

Surface structures of layered compounds treated with alkali-metal hydroxide solutions studied by scanning tunneling microscopy

Koji Miyake and Hidemi Shigekawa

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

Ordered 2×2 and $\sqrt{3} \times \sqrt{3}$ superstructures with charge density modulation were observed by scanning tunneling microscopy (STM) on highly oriented pyrolytic graphite surfaces treated with MOH ($M=\text{Na}, \text{K}$) aqueous solutions. Charge transfer from intercalants to host graphite was observed, as previously seen on stage-1 alkali-metal intercalations. On the other hand, for the MoS₂ crystal treated with the same solutions, the host MoS₂ lattice was observed together with island structures with low charge density formed by intercalants. Some electronic states seemed to be formed between the MoS₂ band gap.

Layered compounds, such as graphite and transition-metal dichalcogenides, are known to intercalate various kinds of atoms or molecules, forming new materials called intercalation compounds. Since these intercalation compounds have new properties differing from those of host materials, they have attracted considerable attention. When materials are intercalated in every "n" host interplaner gap, the structure is defined as having stage-"n". Among the various stage structures, only the first and second stages have been studied in detail. For example, scanning tunneling microscopy (STM) was performed on the stage-1 alkali-metal graphite intercalation compound (M-GICs: $M=\text{Li}, \text{K}, \text{Rb}, \text{Cs}$) surfaces [1-3], and structures such as 2×2 and $\sqrt{3} \times \sqrt{3}$ superstructures were observed directly, confirming the results of X-ray diffraction measurements. Compared to the GICs where intercalants have ordered structures as mentioned above, detailed structures of the MoS₂ intercalation compounds remain to be clarified.

In this paper, we present the results of STM observation of the MOH ($M=\text{Na}, \text{K}$)-treated HOPG (highly oriented pyrolytic graphite) and MoS₂ crystals. Samples were prepared by introducing dropwise MOH ($M=\text{Na}, \text{K}$) aqueous solutions onto freshly cleaved HOPG and MoS₂ surfaces or dipping HOPG and MoS₂ crystals into MOH aqueous solutions. STM was performed in air at room temperature by using a Pt/Ir tip. All STM images were taken in the constant height mode.

Recently, we found that HOPG crystals treated with NaOH solutions form a stage-8 intercalation compound, and that 2×2 and $\sqrt{3} \times \sqrt{3}$ superstructures were observed on the surface using STM [4]. Similar superstructures were also observed on a KOH-treated surface. Figure 1 shows an STM image of a KOH-treated HOPG surface ($V_t = -20\text{mV}$, $I_s = 2.0\text{nA}$). The distance between protrusions is about 0.42nm, corresponding to a $\sqrt{3} \times \sqrt{3}$ superstructure of the HOPG substrate.

According to tunneling spectroscopy of the MOH-treated HOPG samples, an increase in the charge density near the Fermi level after the treatment was observed as shown in Fig. 2, indicating a charge transfer from the intercalant to the host graphite, similarly to the case of alkali-metal GICs.

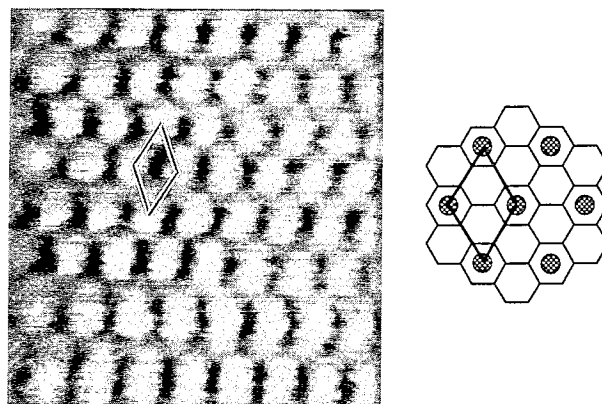


Fig. 1 STM image of KOH-treated HOPG surface (30nm \times 30nm).

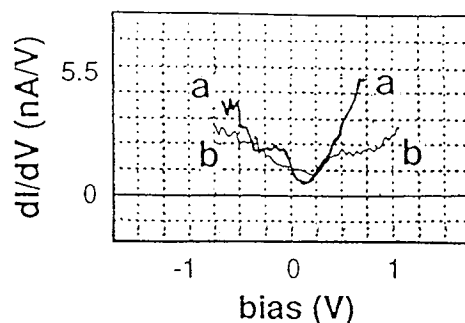


Fig. 2 Tunneling spectroscopy of a HOPG surface before (indicated by "b") and after (indicated by "a") NaOH treatment.

When a HOPG surface was treated with NaOH solution, a new $\sqrt{3} \times \sqrt{3}$ structure formed by three different kinds of protrusions was found on the surface, as shown in Fig. 3(a), in addition to the 2×2 and $\sqrt{3} \times \sqrt{3}$ structures previously reported [4]. In comparison with the graphite lattice shown together in Fig. 3(a), a schematic structure for the $\sqrt{3} \times \sqrt{3}$ superstructure is drawn in Fig. 3 (b), which is similar to that previously observed on a CsCs-GIC surface [5].

Figure 4 shows an STM image obtained for a NaOH-treated MoS₂ surface. In the case of MoS₂, contrary to the results obtained for the MOH-treated HOPG crystals, the substrate lattice was imaged even after the treatment, and we could not find superstructures on this surface. However, dark island regions were observed, as indicated by arrows in Fig. 4.

In a previously proposed model [6], charge transfer from intercalants was thought to just occupy the upper *d* band of MoS₂ without any modification of the band structure. However, tunneling spectroscopy of the treated surface (Fig. 5) showed that in addition to the decrease in the charge density of filled states, new structures seemed to be formed between the band gap, contrary to the previous model mentioned above. Since the change in the spectrum was magnified at the island structures, more intercalants are expected to exist there. These results suggest that some new mechanism must be introduced to explain the properties of MoS₂ intercalation compounds.

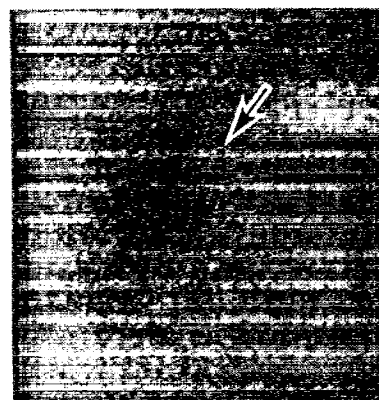


Fig. 4 STM image of NaOH-treated MoS₂ ($V_t = 150\text{mV}$, $I_s = 2.0\text{nA}$, $20\text{nm} \times 20\text{nm}$).

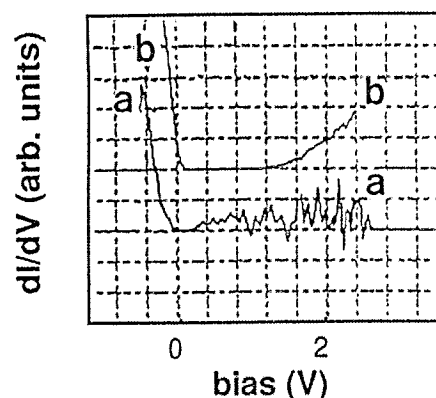


Fig.5 Tunneling spectroscopy of MoS₂ surface before (indicated by "b") and after (indicated by "a") NaOH treatment.

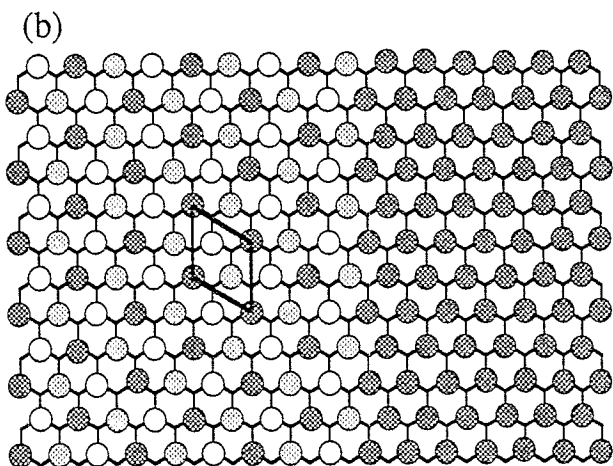
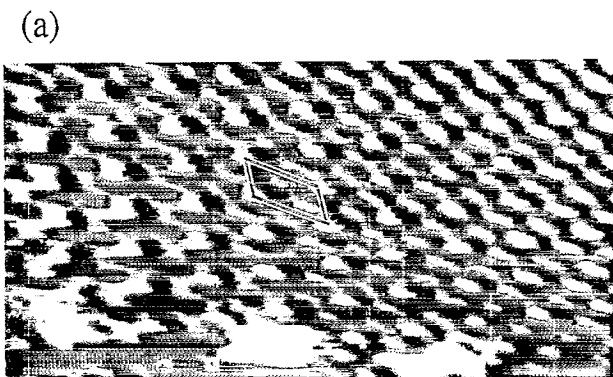


Fig. 3 (a) STM image of a $\sqrt{3} \times \sqrt{3}$ new structure observed on a NaOH-treated HOPG surface and (b) its schematic structure.

This work was supported in part by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. Supports from IZUMI, KURARA, and MIKITANI Research Foundations are also acknowledged.

References

1. H. P. Lang, R. Wiesendanger, V. Thommen-Geiser and H.-J. Guntherodt, *Phys. Rev. B* 45 (1992) 1829.
2. H. P. Lang, V. Thommen-Geiser and R. Wiesendanger, *Ultramicroscopy*, 42-44 (1992) 624.
3. S. P. Kelly and C. M. Lieber, *J. Vac. Sci. Technol.*, B 9 (1991) 1068.
4. K. Miyake, Y. Aiso, M. Komiyama and H. Shigekawa, *Scanning Microscopy*, to be published.
5. D. Anselmetti, V. Geiser, D. Brodbeck, G. Overney, R. Wiesendanger and H. J. Gunterodt, *Synthetic Metals*, 3 8 (1990) 157.
6. R. B. Somoano, V. Hadek and A. Rembaum, *J. Chem. Phys.*, 5 8 (1972) 697.