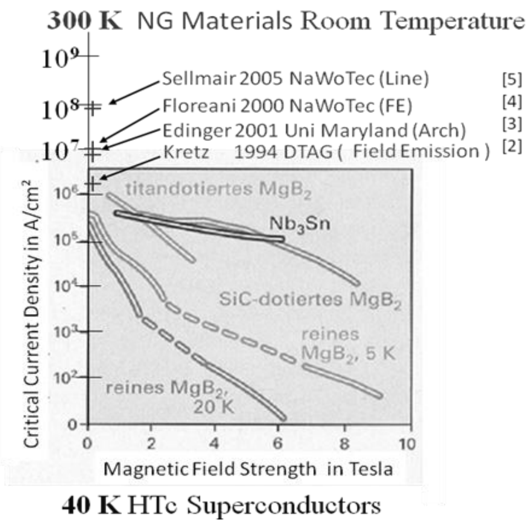


Fig. 5: Comparison of the critical current density for HTc Superconductors at 40K and with FEBIP produced NG materials from Au and Pt precursors at room temperature 300K [10].

III. CONCLUSION

Focused electron beam induced processing is a modern bottom up nanostructure fabrication technology. The theoretical explanation of the experimentally observed characteristics of such materials is a formidable task, and needs to be achieved.

The technical exploitation of NGM allows many ground breaking applications for miniaturized and macroscopic structures and systems. A design of a miniaturized triode with a field emission cathode and a beam parallel to the wafer surface was used for an electron-beam 10 digit dial system with miniaturized lenses[12], and a Smith Purcell THz source design [3].

FEBIP also allows building large area IR to x-ray image intensifiers, photovoltaic cells and massive parallel beams. With field emitter electron sources a miniaturized Orbitron pump can be developed to evacuate payload chambers on small wafers carrying the special 3D-constructions for nanoelectronics [13]. Such pumps can evacuate free-electron electronics, field-emitter lamps, and other vacuum nano-electronics devices. Miniaturizing typical electron tubes allows accessing of much higher frequencies in amplification and radiation generation. This leads to the design of THz emitting sources based on a miniaturized Dynatron employing two powerful free electron beams for a THz radiation source [14]. Production machines with many parallel high power electron beams are suggested to be fabricated using a self reproducing scheme[15]. Illuminating deposited lines and structures produced by FEBIP did prove that structures act as photo-detectors and optical sensors for near IR-, visible, and X rays. Theoretical development for this experimental result and electrical measurement did prove that very sensitive detectors for IR to X rays can be built for IR- and X-Ray tomography, field-emitter lamps of high brightness and high energy conversion ratio, for fabrication of high current power switches, high current density power cable working at room temperature, and very efficient solar cells with a capability to harvest multi-electrons per photon.

Using these materials in electric power distribution field emitter switching devices which contain thousands of NGM field emitters in power distribution system can be built. They can be switched on and off with < 100 V and can replace mechanical plasma tube power disrupters. Large emitter tip arrays allow construction and use of energy efficient field emitter lamps. For those lamps arrays of NGM tips are assembled in an emitter- extractor planar structure. Such lamps will efficiently convert up to 65% of input energy into light. They will be far superior to present LED technologies.

Also high power miniaturized X-Ray sources can be achieved, which have finer beam spots than conventionally reached with CNT or Reticulated carbon cathodes [16]. Finally thin NGM layer photon detectors of high sensitivity and high power harvesting capability become possible, which can collect energies as low as 60 meV (□ = 20 µm without additional cooling) and therefore release up to 15 times more electrons from visible light quanta than silicon solar cells, and 2 to 4 times higher electron numbers than HgCdTe- IR detectors[17], which have 250 meV band gap. NGM detectors have the advantage, not to need an active Peltier cooler for operation when detecting near to far infra-red photons. Such detectors could lower the X-Ray dose required in medical investigations by a factor >10. This would protect humans during medical investigations and treatments.

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