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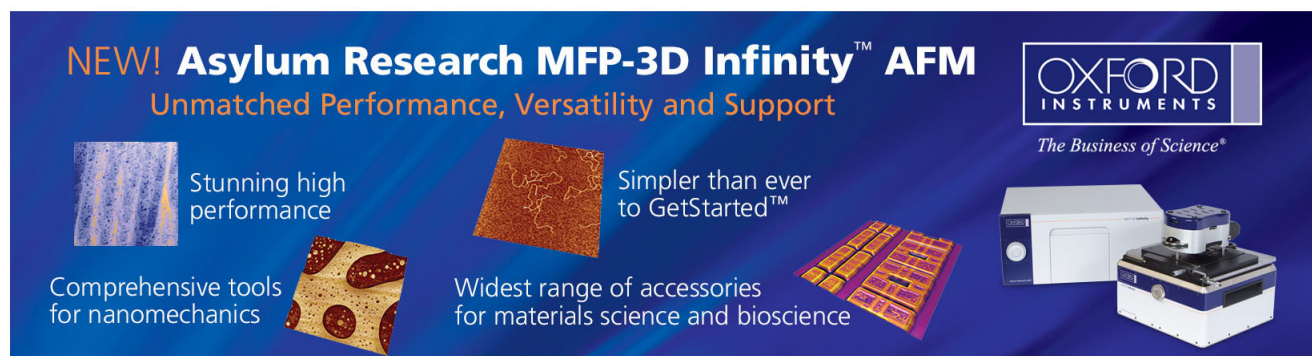
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Tailoring thermopower of single-molecular junctions by temperature-induced surface reconstruction

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Recent experiments revealed that surface reconstruction occurs at around 300–400 K in the interface of C_{60} adsorbed on Cu(111) substrate by scanning tunneling microscope techniques. To understand effects of such reconstruction on thermopower, we investigate the Seebeck coefficients of C_{60} single-molecular junctions without and with surface reconstruction as a function of temperature at different tip-to-molecule heights from first-principles. Our calculations show that surface reconstruction can enhance or suppress Seebeck coefficients according to junctions at different tip heights. We further observe that the Seebeck coefficient of the junction at $d = 3.4$ Å may change from p- to n-type under surface reconstruction. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4769814]

Thermoelectricity involves the conversion between thermal and electric energies. Research on thermopower is important to understand the renewable energy system that converts waste heat to useful electric power.[1] Thermopower (also called the Seebeck coefficient) describes a thermoelectric phenomenon by which thermal energy is converted into an electric current via a temperature difference. The Seebeck coefficient, defined as dV/dT, where dV is the voltage difference caused by the temperature difference dT, is the most important physical quantity for characterizing thermoelectric properties. In recent years, fundamental properties of the Seebeck coefficient and thermoelectric figure of merit (ZT) single-molecule thermoelectric junctions have attracted many theoretical[2–14] and experimental[15–19] attentions, thereby providing new opportunities and challenges for exploring the nanoscale renewable energy system. Single-molecule thermoelectric junctions may have promising use in revolutionizing the design of next-generation energy conversion devices at the nanoscale level. For example, single-molecule junctions may be considered as gate effect controllable nano-refrigerators for appropriate external biases in a range between the lower and upper threshold voltages. Nano-refrigerator can perform better than bulk thermoelectric refrigerators with the same thermoelectric figure of merit ZT due to the suppression of local heating via the size minimization, which prevents the overwhelming Joule heating in the bulk system.[20,21] Single-molecule junctions may also be considered as self-powered transistors.[22]

The appearance of high-temperature superconductivity in a doped C_{60} has inspired the study of the mechanism of electron transfer of a C_{60} monolayer on a metallic surface.[23,24] Recent scanning tunneling microscope (STM) experiments reported that interface reconstruction occurs at around 300–400 K for the C_{60} molecule adsorbed on the Cu(111) surface.[25]

Total energy calculations showed that the C_{60} molecule tends to dig a seven-atom vacancy on the Cu(111) surface, where the geometry increases the adsorption strength that compensates for the energy cost of vacancy creation.[25] In the bulk crystal, structural transition can cause a significant change in the Seebeck coefficient. For example, vanadium dioxide (VO_2) undergoes phase transition from a rutile (high-temperature) to a monoclinic (low-temperature) crystal at 68 °C. An abrupt change of the Seebeck coefficient occurs at 68 °C due to structural phase transition.[26] This illustrates that discontinuities can happen in the Seebeck coefficients of the bulk crystals as a function of temperature. However, no study has ever discussed such effects in nanojunctions, which motivates us to investigate the possible abrupt changes in the temperature profile of Seebeck coefficients in nanojunctions. The system we choose to investigate is an STM–C_{60}–substrate junction. Such a junction undergoes surface reconstruction at around 300–400 K when the Cu(111) substrate is heated. This study suggests for the time a possible way for experimentalists to explore the temperature-discontinuities of the Seebeck coefficients in molecular junctions. This technique may have considerable impact on the *in situ* characterization of single-molecule junctions.

To determine the effect of surface reconstruction on the Seebeck coefficient, we calculate the Seebeck coefficients of C_{60} single-molecule junctions with and without surface reconstruction. The C_{60} single-molecule junctions are modeled as a C_{60} molecule probed by STM. The STM tip is composed of five tungsten atoms and the C_{60} molecule is adsorbed on the Cu(111) surface, as shown in Fig. 1. The optimized structures of C_{60} single-molecule junctions in the unreconstructed and reconstructed cases are relaxed using the Vienna *ab initio* simulation package (VASP). In the reconstructed cases, a vacancy atom is initially dug on the Cu(111) surface, and the optimized geometry of C_{60} adsorbed on the Cu(111) surface is obtained using VASP to relax the

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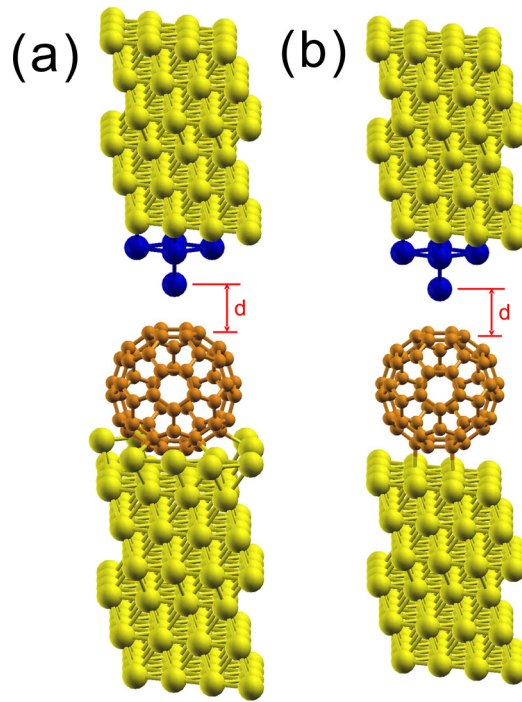b)Electronic mail: yuchangchen@mail.nctu.edu.tw.

FIG. 1. The schematics of C$_{60}$ single-molecule junctions in which the C$_{60}$ molecule (bronze) is adsorbed on the Cu(111) surface (yellow) with an STM tip composed of tungsten atoms (blue) (a) with and (b) without surface reconstruction on Cu(111) substrate. d is the tip height.

structure. Consequently, the C$_{60}$ molecule sinks one-atomic–layer into the Cu(111) surface. The previous first-principles study shows that C$_{60}$ can sit at an fcc or an hcp site, and the latter case is slightly energetically favored than the former. Hence we adopt the hcp-site model in calculating the thermal power of the reconstructed case. The reconstructed surface involves a higher amount of charge transfer from the C$_{60}$ molecule to the Cu(111) substrate. Thus, the transmission function is highly relevant to the surface configurations. Subsequently, we apply Nanodcal to calculate $\tau(E)$, the sum of the transmission probabilities from all channels, of STM-based C$_{60}$ single-molecule junctions with and without surface reconstruction. Nanodcal is an implementation of density functional theory (DFT) within the Keldysh nonequilibrium Green function formalism (NEGF). The overall structure can be divided into three regions: left lead, right lead, and center scattering region. The center scattering region contains a C$_{60}$ molecule, five tungsten atoms to represent the STM tip, and three layers of crystal planes in Cu(111) from the top and bottom electrodes.

To calculate Seebeck coefficients, the current I through the STM-based C$_{60}$ single-molecule junction is initially considered in a Landauer-Büttiker formalism

$$I(\mu_L, T_L; \mu_R, T_R) = \frac{2e}{h} \int dE (f_E^R - f_E^L) \tau(E), \qquad (1)$$

where the Fermi–Dirac distribution functions are $f_E^{L(R)} = 1/[\exp((E - \mu_{L(R)})/k_B T_{L(R)}) + 1]$, where $\mu_{L(R)}$ and $T_{L(R)}$ are the chemical potential and temperature in the left (right) electrode, respectively. To obtain Seebeck coefficients, we assume that the nanojunction is not connected to an external battery and in thermal equilibrium, such that $\mu_L = \mu_R = \mu$

and $T_R = T_L = T$. When an infinitesimal temperature dT is applied to the right electrode, the Seebeck effect induces a voltage difference, dV, across the nanojunction. The Seebeck coefficient is calculated by letting $dI = I(\mu, T; \mu, T + dT) + I(\mu, T; \mu + edV, T) = 0$. By expanding the Fermi-Dirac distribution functions in dI to the first-order in dT and dV, the Seebeck coefficient ($S = dV/dT$) is obtained[27]

$$S(\mu, T) = -\frac{1}{eT} \frac{K_1(\mu, T)}{K_0(\mu, T)}, \qquad (2)$$

where

$$K_n(\mu, T) = -\int dE \tau(E)(E - \mu)^n \frac{\partial f_E(\mu, T)}{\partial E}. \qquad (3)$$

Equations (2) and (3) are applied to calculate the Seebeck coefficients in this study. In the low-temperature regime, Eq. (2) can be further simplified using the Sommerfeld expansion[27]

$$S \approx -\frac{\pi^2 \kappa_B^2 T}{3e} \frac{\frac{\partial \tau(\mu)}{\partial E}}{\tau(\mu)}. \qquad (4)$$

The simplified equation above clearly shows that the Seebeck coefficient is positive (or negative) if the slope of the $\tau(E)$ is negative (or positive) near the chemical potential. This correlation demonstrates that the Seebeck coefficients, which are related to both the magnitude and slope of $\tau(E)$, can yield more information on the underlying electronic structures than I-V measurements, the latter of which are merely related to the magnitude of $\tau(E)$. Equation (4) predicts that the temperature dependence of the Seebeck coefficient is linear due to the first-order Sommerfeld expansion. For effects such as magnetic field asymmetries in the Seebeck coefficient due to inelastic scattering,[28] going beyond the first-order Sommerfeld expansion is crucial.

In this letter we compare Seebeck coefficients with and without surface reconstruction in C$_{60}$ single-molecule junctions as a function of temperature for junction. In both cases, we also investigate the effect of the tip heights (denoted by d) on the Seebeck coefficients, where d is the distance between the STM tip (the bottom tungsten atom) and the top edge of the C$_{60}$ molecule. Figures 2(a) and 2(b) compare the functions $\tau(E)$ of C$_{60}$ single-molecule junctions with and without Cu(111) surface reconstruction for various tip heights $d = 2.1$, 2.3, 2.77, and 3.4 Å. The comparison shows that surface reconstruction generally enhances the transmission probabilities at the Fermi level for all junctions with different d values. The result manifests that a higher conductance is expected when surface reconstruction occurs, which is remarkably consistent with the experimental measurements. The enhanced conductance caused by the surface reconstruction is possibly due to the shorter tip-to-substrate distance and larger contact surface between the C$_{60}$ molecule and the substrate. After surface reconstruction, the indentation of the Cu(111) surface exerted by the C$_{60}$ molecule shortens the tip-to-substrate distance. The shortened tip-to-substrate distance decreases the width of the potential barrier and increases the transmission probabilities, thus increasing
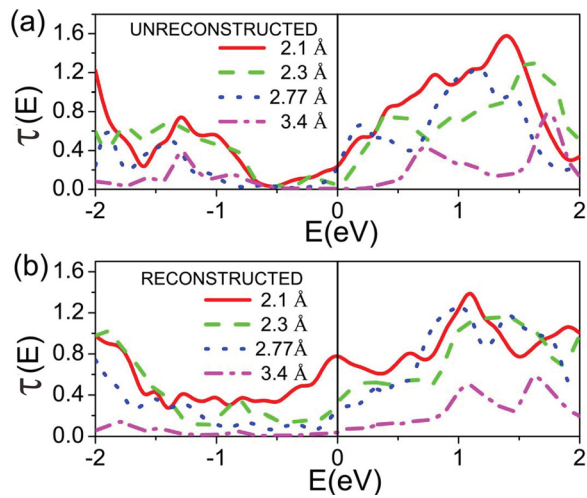
FIG. 2. $\tau(E)$ calculated using nanodcal as a function of temperature for various STM tip heights $d = 2.1$, 2.3, 2.77, and 3.4 Å in two scenarios: (a) with surface reconstruction and (b) without surface reconstruction. $\tau(E)$ is the sum of transmission probabilities from all channels.

the conductance. The junction with $d = 2.1$ Å in the reconstructed case has a larger $\tau(E)$ at the Fermi level due to a much shorter tip-to-substrate distance than the other three junctions with $d = 2.3$, 2.77, and 3.4 Å.

We investigate Seebeck coefficients with (from 300 to 500 K) and without (from 0 to 400 K) surface reconstruction from for C_{60} single-molecule junctions with various tip heights $d = 2.1$, 2.3, 2.77, and 3.4 Å, as shown in Figs. 3(a)–3(d). Initially, we observe that the tip heights can modulate the magnitude of Seebeck coefficients of C_{60} single-molecule junctions. Unlike the conductance that is merely proportional to the magnitude of the transmission function, the Seebeck coefficient is related to both the magnitude and slope of the transmission function. This phenomenon results in more complicated relationships between the Seebeck coefficient and

d than between the conductance and d. For example, junctions with shorter tip heights ($d = 2.1$, 2.3, and 2.77 Å) show n-type behavior (negative Seebeck coefficients), whereas the junction with the largest tip height $d = 3.4$ Å shows p-type behavior (positive Seebeck coefficient) in the low-temperature regime (from 0 to 300 K). On the contrary, the conductance generally decreases exponentially with increased d because the transmission probability decreases exponentially with increased d due to larger contact potential.

There is experimental evident showing that surface reconstruction occurs when the temperature is increased to around 300–400 K in the C_{60} single-molecule STM junction. Regarding the abrupt changes in the temperature profile of Seebeck coefficients caused by surface reconstruction, the ranges of temperatures within which the surface reconstruction is expected to occur are shaded in Figs. 3(a)–3(d). The point to observe is the abrupt changes in the temperature profile of Seebeck coefficients for each junction. We note that there is a discontinuity in the temperature profile of Seebeck coefficients at the surface reconstruction temperature when surface reconstruction occurs. Particularly, for the junction with $d = 3.4$ Å, the Seebeck coefficient can even change from positive (p-type) to negative (n-type) when surface reconstruction occurs. The Seebeck coefficient is not only related to the magnitude but also to the slope of the transmission function, which produces salient differences between the conductances and Seebeck coefficients due to the effects of surface reconstruction. These results can be seen in the following discussions. Figures 3(a)–3(d) show that surface reconstruction can enhance the magnitudes of Seebeck coefficients for junctions with $d = 2.3$ and 3.4 Å and suppress the magnitudes of Seebeck coefficients for junctions with $d = 2.1$ and 2.77 Å. This finding is in sharp contrast to the effects of surface reconstruction on conductances. The effects of surface reconstruction always enhance the conductance for a
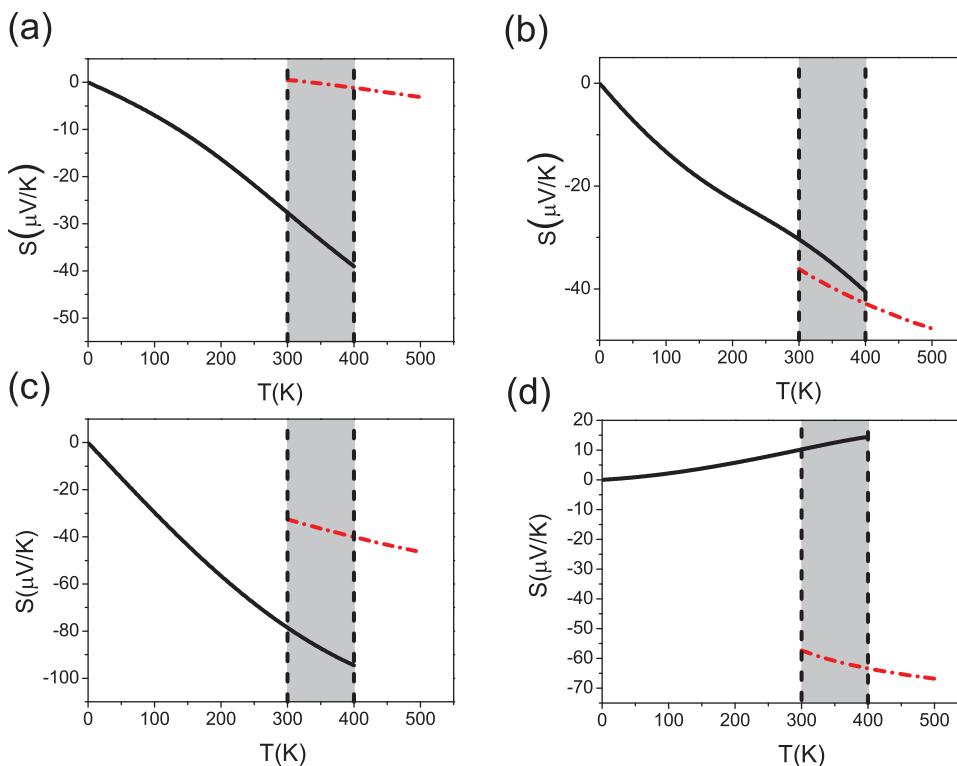

FIG. 3. Seebeck coefficients of C_{60} single-molecule junctions without (solid black line) and with (red dashed-dotted line) surface reconstruction as a function of the temperature T for various tip heights $d =$ (a) 2.1 Å, (b) 2.3 Å, (c) 2.77 Å, and (d) 3.4 Å. The shaded areas represent the range of temperatures within which surface reconstruction is expected to occur. The left (right) of the shaded areas denote the well-defined unreconstructed (reconstructed) phase.

given junction because the indentation of the Cu(111) surface exerted by the C_{60} molecule shortens the tip-to-substrate distance and thus increases the transmission probability. A more detailed understanding of this relationship can be gained by investigating Eq. (4) and Fig. 2.

In conclusion, a discontinuity at the surface reconstruction temperature can happen in the temperature profile of Seebeck coefficients in single-molecule STM junctions. To illustrate the possible abrupt changes in the temperature profile of Seebeck coefficients, we theoretically investigate the Seebeck coefficients of C_{60} single-molecule junctions with and without surface reconstruction. The reconstruction induces the indentation of the Cu(111) surface exerted by the C_{60} molecule. Surface reconstruction enhances charge transfer from the C_{60} molecule to the Cu(111) surface, which leads to crucial changes in electronic structures. Consequently, abrupt changes in the conductances and temperature profiles of Seebeck coefficients occur at the surface-reconstruction temperature around 300–400 K. The junction with $d = 3.4\,\text{Å}$ can even change the sign of the Seebeck coefficient from positive (p-type) to negative (n-type) at that temperature. The Seebeck coefficient is related to both the magnitude and slope of the transmission function, whereas the conductance is merely determined by the magnitude of the transmission function at the Fermi level. Consequently, the effects of surface reconstruction on Seebeck coefficients are more complicated than that on conductances. We illustrate this point by comparing the effects of surface reconstruction on the conductance and Seebeck coefficient. Surface reconstruction generally enhances the conductance as experimentally shown due to the shorter tip-to-substrate distance caused by surface reconstruction. On the other hand, surface reconstruction can enhance ($d = 2.3$ and $3.4\,\text{Å}$) or suppress ($d = 2.1$ and $2.77\,\text{Å}$) Seebeck coefficients depending on different tip heights d. We suggest that future STM experiments explore the temperature-discontinuities of the Seebeck coefficients, with C_{60} as one of the best candidates.

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