

Energy level alignment of single-wall carbon nanotubes on metal surfacesSylvain Clair,^{1,2} Yousoo Kim,^{2,*†} and Maki Kawai^{2,3,‡}¹*Aix-Marseille Université, IM2NP, CNRS UMR 6242, Campus de Saint-Jérôme, Case 142, F-13397 Marseille Cedex 20, France*²*RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*³*Department of Advanced Materials Science, The University of Tokyo, Chiba 277-8561, Japan*

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We studied the electronic configuration of single-wall carbon nanotubes adsorbed on well-defined Au(111) and Cu(111) surfaces. We found opposite behaviors for their energy-level alignment with metal: nanotubes are p-doped on Au(111) and n-doped on Cu(111). The doping level is not uniquely defined for a particular metal surface but rather exhibits a distribution depending on several uncontrolled factors such as nanotube geometry and adsorption configuration.

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I. INTRODUCTION

Single-wall carbon nanotubes (SWCNT) are seen as highly valuable materials for potential application in nanoelectronic-device architectures, as confirmed by the large number of related studies.¹⁻³ There remain, however, important challenges to overcome before their application in real devices can be utilized, such as achieving proper control and reproducibility of their characteristics. In particular, the problem of contacting a nanotube to a metal is crucial as its conduction properties may be restricted to the interface conditions with the electrodes.^{2,4-7} Furthermore, the achievement of a simple and efficient method to control the doping of nanotubes is still missing. Our scanning tunneling microscopy (STM) study shows that the charge transfer-induced interface dipole created when a nanotube is adsorbed to a metal surface directly governs the doping level of nanotubes. While it is known that SWCNT on Au(111) are p-doped,⁸ we found that it is possible to produce n-doped SWCNT on Cu(111). The detailed comprehension of the doping behavior, however, includes—besides the difference in work functions (WF) of metal-SWCNT—a large number of mainly uncontrolled parameters related to the exact epitaxial conditions on a crystalline surface.

The early STM experiments on SWCNT have provided highly valuable details on their structure and their related electronic properties.⁸⁻¹⁷ However, little attention was given to the effect of the adsorption to a metal substrate, and essentially only Au(111) surfaces were used. Here we propose systematic investigations on the interaction of a SWCNT with well-defined Au(111) and Cu(111) metal surfaces. The nanotubes were deposited *in situ* via a vacuum-compatible dry contact transfer (DCT) technique,¹⁷⁻¹⁹ which provides a surface free of impurities. The STM was subsequently used to locate and analyze isolated SWCNT on a clean substrate.

II. EXPERIMENTAL METHOD

Measurements were performed in an ultrahigh vacuum (UHV) low-temperature (4.7 K) STM (Omicron LT-STM) operating with a tungsten tip. The Au(111) and Cu(111) substrates were prepared following standard UHV procedures with repeated cycles of argon-ion sputtering and annealing providing an atomically clean surface. HiPco-produced SWCNT

(Carbon Nanotechnologies, Inc.) with a mean diameter of ~ 1.0 nm were deposited *in situ* onto the surface at room temperature via the vacuum compatible DCT technique.¹⁷⁻¹⁹ In some cases, the samples were postannealed up to ~ 600 K for one hour. Scanning tunneling spectroscopy (STS) data was obtained through lock-in detection of the ac tunneling current driven by a 797-Hz, 10-mV (rms) signal added to the junction bias under open-loop conditions (bias voltage here is defined as the sample potential referenced to the tip). The $dI/dV(r, V)$ maps were created by acquiring a series of STS spectra along the top of a nanotube; the feedback loop was briefly closed before each spectrum acquisition. STM images were partly processed with the WSxM software.²⁰ The nanotube types were identified from STM/STS data following the procedure described by Wildöer *et al.*⁸

III. RESULTS AND DISCUSSION

The DCT deposition technique results in isolated individual nanotubes that are mostly (but not exclusively) aligned along the substrate crystallographic high symmetry direction.¹⁸ The cleanliness of the substrate is considerably enhanced as compared to the traditionally used drop-casting deposition method. On Au(111) the chevron pattern of the surface reconstruction is clearly observed around the nanotubes, and atomic resolution imaging of the substrate is routinely obtained. Furthermore the DCT technique obviates the need to sonicate the SWCNT dispersion in order to debundle the tubes, a process that potentially leads to defect formation on the nanotube surface²¹ or chemical reaction with the solvent.^{22,23} The system nanotube/metal surface is thus unambiguously defined.

According to tight-binding calculations,^{2,24,25} the local density of states (LDOS) of a SWCNT present singularities arising from its one-dimensional character (van Hove singularities). Additionally, a nanotube can be of a metallic or semiconducting type depending on its geometry. STM of adsorbed SWCNT allows for a complete characterization of the tube:⁸⁻¹⁰ chiral angle and diameter can be measured on atomically resolved images, and STS gives direct access to the LDOS. It was thus shown that the configuration of adsorbed nanotubes is in good agreement with what can be expected for free-standing tubes.⁸⁻¹⁷ However, because of the interaction with the substrate, fine effects take place such as a broadening

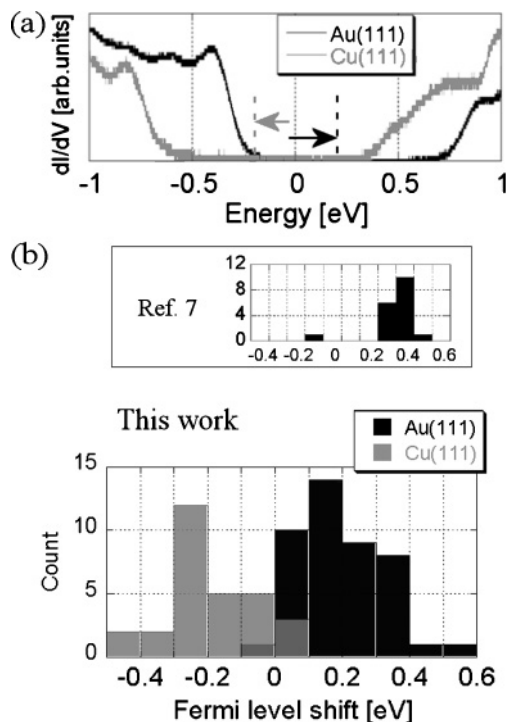


FIG. 1. (a) Differences in STS for a (7,3) nanotube adsorbed to Au(111) and Cu(111). (b) Distributions of Fermi-level shifts measured for various nanotubes on Au(111) and on Cu(111). The statistics include metallic and semiconducting tubes, which behave similarly.

of the van Hove singularities resulting from hybridization with surface wave functions.^{8,26} In the region around the Fermi level, the STS spectrum of a nanotube adsorbed on a metal is not symmetrically positioned around the zero bias voltage. For Au(111), the middle of the band gap is measured above the Fermi level by a few hundred meV [Fig. 1(a)], which is in agreement with previous measurements^{8–10,13,15} and calculations.^{26–30} Note that in the case of metallic tubes, similar behavior is found when considering the middle point between the first van Hove singularities. In the literature, to our knowledge, STM studies on carbon nanotubes (CNT) on metals are, with few exceptions,^{16,17,31} exclusively limited to the Au(111) surface,^{8–15} and in fact little detail is given concerning this asymmetry in the gap and the shift of the Fermi level. Owing to the particular deposition method we used, we found we were able to investigate nanotubes adsorbed on a different metal surface, namely Cu(111), as well as substantial differences in the electronic behavior thereof as compared to Au(111). After systematic analysis of the geometry of approximately 25 nanotubes on both surfaces following the procedure described by Wildöer *et al.*,⁸ we were able to characterize a small number of tubes of exactly the same type but adsorbed on different substrates. Typically, as for the case of the (7,3) tube presented in Fig. 1(a), the gap width and the STS spectral-line shape are identical, but the spectra are shifted in energy one relative to the other. Whereas on Au(111) the Fermi energy is shifted toward the valence band, i.e., the nanotube is the electron donor, on Cu(111) the Fermi energy is shifted towards the conduction band, i.e., the nanotube is the electron acceptor. Similar behavior

(opposite Fermi-level shift) was observed for all the tubes regardless of their semiconducting or metallic type. Whereas CNT doping is done traditionally through chemical modifications such as exohedral functionalization^{32,33} or ion implantation,³⁴ these findings clearly provide a simple way for efficient control of the doping level of carbon nanotubes on surfaces: the nature of the substrate itself can directly steer the polarity of the charge transfer in a pristine carbon nanotube.

We found, however, that the shift in Fermi level is not uniquely defined for a particular metal surface but rather exhibits a distribution. Figure 1(b) reports the statistics found for a series of nanotubes adsorbed on both surfaces. The mean value obtained is 0.20 eV for the case of Au(111) and -0.15 eV for the case of Cu(111), and the standard deviation is 0.13 eV. Indeed Wildöer *et al.*⁸ reported a similar distribution on Au(111) with a mean value of 0.25 eV [Fig. 1(b), inset]. Interestingly, the distributions for Au(111) and Cu(111) slightly overlap, and a few n-doped (resp. p-doped) nanotubes are found on Au(111) [resp. Cu(111)]. Variations in Fermi-level shift are found on different nanotubes depending on their geometries, as well as their adsorption configurations on the surface. In principle, for the case of a nanotube on an ideal metal surface, various parameters may be responsible for minor variations in the Fermi-level position, i.e., contacting effects,³⁵ rotational and longitudinal epitaxial position,^{17,36} or compressive stress.²⁸ However, we could not find any correlation between Fermi-level shift and tube chirality, diameter, or orientation with respect to the substrate. Moreover, we found that metallic and semiconducting tubes behave in similar ways. In fact the exact epitaxy conditions are in most cases impossible to assign, but their influence is clearly not radically decisive. For instance, we could find examples of curved nanotubes that do not show variations in their electronic structure and exhibit a constant Fermi-level shift. Figure 2 illustrates the different cases that can be found

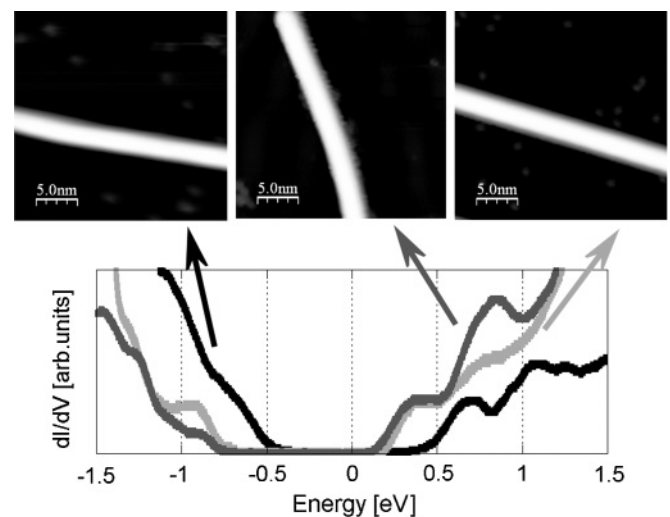


FIG. 2. Differences in STS for three different (6,5) nanotubes adsorbed on Cu(111) with similar environments but showing different relative Fermi-level shift. Two of the nanotubes (left and right) have similar orientation but their Fermi level are shifted by 0.25 eV relative to each other, and the two nanotubes forming an angle of approximately 55° (middle and right) have very close Fermi-level positions.

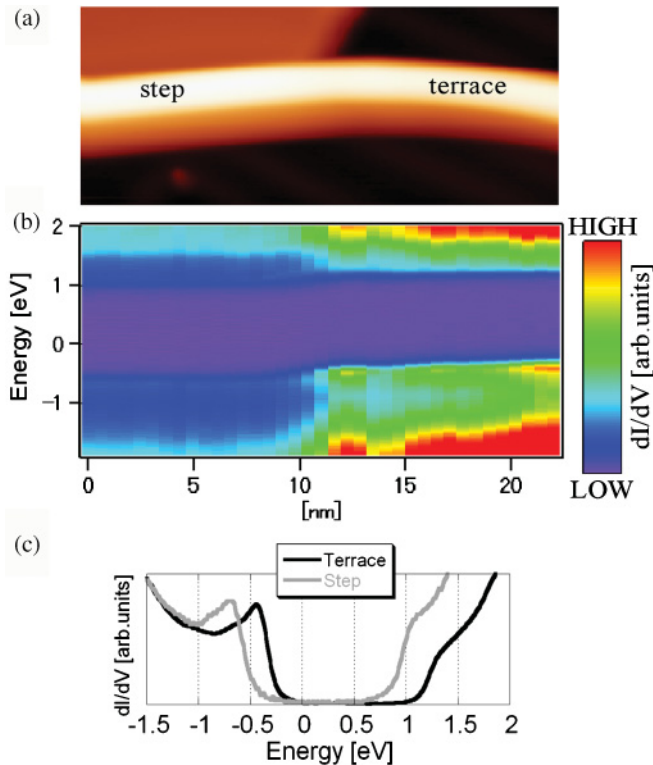


FIG. 3. (Color online) Nanotube (5,3) on Au(111) leaving a step edge. (a) STM topographic image. (b) The dI/dV map along the nanotube length (set point 0.9 V, 0.3 nA). (c) STS spectra taken from (b) along the step and on the terrace; the difference consists of a relative shift of ~ 0.3 eV.

for three different nanotubes of the same chirality adsorbed on Cu(111). Two of the nanotubes have similar orientation but their Fermi level are shifted by 0.25 eV relative to each other, and the two nanotubes forming an angle of approximately 55° have very close Fermi-level positions.

Also, variations can be found locally on a single nanotube. Figure 3 shows the configuration change observed on an individual nanotube depending on its local environment. Here a tube is lying along a substrate atomic-step edge (on the lower terrace) on the left part of the image and is continuing freely on the terrace on the right part of the image. The $dI/dV(r, V)$ map [Fig. 3(b)] demonstrates two distinct electronic configurations corresponding to these two spatial regions. These consist of two different STS spectra simply shifted by 0.27 eV with respect to each other [Fig. 3(c)]. In this example, the density of states (DOS) is less asymmetric toward the Fermi level for the nanotube lying along the step edge than on the terrace, but this finding is not the general case; indeed, the opposite case was also observed. The transition region extends over ~ 4 nm. Similar variations in the shape and position of the DOS were observed for C_{60} , another carbon-based π -electron molecule. On Au(111) these changes were related to the Smoluchowski effect,³⁷ i.e., the interactions of the molecules with a charge-depleted region along the step edge.³⁸ The nanotube case is, however, more complex as we could not extract even a simple rule for the shift direction.

The fundamental difference in the doping level of nanotubes on Au(111) and on Cu(111) can be understood by looking at

the WF of the metals. With a WF of 5.31 eV, Au(111) has a higher electroaffinity than Cu(111) (WF 4.98 eV),³⁹ resulting in the observed opposite behavior. At the interface between the metal surface and the nanotube, the adsorption induces a rearrangement of the electron distribution depending on the bonding type (Van der Waals, electrostatic, covalent, ...).⁴⁰ Following this charge transfer, a dipole layer is created that results in a shift in the vacuum level.^{41,42} STM data on C_{60} molecules shows similarly a different behavior on Cu(111)⁴³ and on Au(111),^{38,44} but in this case the Fermi-level shift is also accompanied by a change in the molecular energy gap. Elucidating the precise electronic configuration of a carbon nanotube adsorbed on a metal surface is a rather delicate matter as it is closely related to the exact epitaxy between the nanotube-carbon atoms and the substrate-metal atoms.¹⁷ The large number of possible nanotube geometries and adsorption configurations makes it a very complex system. This is the reason why various situations are found in our STM data, which is acquired locally and for individual tubes. Thus while the data is limited and it is difficult to extract the relevant parameters, a general trend is clearly demonstrated. Similar difficulties are found when trying to clarify the electronic configuration of double-wall carbon nanotubes, as the number of possibilities for the geometric-atom arrangement is quasi-infinite.^{45,46}

The WF of carbon nanotubes as measured by photoemission is $W_{CNT} = 4.8$ eV^{47,48} and is lower than the WF of both Au and Cu. Along the WF difference between CNT and metal therefore fails to explain the nature of transfer doping. Recent theoretical works proposed a phenomenological model for the electronic configuration of graphene (Khomyakov *et al.*⁴⁹) or carbon nanotubes (Nishidate *et al.*³⁰) adsorbed on metals. Here the interface dipole is decomposed into a charge-transfer dependent term and a short-range repulsion-interaction term ΔV_c , which results from the overlap of the wave functions of the metal and the adsorbate. Interestingly, the latter term depends only very weakly on the metal substrate so that it represents an intrinsic quantity of the adsorbate, which is

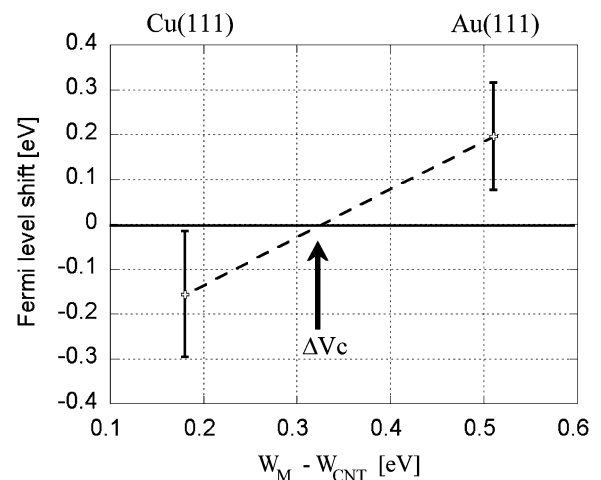


FIG. 4. Fermi-level shift as a function of metal-CNT WF difference $W_M - W_{CNT}$. Following the phenomenological model proposed by Khomyakov *et al.*,⁴⁹ we can estimate ΔV_c at approximately 0.33 eV.

similar to the concept of a charge-neutrality level developed for metal/organic junctions.^{42,50} In this model adsorption on a (virtual) metal with a WF of W_M exactly equal to $W_{CNT} + \Delta V_c$ would produce no charge transfer and therefore no Fermi-level shift. In all other cases, the sign of the Fermi-level shift is related to the sign of the quantity $(W_M - W_{CNT} - \Delta V_c)$. From our experimental data (Fig. 4) and following Khomyakov *et al.*,⁴⁹ we can estimate the parameter ΔV_c from the virtual metal WF that would cancel the Fermi-level shift, and we found $\Delta V_c \approx 0.33 \pm 0.15$ eV. This value accounts for our previous data on the low WF surface Ag(100) (WF 4.64 eV³⁹) where a negative doping was found.^{16,17} However, our results are in contradiction with Nishidate *et al.*³⁰ who calculated a ΔV_c value of 0.13 eV that would predict no charge transfer for SWCNT/Ag(100). One reason for this discrepancy might be that they considered a large diameter tube with a (calculated) low WF (4.48 eV). Regardless, because of the multiple configuration types that can account for a SWCNT-metal system, as illustrated above, the achievement of predictive calculations is certainly a delicate matter.

IV. CONCLUSION

In summary, the (average) shift of Fermi level for carbon nanotubes, or the n- or p-type doping (average) behavior is related to the CNT-metal WF difference and the sign of the

quantity $(W_M - W_{CNT} - \Delta V_c)$ with $\Delta V_c \approx 0.33 \pm 0.15$ eV. We previously reported data on Ag(100) where the Fermi-level shift was negative and of a similar order of magnitude to Cu(111), which was in agreement with the low WF of silver. However, the shift of the Fermi level is not uniquely defined for a particular metal surface but rather exhibits a distribution. The precise electronic configuration of a SWCNT adsorbed on a metal surface is indeed closely related to the exact epitaxial conditions between the nanotube-carbon atoms and the substrate-metal atoms; the large number of possible nanotube geometries and adsorption configurations makes it a highly complex system.

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