

Interaction between Tip and HOPG Surface Studied by STS

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Transformation of highly oriented pyrolytic graphite (HOPG) is investigated by scanning tunneling microscope (STM) and its spectroscopic mode, scanning tunneling spectroscopy (STS). This transformation is caused by the interaction between tip and HOPG surface because HOPG takes the layer structure. The aim of the study was to attempt to establish more quantitative measure of the HOPG surface. STS spectra exhibited clear dependence of the separation between tip and surface. The feature of this difference in STS spectra could be classified two. However, the STS spectra are not changed largely when tip is very close to the surface. Current distance (*I*-*s*) characteristic is presented along with the interpretation of the result.

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Highly oriented pyrolytic graphite (HOPG) is widely used in the measurement by scanning tunnelling microscope (STM)¹⁾ as a standard sample to check the atom-resolving ability of the apparatus. HOPG has following good properties as a standard sample for STM. It easily offers an atomically flat and clean surface just by peeling off the surface layer with a mending tape. It is electroconducting, and also its surface corrugation is large due to the presence of surface dangling bonds compared with other materials such as metallic samples. However, some disadvantages of HOPG, such as the formation of flakes and the tip-induced surface deformation, were also reported.²⁾³⁾ Some unusual related phenomena had been reported in the STM investigation of HOPG,⁴⁾⁵⁾ such as the giant corrugation and many artefacts. Hence, the electronic state of HOPG was not investigated by STM in detail.

In this paper, scanning tunnelling spectroscopy (STS) measurement was used to investigate the electronic property of HOPG. The change in the STS spectra is discussed in relation to the tip-induced deformation of HOPG.

Experimental

The applied bias voltage (*V*) dependence of the tunnel current (*I*), i.e. the *I*-*V* characteristics of freshly cleaved surface of HOPG were measured using mechanically sharpened Pt/Ir (80/20%) tip at ambient condition. The STM equipment used was Nanoscope E of Digital Instruments. The measurement was always commenced by observing the carbon atoms of HOPG surface so as to ensure that the tip is sharp enough.

At the beginning of the measurements of the *I*-*V* characteristics, the bias voltage was always set at 50mV, while the initial tunnel current (set-point current) was varied between 0.2nA and 2.2nA at 0.05nA step. It should be noticed that the separation between the tip and the HOPG surface decreases as the set-point current increases. The *I*-*V* characteristics were measured five times at a same place on the HOPG surface, and this procedure was repeated at five different places with the

same set-point current. 512 tunnel current data were taken between -1.0V and 1.0V. The *I*-*V* characteristics were transformed to $(dI/dV)/(IV)$ characteristics by numerical calculation to obtain STS spectra. In order to reduce the noise on $(dI/dV)/(IV)$ characteristics, some Savitzky-Golay numerical low-pass filtration was applied.

It was hard to obtain qualitatively good STS spectra with high spatial resolution and high energy resolution because the measurement was operated in air. In order to overcome these difficulties, every spectrum was obtained by averaging over 25 equivalent spectra. Thus, the spatial information in the atomic scale was lost.

Results and Discussion

The bias voltage dependence of the $(dI/dV)/(IV)$ calculated from the *I*-*V* characteristics was obtained with the set-point current ranging from 0.2 nA to 2.2 nA at 0.05nA. The obtained spectral profiles resembled each other, but the profile exhibited apparent change at the set-point current of ca. 1.1 nA. Figure 1 shows the selected spectra. At a set-point current below 1.1 nA, the bottom of the curve is located around 230 mV, while at over 1.1 nA, the bottom shifts to around 300 mV. Figure 2 shows the set-point current dependence of the bias voltage of the $(dI/dV)/(IV)$ minimum (STS_{min}). It should be noted that the tip-sample separation decreases as the set-point current increases. At a set-point current below 1.1 nA, the STS_{min} tends to increase gradually from 200 mV, and jumps at around 1.1 nA to 300 mV. At over 1.1 nA, the STS_{min} is almost constant but only increases slightly.

Theoretically, the $(dI/dV)/(IV)$ value represents the local density of states (LDOS).⁶⁾⁷⁾ Therefore, the difference in the STS spectra corresponds to the difference in the electronic state of the sample surface. Since HOPG is known to deform upon approach of the tip due to the pressure of the tip, this change in the STS spectra should be attributed to the deformation of HOPG. However, the STS curve is severely affected at low set-

point current rather than at high set-point current. This fact suggests that the deformation of the HOPG surface is induced at large tip-sample separation. From the investigation by atomic force microscopy measurement,⁸⁾ the tip senses first an attractive force and then a repulsive force from the surface upon approaching. At large tip-sample separation, the sample should sense an attractive force from the tip enhanced by the applied voltage. Figure 3 shows the model image this attractive force and deformation of the surface induced by the attractive force. The attractive force separates the surface layer from the bulk of HOPG, and induces a difference in LDOS. This assumption is highly probable, since it accords with the fact that the HOPG surface tends to form flakes of carbon atoms in the STM measurement. Separation of surface layer from the bulk should result in formation of flakes. Since STS changes only slightly at high set-point current, the deformation should be ceased at this condition, but HOPG should start to deform by the pressure of the tip.

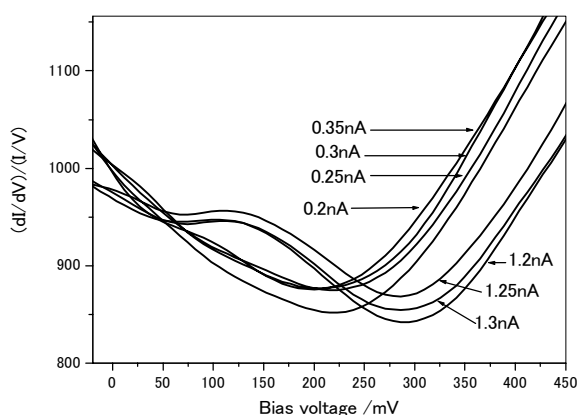


Fig. 1 Bias voltage dependence of $(dI/dV)/(I/V)$ curve.

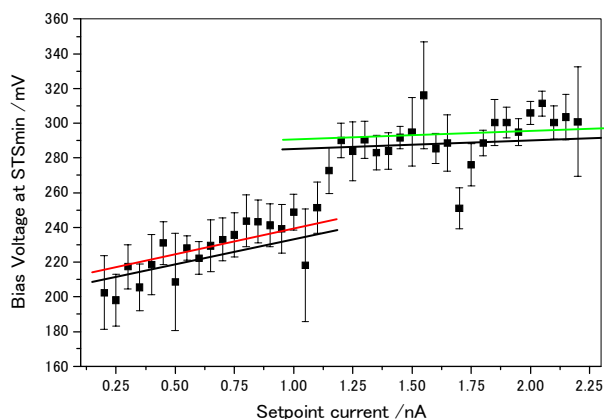


Fig. 2 Set-point current dependence of the voltage of $(dI/dV)/(I/V)$ minimum (STSmin).

Looking back on Figure 1, it is clear that the difference in STS is severe at positive bias voltage higher than +250mV. In this voltage region, the electron tunnels from the negatively biased tip to the vacant state of HOPG. Thus STS shows that the vacant state of HOPG shifts towards higher energy side by the approach of the tip. Considering the deformation of the sample discussed above, the vacant state shifted to lower energy side by the separation of the surface layer. This is not unusual since by the separation from the bulk, the π -conjugation of the surface

layer is enhanced by cutting off the weak σ bond-like interaction between the layers, consequently lowering the energy of LDOS. The σ bond-like interaction present at high set-point current should also cause a localisation of LDOS, and consequently generates a low-energy LDOS. The peak at around 120 mV generated at > 1.1 nA must be the low-energy LDOS just discussed.

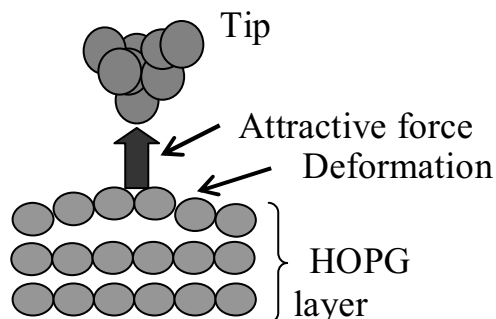


Fig. 3 Schematic illustration of the deformation of HOPG induced by the attractive force between tip and HOPG.

Conclusion

The I-V characteristic measurement and scanning tunnelling spectroscopy measurement were successfully applied to evaluate the electronic state of HOPG. The change in surface electronic state induced by the approach of the tip to the HOPG surface was concluded as caused by the deformation of HOPG. The attractive force present between the tip and HOPG is concluded as the major factor that causes the separation of the surface layer of HOPG.

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