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Formation and Field-Emission of Functionalized Nanostructures : Theoretical Investigation of Nanotube-Based Nanodevices

	KHAZAEI Mohammad
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		かざえい　　もはめど	
氏	名	KHAZAEI, Mohammad	
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指 導 教 員		教授　川添　良幸	
論 文 審 査 委 員		主査　東北大学教授　川添　良幸	東北大学教授　粕谷　厚生
		東北大学教授　畠山　力三	東北大学教授　岩佐　義宏

論 文 内 容 要 旨

In this thesis, we introduce a general formalism for investigation of field emission from any kind of nanostructured surfaces including protrusion, impurity and defects. The introduced method is based on first principles local density of states and effective potentials. It gives us the ability to estimate the current emission from any individual energy state at any point of nanostructure's surface. Hence the experimental field emission spectroscopy images can be interpreted. Through this modeling the current emission is related the two main factors: local density of states on the emitting surface and the tunneling probability of electron through the structure-vacuum barrier. The role of these two factors is discussed separately for interpretation of the emission patterns. The experimental field emission spectroscopy images are explained as local density of states at the structure-vacuum barrier, weighted by the probability of electron tunneling as it is observed in Fig.1. This method is applied to calculate the current emission from pristine capped carbon nanotubes and cesium doped capped nanotubes. The model excellently reproduces the experimental field emission patterns of pristine capped nanotubes, i.e., presence of pentagon and hexagon ring with dark center and dark boundary line between two connecting bright neighboring rings. The role of electron effective mass on current emission is discussed. It is observed that cesium adsorbates even with a low doping ratio of one dopant per nanotube increase the current emission more than 2.5 times irrespective of electron effective mass [1].
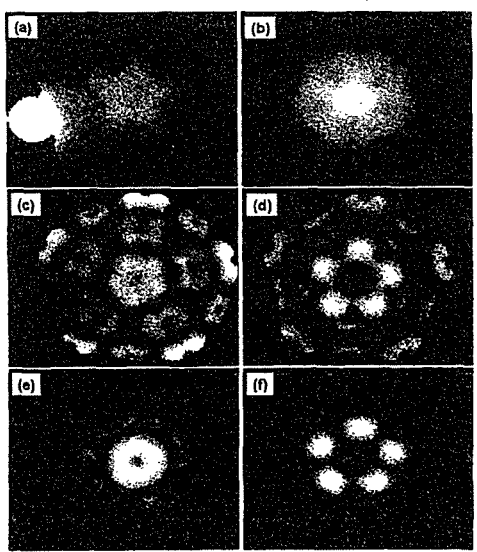
Figure 1. The tunneling probably, (a) and (b), local density of states at left turning point, (c) and (d), obtained current emission pattern, (e), (f) for two different Cs doped structures with a Cs adsorbed or trapped at the tip.

In order to calculate field emission using of first-principles, we need to have precise atomic coordinates of the nanostructure for calculating the corresponding electronic structure. For getting close to experimental results, we should have similar nanostructures used in experiments. Hence, we have performed ab initio molecular dynamics to prepare the atomic coordinates of the nanostructures with first-principles accuracy and similar to those observed in experiments. In recent experiments carbon nanotubes with high chemical stability even under strong electric field [2] and high aspect ratio are shown to be one of the promising materials for making field emission devices with low threshold voltage. The current emission from the carbon nanotubes can be changed significantly using dopants. Cesium is one of the elements that have a large atomic diameter and very low electronegativity. It donates its electron to the nanotube's lattice easily. Consequently, it changes the electronic structure of the nanotubes. The experimental results show that the current emission is increased more than ten times after Cs deposition [3,4]. These experimental observations motivate us to consider how Cs affects the electronic structure of carbon nanotubes to increase the current emission by using our proposed modeling.
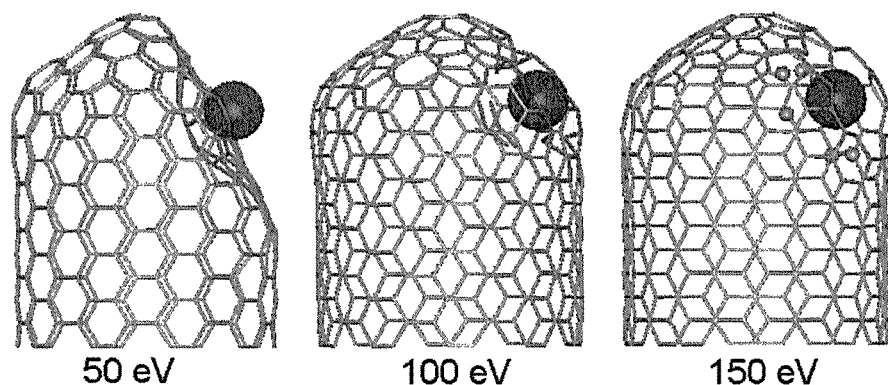

50 eV **100 eV** **150 eV**

Figure 2. The results of Cs collisions at different kinetic energies, 50, 100, and 150 eV.

The Cs-doped structures are prepared in accordance to the recent experiments that were able to encapsulate the Cs inside the carbon nanotubes by irradiation method [5]. Our ab initio molecular dynamics simulate the experimental condition of Cs ion irradiation experiments. The results clarify the process of Cs adsorption and encapsulation at the carbon nanotubes with large and small diameters. The results are compared with Raman scattering spectroscopy experiments, and are in very good agreement. Considering three relevant factor of collision, i.e., impact position, impact angle, and kinetic energy of dopant, we have shot Cs^+ toward (10,10) capped and stem armchair carbon nanotubes. Figure 2 shows that that the Cs^+ with kinetic energy 50 eV is adsorbed on the surface irrespective of the impact angle and impact position. The Cs^+ with kinetic energy 100 eV can make a hole, if the collision route is aiming toward the nanotube axis. If the rout is aiming away from the nanotube axis, the Cs^+ will tear the nanotubes' surface and will be scattered off. This makes it possible for other Cs ions to get encapsulated via the torn region. The Cs ions whose energies are 150 eV and aim toward the nanotube stem get encapsulated with minimal deformation of the collision region. Cs^+ encapsulation, which is further supported by Raman scattering spectroscopy experiments, is useful in making nanojunction, in agreement with experimental results, with potential application in nanoelectronics. The energy transfer rate to the highly curved regions of the nanotube (i.e., at the cap) is seen to be lower than the corresponding rate in collision with the stem. At high kinetic energies (100 and 150 eV), our calculations show that the Cs^+ transfers more than 70% of its kinetic energy to the carbon atoms at the impact position. Therefore, the carbon atoms at the impact position are detached from the nanotube. The detached carbon atoms, which are not able to escape from

inside of the tube, get attached to the opposite side of the nanotube wall in a local sp^3 structure. At low kinetic energy, i.e., 50 eV, the whole energy of Cs^+ is transferred to the carbon lattice. The created deformation wave diffuses to the whole system. Hence, the deformation at 50 eV, although being temporarily larger than those of 100 and 150 eV, is remedied, and the Cs^+ remains adsorbed on the tube [6].

Our simulations also show that Cs^+ gets adsorbed on long, thin (5,5) carbon nanotubes under Cs^+ bombardment at 50 eV. However, it is desorbed by reflected distortion wave in short nanotubes attached to hard substrates. The distortion wave velocity for (5,5) nanotubes is estimate to be 0.10 Å/fs that is similar to that of (10,10) armchair nanotubes, but 0.4 times that of (10,0) zigzag nanotubes, showing that zigzag tubes are stiffer. After collision, the short nanotubes nearly restore their initial geometries within a very short time interval. This shows the great stability of short nanotubes against high strain. At higher collision energies (100 and 150 eV) the behavior of short and long nanotubes are the same; it is observed that the Cs^+ is trapped in the middle of the created hole along the routes aiming toward the nanotube axis. The detached carbon atoms are adsorbed inside the nanotube in local sp^3 structures. Our simulations support the usage of short thin nanotubes in atomic force microscopy, and of doped, long thin nanotubes in field emission devices [7].

The binding energy calculations show that inside the nanotube, especially within the cap, is a favorable position for the Cs atoms as compared to outside adsorption. It is due to collective Coulomb interaction between the ionized Cs and negatively charged carbon atoms that envelop the Cs inside the nanotube as compared to weaker interactions when the Cs has adsorbed outside. It might be the reason for the fact that in many of the growth mechanisms, the deposited catalysts are found within the capped tip of the tube [7].

From energy spectra calculations it is observed that Cs doping at the cap results in almost vanishing HOMO-LUMO gap and reduction of the work function of up to 1.0 eV. The created dipole field explains work function reduction after Cs deposition on carbon lattice. By Cs ionization on the lattice, repulsion between the electrons inside the nanotube increases. Hence the energy levels are shifted to higher energies. Also, after Cs adsorption, the extension of π electrons of carbon atoms toward the vacuum at the adsorption site decreases. The π electrons are extended into the barrier to decrease the repulsion energy and to minimize their kinetic energies. Therefore, the π electrons are in prison inside the nanotube after Cs deposition which helps the energy levels to be shifted to higher energies (decreasing work function), and the repulsion between π electrons outside the nanotube decreases which helps to decrease the height of the effective potential in the vacuum side (increasing tunneling probability of the electrons). These are some of the reason for the enhancement of current emission after Cs deposition. It is also observed that the states near Fermi energy get more localized at the cap in doped structures as compared to pristine one. For the periodic stem structures, we observe that the presence of dangling bonds in Cs doped configurations generates extra levels within the pseudogap [8]. It shows the tendency of Cs doped structures for becoming a superconductor.
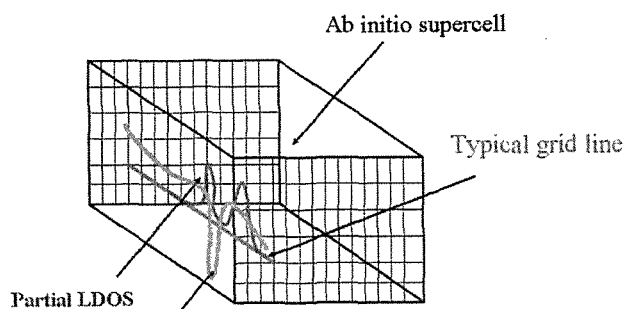

Figure 3. The ab initio supercell divided by the grid lines. The emission current is calculated along each line using partial LDOS and the potential energy.

To calculate field emission current from any kind of nanostructures, Penn-Plummer model [9,10] is adapted to first principles electronic structures. The supercells in ab initio calculations are generally discretized by introducing a fine grid as shown in Fig. 3. The grid divides the supercell face perpendicular to the emission direction into small surface elements. The emission current along individual grid lines parallel to the emission direction is calculated using Penn-Plummer method. Hence, the total current will be the superposition of current emission from all individual grids. Through this model, the effect of impurities, defects, and protrusions on current emission and emission patterns can be discussed. For example, in the case of Cs doped capped nanotubes with a trapped Cs at the tip, constructed by detachment of pentagon ring, it is observed that most of current emission comes from the created dangling bonds, and not from Cs atom as seen from Fig.1(f) [1].

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論文審査結果の要旨

　　本論文は、ナノ構造体からの電子放出特性に関する量子力学の理論体系を確立し、その動的プロセスをスーパーコンピューターを活用した超大規模第一原理分子動力学シミュレーション計算により定量的に明らかにしたものである。特に、実験との共同研究により、セシウム原子をカーボンナノチューブにドープした場合の電子放出量の増大に関する詳細な数値計算を実行し、薄型テレビ等への応用を議論したもので、全編8章よりなる。

　　第1章は序論である。

　　第2章では、本研究の理論的基盤である量子多体系の電子密度を第一原理計算によって求めるための密度汎関数理論と、それを適用したナノ構造体に関する具体シミュレーション計算に用いられる局所密度近似と擬ポテンシャルについて詳述している。

　　第3章では、アルカリ金属原子の代表として実験的に用いられているセシウム原子を加速してカーボンナノチューブへ衝突させる過程の第一原理分子動力学シミュレーション計算を実行した結果を実験との比較で述べている。数十 eV での衝突により、セシウム原子はナノチューブ表面に付着し安定構造を構成することが示された。ラマン散乱実験との比較検討を行い、原子構造に関する良好な一致を得た。

　　第4章では、カーボンナノチューブの長さとドーピングの最適位置の関係を第一原理分子動力学シミュレーション計算によって明らかにした。

　　第5章では、第一原理計算により、セシウム原子をドープしたカーボンナノチューブの電子状態の詳細を明らかにすることにはじめて成功した。

　　第6章では、カーボンナノチューブからの電子放出過程を、ＷＫＢ近似とバーデン法等を適用し、ペン・プラマー理論により理論的に考察した。

　　第7章では、第一原理計算をペン・プラマー理論に適用し、電子放出過程の量子理論を構築し、セシウム原子ドーピングによるナノチューブの仕事関数への影響を明らかにした。また、電子の有効質量の電子放出への影響を定量的に示した。

　　第8章は総括である。

　　以上要するに、本論文は、アルカリ金属をドープしたカーボンナノチューブからの電子放出特性を第一原理シミュレーション計算によって明らかにしたもので、その薄型テレビの電子放出源等への応用を可能としたナノテクノロジーの画期的な成果であり、材料物性学の発展に寄与するところが少なくない。

　　よって、本論文は博士（工学）の学位論文として合格と認める。