# Applications of nano-composite materials carrying GA/cm² current density due to a Bose-Einstein Condensate at room temperature produced by Focused Electron Beam Induced Processing for many extraordinary novel technical applications.

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# Principle of Fine Line 3-Dimensional Lithography using Electron-Beam Induced Deposition and Etching

TEM 30 to 200 kV
SEM 1 to 30 kV
2 nm spot
1 pA to 10 nA

Cracking of adsorbed molecules by electrons of high energy
**Power density: 60 MW/cm$^2$**, corresponds to
one quarter of the temperature at the surface of the sun, or
Radiation damage dose 100 m off the center of the atomic bomb
-> Deposition of fragments
-> Evaporation of vaporized radicals
-> Evaporation of volatile reaction products of precursor and sample

# Amorphous deposits

Precursor Mo $(CO)_6$

JEOL 840F
Cold W <311>-FE source
20 kV 3 nA

Deposit: Amorphous

Mo, MoO, MoC

Similar from W $(CO)_6$
W, $W_2O_3$, $W_2C$

TEM image
R. Scholz MPI Halle

High extraction voltage needed
due to „large“ tip radius (10 nm)

**Material can carry 160 kA/cm²**

# Metal crystals in a Fullerene matrix

**Dimethyl-Gold-Trifluoro-Acetyl-acetonate**

**Crystal size**
**Au: 3-4 nm**
**I max: 1 Ga/cm²**

**Cyclopentadienyl-Platinum-Trimethyl**
**Pt: 1,8 – 2,1 nm**
**I max: >1 Ga/cm²**

**NGM nanogranular materials**
aggregate during deposition with crystals showing no percolation.

# Giant Current Density in Koops-GranMat® and anomalous high currents explained as a Bose-Einstein Condensate at Room Temperature

| | | |
|---|---|---|
| Review FEBIP | $MA/cm^2$ | Koops, H. W. P.; et al. Jpn. J. Appl. Phys. 1994, 33, 7099-7107 |
| Au/C Field Emitter | 2<br>at tip 1000 | Kretz, J.; Rudolph, M.; Weber, M.; Koops, H. W. P. Microelectron. Eng. 1994, 23, 477-481 |
| Pt/C Field emitter | 2 | Koops, H. W. P.; Schössler, C.; Kaya, A.; Weber, M. J. Vac. Sci. Technol. 1996, B14, 4105. |
| Pt/C Wire arch | 15 | Edinger, K.; Rangelow, I. W.; Gotszalk, T. J. Vac. Sci. Technol. 2001, B19, 2856-2860 |
| Pt/C Fe Emitter | 10 | Floreani, F.; Koops, H.W.P.; Elsäßer, W. Nuclear Instruments and Methods in Physics Research A 2002, 483, 488-492. |
| **Pt/C Fieldemitter** | 100 | J. Sellmair, NaWoTec, communication |
| HTc Superconductors 40 K | | |
| Titan doped $Mg B_2$ | < 1 | P.C. Canfield, D. Budko, Spectrum d. Wiss. Juni 2005 p. 56 |

The slow x,y,t- stream program controlled lithography generates metal nanocrystals with 2 to 4 nm diameter embedded in a carbon matrix material of 1 nm thickness. Spot exposure times needed are 10 msec . For field emitters a large foot area ( >500 nm diameter) must be deposited to allow the hopping of electrons from the connector metal into the excitonic states

# High-power density type resistor

The 40 KOhm depend on the area of overlap of the Koops-GranMat to the Gold-connector **The line resistivity itself is zero !**

Courtesy of NaWoTec

2006

J. Sellmair

Application for Access at KNMF:

# Experimental Method

Measurements by Ankit Machanda PHD Thesis INT 2016

The experiment shall render the conditions to produce Pt/C routinely with FEBIP.

First experiments showed extremely high current conductivity > $10^9$ A/cm²

Figure2: Measurement of Pt/C resistivity (INT)after first set of experiments to optimize settings

# 3-D Lithography uses x, y, and t beam control for Koops-GranMat®.

Lithography systems with GDSII-layout exposure control can not return to a position with a changed dwell time. This requires loading a new pattern file.

**Therefore FEBIP/GDSII deposition systems failed to build Koops-GranMat®**

**Dwell-time > 10 msec**

(courtesy U. Koops)

**Illustration of FEBID / GDSII:**
**M. Huth, Beilstein J. Nanotechnol. 2012, 3, 597-619**
**Stepping time 100 nsec /pitch**
**Dwelltime < 14 µsec**

# Superconductivity – Charges and Spins (Magnons) balance each other

For Superconductivity a **quantum collective wave**, **the condensate,** is formed by a large number of electrons.
The "Pauli exclusion principle" only allows the existence of such a condensate if the waves which compose it are carried by particles called Bosons.
Unfortunately, electrons and holes are Fermions, not Bosons. One energy state can be occupied only by 2 electrons with opposite spin ( Fermi-Dirac Statistics).
**Leon Cooper [of Bardeen, Cooper and Schrieffer] showed, that in order to form a condensate, electrons must form pairs first.**
**Indeed, a pair of electrons, a Cooper pair can form a Boson** ( Maxwell statistics) . In conventional superconductors, the creation of electron pairs and the formation of the Bosons in the condensate happens instantaneously.
Charge: 2, Spin: 1/2 – 1/2 = 0**.**
**The dimension is up to 600 nm diameter**. (Source : CNRS)

**2 Electrons repel each other**
**2 Bohr Magnons (Spin) attract e.o.**

**However that happens only, if no phonons destroy the e-e binding by high temperature lattice vibrations.**

**Therefore Superconductors must be cooled below TC!**

**Superconductivity does not rely on vibrating ion cores of the crystal lattice ( as taught by Cooper) but exists, since 2 electrons with antiparallel spin balance the electric and magnetic forces and form large BOSONS having 600 nm diameter**

D. S. Inosov et al. "Normal-state spin dynamics and temperature-dependent spin-resonance energy in optimally doped $BaFe_{1.85}Co_{0.15}As_2$", *Nature Physics* **6**, 178 - 181 (**2010**)

B. Steele, **"Magnetism glues Cooper-Pairs",** Cornell Chronicle July 28, **2014,**

J. C.S. Davis, Cornell**,** S. Avici et al. *Nature Comm.* 5, Article:3845, 22.5. **2014**

CNRS http://www.supraconductivite.fr/en/index.php supra-explication-cooper, Excerpt from http://www.supraconductivite.fr/en/index.php?p=recherche-#supra-explication, http://www.cyclopaedia.fr/wiki/Cooper_electron_pair

**The classical Bose Einstein Condensate happens at super low temperatures. (**Extract from Wikipedia.)

At zero Kelvin (absolute zero) all molecular motion stops.
Scientists can get a temperature only a few billions of a degree above absolute zero. When temperatures get that low, you can create a BEC ( Bose-Einstein Condensate) as Cornell and Weiman did it with rubidium (Rb) by cooling to 0,5 µK. The group of rubidium atoms sits in the same place, creating a "super atom." There are no longer thousands of separate atoms. **All their highest orbitals overlap** which gives the condition that electron and holes can form Bosons and all occupy the same level. **Their motion becomes coherent**

**Electrons and holes having parallel spin in an excitonic condensate level form also pairs, if the material is very cold** ( Boer et al. **1962**)

**Koops-Pairs ( Electron and hole) are observed at room temperature since 1994.**
The nanogranular compound material is **"frozen in"** by epitaxial crystallisation of metal nanocrystals at 400 °C in a fullerene matrix at 150°C and cooling down to room temperature 20°C .
During the FEBIP deposition process a power density up to 60 MW/cm² is used .

# Bohr's stability conditions employed to orbital Eigenstates above the crystal surface gives a much smaller level splitting than the bandgap is in semiconductors ( H.W.P. Koops, U. Koops 2009)

In Koops-GranMat one nano-crystal is composed from ca.1000 atoms in a single crystal form. The crystal is embedded in a Fullerene matrix which is also geometry quantized.

**Overlapping Excitonic surface orbital electron states form the condensate .**

**Wavelength of electrons at Fermi level is ~ 2 nm (Pt/C)**

Bohrs Eigenvalue in circular states at the crystal rim :
Surface Orbital (n λ), n= 3 at 2 nm diameter crystals

**Overlapping surface orbital states n= 5 λ form BEC condensate**

**Nanocrystal Pt/C 2nm or Au/C 4 nm diameter, separation 1 nm**

**The energy difference between excitonic levels is 125 meV ( Pt/C) and 65 meV (Au/C)**

# **Koops-GranMat® is** a cluster of excitons at room temperature, explained by Bohr's atom model. It contains **Koops-Pairs** in a **condensate** formed by overlapping excitonic surface states

200 nm

**2 charges – Electron, + Hole attract each other**

**2 Bohr Magnons (Spin) repell each other**

**The Maxwell energy distribution of charges in thermal distribution in the contact area supplies the current.**
**If the contact area is not large enough, the Gold contact area will melt**
**( as observed several times)**

# All Bosons are coherent

Investigating field electron emission from such materials Takai and Murakami in 2008 found a coherent emission from several sites , indicated by Young's interference patterns

Fig: a: Pt/C deposit , b: Tip after RIE etching, right: fringe-like electron-emission pattern observed in field emission in the far field from a Pt field emitter fabricated by electron-beam-induced deposition.

K. Murakami, F. Wakaya, and M. Takai, "Observation of fringelike electron-emission pattern in field emission from Pt field emitter fabricated by electron-beam-induced deposition,"
J. Vac. Sci. Technol. B, vol. 25, no. 4, pp. 1310-1314, **2007**

**Bose and Einstein published the formula for a Temperature of a Condensate in 1929** depending on the particles density and their mass.
With this formula one obtains for Rubidium atoms BEC at 0,5 µK. For 2 d double quantum wells of of Butov and Remeika: 50 mK, and for Pt/C-Koops-GranMat® 300 K, as it was observed

H. Koops, H. Fukuda, "Giant current density via indirect exciton orbit overlapping in polarized nanogranular materials" J. Vac. Sci. Technol. B 33, 02B108 (2015), http://dx.doi.org/10.1116/1.4904732

# Electron- Hole Excitons are temperature dependent

J.M.Blatt K W Böer Werner Brandt stated in 1962 **Electron - Hole - Excitons, can only be investigated in very cold materials**
(John M. Blatt, K. W. Böer, and Werner Brandt ,“ **Bose-Einstein Condensation of Excitons**” Phys. Rev. 126, 1691 – Published 1 June **1962.**)

**Cold materials contain no phonons!**

**Either you cool the material or you use only nm size crystals!**

H. Lamb, Proc. London Math. Soc, 13, 187 **(1882)** stated:
**In Crystals smaller than 5 nm diameter, phonons cannot exist !**

Michael R. Geller, and co-workers published:“Theory of electron–phonon dynamics in insulated nanoparticles” Physica B 316–317 430–433 (2002). They stated:

**Nanocrystals with dimension smaller than 5 nm can only adopt phonons with < 2 meV or 23 K!**

**This statement lifted the curtain for the existence of electron-hole pairs in Koops-GranMat® at room temperature.**
Here Crystals are smaller than 5 nm and are frozen in into a Fullerene matrix.

**The material is Super Cold at room temperature**

The **low bandgap energy** in the Koops-GranMat® emitters can be explained by low energy difference of the excitonic surface orbital states.
The high brightness of the emission is given by the huge Boson number in the outer excitonic surface orbitals forming the condensate level.
Although these high density electrons produce the electric field outside the tip, the field inside the tip is normalized (shielded) by their counterpart holes in the nano-particles at the emission site.
Photo-induced emission current is observed at low extraction voltage, since photo-irradiation elevates electrons to higher exciton energy levels.
The required energy is 125 meV (Pt/C)
And 65 meV (Au/C)

**Overlapping higher excitonic states allow free motion of electrons and holes, Bosons, especially under the influence of an external electrical field E with a gradient**

# Nanocrystalline compound materials absorb light

Room-Temperature EBID NGM IR-Vis- THz detector

Metal single crystals in a carbonaceous matrix (Fullerenes) show high VIS light absorption

**Field emission characteristics of NGM Diode under red light illumination (1,3 eV)**

**Pt/C NGM photocell = 72 mW/cm²**
**Typically Si solarcell = 20,4 mW/cm²**
**Experiment not optimized**

**Pt/C :120 meV are needed for the excitation of one electron:**
**This means 1 red quant of 1300 meV can free 10 electrons!**
**Au/C : needs 60 meV to free 1 electron (1 Quant: 20 electrons !)**

H.W.P. Koops, A. Kaya, M. Weber, "Fabrication and Characterization of Platinum Nanocrystalline Material Grown by Electron-beam Induced Deposition", J. Vac. Sci. Technol. B 13(6) Nov/Dec (1995)

# Applications of Koops-Gran Mat®

**Electrons in vacuum are much faster than electrons in semiconductors: K. Shoulders 1956**

**This leads to Micro-tube applications in a miniature vacuum system with Orbitron pump.**

**Field emitter tips from Koops-GranMat® can deliver up to 1 mA , which is supplied from a gold conductor at the foot of the Field-emitter in a square area of 660 nm diameter.**

**Vacuum diodes and micro triodes of 1 µm length with a cathode to grid capacity of 240 aF allow operation as switching amplifiers above 3 GHz up to 6 THz with a high S/N > 6**

**Field emitter arrays can switch KA with 70 V using cm² large devices for power distribution**

**High current switch: 1 KA/ 0,7 x 0,7 mm² by an array of 1 Mio tips with 0,66 µm separation**

**Current transport of 20 A per fiber with a current density of 1 GA/cm² allows coating a glass or plastic fiber of 100 µm diameter with Pt/C and a layer thickness of 50 nm.**

**Thin large area deposited layers can serve as solar energy converters with a > 3 times higher efficiency than Silicon or other solar cells of today. Night vision with Near infrared detectors, without cooling is possible.**

**A 1 Watt Dynatron with 1 to 6 THz power sources enables effective homeland security**

# 2 Needle prober Fe-experiment with 10 emitter tips
# Height of left needle anode is 1 µm above the emitter array

120 µA = 0.12 mA current is emitted from 10 tips with 20 nm rod diameter
Current carrying area 400 nm² = $4.10^{-12}$ cm² at the 5 footpoints of Pt/C
Current density: 0,48 GA/cm² = 480 MA/cm².

The gold layer can carry only 240 kA/cm²!! :

This results in Explosion of the molten Au pad

Explosion of the molten Au pad

# Micro-Triode a THz Switching Amplifier

The mean free path between air molecules at 1 bar is 0.3 µm.
A microtriode of 0.3 µm length does not require a vacuum pump, since there is ultra high vacuum between the gas molecules.
The cathode-grid capacitance of a microtriode is in the range of fF.
Such a system can switch and amplify in the upper 100 GHz regime.

Schematic and constructed microtriode

HansWP Koops
HaWilKo GmbH

# Schematic of a stand-alone Device with Orbitron pump and Bayard Alpert Vacuum Measurement for the operation of a Dynatron-Oscillator with THz-sender for 1 W

# Layout of the THz IR radiation source with Dynatron Oscillator

Two free beam micro-triodes are controlled by the oscillator voltage, but with by C12 reversed voltage with opposite phase and beam direction. They emit electron pulses as THz emitters inside a resonator.
The IR radiation emitter aperture matches the travel of the electron pulse, which is acellerated to the voltage A, in ½ period of the oscillator voltage

Fabrication by lithography and EBID with 0D-material (HaWilKo Patent 2010).

# Characteristics for IR-sources in the 0.2 to 10 THz range

**Stability requirements of electrostatic elements limits the usable voltage in miniaturized beam sources**

**Experimentally 100 V can be used with metal line distances as small as 1 µm.**

**Electrons reach by acceleration to 100 V a speed of 6 µm / psec.**

**The oscillator voltage cuts the DC beam in charge pulses of half a wavelength in length, which corresponds to half the time span of a period.**

**For example: at 500 GHz the pulse length is 1 psec.**

**To clearly separate the two electric fields, each beam must pass an aperture of 6 µm diameter located in the center of the resonator through which the electric and the magnetic field of the Hertz Dipole radiation is delivered into the resonator having a dimension of half a wavelength, which is 300 µm at 500 GHz.**

| Frequency THz | Wavelength µm | Resonator E0 µm | 1 Electron pulse at 300 V travels µm = IR window µm | S/N at 1 mA DC |
|---|---|---|---|---|
| 0.2 | 1500 | 750 | 45 | 173 |
| 0.5 | 600 | 300 | 18 | 77,5 |
| 1 | 300 | 150 | 9 | 54 |
| 5 | 60 | 30 | 1,8 | 24,6 |
| 10 | 30 | 15 | 0,9 | 17 |

# Conclusions

- Metal nanocrystals with 2– 4 nm-diameter packed in a Fullerene matrix are produced by FEBIP from organometallic precursors using slow step deposition and sequential epitaxy
- Electrical resistance measurements show no line resistance but a contact resistance which depends on the contact area
- Using Bohr's Atom model around the Pt crystals overlapping surface orbital Eigen-states were found, which overlap to similar states of neighboring crystals and form a Boson- condensate according to Bose's and Einstein's theory
- This transition of electrons and holes from Fermions to Bosons by (Koops-Pairs) allows to explain the Hyper Giant Conductivity Observed at Room Temperature in Metal/Carbon compound materials
- The theory of Bose renders the temperature for the formation of the Bose - Einstein condensate for Rb: 0,5 µK, 2D Litho: 50 mK and Koops-GranMat®: 300K, as they were observed
- **Koops-GranMat® requires no cooling.**
  **It can revolutionize electronics energy transport and photonics**

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„Imagination is more important than knowledge.
Knowledge is limited, imagination embraces the world". AE

**Thank you for your attention**