Hypergiant –conducting nanogranular compound materials, as IR-photon detectors forBoson-current transport at room temperature with GA/cm² current carrying capability

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I. Introduction

In vacuum nano electronics different electron sources are used. They usually consist of hot or cold zirconia, tungsten, or carbon tips, the latter being in diamond or nanotube form. Electron sources of a special composite of precious metal crystals, which are embedded in a fullerene matrix, were first developed in 1992 at the Research Institute of Deutsche Telekom FTZ in Darmstadt, Germany. With those very high emission current densities were achieved and were brought to applications. Outstanding room temperature conductivities were achieved with these nanogranular composite materials, and are presented here along with a model to explain the measured data,

II. Currents from conventional emitters

Typical metallic or even single carbon (carbon nanotube) emitters only start their current field emission above several 100 V and never reach emission currents of mA. Although the geometries of these conventional and the new emitter tips are very similar, in the case of pure platinum or carbon spikes, the work function for platinum of the electrons is 5.4 eV and for carbon 4.8 eV. Therefore, very high extraction voltages are always required with these field emitters, and the maximum emission currents are at 10 µA for Pt. Carbon nanotubes reach 0.1 µA, since they vaporize their carbon atoms from the tip due to the ohm resistance of the nanotube [[1]].Also, metal field emitter tips do not reach current emissions greater than 10 µA due to the internal resistance of the wires. These then melt due to the high resistance at elevated temperature. Successful deposition experiments arrive with carbonyls of the metals, preferably tungsten hexa-carbonyl. However, these compounds showed emissions as known from standard field emitters, i.e. they gave a maximum emission current of 10 µA, and required high extraction voltages of> 1 kV, see also [[2]].

III. Nanogranular composites for high-performance electron sources

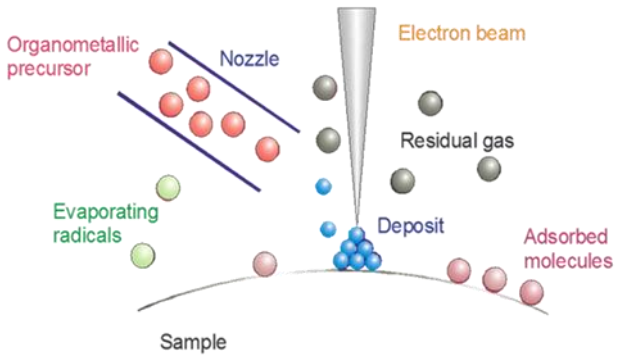

Figure 1: Deposition of emitter tips using nano-granular compound materials.

Organometallic compounds have been used to prepare the electron sources described above.For this purpose, the selected organo-metallic materials were supplied by commercial manufacturers[[3]], which have a low vapor

pressure at room temperature. They were supplied from a reservoir in a molecular beam to the deposition site by means of a cannula, see figure 1. The nanogranular emitters grow due to

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theelectron scattering in the heavy metals to a relatively blunt tip of about 10 nm radius of curvature. The material is not monocrystalline - as in conventional emitters - but grows under the high dose of the primary beam to metal crystals of 2 to 4 nm diameters, which are embedded in a fullerene crystal matrix having 1 to 2 nm diameters. During the growth the metal nanocrystals solidify at 500°C and are encapsulated by the fullerenes at 150 °C, see figure 2.

The tip material is polycrystalline. It is composed of very small metal crystals, each containing about 800 metal atoms embedded in an enveloping phase of fullerenes (Bucky-balls).

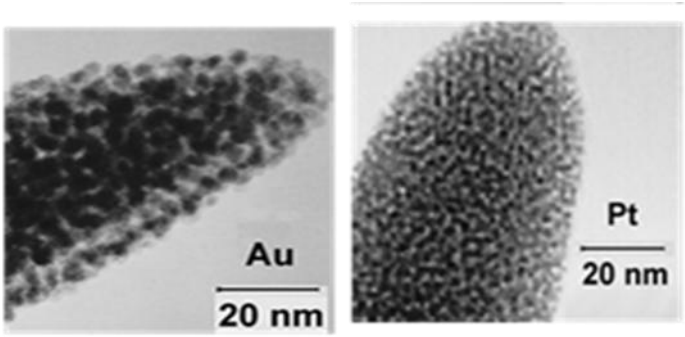

Fig. 2. Nanogranular compound field emitter tips. Left: Gold with crystal diameters of 4 nm, grown with Gold-Acetylacetonate-tri-methyl. Right: Platinum, grown from cyclopentadienyl-platinum-tri-methyl methyl to diameters of 2 nm.Both experiments: 20 kV electrons, 1 nA electron current, focused to 4 nm spot.(300 kV TEM images by MPI Halle).

The deposited tips, which were used for the photographs in the TEM were deposited in the JEOL 840 SEM at Telekom with nA electron current on edges of standing mounted copper object carrier grids. This allowed to image the tips in horizontal position in the TEM, and avoided the scattering contrast contribution of a carrier foil.

To understand the materials better, work function measurements were performed, see figure 3, left. They resulted in activation energies for variable range hopping for Pt/C and Au/C in the meV range! This result indicated that the nanogranular compound material is well suited for energy harvesting in the IR region. Also the construction of the compound materials with many layers of crystals, having the same energy gaps for excitonic energy levels enhances the sensitivity of the material to absorb light of all frequencies from IR to UV! Figure 3, right, shows a white-light optical image in reflection. On an silicon base coated with SiO_2gold contact areas were structured, which allowed 3 lines (green) to be deposited with 20 kV electrons. Using the Pt-cyclopentadienyl-tri-methyl-methyl precursor 3 bridges were deposited, which are broadened by the forward and back scattered electrons by additional deposition. This material looks black in the light microscope, indicating that all photons of the white spectrum from the lamp were absorbed by the nanocrystalline deposit.

As a result, the required extraction voltage for field electron emission was much lower than with metal single crystal emitter tips. Thus, gold / carbon nanogranular emitters, delivered the first emitted electrons starting at 8 V, and terminated the emission at extraction voltages of 24 V at an emission current near 1 mA. The emitter-extractor distance was less than 0.8 µm, see figure 4. The same applies to the Pt/C emitters, which began to emit at 15 V and ended at 75 V with an emission current of 1.4 mA or an emission current density of 1.4 GA / cm².

Electrons emanating from the emitter tip were coherent, as seen in the far field, by registering several patterns of interference fringes. This measurement confirms that the electrons emitted from the field emitters are coherent, indicating that they come from coherent bosons existing in the tipmaterial [4].

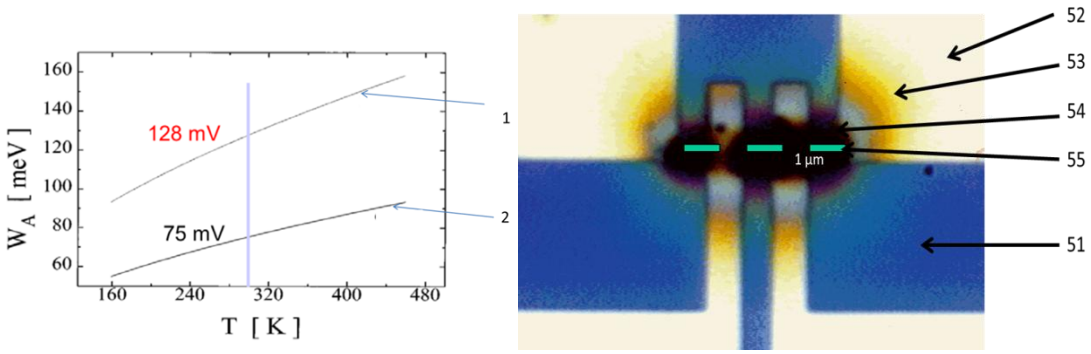

Fig. 3. Left: Activation energies for variable range hopping for Pt/C (1) and Au/C (2) [5].
Right: Optical photograph with white light illumination. Optical sensitivity of a line deposited with Pt/C (55) green: beam trace. Back scattered nanocrystalline deposit: black (54); blue area (51): SiO_2 on Si base material. Interference colors(53): insulating deposit. White areas: (52) Gold contact layers).

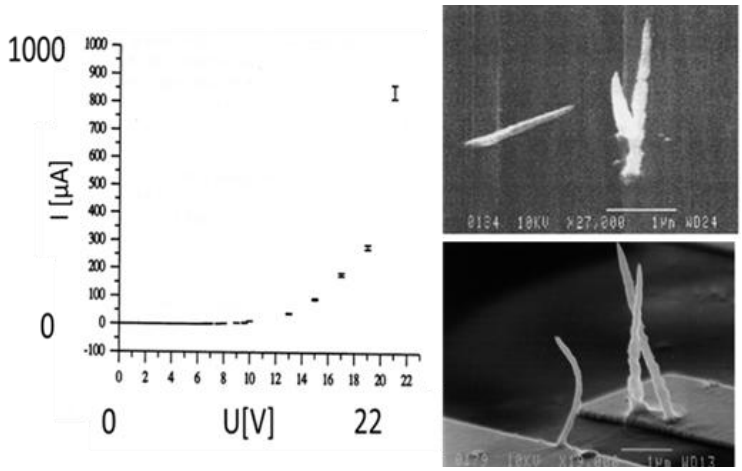

Fig. 4: Left: Au/C emission curve. Right Top: Diode- Source before the measurement: left: emitter, right extractor in x-shape. Right Bottom: Structure obtained, after the emission curve stopped [6]. The bent form of the emitter originated from implantation of water molecule ions sputtered from the anode and implanted at the cathode side facing the anode. This implantation can be prevented by using a potential saddle point between cathode and anode with a potential higher than the anode potential. This prolongs the lifetime of the emitter [7,8].

IV. Model to explain the hyper giant emission current densities

One explanation was formulated by Inosov et al. in 2010 of the superconductors using Cooper pairs and their high currents of up to 1 MA / cm² in wires, which are cooled to 40 K[9]. This provided the impetus for the formulation of a model to explain the hyper giant current carrying capacity of the novel nanogranular composite materials. Inosov and colleagues recognized that the Cooper pairs being formed from two electrons having antiparallel spin can reside as Bosons at the same energy level. This allows current densities of 1 MA/cm² in the material.

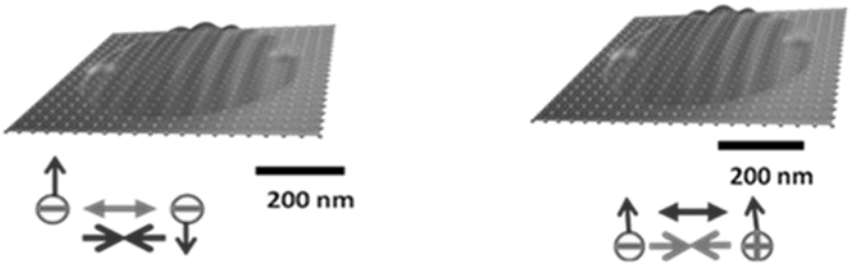

Figure 5: Left: Cooper pair, 2 charges repel, but antiparallel spins attract and balance the boson. Right: Koops pair, electron (-) and hole (+) attract, but the parallel spins repel and stabilize the Boson to a diameter of 600 nm.

The only difference between Cooper pairs and Koops pairs is in the sign of the charges and for the magnetic forces.

This is predicted by Maxwell's theory. However, for Cooper pairs cooling with liquid nitrogen to at least 40 K was required.
But our experiments with Koops pairs were performed at room temperature: 300 K!

Considering that by electron beam obtained Au/C or Pt/C deposits are nanocrystalline composite materials, with crystallite diameters of Pt (2 nm) or Au (4 nm), each encased in a layer of fullerene crystals. This means that now 2 conductive phases touch each other. Therefore, it is concluded that 2 work functions (Pt: 5.4 eV or Gold: 5.0 eV and Carbon: 4.8 V) are in contact and immediately form a common average Fermi level (Pt / C: 5.1 eV, and Au / C: 4.9 eV) into which the carbon must give up its electrons and thus the platinum or the gold is negatively charged. The energy states above the common Fermi level are empty, and extend through the whole composite matter.

At room temperature, electrons in the adjacent metals are excited by the Maxwell energy distribution in the conduction band, and they can occupy the empty energy levels in the Pt / C or Au / C material and immediately form after Bose Bosons from electron and hole with parallel spin. This behavior is made possible by the fact that crystals with a diameter of less than 5 nm can no longer carry phonons [[10], [11]]. These Bosons are at the same energy level, and are coherent, and can be up to 10^{28} / cm² in number. And since the material is no longer a pure metal that obeys the Fermi energy distribution, with only 2 electrons per level, but it is now composed by Bosons, which have a dipole moment (+, -) with many particles in the same level, similar to lasers. For data comparison: high temperature super conductors (HTc) reach at 40 K with titanium doped magnesium-di-boride < 1 MA/cm^2 ! [see table 1: 17], but the nanogranular composite materials reach up to 1 GA/cm².

V. History of the discovery of nanogranular compound materials for electron sources and other applications.

Material combination of emitters	Maximum obtained current carrying capability	Temperature T [°C]	Investigation at	Citation
Nanogranular compoundmaterials:				
Au/C	2 MA/cm², 10^3 MA/cm²(tip)	RT	Measured in UHV (TU Darmstadt)	[12]
Pt/C	2 MA/cm²	RT	Measured in UHV (TU Darmstadt)	[13]
Pt/C	15 MA/cm²	RT	Measured at wire archUniv. Maryland USA	[14]
Pt/C	10 MA/cm²	RT	Measured in HV (DTAG)	[15]
Pt/C	100 MA/cm²	RT	Measured in HV (NaWoTec, D)	[16]
Me/Fullerene	>50 MA/cm²	20	Metal in nanogranular matrix, Embedded (Me)	[17]
For comparison: High Temperature Superconductors (HTc):				
TitaniumdopedMagnesiumdiboride	<1MA/cm²	--233,15	Spektrum d. Wissenschaft. 7. 2005	[18]

Table 1: Emission current densities from field-emitters from nanogranular composite materials (FEBIP: Focused Electron Beam Induced Processing), see publications by several authors 1994 to 2005.

VI. But the Bosons cannot move!

The Bosons can be moved only by applying a field gradient of an electric field along the wire. When they reach the end of the wire, the Bosons disintegrate into an electron and a hole. The electron escapes from the substance and goes into vacuum (emission of electrons) or into the conductor of the terminal by tunneling into the conduction band. This explains the electron emission, but also why the work function is so low, and why the current is so much higher than with the emission of electrons from a metal after the Fermi Dirac distribution. Therefore, this electron emission is the solution to the mystery of the hyper giant-current density as it was

measured by our group at FTZ with these nanogranular composite emitter tips.It was also measured at the Helmholtz Institute KIT – KNMF in Karlsruhe, Germany, see figure 6.

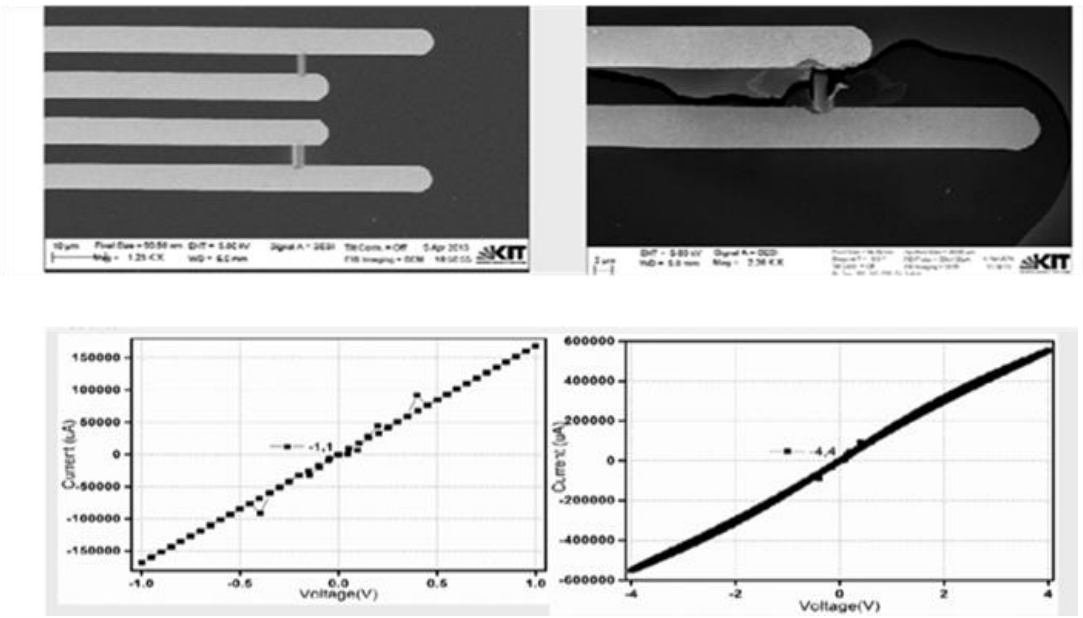

Fig. 6: Top left: Measurement setup to determine the current carrying capability of Pt/C deposit between platinum conducting lines. Top right: an overloaded deposit. The Pt- conducting lines melt but not the Pt/C deposit under investigation. The lower graphs show I/V curves. Left: the current obtained between + 1 V and – 1 V. right: for -4 V to + 4 V. A current up to 0,6 A was possible (with friendly allowance of KIT/ KNMF).[19]

Also, by multiplying the emitter tips in parallel, we had to learn that the size of the matching connecting surface of the structure to the deposited pure metal is limited by its current carrying capacity. By friendly cooperation with Mr. A. Rudzinski of the company RAITH, Germany, we were able to make electrical measurements of the device, see Figure 7.

To increase the available currents, a plurality of emitter tips were deposited in parallel at intervals on cone-shaped deposited contacts on a gold conductor end. When measuring the emission currents from 5 emitters connected in parallel, an emission starting at 15 volts was measured with an increase up to 135 µA total current, which then stopped and completely disappeared at 80 µA, see Figure 7. The explanation for the stop is as follows: Gold as a patterning material can carry 250 kA/cm². The measured current of 135 µA corresponds for the 5 emitter sets already a ten-fold overload and therefore results in melting of the electron emitters. The nanogranular compound materials demand to first build a large area as an connection sheet to the underlying metal, and to deposit only then on top of this structure the electron emitters.

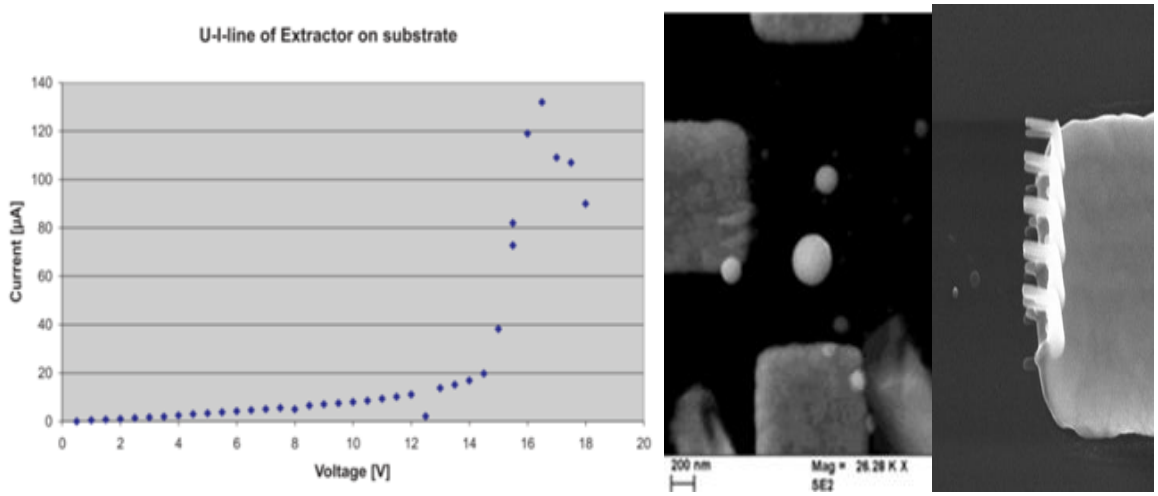

Fig. 7: I/V curve for multiple parallel emitters used to increase the emitted current. Center structure after raising the extraction voltage by 2 Volts, the base material did melt. Right: Emitter structure before starting the experiment

Other experiments showed, that the deposited nanogranular compound material has 0 Ohm resistance, but is controlled in its conductivity by the diameter and property of the contact material only [20].

VII. Koops-GranMat can be applied for harvesting of Greenhouse gas emission in the IR

NASA recorded in a 10 years measurement the in 2009 quoted data-average in W/m² [21].

In addition to the sunlight, which sends 160 W/m² to the earth during the day, the green-house gas molecules in the upper atmosphere send in the infrared window of the earth's atmosphere Infra-Red photons with 340 W/m² directly to earth during the day and the night. This is a 4 fold energy supply compared to that in the visible spectrum. Greenhouse gases emit in the near IR range, e.g. at 128 meV (Pt/C). We can harvest in the near IR the emitted energy with the Koops-GranMat® detector. This is the region, where the atmosphere of the earth is transmitting the IR radiation to the earth with 340 W/m², in day and at night. The atmosphere has a high transmission region at 5 µm to 10 µm, where no absorption loss hinders this energy supply at day and at night.

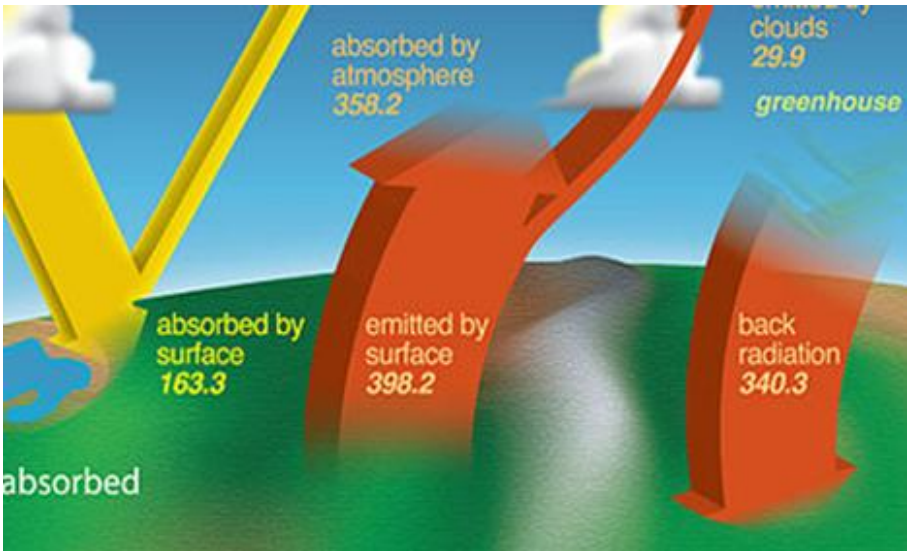

Fig. 8: The earth-near space delivers a lot of greenhouse energy to the earth, day and night.

The water containing atmosphere does not absorb the IR radiation around 7 to 10 µm.

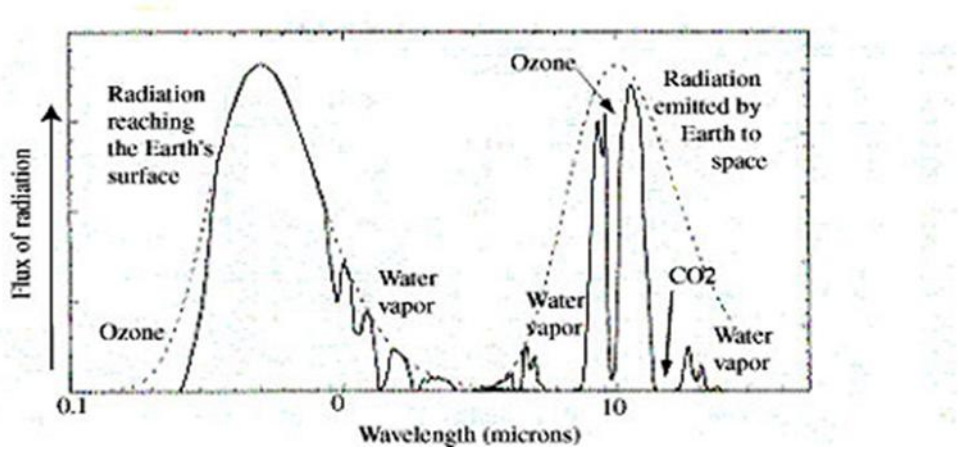

Fig. 9: The IR reception of Pt/C is in the gap before 10 µm, where there is no absorption.

This energy can be absorbed with the panels or films, which are coated with Boson field gradient materials. The energy harvesting requires only a field-gradient in the receiver layers, to move the electrical energy to the user. See figure 9 and 10.To harvest the energy from the green-house gases in the earth atmosphere sheets of glass or polymers can be coated with electron-beam induced deposition materials. Presently Pt/C or Au/C nanogranular compound materials are known. However less expensive materials are also possible, which have a low bandgap, like 0.128 eV for Pt/C compound layers.

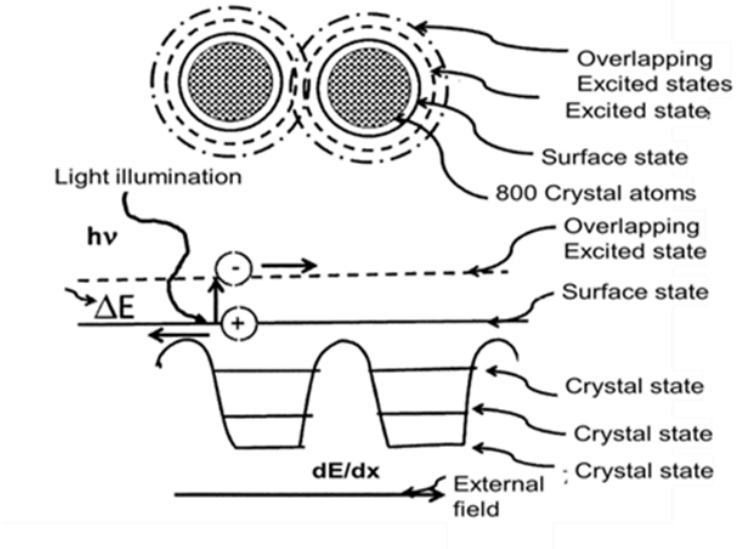

Fig.10.Principle of energy harvesting from the green-house emission using nanogranular compound materials. Since a 2 materials mixture is used, the 2 materials form a common Fermi–level. The Pt-material takes the electrons from the Fullerene crystals, which have therefore holes. The incoming radiation excites the electrons in the Fermi-Level to the level with the holes. There electrons and holes form Bosons in a very high density. They can be moved by an external dipole moment and finally deliver electrons to the outside world for work.

Nano-composit materials, e.g. Pt/C are sensitive in the IR light and can harvest all day and night the IR- light, which is emitted by the Green-House – gases in the upper atmosphere. By switching on a field gradient at the rim of the Koops-GranMat® detector layer the in Bosons stored energy isat the end of the layer released as electrons to the customer.

This material unifies the radiation detector, the storage device, and the energy supply, see figure 11. IR-Solar-receivers are especially useful in areas having a low density of population, but need to use electrical machines like pumps, cars and other tools.

Fig. 11: To move Bosons a field gradient is required, which can propel the dipoles of the Bosons to theend of the field gradient, where they can decay and deliver the charge to a user.

The current supply can be controlled by adjusting the static field gradients or switching them on or off. The principle has been shown, in the experimental stage. Now a larger area layer of 1 cm² is under construction for demonstration.

Later presently existing glass coating machines, which deposit by ion bombardment the coating layers on glass or polymer sheets, can be used by replacing the Sputter-sources with ions by field-emission array electron sources, which deposit the nanocrystalline detector layers from organometallic precursor gases to absorb the IR radiation and convert this finally to electrons or current.

VIII. Conclusions

Nanogranular compound materials offer a possible solution to absorb energy from the space in the earth atmosphere without interruption by day and at night. The green-house gas emission is the powerful source of 340W/m² during day and night. Large area detectors and storage devices are possible, which are far more efficient than present Silicon solar energy panels. The fabrication is possible by small changes in today's glass coating systems. It will be a revolution for the earth energy budget without the need to burn coal or plants. All this energy comes in the end from the sun and the space.

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