I. INTRODUCTION

Endohedral metallofullerenes have attracted much attention as caged molecules with unique structural and electronic properties and a variety of potential applications [1–4]. These studies mainly focused on the electronic structure of magnetic metallofullerenes with encapsulated group-III metal or lanthanide atom, M@C$_{82}$ [5–7]. Various diffraction, spectroscopy, and microscopy techniques [7–16] have been used to characterize these metallofullerenes, which revealed that metal atoms were indeed encapsulated by the carbon cage and that the metal atoms were located off the center of the fullerene cage. Many experimental and theoretical techniques have been employed to characterize the variation of structural and electronic properties of metallofullerenes when it interacted with other compounds or being adsorbed on substrates [16–22]. It has been found that the electronic structures of metallofullerenes at molecular and cluster levels could be significantly modified by the substrates. Such knowledge is of importance for building solid-state devices involving single molecules or structured molecular assemblies.

Scanning tunneling microscopy (STM) is a unique method for structural investigation of adsorbed molecules on the conductive surfaces. High-resolution STM makes it possible to determine the packing arrangements and even electronic structures of fullerene molecules adsorbed on various metal or semiconductor surfaces [19–30]. On the Si(111) substrate, Dy@C$_{82}$ and C$_{60}$ molecules were adsorbed randomly and stably individually on surface, suggesting strong interactions between Si atoms and fullerene molecules [26, 27]. In contrast, the fullerenes are likely bonded to metal surfaces via weak ionic bonds or van der Waals forces [29, 30]. A recent STM investigation of substrate-dependent adsorption of Gd@C$_{82}$ on Cu(111) and Cu(100) showed that the lattice structure of the underlying metal substrates affected the arrangement of the metallofullerenes [20]. It was found that the growth of Gd@C$_{82}$ proceeded in a Volmer-Weber mode and the arrangement of the islands was determined by the molecule-molecule interaction. By comparing high-resolution STM images with molecular orbitals calculated by density functional theory (DFT), Wang et al. gave the geometrical and orientational information of Dy@C$_{82}$ on Ag/Si(111) surface [14].

Here, we present an STM study of Dy@C$_{82}$ molecules deposited onto a Au(111) substrate. The Dy@C$_{82}$ (isomer I) is a metallofullerene in which the Dy atom lies along a C$_2$ axis on the six-membered ring of the C$_{2v}$–C$_{82}$ cage [11, 12]. It promises one of the candidate materials for creating single molecular orientation switching devices owing to the electric dipole moment [16, 31–34] based on the electron exchange between the encapsulated metal atom and the fullerene cage. The control of the texture and the orbital interactions of surrounding Dy@C$_{82}$ molecules on the subnanometer scale is the key to realizing the single molecular orientation switching device using Dy@C$_{82}$. In this work, the coverage-dependent orientations of Dy@C$_{82}$...
molecules on Au(111) are characterized. The orientations of Dy@C$_{82}$ molecules can be derived by the intramolecular patterns. It is found that the adsorption orientations of Dy@C$_{82}$ molecules on Au(111) substrate are both influenced by the fullerene-substrate interaction as well as the dipole-dipole interaction between the fullerenes.

II. EXPERIMENTS

The Au(111) substrates with well-defined terraces and single atomic steps were fabricated by thermal evaporation of gold film of $\sim$160 nm thickness onto mica. Several cycles of Ar$^+$ (600 eV) sputtering and annealing were used to clean and flatten the Au(111) surface in the preparation chamber of an Omicron ultrahigh vacuum (UHV) LT-STM system. The Dy@C$_{82}$ (isomer I) was produced by dc arc-discharge method followed by purification and isolation via multistage high-performance liquid chromatography as described elsewhere [6, 7]. The resulting solution of Dy@C$_{82}$ in toluene was hermetically sealed in darkness. A small amount of solid powder of Dy@C$_{82}$ was obtained in a tantalum crucible by evaporation of solvent in a dry box. The powder was degassed thoroughly at 450 °C and then a low coverage of Dy@C$_{82}$ was deposited onto Au(111) surface at approximately 400 °C. Furthermore, to control the molecular coverage intermediate between full monolayer and isolated molecules, we prepared another samples by drop casting 10 $\mu$L of dilute solution of Dy@C$_{82}$ in toluene onto the Au(111) substrate. The samples were subjected to a post annealing process at about 300 °C to remove residual solvent or impurities. STM experiments were carried out at a base pressure below 10 nPa with an electrochemically etched tungsten tip, which had been subjected to a careful cleaning treatment. Deposition of a suitable amount of Dy@C$_{82}$ was checked using STM at room temperature. And then the substrate was cooled to liquid N$_2$ temperature (80 K) for the detailed characterization, where the rotations of the molecules were frozen out and high-resolution images of the molecular orbital structure were obtained. All STM images presented in this work were acquired in the constant current mode.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical STM image of Dy@C$_{82}$ (10 molecules/(100 nm)$^2$) on Au(111) surface. The bright near-circular features correspond to the individual Dy@C$_{82}$ molecules. The typical 22$\times$$\sqrt{3}$ herringbone reconstruction features of Au(111) surface can be observed on the bare gold substrate. As the case for La@C$_{82}$ on Ag/Si(111) surface [25], it can be found that the molecules are able to diffuse on the surface at room temperature and become bound at reactive sites where there are unsaturated dangling bonds. Some molecules in the sample prepared by sublimation of Dy@C$_{82}$ on the gold surface can be observed on the terrace, however, most of the molecules are present at step edges, indicating their easy migration during deposition because of the weak interaction with the substrate. This is in sharp contrast to the adsorption of fullerenes on Si(111) surface [26, 27], in which the fullerenes such as C$_{60}$, Dy@C$_{60}$, and Dy@C$_{82}$ do not freely migrate.

Figure 1(b) is a higher resolution image showing the internal patterns of three Dy@C$_{82}$ molecules adsorbed on the terrace. It is observed that there are several kinds of intramolecular patterns of the Dy@C$_{82}$ molecules adsorbed on the same image conditions, indicating various molecular adsorption configurations. The intramolecular patterns in the STM images depend strongly on the bias voltages. Figure 1(c) and (d) show two images of the same molecule at different sample bias voltages. The empty states image (Fig.1(c)), taken at +1.7 V, show some bright pentagon and hexagon rings. These patterns are believed to be most directly related to the cage structure of the
fullerene [14, 28]. In the filled states image (Fig.1(d)), taken at −1.7 V, the molecule appears as several slightly curved bright stripes. Such an intramolecular pattern has been observed in STM images of other fullerene molecules such as C_{60} and C_{70} adsorbed on different surfaces, and ascribed to the combined contributions of the fullerenes and substrates [27].

Further deposition of Dy@C_{82} onto Au(111) substrate leads to the formation of cluster chains along the steps as shown in Fig.2(a). Previous STM studies of Y@C_{82} [32] and Nd@C_{82} [33] on surfaces revealed the presence of pairs and small clusters of molecules at low coverage. These observations are attributed to the permanent dipole moment of the molecules. The STM image in Fig.2(a) also shows that regularly spaced chains of three and four molecules predominate at the straight step edges. The spacing of the molecules in the chains is 1.14–1.16 nm, similar to the nearest neighbor distance of the (111) face of bulk fcc Dy@C_{82} [11].

Intervals among these chains seem periodic to some extent. It is shown that this periodic behavior is due to selective adsorption at the steps where they intersect the fcc regions of the reconstructed surface [30]. High-resolution STM images (Fig.2 (b) and (c)) show different intramolecular patterns in the clusters such as a short chain and one trimer. Considering the selective adsorption sites and the multiple adsorption configurations of Dy@C_{82} molecules, these cluster structures at this molecular coverage are dominated by the adsorbate-substrate interaction rather than the dipole-dipole interaction between the metallofullerenes which is expected for Dy@C_{82} [7].

With the increasing of the coverage, the adsorbed molecules occupy almost all the edge positions; Dy@C_{82} islands are thereafter formed extending out from the step edges on both the upper and lower terraces (Fig.3). Locally, the crystallographic directions of the islands are maintained across the step edges as shown in Fig.3(a). However, at this coverage various domain orientations are observed, unlike the case for Gd@C_{82} on Cu(100) with one domain orientation [20]. As shown in Fig.3 (a) and (b), the domains of Dy@C_{82} can take any one of the following orientations: 0°, ±7°, or 30° rotated from the close packing directions of gold atoms on Au(111). Domain boundaries due to merging growth fronts are observed as shown in Fig.3(b). Therefore, the growth of Dy@C_{82} islands at room temperature is not epitaxial on the Au(111) surface. The arrangement of these islands is presumably dominated by the molecule-molecule interaction. In the magnified image (Fig.3(c)), we find that these molecules aggregate into a quasi hexagonal close packed (hcp) domain, similar to the fcc (111) structure. The cross-sectional profile (Fig.3(d)) through the island shows that the nearest neighbor distance of the molecules is 1.14 nm, an intermolecular separation same as Dy@C_{82} bulk crystal [11]. A number of larger bright spots are observed on the islands. These spots are about 0.2 nm higher than the other molecules, con-
FIG. 4 Filled states (−0.8 V, left) and empty states (+0.8 V, right) current images showing molecular details of the same area of a Dy@C_{82} island on Au(111), size is 9 nm×6 nm, I_{set}=0.1 nA. Circles show three molecules with different intramolecular patterns labeled as A, B, and C. Dot signs are superimposed on the graphs to show the same molecules in each image.

siderably lower than that would be expected for a second layer molecule. The larger bright spots may be due to larger fullerene molecules which appear as random point defects and do not appear to distort the positions of the surrounding molecules.

In a bulk Dy@C_{82} crystal, the molecule is orientationally disordered around the C_{2} axis of the C_{2v}-C_{82} cage at room temperature [12]. When adsorbed on a solid surface, it presents different ratchet-type rotation according to the molecule-substrate interaction. On Si(111) surface the rotations of Dy@C_{82} molecules are frozen out leading to the first observation of the internal structures at room temperature [26]. On Ag/Si(111) surface, various intramolecular patterns of individual Dy@C_{82} molecules can be obtained at 5 K, ascribed to a small subset of all of the possible orientations on the surface [14]. As for Au(111) surface, we could not observe the intramolecular patterns at room temperature (see the close-up STM image of an island in Fig.3(c)). Therefore, on Au(111) surface the interaction is presumably weaker and the Dy@C_{82} molecules rotate at room temperature even in the close packed overlayer. To characterize the molecular orientations of Dy@C_{82} molecules on monolayer islands, we have acquired filled states (−0.8 V) and empty states (+0.8 V) current images of the same area of a Dy@C_{82} island at 80 K, as shown in Fig.4. The images show many different orientations of the Dy@C_{82} molecules on the Au(111) surface. Overall three orientations are found to be abundant, assigned to different dot signs (see Fig.4). Comparing the molecules A, B, and C in both images, we find that molecules A and B adopt the same adsorption orientation on the substrate except for an oblique angle with respect to each other in the surface plane. This process permits recognizing the molecules with same orientations on an island.

As the coverage approaches 1 ML, grain boundaries come into being due to the different oriented domains in the Dy@C_{82} overlayer on Au(111). Post-deposition annealing is required to reduce the kinetic barriers for relaxation of the overlayer and surface atoms. In addition, well-ordered overlayers can be achieved by multilayer deposition followed by annealing of the sample to desorb those molecules that did not directly bond to the surface. Figure 5 shows STM image of Dy@C_{82} molecules adsorbed on Au(111) at a coverage close to a complete monolayer, with a high density of voids and single vacancies. The nearest neighbor distances in this long-range-ordered monolayer are equal to the ones in the above-mentioned hcp islands, within the measurement error of STM. Figure 6(a) shows a high-resolution STM image revealing the molecular orientations of Dy@C_{82} molecules. Three preferable orientations of the Dy@C_{82} molecules are found in the two-dimensional hexagonal close packed overlayer, as the molecules labeled as I, II and III, which appear the similar “stripe” patterns. Equally oriented molecules form small domains [22] consisting of several molecules within the monolayer islands as shown in Fig.6(a), where colored lines are superimposed on the molecules at the bottom region for visualization of domains. On Cu(111) surface [20] the uniform feature of individual Gd@C_{82} molecules in the arrays indicated that the molecules adopted the same adsorption configurations. As for Au(111) surface, the interaction is presumably weaker, and correspondingly we do not observe a predominate molecular orientation.

In order to understand the molecular orientations in Dy@C_{82} monolayer, we have carried out DFT calculations on a free Dy@C_{82} molecule using the molecular...
The molecular orientation is derived by matching the Kohn-Sham molecular orbital from DFT with the striped molecular orbital patterns from the STM image of Dy@C$_{82}$ molecules. Initially, we set the Dy@C$_{82}$ molecule with a standard orientation in which the C$_2$ axis is defined as the z direction. (c) Diagram of one molecular orientation according to type I molecules. The three Euler angles relative to the standard orientation are $\alpha=198^\circ$, $\beta=96^\circ$ and $\gamma=207^\circ$, respectively. (d) Kohn-Sham molecular orbital of $-1.21$ eV from DFT for Dy@C$_{82}$ with an isovalue of $1.0 \times 10^{-3}$ e/Å$^3$, corresponding to the orientation shown in (c). (e) Schematic graphs showing the molecular alignments along one of the close-packing direction of the Dy@C$_{82}$ monolayer. Arrows represent dipole moments of Dy@C$_{82}$ molecules.

IV. CONCLUSION

We have investigated the adsorption behavior and molecular orientation of Dy@C$_{82}$ isomer I on Au(111) at different coverages. STM images show that small amounts of molecules are preferentially adsorbed on the step edges. With the increasing of the coverage, the adsorbed molecules occupy almost all the edge positions and formed cluster chains along the step edges. The Dy@C$_{82}$ islands are thereafter formed on the terraces with various domain orientations. The Dy@C$_{82}$ molecules rotate at room temperature even in the close packed overlayer. Therefore, the growth of Dy@C$_{82}$ islands at room temperature is not epitaxial on the Au(111) surface.

High-resolution STM images at 80 K show that Dy@C$_{82}$ molecules present various molecular orientations at low coverage. When the coverage approaches 1 ML, ordered islands consisting of small domains of equally oriented molecules are observed. The Dy@C$_{82}$ ellipsoid prefers the adsorption configurations with the
major C$_2$ axis approximately parallel to the surface of the substrate. Three preferable orientations of the Dy@C$_{60}$ molecules are found in a two-dimensional hexagonal close packed overlayer. These observations are attributed to the fullerene-substrate interaction and dipole-dipole interaction between the metallofullerenes.

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