High field induced deposition of nanogranular materials for electron sources

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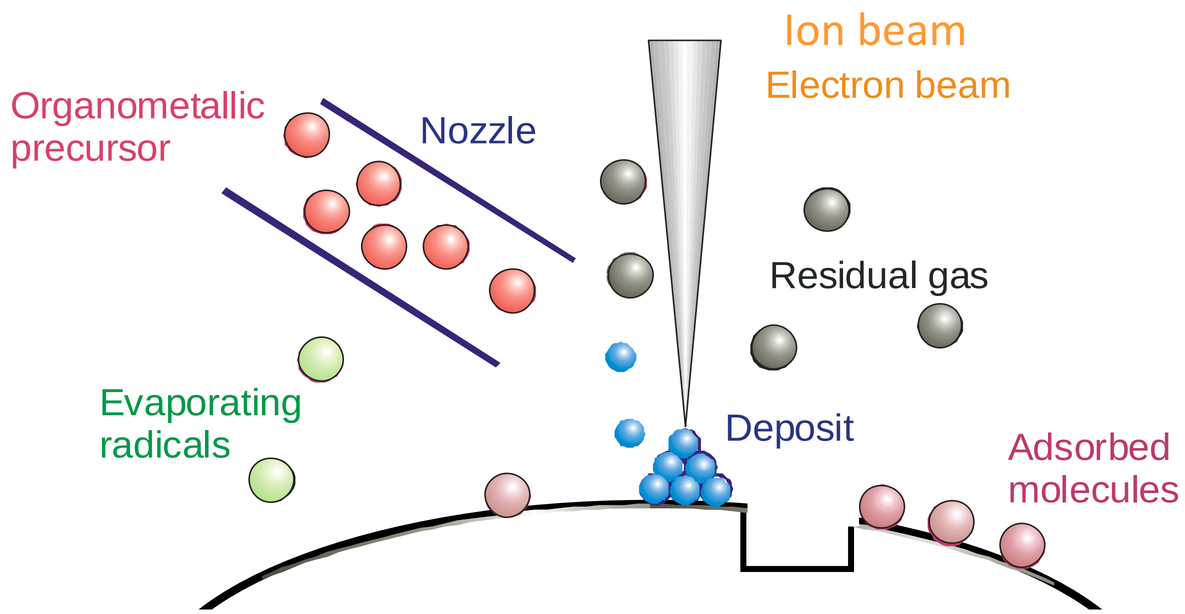
Darmstadt, **Art Nouveau** Centre, brought a new arts at Expo 1902, 1904

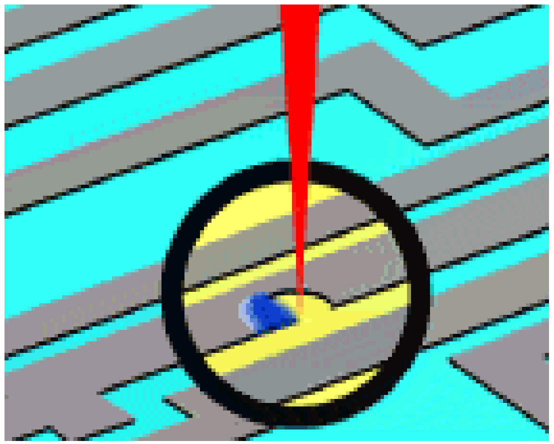
At German Telekom Research Centre FTZ in 1994 a **new material** was discovered:

It can replace cooled superconducting materials in present applications and will revolutionize electronics, THz switching, photonics, and energy transport

Magnetism glues Cooper-Pairs and Koops-Pairs: B. Steele, Cornell Chronicle July 28, 2014, J. C. Séamus Davis, Cornell, S. Avici et al. Nature Comm. 5, Article number:3845, 22. 5. 2014D. S. Inosov et al. NATURE PHYSICS VOL 6 , 178 March 2010

Electron beam induced deposition and etching is used to produce Koops-Pairs in Koops-GranMat® using 3 - d Nano Printer





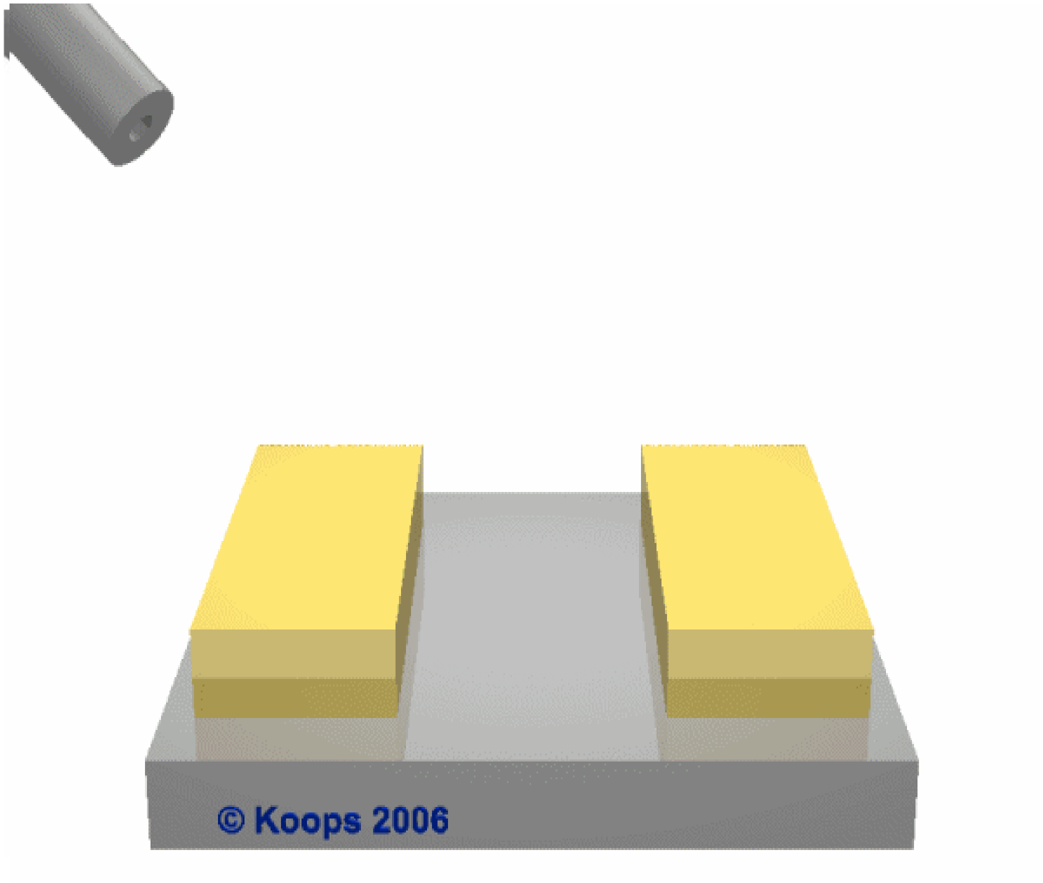
Technical application
Electron beam photo-mask repair: NaWoTec / Zeiss

- Adsorption of precursor molecules
- Exposure with focused charged particle beam (60 MW/cm^2)
- Pixel exposure dwell-time must be > 10 msec
  - Reaction and Immobilization of Precursor → Deposition
  - Reaction with Substrate and Volatilization → Etching

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 find Koops-GranMat®



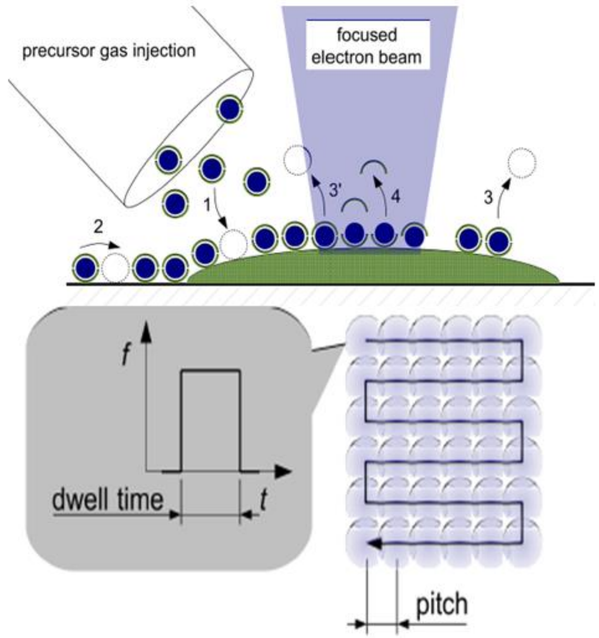


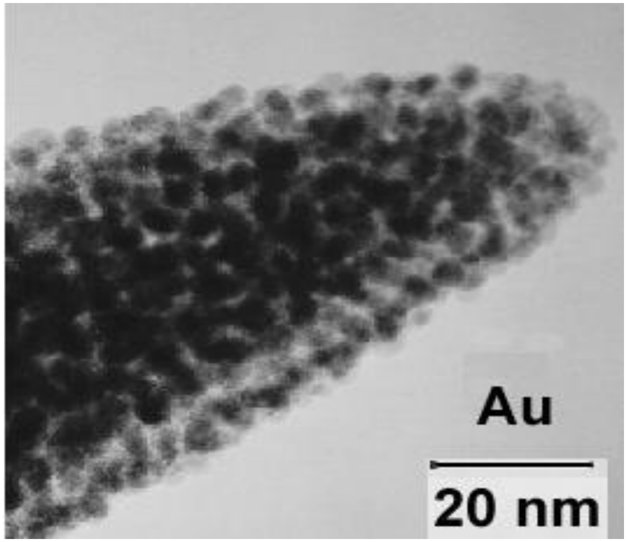
Illustration of FEBID / GDSII:
M. Huth, Beilstein J. Nanotechnol. 2012, 3, 597-619
Stepping time 100 nsec /pitch
Dwelltime < 14 µsec

(courtesy U. Koops)

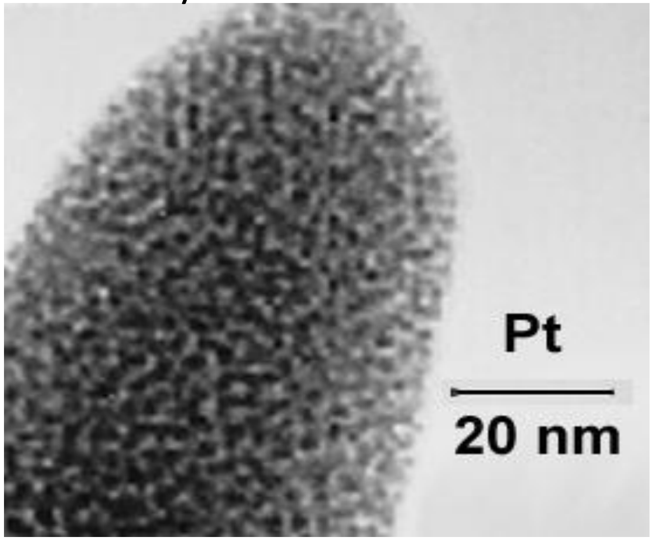
Koops-GranMat® Metal crystals in Fullerene – C -- matrix

Nanogranular material

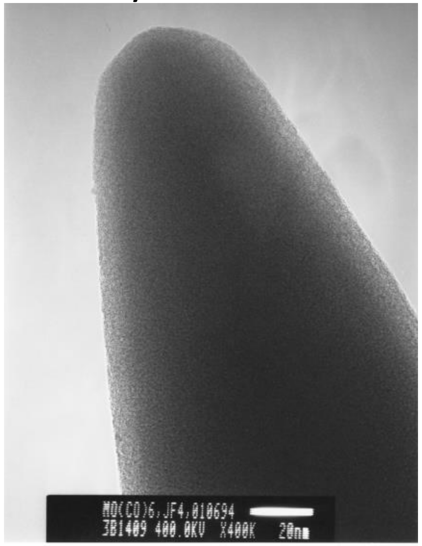
Dimethyl-Gold-Trifluoro-Acetylacetonat



Cyclopentadienyl-Platinum-trimethyl

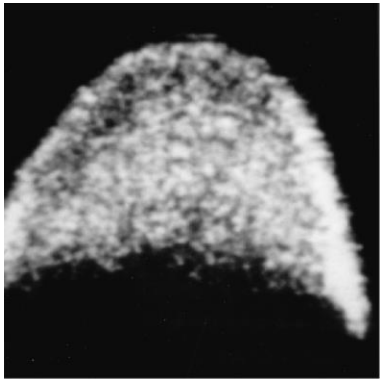


Molybdenum Hexa-carbonyle

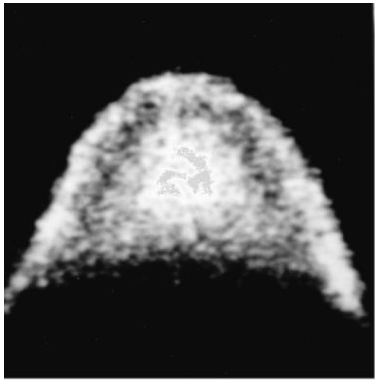


The ratio of refresh-time to dwell time renders a less dense deposit, and no longer a condition to form Koops-GranMat®

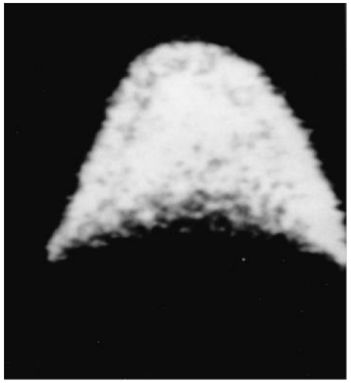
pulsed 0.2 t- on



pulsed 0.5 t-on



continuous beam



Motivation: Novel nano-granular matrix materials for FE- Nanofabrication are needed

Characteristics: High current density (GA/cm^2) at 1 mA in a wire of 70 nm diameter, at room temperature without thermal destruction is required.

Solution: Field emitter tips from materials with Bose-Einstein Condensation at Room temperature deliver at >10 MeV/cm field strength at the tip of 10 nm radius at < 70 eV extraction voltage from a spot of 2 nm diameter a current density up to 3 GA/cm^2 in a total current of 1 mA .

Material: A sinter process under e-Beam exposure renders metal nanocrystals with a diameter of 2 nm (Pt/C) or 4 nm (Au/C) with 1 nm distance which are embedded in a fullerene matrix. Pt/C as Au/C form a common Fermi energy level. Metal: negative charged, C: positive charged. Electrons and holes form Koops-Pairs. For geometry reasons, the crystals cannot transport high phonon energies, but only <2 meV, which corresponds to < 23 K, as it is required for High TC Superconductors.

New Name: Koops-GranMat®, is composed by Koops-Pairs, formed by excitonic energy level electrons (-, Spin up), and holes (+, Spin up), which form immediately Bosons (Charge 0, Spin 2), and are coherent.

Focused Electron Beam Induced Processing (FEBIP), (0.5 nA, 20 kV, spot 2 nmØ) produces nanocrystalline deposits (percolating Metal-, -oxide, –nitride crystals in a mixture)**,** or **Metal single crystals in Fullerene – C – matrix from Cyclopentadienyl-Pt, or Au-tri-fluoro-acetylacetonate at a Rate of 1 µm / min @ 100 Monolayers/sec molecule supply rate. These compound materials are name protected as Koops-GranMat®**

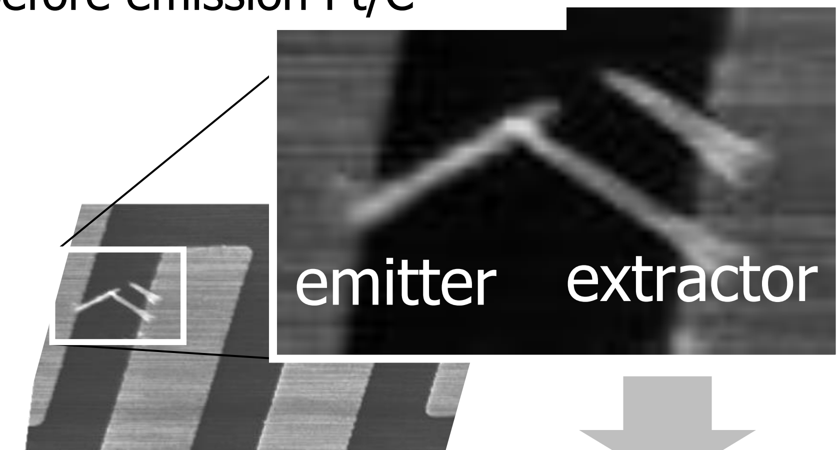
The deposit **– Metal and Carbon crystals percolate and form a common Fermi level** at ca. 5 eV. This charges Pt (Work function W= 5,1-5,9 eV) or Au negative and the C-matrix positive (W= 4,81 eV). Contact : Au (Work function (W) 4.9 eV);

Excitonic surface orbitals around the Pt-crystals overlap and form the one energy level throughout the material needed for a Bose-Einstein Condensate (BEC).
Electrons in the Pt excitonic surface orbitals and holes in the C-matrix, having parallel spin can form Bosons (Koops-Pairs: e-,h+, parallel spin) and occupy the BEC with millions of Bosons, like in lasers.
Koops-pairs are similar to Cooper pairs, but have just reversed polarities.
This leads to Hyper Giant Conductivity Observed at Room Temperature.

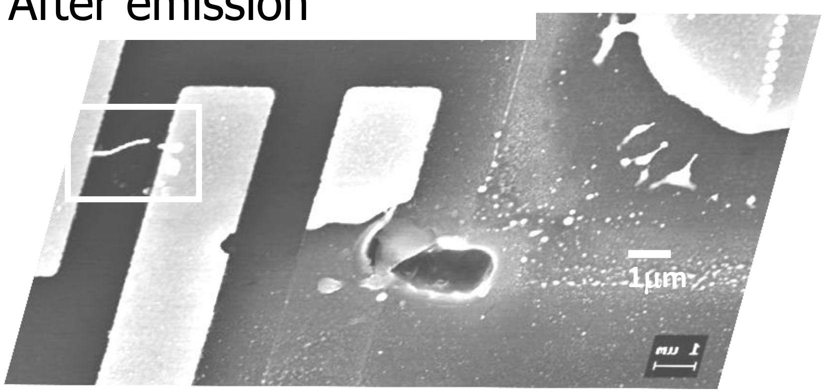
Crystals of < 4 nm diameter result in a geometry quantization for acoustic phonons with energy < 2 meV (23 K). The material is super-cool, which allows the Bosons

Giant emission current is obtained in vacuum electronics device made from Pt/C Koops-GranMat®. FN-plot shows field emission

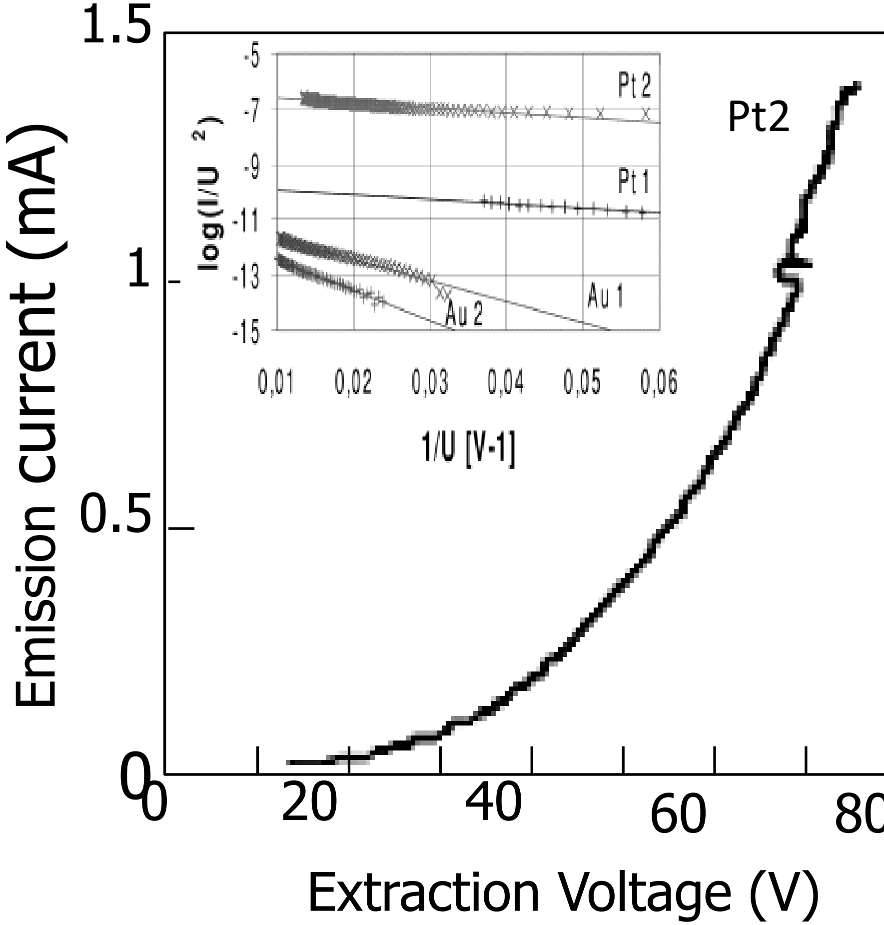
Before emission Pt/C



After emission



Power density at impact 2 10^8 W/cm²

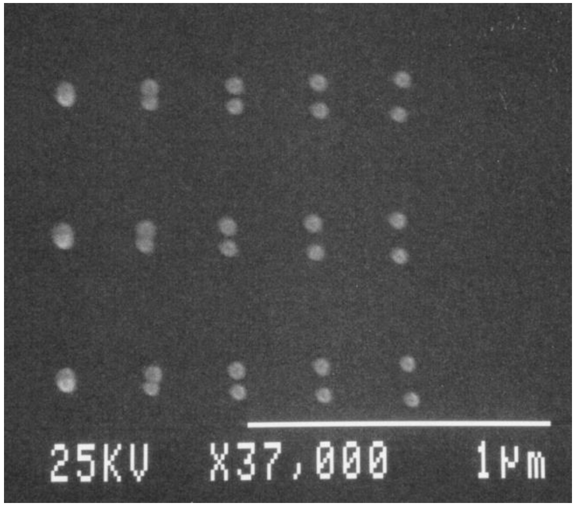


F. Floreani et al. Microelectronic Engineering 57–58 1009 (2001)

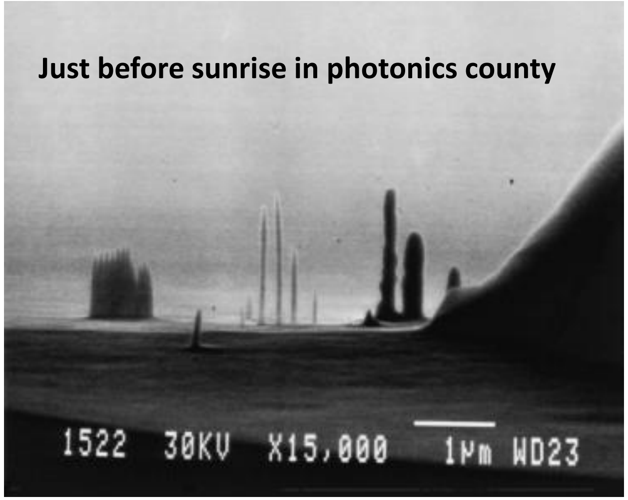
Experimental evidence of the repeatable production of Koops-GranMat® over the last 20 years

Review FEBIP	MA/cm²	Koops, H. W. P.; et al. Jpn. J. Appl. Phys. **1994**, 33, 7099-7107
Au/C Field Emitter	2 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 wire	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

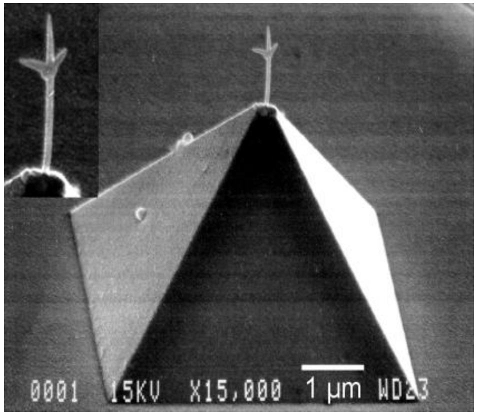
Applications



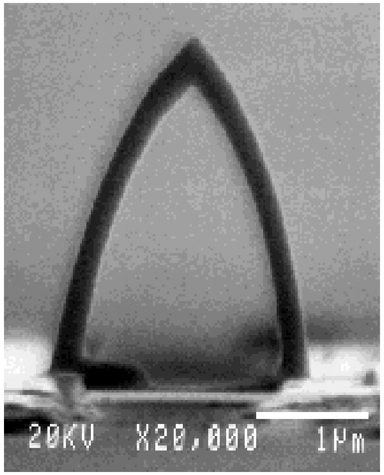
Dots as Calibration pattern



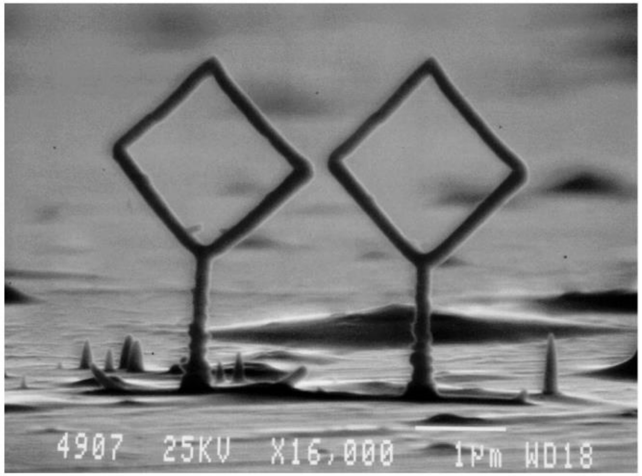
Rods for photonic Crystals



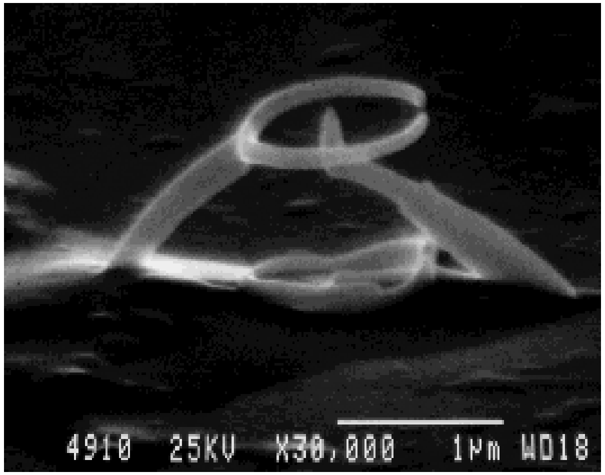
STM 3- Point tip for AFM sidewall probing



Resistive arch



IR antennas



Electron source with low capacitance (24 aF)

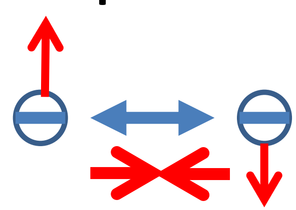
H.W.P.Koops et al. 1997 at Telekom Research Centre, FTZ Darmstadt, Germany

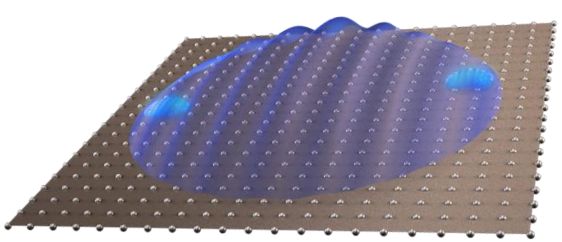
Superconductivity – Charges and Spins (Magnetons) balance each other

(D. S. Inosov et al. "Normal-state spin dynamics and temperature-dependent spin-resonance energy in optimally doped BaFe1:85Co0:15As2" Published ONLINE : 20 December 2009 DOI: 10.1038/NPHYS 1484, and NATURE PHYSICS Vol 6 , 178, March 2010 and S. Avici et al. Nature Communications 5,Art. Nr. : 3845,22.5.2014)

For Superconductivity a **quantum collective wave**, **the condensate,** is formed by a large number of electrons. A **pair of electrons, a Cooper pair can form a Boson** (Maxwell statistics) . The "Pauli exclusion principle" only allows the existence of such a condensate if the waves which compose it are carried by particles called Bosons. In conventional superconductors, the creation of electron pairs and the formation of the condensate happens instantaneously.
Charge: 2e, Spin: 1 – 1 = 0**. The dimension is up to 600 nm diameter**. (CNRS)

2 Electrons repel each other,
2 Bohr Magnetons (Spin) attract each other
However that happens only,
if no phonons destroy the e-e binding
by high temperature lattice vibrations.
Therefore Superconductors must be cooled below TC!





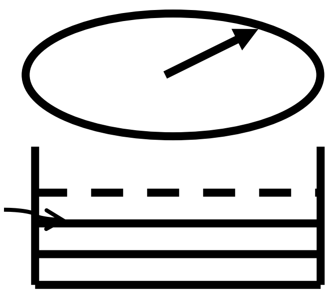
Cooper-Pair

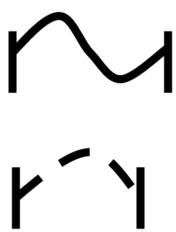
200 nm

Molecular surface orbital computation can handle today ca. 300 atoms, but not >1000 per crystal , nor the interaction of > 3000 metal atoms with an intermediate carbon phase. Therefore a **semiclassical approach** is the application of **Bohr's atom model** to explain excited surface Orbital states.Nanocrystal diameter Pt/C: 2 nm or Au/C: 4 nm

Overlapping electron states allow the formation of a Bose-Einstein Condensate, having 1 common energy state throughout the material

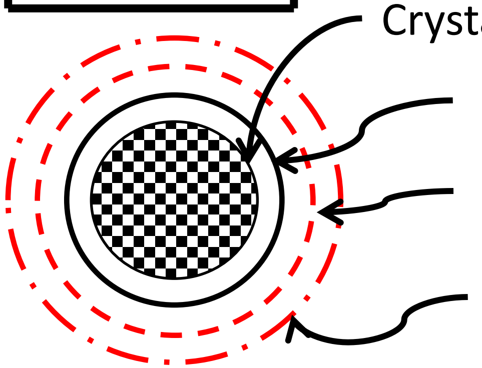
Electrons (-,↑) and holes (+,↑) combine to a Boson: (Charge 0, 2 magnetons, strong dipole moment), and leave the Fermi-Dirac statistics (only 2 electrons per energy state), to form **Bosons following Maxwell statistics, allowing unlimited number of now coherent Bosons in the state.**





Bohrs Eigenvalues for circular Surface Orbitals (n λ)

Bohr's Eigenvalue transmission states(mλ/2)



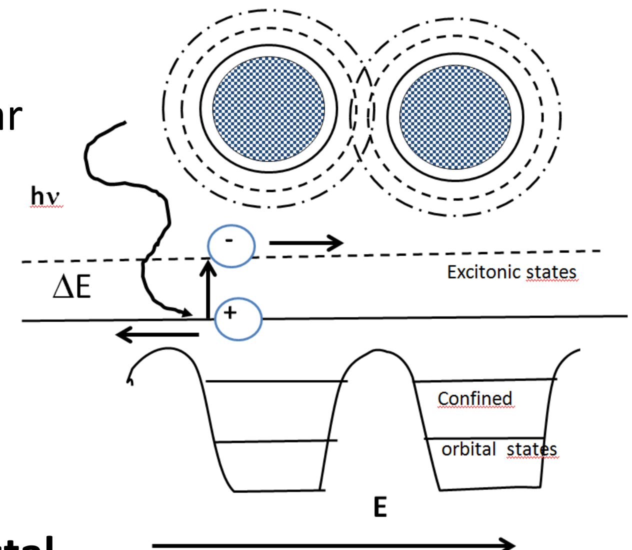
Crystal surface n = 3, λ= 2nm

n=4 **exitonic orbital, ΔE 125 meV**

n=5 overlaps to n=5, 6 of next crystal

this forms the energy level for the **condensate**

n=6

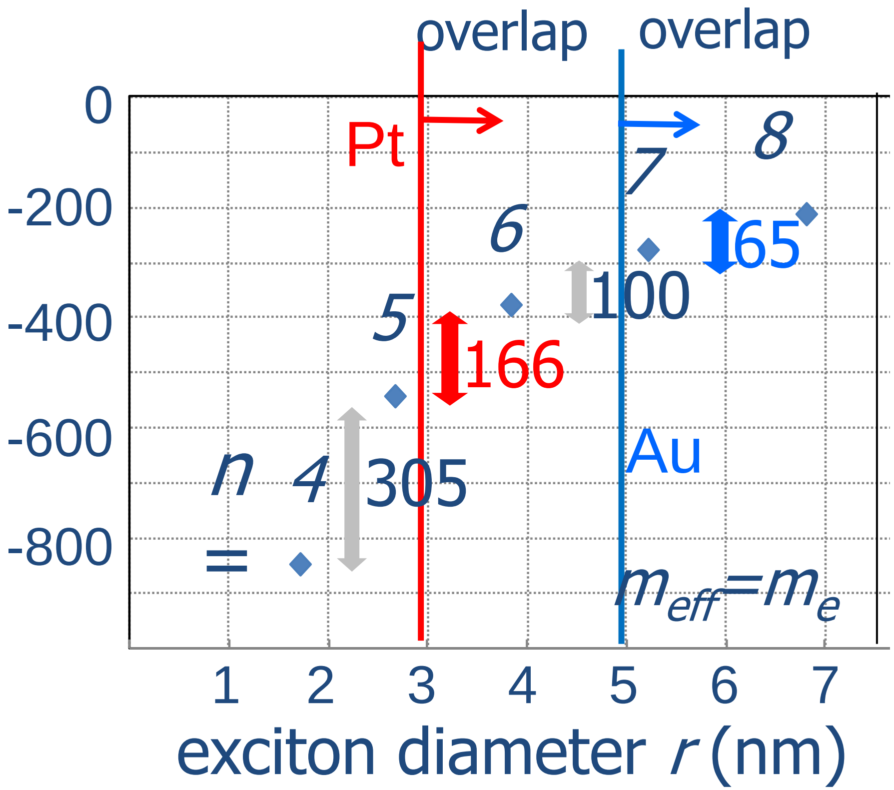


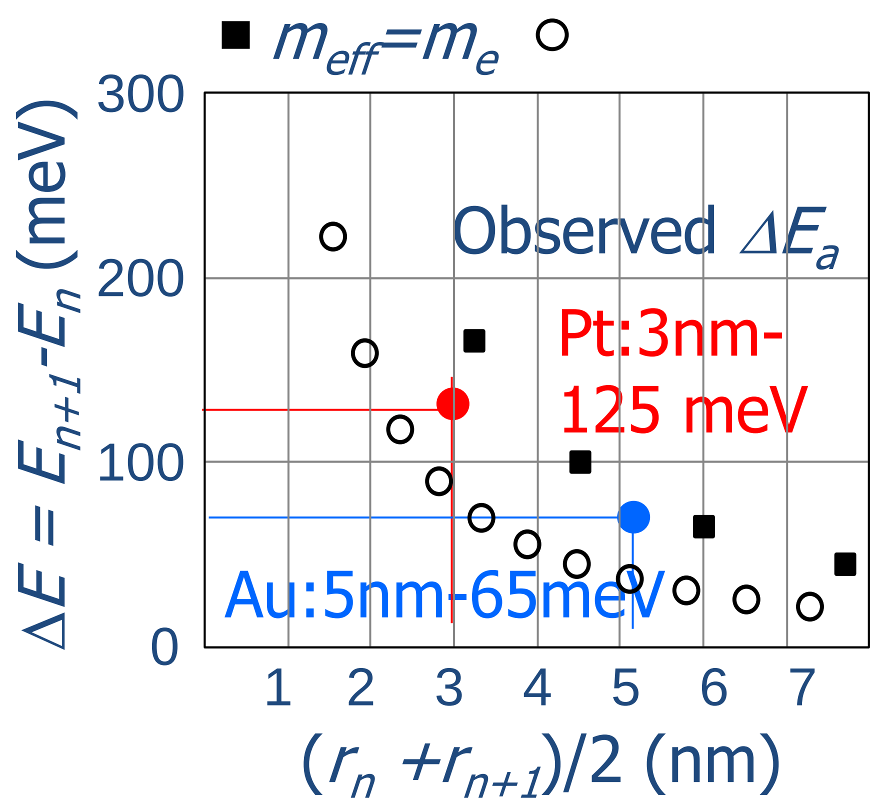
Approximated with Bohr's model

Predicted ΔE between confined and overlapping orbits agree with observed ΔEa

Bohr's model

Bohr radius: $r = \varepsilon n^2 h^2 / (\pi m_{eff} e^2)$ Energy level: $E = - m_{eff} e^4 / (8 \varepsilon^2 n^2 h^2)$



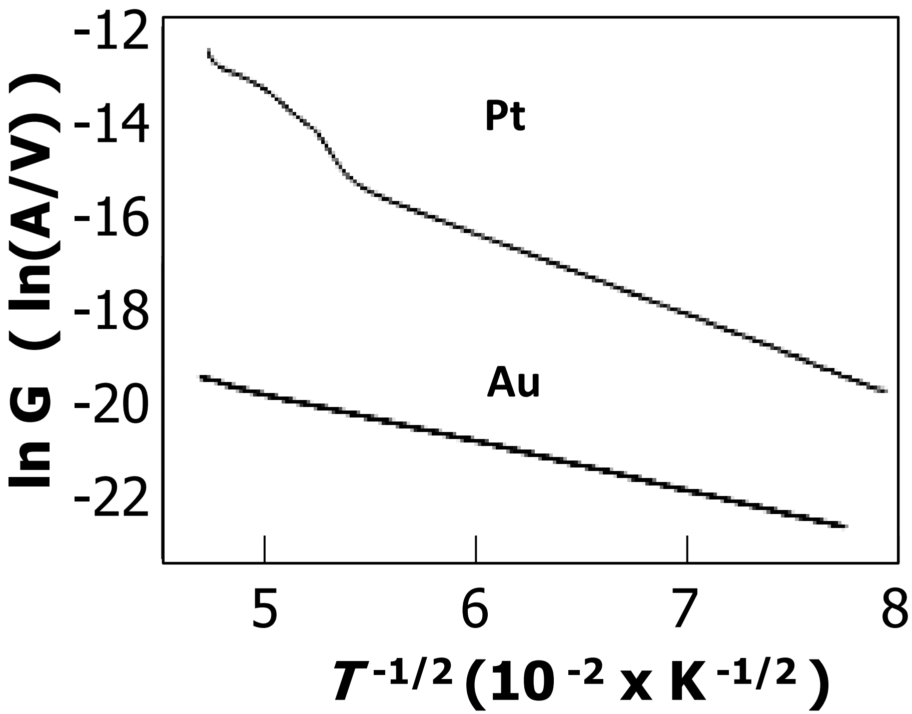


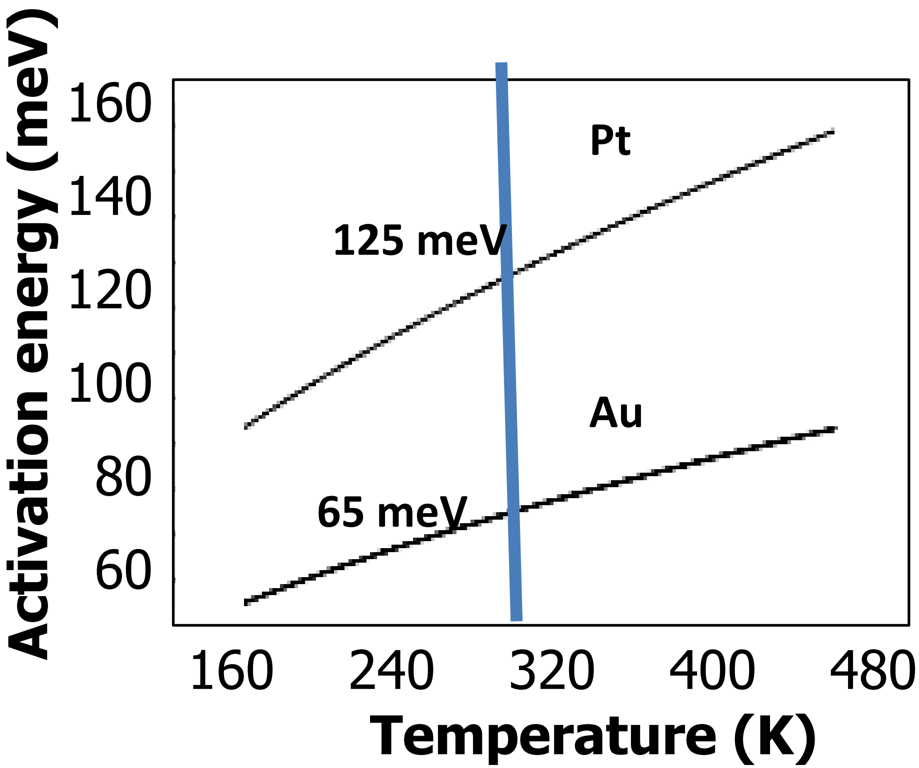
Koops-GranMat®   Pt/C, Au/C

Conductance G has a Negative Temperature Dependency due to **Hopping** in the contact area of the gold line to the deposited line

Activation energy

(Pt/C: ~125meV, Au/C: 65 meV)
RT



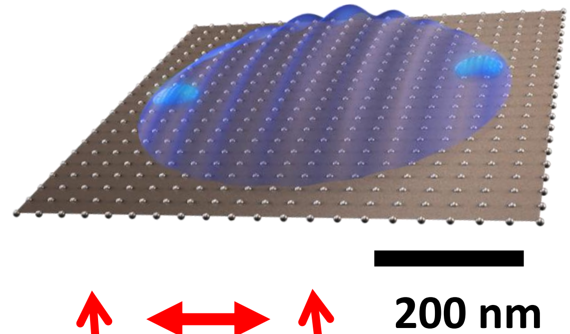


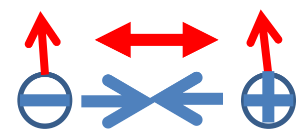
H.W.P. Koops, A. Kaya, M. Weber J. Vac. Sci. Technol. B 13(6) Nov/Dec (1995) 2400-2403

Bose Einstein Condensate (BEC)

In BEC 2 Charges Electron – and Hole + attract each other, 2 Bohr Magnetons (Spin) repel each other

However the laws for repulsion or attraction stay the same, just the sign changes, therefore **the sizes remain the same for BCS or BEC Bosons.**





Such a Boson, however, has a strong dipole moment. The extraction voltage forms an electrostatic field with a field gradient.
Dipole moment times field gradient represents a force on the dipole and moves the charged Koops-Pair
This moves the Boson until one part feels the field gradient at a FE-tip, and then the Boson decays, and releases the electron. The hole immediately catches the next electron and forms again a Boson. Since Bosons move without friction inside the Koops-GranMat® a huge current is flowing, as experimentally measured:
1 mA per emitter, at > 3 GA/cm^2 current density at the tip.

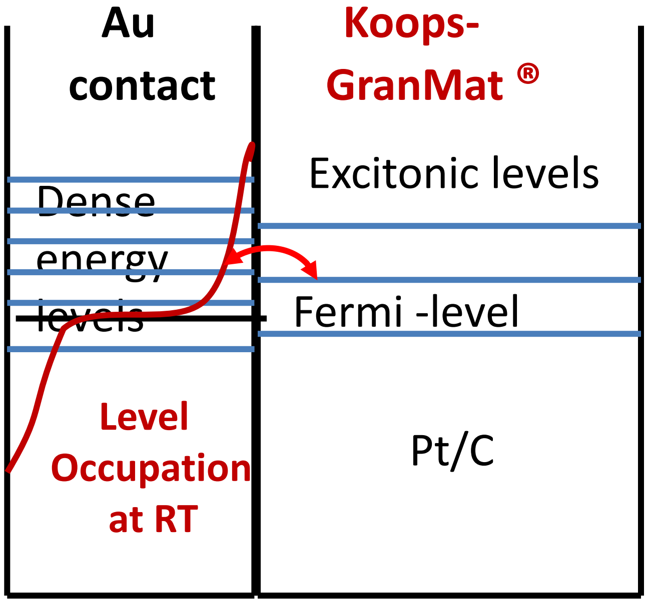
The calculated temperature for the Bose-Einstein-Condensation is higher than room temperature (300K) , according to Remeika's Theory (2012)

Koops-GranMat® : a cluster of excitons, explained by Bohr's atom model

Due to Maxwell – Boltzmann temperature distribution of electrons in the dense states of the conduction band, electrons in the Au contact metal can have at room temperature a high energy and supply those to 5~6 λ Exciton orbits in Pt., and to the 7/8 λ exciton orbits of the gold crystals.

Since the excitonic energy levels in the BEC material are overlapped, also higher excited electrons can be in the higher levels even more overlapped. These levels allow to form a Condensate, and contain BOSONS from electrons and holes, having parallel spin, and contribute to the current carrying characteristics.

The Maxwell energy distribution of charges in thermal distribution supplies the current. If the current in the supplying contact area is not large enough the Gold contact area will melt.



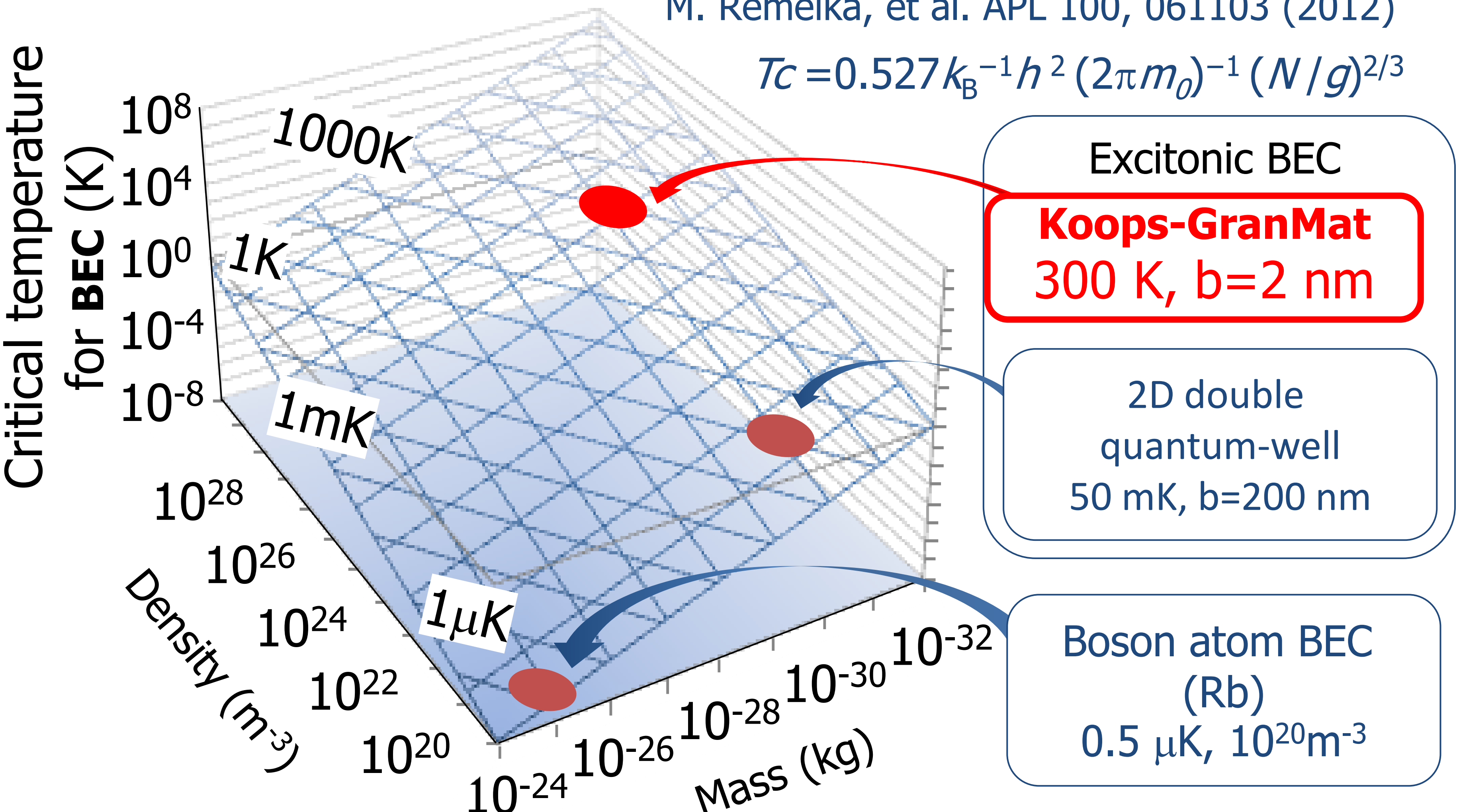
Under an externally applied electric field with a gradient inside the material, the Bosons are moved to the contact, where they decay into electrons and holes. This separation of electrons and holes **results in current transport and coherent emitted electrons**

Quantum Condensation Temperatures calculated after Remeika

Critical temperature calculated for BEC in Koops-GranMat® gives **~ RT** because of high density and small mass of electron

M. Remeika, et al. APL 100, 061103 (2012)

$$Tc = 0.527 k_B^{-1} h^2 (2\pi m_0)^{-1} (N/g)^{2/3}$$



Hans W.P. Koops
HaWilKo GmbH

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.

Field emitter tips from Koops-GranMat® can deliver up to 1 mA , which is supplied from a gold conductor 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 cm^2 large devices for power distribution

High current switch: 1 KA/ 0,7 x 0,7 mm^2 by an array of 1 Mio tips with 0,66 µm separation

Coating a glass or plastic fiber of 100 µm diameter with Pt/C and a **layer thickness of 50 nm** allows to **transport current** of 20 A per fiber with a current density of 1 GA/cm^2.

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.

These layers can also serve as NIR infrared detectors, without cooling.

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 an approximation like Bohr's Atom model around the Pt crystals overlapping surface orbital Eigen-states were found, which overlap to similar states of neighboring crystals and allow 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 Remeika 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® is capable to revolutionize electronics and photonics

Acknowledgments

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

Thank you for your attention