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Focused Electron Beam Induced Processing Renders at Room Temperature a Bose-Einstein Condensate in Koops-GranMat

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Abstract: Focused Electron Beam Induced Processing allows to generate nanocrystalline materials with metallic conductivity and also nanogranular materials with metal crystals embedded in a fullerene matrix, which shows at room temperature 1000 times better conductivity than superconductors at 40 K due to a Bose Einstein Condensate. Resistors and field emitters carry > 50 MA/cm² current density and deliver up to 1 mA current by field emission, when having an enlarged foot point contact to normal metal like Gold. An explanation for the different characteristics is given. The reason for the generation of the Bose Einstein Condensate is explained, and applications are described.

Keywords: Field emission, Focused electron beam induced processing, GDSII-layout exposure control, x,-y,-t,-nested loop exposure control, 3-d e-beam printing, Super conductivity, Cooper pairs, Bose Einstein Condensate, Koops-Pairs, Applications.

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1. INTRODUCTION

In 1994 a novel material, now called Koops-GranMat® [1], was discovered at FTZ, the German Telekom Research Centre at Darmstadt. This novel material is now understood to have extraordinary characteristics caused by a Bose-Einstein Condensate at room temperature, which makes it possible to replace cooled superconducting materials, and offers the chance to revolutionalize many tasks: energy transport and distribution, high frequency electronics above 30 GHz, THz switching and spectroscopy, materials analysis, photonics and energy harvesting.

The long lasting discussion how this novel material has been generated, but could not be reproduced by other researchers is now understood [2].

I. ELECTRON BEAM INDUCED DEPOSITION AND ETCHING

A. Early work

With the development of early electron microscopes since 1930, which challenged the resolving power of optical microscopes, the influence of the electron beam in the microscope and its vacuum conditions was found to change the samples. Heide [3] investigated this influence of the sample temperature and the water content in the microscope and explained it by etching with water or deposition of contaminants. Later the destruction of Nitrocellulose films was used by Rau [4] to structure the sample carrier foil with electrons, ions and X-rays and showed the deep etched groves by shadow evaporation in the TEM. These processes were applied to generate transmission gratings for spectroscopy of soft X-Rays from ionized carbon with□□= 4,4 nm from flares of the sun [5]. Since field aberrations in electron projection systems for the production of 50 nm node like transmission line gratings were to be measured [6], organometallic precursors were employed in the sample containing sub cells to record gratings in the image field of the projection systems, and to overlay in double exposures the undistorted centre part of the image field with the edge parts of the image field in a half dose double exposure. The appearing moiré patterns allowed measuring the distortions with sub nm resolution. Later 80 µm diameter quantum dot field arrays could be fabricated with 200 nm square size using gold precursors in a TEM with Twin lens and a material supply integrated in the sample holder [7].

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B. Recent Findings

Triggered by a relocation of an SEM with liquid nitrogen baffle, used to absorb the ultra high vacuum capable diffusion pump oil and it's vapours, we built by electron beam induced deposition a 10 µm high carbon needle having a diameter of 200 nm [8], and also Atomic Force Microscope (AFM) needles on top of the tip of the cantilevers, as well as on etched tungsten needles. Later 3-tip pointed AFM structures were deposited and allowed to probe the deep trench etching in the semiconductor storage devices [9]. When investigating very different organometallic precursors for their structure of the deposited material by using high resolution TEM at MPI Halle and TU Darmstadt, very different characteristics of the deposited material were found [10]. Very fine granular composites based on compounds of carbonyls were discovered, see Figure **1** left. The material crystals percolate and the current conductivity stops at 156 kA/cm². However, with Gold acetyl-acetonates and cyclopentadienyl Pt compounds, a nanogranular crystalline compound material with a Fullerene type matrix between non percolating metal crystals was found; see Figure **1**, middle and right. The metal and the carbon form a common Fermi level at about 5 eV, charging the metal negative, and the carbon compound positive. The Fullerene embedding matrix allows that surface orbital states around the platinum or gold nanocrystals can be formed and occupied with electrons from the due to Maxwell temperature distribution at room temperature occupied conduction band levels of the connector material. Those can enter by hopping into the excitonic surface orbitals around the metal crystals, and immediately form Bosons with the holes from the carbonaceous matrix.

The Pt/C and Au/C materials delivered in field emission outstanding currents > 1 mA, and also emission current densities up to 3 GA/cm², without any sign of melting at the tip. All three materials were deposited using dwell times > msec or continuous deposition at one spot with a beam current < 2 nA and up to 20 keV accelleration voltage from a cold 310 oriented field emitter. The energy density at the sample ranged up to 60 MW/cm², which corresponds to 0.3 of the energy density at the surface of the sun, or is aequivalent to the radiation damage dose at a distance of 100 m from the atomic bomb. The molecules are totally stripped from ligands and the metal atoms could crystallize at 380°C to 400°C to nanocrystals of 2 nm diameter (Pt) or 4 nm diameter (Au), until the fullerenes started to crystallize at 150°C and stopped the metal crystal growth, respectively initiated the growth of the neighboring crystal. This process led to a homogenuous compound material of Pt/C or Au/C [12].

II. MECHANISM OF CONDUCTION IN NANOGRANULAR MATERIAL AND KOOPS-GRANMAT®

Nanogranular material deposited from metal-carbonyl precursors shows in the high resolution TEM image very small, crystals, which all percolate and are composed from conductors of very similar conductivity. Therefore this material behaves like a resistor with conductivities in the range of a few µOhm cm. The Koops-GranMat® materials however have non percolating large metal crystals of up to 1000 atoms, which are pure metal, and are embedded in a fullerene or nano-diamond carbon matrix. The average thickness of the C-matrix is 1 nm. The metal crystals are surrounded by surface orbitals around the crystal, which can also be excitonic orbitals. Due to the large orbital diameter and the low binding energy the electrons which are occupying such orbitals have according to the Bohr Theory a wavelength of 2 nm. Since the crystals are 2 nm in diameter, the energy difference between the excitonic orbitals in the case of Pt/C was 125 meV, and for Au/C 65 meV, see Figure **2**.

According to Bose it is a precondition that a condensate energy level of one energy exists throughout all the material. This is the case, since surface exciton orbitals with n > 5 overlap with the levels n >5 of the neighbouring metal crystal. This allows 2 Fermions, electron and hole, to combine to 1 Boson. Excitons, electron-hole pairs, were predicted by Boer *et al*. in 1961 to condense at low temperature and high density. In superconducting materials Cooper-Pairs have charge 2, and spin 0. In Koops-GranMat® having Koops-Pairs one electron and one hole have charge 0, and 2 parallel spins: have spin 1. The Condensate level can then be populated by very many Bosons, which was observed in our experiments. The Bosons are all coherent. This results in

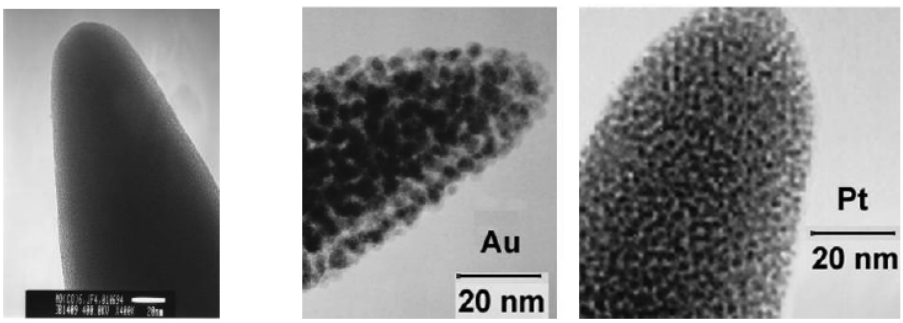

Figure 1: Left carbonylic deposit with percolating nanocrystals from Mo(CO)6. Middle and right: Non-percolating crystals from Di-methyl-Au-acetyl-acetonate, middle, and from Pt-cyclopentadienyl-trimethyl, right, are embedded in a Fullerene matrix [11]. Au crystals have 4 nm diameter, Pt crystal 2 nm diameter.

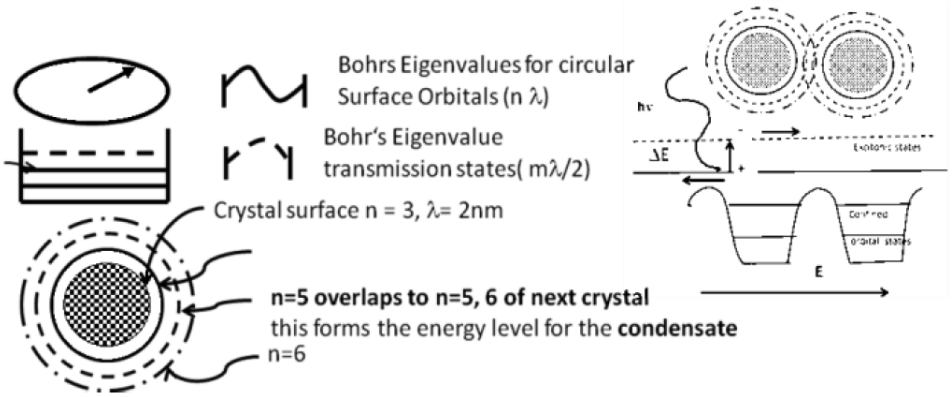

Figure 2: Excitonic orbitals around the nanocrystals overlap with such of the neighbouring crystals and form a Bose-Einstein Condensate [13], which extends through all the deposit.

coherent electron emission from field emitter tips build with Koops-Pairs. This was observed imaging in the far field three Young's interference patterns from one Pt/C emitter tip [14].

Using a theory from L. Butov and M. Remeika, the temperature for the forming of the Bose Einstein Condensate could be calculated, see Figure **3** [15].

III. CONDUCTION IN KOOPS-GRANMAT ® IS MADE POSSIBLE BY THE MAXWELL STATISTICS DISTRIBUTING ELECTRONS IN THE CONDUCTION BAND OF GOLD AS A CONTACT MATERIAL

The activation energy for supplying of electrons from normal metal conduction band levels to the Koops-GranMat® was measured with a Poole-Frenckel setup to be for Pt/C 125 meV, and for Au/C 65 meV [16]. Theoretically the excitonic surface orbitals show these energies as a band gap for the excitonic surface orbitals around the crystals [17]. This result corresponds to the measured data.

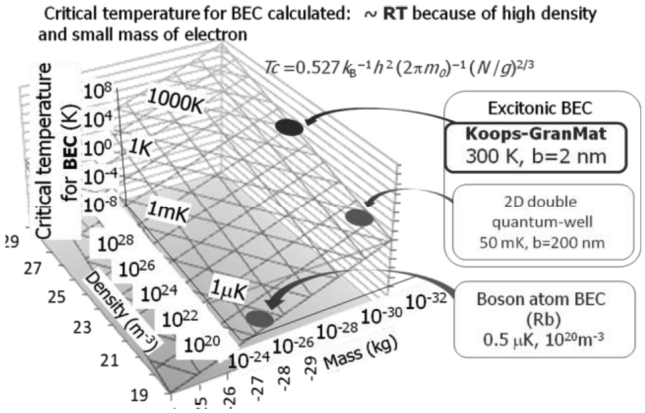

Figure 3: Calculated Bose-Einstein condensate temperature TC BEC as a function of the mass and the density of bosons for Rubidium (0.5 μK), for the excitonic BEC in 2D-double Quantum wells (50 mK), and for excitonic BEC in Koops-GranMat (300 K).

A: Energy states in Koops-GranMat®

Table **1** shows the result of the use of Bohr's atom model to estimate the energy and diameters of the excitonic orbital states. Bohr radius $r = \varepsilon n^2 h^2 / (\pi\ m_{eff}\ e^2)$; Energy level: $E = m_{eff}\ e^4/(8e^2 n^2 h^2)$

B: Current Conduction from the Connecting Metal to the Koops-GranMat®

In Figure **4** is the energy level situation depicted. From the 3D Gold metal contact at the border to Koops-GranMat® energy levels electrons hop into the excitonic levels around the metal crystals. Since the contact is normally at room temperature, the energy levels of the metal conduction band are partially occupied, even at higher voltage, due to the in this material acting Maxwell temperature law for level occupation. Since in the Koops-GranMat® the overlapping energy levels of the condensate are about 250 meV above the room temperature, such levels would normally not be occupied. But due to the energy distribution due to the Maxwell statistics in the connecting gold material, several electrons have already the energy to tunnel directly into the excitonic energy level of the BEC condensate. Now a current can flow to the Koops-GranMat®, and form Bosons and result in current flow with zero resistance by coherent Bosons. Since the Koops-pair has a compensated charge but a strong dipole moment, the Boson can be moved only by an inhomogeneous electric field, or an electric field with a gradient.

IV. GIANT CURRENT CARRYING CAPABILITY IS OBSERVED IN KOOPS-GRANMAT®

When measuring the field emission and the conductivity in deposited lines between gold contacts not really understandable values were measured. Field-emission measurements using Au/C rendered a maximum emission current of almost 1 mA at 22 V extraction voltage [18], and from Pt/C of 1.3 mA at 70V [19]. Typical Mo emitters stop emission at 10 μA but at an extraction voltage > 100 V [20]. In comparison to the current density values known for superconductors a similar mechanism was to be assumed [21].

In Table **2** a comparison is given for current densities in superconductors, see last line, and also for Koops-Gran-Mat®

Table 1: Using Bohr's Model: The Predicted E between Confined and Overlapping Orbit Agree with Observed Ea for Pt and Au

Material	Exciton diameter r (nm)	Exciton number	Energy difference E (meV)	Observed EA (meV)
Pt	3	5-6	166	125
Au	7	6-7	65	65

which surpasses the values for superconductors by orders of magnitudes.

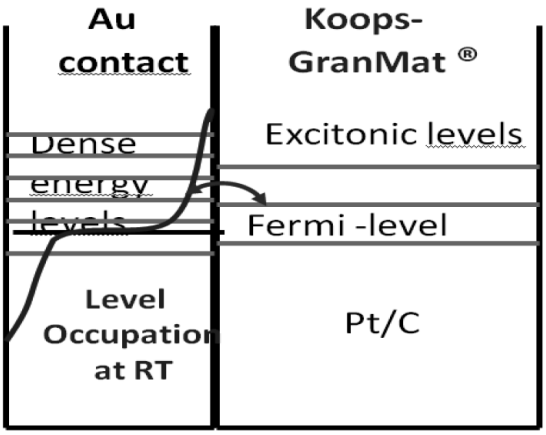

Figure 4: Energy levels and electron occupation at room temperature at the contact of metal and the Koops-GranMat®. The Maxwell statistic lifts the electrons in the conduction band of the contact material gold up to the common Fermi-level and allows a direct tunneling into the Koops-GranMat®.

Table 2: Comparison of the Capability to Carry Current Densities for Superconductors and Koops-GranMat®, as Measured at the German Telekom Research Centre [8, 9, 15, 22, 18] and by other Researchers at NaWoTec [22] and at University Maryland [23]

Review FEBIP	MA/cm²	[8]
Au/C Field emitter- RT	2, at tip 1000	[9]
Pt/C Field emitter- RT	2	[15]
Pt/C Wire arch- RT	15	[22, 23]
Pt/C FE Emitter- RT	10	[18]
Pt/C Wire - RT	100	[21]
HTC Superconductors Ti/MgB2-40 K	< 1	[20]

A: Superconductivity and Bose Einstein Condensate BEC at Room Temperature

Superconductivity, as it was explained by Bardeen, Cooper, Shrieffer, did not teach the truth [24]. Just recently a group of scientists from Max Planck foundation, CEA-CNRS, University Dresden, Munich, and Goettingen, published a statement " Our observations point to a surprisingly simple theoretical description of the spin dynamics in the iron arsenides and provide a solid foundation for models of magnetically mediated superconductivity" in 20.12.2009 [25]. Also B. Steele stated in 2014, "Magnetism glues Cooper-Pairs" [26]. This statement was based on the work of J. C. S. Davis, Cornell University and S. Avici *et al*. May 2014 [27], who published measurements which confirm that the Cooper pair is stabilized by a balance of charges and spins. The same statement was given in a movie by CNRS in Youtube showing how the Cooper pairs form and then finally all Cooper pairs become Bosons, and form a coherent wave in the superconducting material [28]. The Bosons in this case are formed from 2 electrons, having antiparallel spin. This spin configuration stabilizes the Boson at a diameter of 600 nm!, see Figure **5**, left. Having encountered in our by FEBIP produced Koops-GranMat® the capability to transport current densities at room temperature which are > 1000 times the value of HTC-Superconductors, I defined " Koops-Pairs" as Bosons, formed by an electron and a hole but having parallel spin, see Figure **5**, right. In contradiction to this finding, early work of Böer and coworkers in University of New York, USA states, that excitonic electron and hole pairs can exist only at very low temperatures [29].

In the Pt/C- nanogranular matrix compound, as in the Au/C compound generated by high dose FEBIP, two phases of different work function are touching (Pt: 5,3 eV, C: 4,8 eV, or Au: 5,0 eV and C: 4,8 eV). Since the metal crystals are embedded by a fulleren type matrix, the metals attract the electron from the C and form a common Fermi level. Due to this situation, the metals become negative, and the C-matrix becomes positive. Due to Bohrs atom theory and the Heisenberg equation for energy Eigenstates it is possible that above the common Fermi level unoccupied energy levels exist, which can be occupied by electrons, which are delivered from the conduction band of the gold contact. The Bohr- theory gives for the surface orbitals around the metal crystals energy levels with an energy separation of 125 meV for Pt , and 65 meV for the gold crystals. These excitonic surface orbitals, also follow the Bohrs atom theory, which means, that only energies exist, which allow full wavelength in the perimenter. The excitonic surface orbital which has a perimeter of 5□□□and higher, however overlap to the ones from the neighbouring crystal. Therefore in the Koops-GranMat® a Bose Einstein Condensate can form, and paired Fermions can transit to Bosons. These Bosons are formed from a surplus of electrons and also a surplus of holes in the C-matrix, and these Bosons can occupy this energy level with very many Bosons in parallel, which also become coherent, like in a Laser. This happens at room temperature.

Superconducting material must be cooled, since the material is built as macroscopic crystals in the chemical composition, and such large crystal areas can support high energy

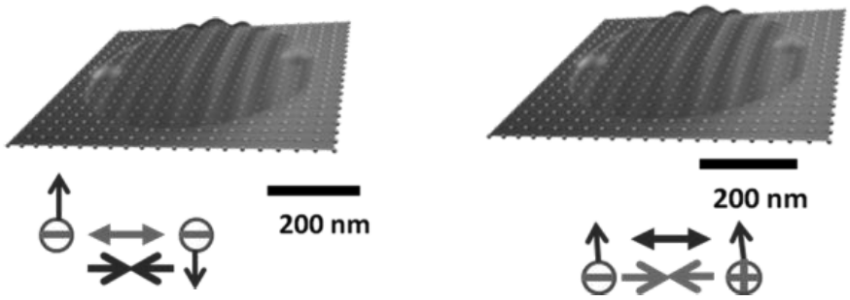

Figure 5: Left: Cooper Pair, 2 charges repell each other, but antiparallel spins contract the charges and balance the Boson. Right: Koops-Pair, electron (-) and hole (+) attract each other, but the parallel spins repell each other and stabilize the Boson to a diameter of 600 nm. The only difference between Cooper-pairs and Koops-pairs is in the signs of the charges or of the magnetic force. There is no change in the law for the forces, but the signs are changed.

phonons, which disturb the balancing forces. This makes it, that only below a jump temperature, the Bosons can be formed and the resistivity becomes zero.

Koops-Pairs are generated due to the difference of the epitaxial growth temperature of metal (ca. 380 to 400 °C) and carbon or Fullerenes (at 150°C). The growing matter is frozen in to a nanogranular metal crystals structure which is embedded in an at lower condensation temperature formed C-Fullerene matrix. Since this formation is generated during the cooling of the nanogranular matrix compound material according to laws of “mother nature” during the deposition process, all the material has the same characteristics, no matter how long the wire is built.

According to Geller [30], a 5 nm diameter silicon ball, which is positioned on a Si metal layer can adopt only 10^{-4} of the heat in the silicon wafer. This corresponds to 2 meV or 23 K. In our case, however, the metal crystal and the substrate are both made from the same metal, but not percolating, but insulated with respect to each other by a Fullerene matrix. Therefore much less than 10^{-4} of the substrate temperature can be adopted. That makes the nanogranular matrix material to be “super cool”, and this characteristic allows the Bose -Einstein Condensate to be built even at room temperature of the ambient material. As experiments showed is the contact resistance quite high, up to MOhm with contact areas of 50 x50 nm². However enlarging the contact area from Koops-GranMat® to the metal reduces the contact resistance, and needs to be designed accordingly to the amount of current which shall be transported from the contact material e.g. Gold (250 kA/cm²) to the Koops-GranMat®. For example, a current of 10 A requires a contact area of 66 µm diameter.

In earlier experiments miniaturized Field-Electron sources delivered electrons at voltages below 100 V and up to 1 mA current. This is of great importance for electronics**,** high speed switching amplifiers, high power sources for IR, THz (up to 6 THz and 1 W) and X-Rays, switchable sources for Brachy-therapy, high current switching, high resolution detectors and sensors for IR, Vis, UV and EUV, detectors for X-ray tomography and X-ray phase contrast imaging.

The construction of self reproducing miniaturized optics for massive parallel particle optics [31] and for the application of scanning- electron- and -ion-microscopes for the semiconductor industry becomes possible**.** With such specially developed adapted multiple beam production machines many novel products can be produced in an economic way, like large area sheets for catalysators, solar cells, long power distributing cables, low voltage high current switches, field-emitter lamps with 65 % efficiency!!, field emitter displays, and many more optical and electronic devices. See the attached patents [32-35].

V. CONCLUSIONS

The applications of Koops-GranMat® can revolutionalize the electronic technology in a dramatic way, with the capability of >100 times of what super-conducting materials can do, but with the advantage to operate at room temperature and having no need for expensive cooling systems.

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