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DSE3T (Nano Materials and Applications)

Topic – Electron Transport (Part – 2)

We have already discussed part 1 of this e-report.

Now let us continue part 2 of it.

Tunnelling Between Nanostructures:

In the case of metallic islands in which the density of states is high, Coulomb blockade effects dominate the transport properties of the networks. In the case of semiconductor nanocrystals, the conductivity is also determined by the quantization of the energy levels induced by the quantum confinement. In both cases, the disorder arising for example from the dispersion in size and shape of the nanostructures plays an essential role. Therefore, elastic tunnelling between neighbour nanostructures is rather unlikely (Fig. 1) and one must consider inelastic tunnelling between non-resonant states, which requires to take into account the electron-phonon coupling. We assume that an injected electron only couples to phonons localized in the nanostructure where it resides, which is a reasonable assumption for weakly coupled nanostructures. Atomic vibrations in the barrier may lead to a modulation of the barrier height but we do not consider this effect here. When an electron is transferred from one site to another, there is an emission or absorption of phonons as required by the conservation of the total energy.

The coupling mechanism has been basically described in the following way. When an extra carrier is introduced into a nanostructure, there is a relaxation of the atoms toward a new equilibrium situation. The relaxation energy is defined as the Franck-Condon shift (for site 1). In order to simplify the problem, we assume as usual that the total energy is a quadratic function of $3N_1 + 3N_2$ configuration coordinates where N_1 and N_2 are the numbers of atoms in the nanostructures 1 and 2, respectively. The probability per unit time for the transfer of an electron from a site 1 to a site 2 is obtained from the Fermi golden rule as

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$$W_{i \rightarrow j} = \frac{2\pi}{\hbar} \sum_{i, n_1, n_2} p(i, n_1, n_2) \times$$

$$\left[\sum_{f, n_1', n_2'} |\langle f, n_1', n_2' | V | i, n_1, n_2 \rangle|^2 \delta(E_{f, n_1', n_2'} - E_{i, n_1, n_2}) \right]$$

where $|i, n_1, n_2\rangle$ and $|f, n_1', n_2'\rangle$ denote the initial and final states of energy E_{i, n_1, n_2} and $E_{f, n_1', n_2'}$ respectively and $p(i, n_1, n_2)$ is the probability to find the system in the state $|i, n_1, n_2\rangle$. The integers n_1, n_2, n_1', n_2' label the vibronic configurations on each site.

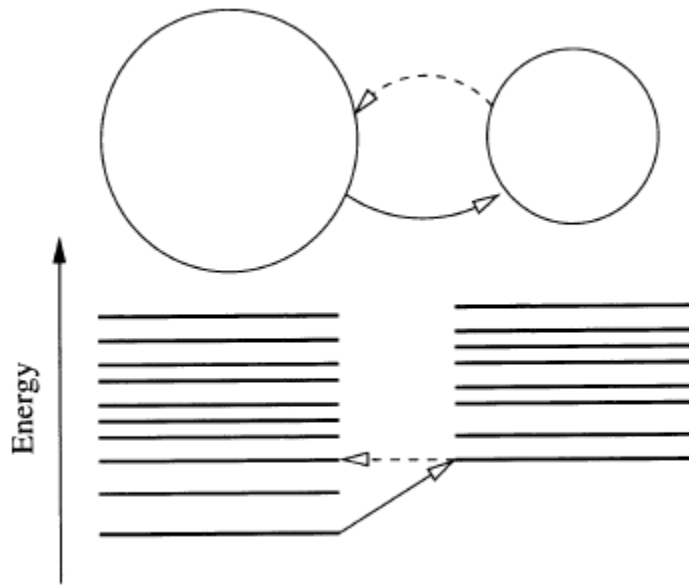


Fig. 1

Simpler expressions can be obtained when all phonons frequencies in a nanostructure can be approximated by a single one (here ω_1 and ω_2). Then one can sum the intensity of all possible transitions corresponding to the same difference in total energies between the final and initial states, for example differing by p_1 phonons of energy $\hbar\omega_1$ and p_2 phonons of energy $\hbar\omega_2$. Then we have

$$E_{f, n_1', n_2'} - E_{i, n_1, n_2} = E_f - d_{FC}^{(2)} - E_i + d_{FC}^{(1)} + p_1 \hbar\omega_1 + p_2 \hbar\omega_2$$



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where the Franck-Condon shifts (d_{FC}) correspond to the relaxation energy when the nanostructure is occupied by one electron. The total intensity of these transitions is equal to $W_{p1} \times W_{p2}$.

Injecting this in the previous equation we obtain

$$W_{i \rightarrow j} = \frac{2\pi}{\hbar} \sum_{i,f} p(i) |\langle \phi_f | V | \phi_i \rangle|^2 \times \left[\sum_{p1,p2} W_{p1} W_{p2} \delta(E_f - d_{FC}^{(2)} - E_i + d_{FC}^{(1)} + p_1 \hbar \omega_1 + p_2 \hbar \omega_2) \right]$$

In the case of strong electron-phonon coupling ($S_1 = \frac{d_{FC}^{(1)}}{\hbar \omega_1} \gg 1$ and $S_2 = \frac{d_{FC}^{(2)}}{\hbar \omega_2} \gg 1$)

$$W_{i \rightarrow j} = \frac{2\pi}{\hbar} \sum_{i,f} p(i) |\langle \phi_f | V | \phi_i \rangle|^2 \frac{1}{\pi \mu} e^{-\frac{(\Delta - d_{FC}^{(1)} - d_{FC}^{(2)})^2}{\mu^2}}$$

where $\mu = \sqrt{2S_1(\hbar \omega_1)^2 \coth\left(\frac{\hbar \omega_1}{2kT}\right) + 2S_2(\hbar \omega_2)^2 \coth\left(\frac{\hbar \omega_2}{2kT}\right)}$ and $\Delta = E_f - d_{FC}^{(2)} - E_i + d_{FC}^{(1)}$ is the energy required to transfer the electron from the site 1 to the site 2. An example of variation of $W_{i \rightarrow j}$ (transition rate) with respect to Δ is presented in Fig. 2.

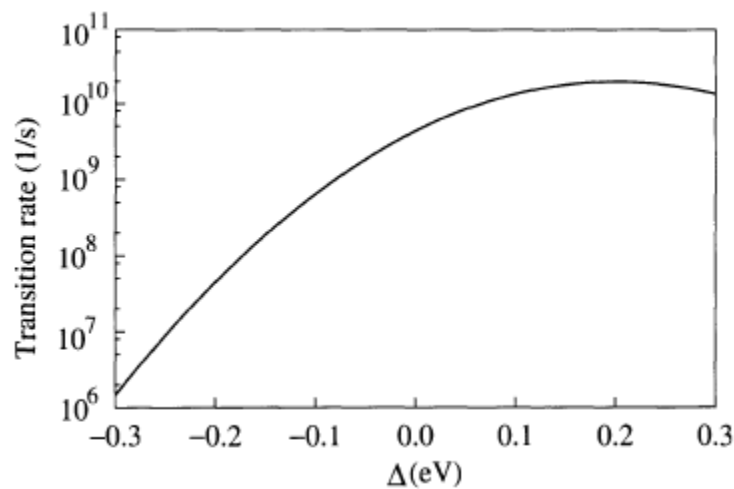


Fig. 2



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Hopping Conductivity:

We consider now a network of nanostructures. Our aim is to present a computational method to calculate the conductivity. We consider systems where the degree of randomness is sufficiently large that the transport of carriers takes place by hopping between neighbouring nanostructures. The disorder may arise under different forms such as the topological or cellular disorder. It was shown that a fixed array of sites can serve as a useful model for topologically disordered systems. Therefore, in the following, we assume a fixed array of sites in which the activated hopping between neighbouring sites i and j is defined by the probability per unit time $W_{i \rightarrow j}$ that was calculated in the previous section and from which we want to determine the dynamic conductivity $\sigma(\omega)$.

The combination of the disorder and of a particular topology of the array may dramatically influence the electrical transport, in particular when the system is close to the percolation limit. Due to these constraints, the diffusion of the electron is anomalous at the microscopic scale, in the sense that the diffusion coefficient D depends on time (the same theory obviously applies to the holes). However, at the mesoscopic scale, when the mean displacement of the electron becomes larger than the correlation length which characterizes the system, a constant diffusion coefficient can be defined, and the diffusion becomes normal. Here we give a simplified presentation of this theory.

Diffusion Coefficient. The diffusion of electrons of density $n(\vec{r}, t)$ at a position \vec{r} and at time t is given by the Fick's law and the charge conservation equation

$$\frac{\partial n(\vec{r}, t)}{\partial t} = \frac{1}{e} \nabla \cdot \vec{J}$$

$$\vec{J} = eD \nabla n(\vec{r}, t)$$

where \vec{J} is the current density. Applying Laplace transformation in the case of a 1D system, we obtain $i\omega N(x, \omega) = D \frac{\partial^2 N}{\partial x^2}$ from which we get

$$N(x, \omega) = \frac{1+i}{2} \sqrt{\frac{\omega}{2D}} \frac{n_0}{i\omega} e^{-\sqrt{\frac{\omega}{2D}} |x| (1+i)}$$

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The coefficient in front of the exponential has been obtained by the Laplace transform of the normalization condition for n_0 electrons in the system, which is

$$\int_{-\infty}^{\infty} N(x, \omega) dx = \frac{n_0}{i\omega}$$

In order to characterize the diffusion of the electrons, we calculate the mean square displacement of the electrons $\overline{x^2}(t)$ at time t defined by

$$\overline{x^2}(t) = \frac{1}{n_0} \int_{-\infty}^{\infty} x^2 n(x, t) dx$$

We obtain that the Laplace transform of $\overline{x^2}(t)$ is related to the generalized diffusion coefficient $D(\omega)$ by $\frac{1}{n_0} \int_{-\infty}^{\infty} x^2 N(x, \omega) dx = \frac{2D(\omega)}{(i\omega)^2}$.

This can be generalized to a system of dimension d as $D(\omega) = -\frac{\omega^2}{2d} \int_0^{\infty} e^{-i\omega t} \overline{r^2}(t) dt$.

This expression is particularly interesting in the case of the hopping transport on an array of localized sites defined by vectors \vec{s} . Let us define the probability $p(\vec{s}, t | \vec{s}_0)$ to find an electron on the site \vec{s} at time t whereas it was on the site \vec{s}_0 at time $t = 0$. Then we can write

$$\overline{r^2}(t) = \sum_s (\vec{s} - \vec{s}_0)^2 \langle p(\vec{s}, t | \vec{s}_0) \rangle$$

So, we deduce the diffusion coefficient as

$$D(\omega) = -\frac{\omega^2}{2d} \sum_s (\vec{s} - \vec{s}_0)^2 \langle P(\vec{s}, \omega | \vec{s}_0) \rangle$$

Using Einstein's relation ($\sigma(\omega) = \frac{ne^2}{kT} D(\omega)$) we get that the conductivity σ can be written as

$$\sigma(\omega) = -\frac{ne^2 \omega^2}{kT 2d} \sum_s (\vec{s} - \vec{s}_0)^2 \langle P(\vec{s}, \omega | \vec{s}_0) \rangle$$

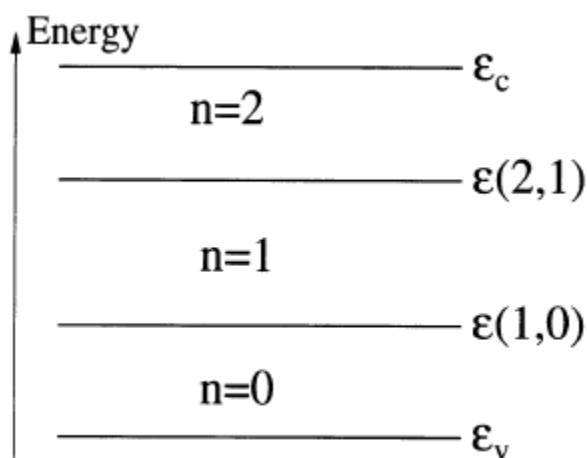


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Deep Level Defects in Nanostructures:

Deep-level traps or deep-level defects are a generally undesirable type of electronic defect in semiconductors. They are “deep” in the sense that the energy required to remove an electron or hole from the trap to the valence or conduction band is much larger than the characteristic thermal energy kT , where k is the Boltzmann constant and T is the temperature. Deep level defects interfere with more useful types of doping by compensating the dominant charge carrier type, annihilating either free electrons or electron holes depending on which is more prevalent. They also directly interfere with the operation of transistors, light-emitting diodes and other electronic and opto-electronic devices, by offering an intermediate state inside the band gap.

Deep level defects are characterized by a strongly localized wave function. One then expects that, a few screening lengths away from the boundary, the wave function of the neutral defect will experience the same local potential as in the corresponding bulk material. This means that the neutral deep level itself remains invariant on an absolute scale at the same position as in the bulk material. It will thus not experience a confinement effect as it is the case for the nanostructure bandgap. Such a property has been extensively used to discuss the Stokes shift of ten observed between luminescence and optical absorption in semiconductor nanocrystals.





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Fig. 3

However this view is too naive and cannot be directly applied to the so-called occupancy or ionization levels $\varepsilon(n + 1, n)$ defined as

$$\varepsilon(n + 1, n) = E(n + 1) - E(n)$$

where $E(n)$ is the total energy of the system with n electrons on the defect (when the corresponding charge state is stable). These ionization levels are the true observable quantities in capture or emission experiments. To illustrate the situation, we choose the basic example of a non degenerate level for which one can have $n = 0$ or 1 or 2 with the neutral state corresponding to $n = 1$. Then one has, if they exist, two ionization levels $\varepsilon(2,1)$ and $\varepsilon(1,0)$ which correspond to the addition of an electron or a hole on the defect, respectively (as shown in Fig. 3). Such quantities are naturally obtained via the resolution of the GW equations which also gives information about the distribution of all other excited quasi-particle states and especially the bandgap limits E_c and E_v of the nanostructure which are affected by the confinement effects. To get simple but accurate conclusions we proceed and split the single-partide GW equations into a bulk-like contribution and a surface polarization term due to the finite size of the system.

The resolution of this problem should be carried out in three steps:

(1) To solve a set of single particle equations, using ab initio or semi-empirical techniques. This will provide us with the single particle energies and wave functions of the system containing the neutral defect: E_d for the deep level, E_c and E_v for the band limits which will include the confinement effect in the presence of the defect. Note that the presence of the defect is not likely to affect seriously the confinement energies since it is an effect of order $\frac{1}{N}$ (N being the number of atoms) while the confinement effect is of order $\left(\frac{N_s}{N}\right)^\nu$ where N_s is the number of surface atoms and the exponent ν is typically between 1 and 2 (the confinement energy in a spherical quantum dot varies like $d^{-\nu}$ where d is the diameter, and therefore $\frac{N_s}{N} \propto d^{-1}$).

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(2) To add a bulk contribution $\delta\Sigma_{bulk}$ to these single particle energies calculated in the presence of the defect. This problem has not been solved yet. However one might anticipate some elements of solution on the basis of the following work. Here, one considers that the local density approximation (LDA) for instance correctly treats the short-range part of the self-energy. $\delta\Sigma_{bulk}$ is then totally determined by the long range part screened by the bulk dielectric constant. This would end up with the bulk $\delta\Sigma_{bulk}$ for the band limits and an intermediate value for the gap state. In any case $\delta\Sigma_{bulk}$, even calculated exactly, would be state dependent.

(3) Finally to add the surface contributions $\delta\Sigma_{surf}$.

Surface Defects in Nanostructures:

Si Dangling Bonds. In silicon, dangling bonds correspond to coordination defects in which a silicon atom has only three equivalent covalent bonds (Fig. 4). The best known case is the P_b centre at the Si(111)-SiO₂ interface. Such defects are also expected to occur at the surface of crystallites as was indeed demonstrated by electron paramagnetic resonance studies of porous silicon.

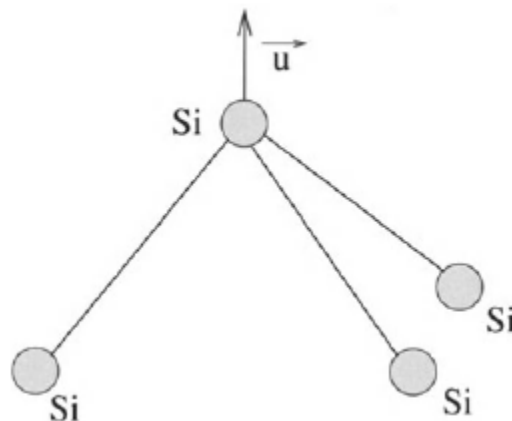


Fig. 4

Let us first discuss the basic physical properties of dangling bonds. The simplest description comes from a tight binding picture based on an atomic basis consisting of sp^3 hybrid orbitals. The properties of the bulk material are dominated by the coupling between pairs of sp^3 hybrids involved in the same

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nearest neighbour's bond. This leads to bonding and anti-bonding states which are then broadened by weaker inter-bond interactions to give, respectively, the valence and conduction bands. In the bonding or anti-bonding picture, the rupture of a bond leaves an uncoupled or dangling sp^3 orbital whose energy is midway between the bonding and anti-bonding states. When one allows for inter-bond coupling, this results in a dangling bond state whose energy falls in the gap region and whose wave function is no longer of pure sp^3 character, but is somewhat delocalized along the back-bonds.

Experimentally this isolated dangling bond situation is best realized for the P_b centre, i.e. the tri-coordinated Si atom at the Si-SiO₂ interface but it can also occur in amorphous silicon as well as in grain boundaries or dislocations. It has been identified mainly through electron spin resonance (ESR), deep level transient spectroscopy (DLTS) and capacitance measurements versus frequency and optical experiments.

Self-trapped Excitons. A puzzling problem concerning the optical properties of semiconductor nanostructures is that there is sometimes a large difference between luminescence energies and optical absorption energies. In fact, optical absorption energy gaps are in agreement with calculated values for crystallites. Only the luminescence energies differ greatly and, for small crystallites, are practically independent of the size. Such behaviours are more consistent with the existence of deep luminescent centres. The problem is that little is known regarding their nature and origin.

We discuss here the possibility of the existence of intrinsic localized states which might behave as luminescent systems. Such states correspond to self-trapped excitons and are stabilized because of the widening of the gap induced by the confinement. This possibility is not restricted to the case of silicon crystallites but is likely to be valid for all types of semiconductor crystallites.

To illustrate the physical basis of such self-trapped excitons let us consider an isolated single covalent bond characterized by a σ bonding state filled with two electrons and an empty σ^* anti-bonding state. The origin of the binding is the gain in energy resulting from having the two electrons in the lower bonding state. Optical absorption in this system leads to the excitation of one electron in

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the σ^* state. In such a case there is essentially no binding and the repulsive force between the atoms dominates so that the molecule eventually dissociates. If, on the other hand, the molecule is embedded in an elastic medium then it cannot dissociate but one ends up with a large distance between the constituent atoms and a reduced separation between the σ and σ^* states. The resulting luminescence energy is thus much smaller than the optical absorption energy, corresponding to a Stokes shift of the order of the binding energy, i.e. ~ 1 eV.

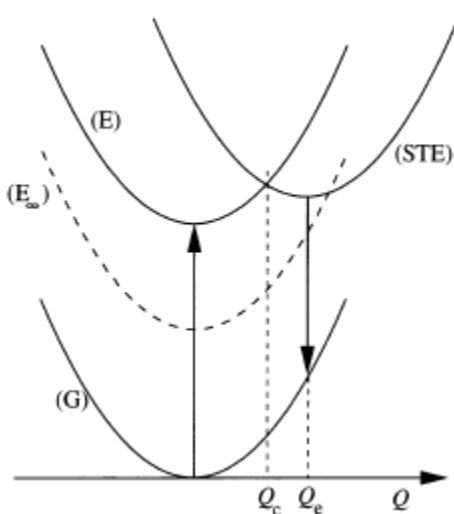


Fig. 5

The applicability of this model to a nanocrystal essentially depends on the possibility of localizing the electron-hole excitation on a particular covalent bond, i.e. of creating a self-trapped exciton. For this, one must be able to draw a configuration coordinate diagram like the one shown in Fig. 5 where the configuration coordinate Q corresponds to the stretching of the covalent bond. For small Q , the ground and first excited states are delocalized over the crystallite and show a normal parabolic behaviour. However, for Q larger than a critical value Q_c , the system localizes the electron-hole pair on one particular single bond, leading to a larger bond length Q_e and a smaller luminescence energy. This self-trapped state can be stable or metastable. An interesting point is that it may exist only for small enough crystallites, in view of the important blue shift as pictured in Fig. 5. Such a self-trapped exciton is likely to be



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favoured at surfaces of crystallites where the elastic response of the environment is weaker than in the bulk.

Thermionic Emission:

Nanoscale electron sources with high electron-emitting performance are of great interest in vacuum nanoelectronics. Resembling traditional thermionic emission sources based on a hot tungsten filament, a hot carbon nanotube or graphene can function as a nanoscale electron source because of its excellent thermal stability and electrical conductivity. Here studies of thermionic emission from single hot carbon nanostructures are overviewed, emphasizing their differences in physics from macroscopic thermionic emission as well as potential applications in vacuum nanoelectronics. Due to their low dimensionality, nanoscale size, and non-equilibrium electron distribution, Richardson's Law, which governs thermionic emission from macroscopic metals, breaks down in the case of thermionic emission from single carbon nanostructures, and an internal electric field in a carbon nanostructure can contribute directly to its thermionic emission. Graphene-based nanoscale thermionic emission sources, source arrays, and vacuum transistors have been fabricated and demonstrated to exhibit the advantages compared to those based on field emission. The advances imply the promise of realizing high-performance nanoscale electron sources and vacuum electronic devices based on thermionic emission.

It is well known that thermionic emission from macroscopic metals is described by Richardson's Law (also known as the Richardson–Dushman equation), where thermionic emission current density (J) is given by the formula

$$J = AT^2 e^{-\frac{\phi}{kT}}$$

where T is the emitter temperature, ϕ is the emitter work function, k is the Boltzmann constant, and $A = 1.2 \times 10^6 \text{ Am}^{-2}\text{K}^{-2}$ is the Richardson constant.

Richardson's Law was deduced on the basis of the Sommerfeld free-electron model where the three-dimensional (3D) free-electron gas follows Fermi–Dirac statistics. The 3D Sommerfeld free-electron model cannot be applied to one-dimensional (1D) CNTs and two-dimensional (2D) graphene. So thermionic

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emission from CNTs and graphene may deviate from Richardson's Law. Liang et al. demonstrated the problem of applying Richardson's Law to thermionic emission from single-layer graphene where electrons behave as massless quasiparticles ($m = 0$), as the mass-dependent expression of Richardson constant in the previous equation becomes questionable. To investigate thermionic emission from single layer graphene, they proposed a model by taking the 2D massless Dirac fermions (electrons in graphene have zero effective mass near the Fermi level) into account. An analytical formula for thermionic emission from single-layer graphene was obtained and is given as

$$J = \beta T^3 e^{-\frac{\phi - E_F}{kT}}$$

where E_F is Fermi energy, $\beta = 115.8 \text{ Am}^{-2}\text{K}^{-3}$. This formula exhibits stronger dependence on the temperature as compared to Richardson's Law. In addition to low-dimensional massless Dirac fermions, electron emission from the surface of single-layer graphene and single-walled CNTs has two additional features that are absent in electron emission from 3D bulky solids, i.e. (1) electrons in the carbon nanostructures are confined in a quantum well along the emission direction because the close proximity of the two surface barriers forms this quantum well and (2) all electrons always locate at the surface.

Reference(s):

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Thermionic Electron Emission from Single Carbon Nanostructures and its Applications in Vacuum Nanoelectronics, Xianlong Wei , Qing Chen, and Lian-Mao Peng, MRS Bulletin

(All the figures have been collected from the above mentioned references)

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