Local electronic edge states of graphene layer deposited on Ir(1 1 1) surface studied by STM/CITS

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Abstract

Scanning tunnelling microscopy and current imaging tunnelling spectroscopy were used to observe electronic structure of the edges of monolayer graphite film deposited on the Ir(1 1 1) surface. The electronic structure derived from the tunnelling spectra revealed peak in electron local density of states very close to the Fermi level. This electronic state was interpreted in terms of localised edge state caused by the topology of the \( p \) electrons networks typical for the zig-zag edges. The observed maximum of local density of states at about 0.2 eV above the Fermi level was ascribed to the presence of resonant state caused by the appearance of disclinations centres in the vicinity of the graphite edges.

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1. Introduction

The tight binding band calculations performed on the single-layer graphite ribbon (graphene) with edges of two shapes, zig-zag and armchair, show peculiar localised state depending on the edge shape [1–4]. The ribbon zig-zag edge shows the localisation of the electrons near the edge and peak in the density of states (DOS) near the Fermi level—localised edge state (LES). The LES stems from the topology of the \( \pi \) electron networks with the zig-zag edge and does not appear in the armchair edge at all [2,3]. The influence of the localised state on the global electronic properties considered in terms of DOS is rather small.
when the ribbon width is large. However, in this case the LES can be observed on the local density of states (LDOS) measured in the vicinity of the zig-zag ribbon edges. Furthermore, the predicted edge state in single-layer ribbon is well reproduced in the zig-zag edges of the multi-layer AB stacking ribbons [5–7]. It suggests that the localised edge state can be even observed on more realistic surface like AB stacked graphite.

The aim of the present investigations is to study the electronic structure of monolayer graphite (MG) film (graphene) deposited on the Ir(1 1 1) surface using scanning tunnelling microscopy and current imaging tunnelling spectroscopy techniques (STM/CITS). Since, this MG is bonded to the metal via Van der Waals forces without electron exchange [8–15], so it can be considered in terms of nearly isolated graphene ribbon. Here we would like to emphasize that there are also some theoretical and experimental results suggesting that interaction between MG and metal substrate is quite strong and contribute to the hybridization of the orbitals between the graphene sheet and the substrate [16–19]. However, we believe that the model with van der Waals forces without electron exchange seems to be more accurate and depicts more experimental evidences than models with strong interaction between graphene and substrate. So, in our experiments MG formed on the Ir(1 1 1) substrate is considered in terms of nearly isolated graphene ribbon.

The presence of natural MG zig-zag edges will enable us to determine whether the LES near the Fermi level exists. Furthermore the obtained results will make it possible to evaluate the role of mutual interactions between graphite layers on the CITS data presented previously [5,7]. It is because some characteristic features on the tunnelling spectra could be smeared due to the weak interlayer bonding, caused by overlapping between 2pz orbitals in the bulk graphite.

2. Experimental details

The Ir(1 1 1) samples with graphite layer covered surfaces were prepared and characterized in the UHV chamber (<10⁻¹⁰ mbar) having Auger spectrometer and electrostatic prism electron analyzer. Energy resolution was ΔE/E < 0.1%, the primary electron density was ~0.1 μA/cm², their energy ~1800 eV. The chamber was equipped with a gas inlet, and a monopole mass-spectrometer was applied to control the residual gas composition. Graphite layer was grown on surface of polycrystalline Ir ribbon of size 40 mm x 1.5 mm x 0.03 mm, which was initially annealed up to 2000 K by passing through it ac current. Being polycrystalline, the ribbon has nearly homogeneous crystalline orientations of surface (1 1 1) for Ir. Graphite layer was chemically deposited from benzene vapour on the surface of Ir(1 1 1) heated up to T = 1700 K. The growth of graphite layer should automatically stop when the surface is covered completely with the monolayer graphite. This is related to the fact that the surface reactivity for benzene dissociation is strongly reduced by the formation of the graphite overlayer. So, in this way of preparation, monolayer graphite coverage for the surfaces is expected. On the surface averaged scale this was experimentally confirmed via observation of the Ir Auger signal reduction by 1.6 times which is near to the theoretical attenuation by one monolayer of graphite [11].

The STM/CITS experiments were performed at room temperature with a commercial VT-STM/AFM system in UHV condition (Omicron GmbH, Germany). During the measurements base pressure was of 2 x 10⁻¹⁰ mbar. The tips used were prepared by mechanical cutting from the 90%Pt–10%Ir alloy wires. In spectroscopic mode, the I/V curves were recorded simultaneously with a constant current image by the interrupted-feed-back-loop technique (current imaging tunnelling spectroscopy mode–CITS). The I/V curves were then stored in a laboratory computer and their voltage derivatives were obtained. After each acquisition sequence the surface was scanned again in order to observe the influence of spectroscopy measurements. In the case of visible surface damages, the spectroscopy data were not taken into account.

3. Experimental results

3.1. STM results

The topography of the clean Ir(1 1 1) substrate is shown in Fig. 1(a). The image clearly shows terraces of triangular shape separated by mostly monoatomic
steps. The steps are oriented parallel to the [1 1 0] direction which is compact direction in the (1 1 1) surface of the fcc crystal. The steps cross each other at angles of 60° and 120°.

The STM image in Fig. 1(b) shows monolayer graphite deposited on the Ir(1 1 1) surface. Furthermore, it is seen that the deposited MG is continuous—covering whole the substrate. In all the STM images, which have been obtained, there was always observed that the graphite layer covering the entire Ir(1 1 1) surface area. It is important to note that there is a crystalline-geometrical accordance between the graphite layer and the Ir(1 1 1) metal surface.

Furthermore, in Fig. 1(c) we show MG terraces with well defined step edges where the triangular symmetry of the Ir(1 1 1) substrate is well visible due to the monolayer graphite thickness. STM images of the regions in the vicinity of the step edges were obtained in constant current and height modes. However, no recognisable periodic structure typical for graphite could be resolved. It may prove that the surface in the vicinity of the edges is not uniform as a result of zig-zag/armchair edges and mechanical deformations, thought away from the step edges atomic resolution was always observed as presented in Fig. 1(d).

The obtained MG fabrication results enable us to carry out STM/CITS measurements at different regions over the graphite terraces with edges. A detailed analysis of the tunnelling spectra will enable...
us to determine whether the tunnelling via localised edge state takes place.

3.2. CITS results

In Fig. 2(a) the constant current image of the Ir(1 1 1) terraces covered by MG is presented. In addition to the topography, the I(V) tunneling spectra at every pixel in the image were simultaneously recorded - CITS. Using the I(V) data, a spatial maps of the quantity $(dI/dV)(V)$ at a given voltage were calculated.

In Fig. 2(b) the map of the $(dI/dV)(V)$ quantity for the sample bias $+0.20$ V is presented. In this picture the bright contrast indicates a large value of the $(dI/dV)(V)$. Since the $(dI/dV)(V)$ is a measure of LDOS, the image corresponds to the surface map of the LDOS at the energy of $0.20$ eV above the Fermi level. Fig. 2(b) shows a high LDOS at MG edges and in the vicinity of the edges, it indicates the presence of electronic localized state close to the Fermi level. Similarly, Fig. 2(c) corresponds to the surface map of LDOS at energy of $0.90$ eV above the Fermi level and indicates that this electronic state disappeared completely at higher energies. This is especially seen for the edge denoted by #1.

It seems to be interesting to analyse single $(dI/dV)(V)$ curves recorded over MG edges. However, firstly we focus on the $(dI/dV)(V)$ curves recorded on pure Ir(1 1 1) surface (Fig. 3).
On these spectra we observe local maximum of LDOS at about 0.35 eV below the Fermi level. In our interpretation this peak can be attributed to the presence of sp-like surface state (SS) which lies in the bulk band gap of the Ir(1 1 1). The nature of the SS is similar to the surface states observed on noble and transition (1 1 1) metals. The energy of the surface state on the Ir(1 1 1) surface estimated from angle-resolved photoelectron spectroscopy (ARPES) measurements equals 0.4 eV below the Fermi level [20]. This value is in good agreement with our tunnelling spectroscopy measurements.

In Fig. 4 the dI/dV(V) curves recorded over MG edges denoted in Fig. 2 by #1 and #2 are presented. The appearance of the local maximum of LDOS at about 0.2 eV above the Fermi level (RS) is presented. The dI/dV curves are shifted in vertical scale for the sake of clarity.

In fact, these two factors i.e. band dispersion (due to the multilayer graphite structure) and additional
resonant states (due to the appearance of fused disclination centres) could cause some problems when distinguishing the localised edge state from the resonant states. Thus estimation of energy of the LES was complicated. In the present experiments the first factor i.e. band dispersion can be significantly minimized. This is because, MG/Ir(1 1 1) structure can be considered in terms of nearly isolated graphene ribbons bonded to the metal via Van der Waals forces without electron exchange. Unfortunately, the second factor i.e. the appearance of additional resonant states cannot be excluded from the experiments for the reason that mechanical deformations always exist in the vicinity of the edges.

A detailed analysis of the conductance maps shows a high LDOS at MG edges and in the vicinity of the edges even at energies very close to the Fermi level. This is presented in Fig. 2(d) for the \( \frac{dI}{dV}(V) \) map recorded at sample bias \(-0.005\) V. The inspection of the \( \frac{dI}{dV}(V) \) curves in the energy range close to the Fermi level \(\pm 0.5\) eV revealed the local maximum of LDOS at about 0.2 eV above the Fermi level (RS) and additional electronic state (LES) at about 0.025 eV below the Fermi level (Fig. 5). In our opinion peak at energy 0.025 eV below the Fermi level can be interpreted in terms of localised edge state caused by the topology of the \( \pi \) electrons networks typical for the zig-zag edges. The RS peak is interpreted in terms of resonant state caused by the presence of disclinations centres in the vicinity of the graphite edges. As was discovered, energy position of the LES and RS did not strongly depend on spatial position.

Hence, we believe that in the experiments carried out over MG edges we were able to resolve both LES and RS states. It was not possible in our previous experiments carried out on bulk graphite edges due to the presence of small band dispersion around the Fermi level. As result, superposition of LES and RS was mainly observed. From the experiments carried out on the MG it is concluded that the zig-zag edges show localisation of electrons near the edges and peak in the LDOS very close to the Fermi level or even at the Fermi level—localised edge state.

4. Conclusions

In summary, we have studied electronic structure of the edges of monolayer graphite film deposited on the Ir(1 1 1) surface.

1. On the pure Ir(1 1 1) surface the observed local maximum of LDOS at about 0.35 eV below the Fermi level was ascribed to the presence of sp-like surface state which lies in the iridium bulk band gap.

2. On the Ir(1 1 1) surface covered by monolayer graphite the surface state at 0.35 eV below the Fermi level disappeared completely. A new local maximum of LDOS at about 0.2 eV above the Fermi level was observed at the graphite edges. This maximum of LDOS was ascribed to the presence of disclinations centres in the vicinity of the graphite edges (resonant state).

3. The additional electronic state at about 0.025 eV below the Fermi level was detected in the vicinity of the monolayer graphite edges, and attributed to the localised edge state caused by the topology of the \( \pi \) electrons networks typical for the zig-zag edges. Even though the atomic resolution on the MG edges was not achieved in our experiments the tunnelling spectra can be used to make quantitative

![Fig. 5. The \( \frac{dI}{dV}(V) \) curves recorded over two different edges denoted in Fig. 2 by \#1 and \#2. The appearance of the local maximum of LDOS at about 0.2 eV above the Fermi level (RS) and additional electronic state (LES) at about 0.025 eV below the Fermi level is presented. The \( \frac{dI}{dV} \) curves are shifted in vertical scale for the sake of clarity.]
conclusions about topological structure of the observed edges.

4. In the tunnelling experiments carried out over monolayer graphite edges it was possible to resolve both localised edge state and resonant state.

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References