

SCANNING TUNNELING MICROSCOPY OF GALENA AND MOLYBDENITE*

LIAO LI-BING (廖立兵), SHI NI-CHENG (施倪承), MA ZHE-SHENG (马喆生)

(China University of Geosciences, Beijing 100083, PRC)

AND BAI CHUN-LI (白春礼)

(Institute of Chemistry, Academia Sinica, Beijing 100080, PRC)

Received April 30, 1990.

Keywords: STM, galena, molybdenite.

STM has rapidly and widely been used in various study fields since it was invented by Binnig and Rohrer^[1] in 1983. Up to now, all the study results obtained by using STM have proved that STM is a powerful device in studying the surface structure of conducting and semiconducting materials.

In 1988, Zheng et al. used STM for the first time in the world to study mineral surface and achieved great success^[2]. But because of the poor electric conductivity, uneven surface, impurities in chemical composition and oxidization of most minerals, it is very difficult to obtain their atomic-resolution STM images. For this reason, we chose galena and molybdenite, which have relatively good electric conductivity and even cleavage surface, as our first study samples. The STM we used was CSTM-9000 type, manufactured by the Institute of Chemistry, Academia Sinica.

I. GALENA

Zheng et al. were the first in the world who used STM to study mineral surface and succeeded in obtaining an atomic structure image of galena (100) surface in vacuum in 1988. In 1989, Michael et al. again studied galena with STM under oil^[3]. But they could only get STM image of galena with atomic-resolution under negative tip bias, and their STM image showed only one kind of atom (Pb or S). Our aim is to obtain high resolution STM image of galena surface in air.

The galena specimen came from Taolin deposit, Hunan Province. It is grey in color and with three groups of perfect cubic cleavages, which make the sample preparation much easier. In order to prevent the specimen surface from being oxidized and absorbing impurities, we experimented on the specimen within 5 h every time after it was cleaved. The tip (tungsten wire with 0.5 mm in diameter) was prepared by electrochemical corrosion in 1.5 mol/L NaOH solution.

* Project supported by the National Natural Science Foundation of China.

Figs. 1 and 2 are images of galena (100) surface with tip biased negatively. These two images clearly show that the atoms are arranged at the corners and centers of a square net. According to the interatomic distances, these images reveal only one kind of atom (Pb or S). This is consistent with the result of Michael et al. Before our study, only imaging galena in vacuum^[2] could obtain images that show both atoms. In this case, one type of atom seems to have protruded at the surface. Zheng et al. postulated that the atom "protruding" was S because of its higher density of state near the Fermi level. According to this explanation, Michael et al. believe that the atoms observed by STM with the tip biased negatively are most likely the S atoms. The calculated atom-atom distances in Figs. 1 and 2 are around 5.8 Å which agrees with the S-S distances on the (100) surface of galena. Michael et al. have also made efforts but failed in obtaining the STM image of galena with positive v_{bias} .

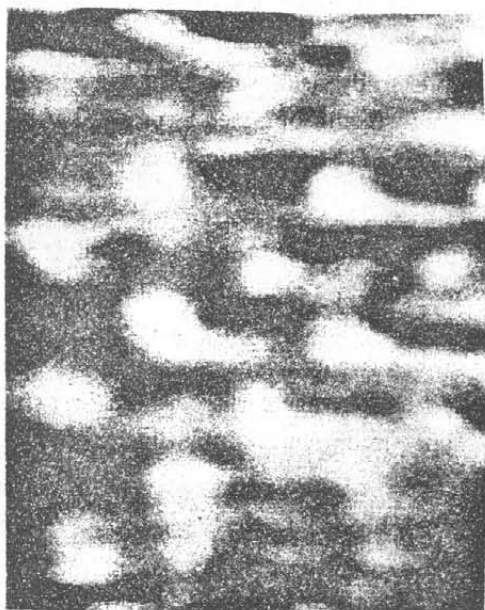


Fig. 1. Atomic-resolution STM image of galena (100) surface. $v_{\text{bias}} = -66$ mV, $I_{\text{ref}} = 0.41$ nA.

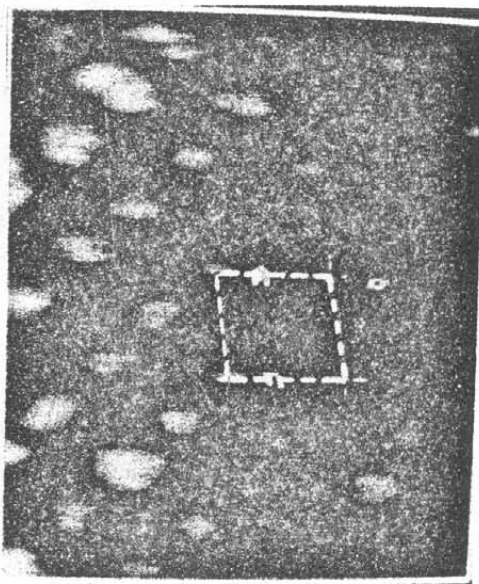


Fig. 2. Atomic-resolution STM image of galena (100) surface. $v_{\text{bias}} = -28$ mV, $I_{\text{ref}} = 0.36$ nA.

Fig. 3 is the atomic-resolution STM image of galena (100) surface which was successfully obtained, in air, with tip biased positively. It reveals clearly two types of atoms. One type is brighter than the other. The calculated interatomic distances are around 3 Å, approximately equal to the S-Pb distances of galena on its (100) surface. So Fig. 3 shows both S and Pb. According to Zheng et al., the brighter atoms should be S.

II. MOLYBDENITE

The surface structure of synthetic MoS_2 has already been studied by Weimer et al.^[4] But natural MoS_2 has never been studied before. The molybdenite specimen of this study was collected from Piaotang, Jiangxi Province. The specimen is greyish white with

perfect (0001) cleavage. Again, tungsten was used as tip material and the preparation methods of the tip and the specimen are the same as that of galena.

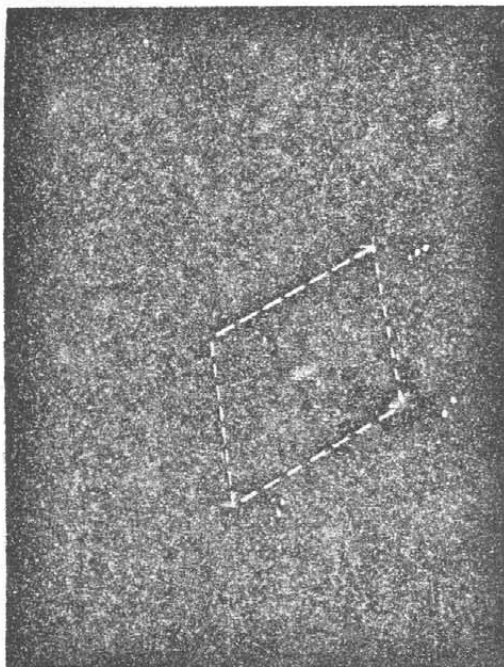


Fig. 3. Atomic-resolution STM image of galena (100) surface. $v_{\text{bias}} = 72$ mV, $I_{\text{ref}} = 0.68$ nA.

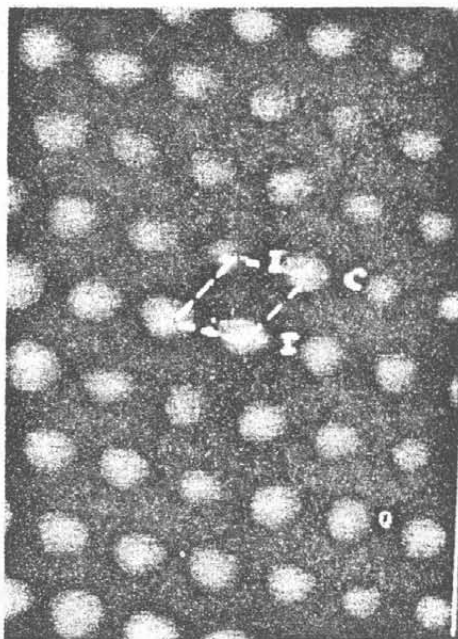


Fig. 4. Atomic-resolution STM image of molybdenite (0001) surface $v_{\text{bias}} = -35$ mV, $I_{\text{ref}} = 0.80$ nA.

Fig. 4 is the STM image of molybdenite (0001) surface. We know from the structure of MoS_2 that it always cleaves between two S layers, so atoms in Fig. 4 can only be S. The S atoms in Fig. 4 are arranged in a hexagonal pattern. The calculated parameter of the hexagonal unit cell is 3.2 \AA which approximately equals a_0 of molybdenite.

Fig. 4 not only reveals the top layer S atoms but also reveals the second layer Mo atoms of molybdenite (0001) surface. It shows that Fig. 4 is of high resolution both longitudinally and latitudinally.

III. BRIEF SUMMARY

In this note, we used a very important new imaging technique, scanning tunneling microscopy, to study the surface structure of galena and molybdenite. We not only obtained the surface STM images of galena and molybdenite, in air and at room temperature, with tip biased negatively, but also successfully obtained the STM image of galena (100) surface with tip biased positively in air which reveals both S and Pb atoms. This is the first time in the world. Our results proved again that STM is a powerful device in studying the surface structure of semiconducting minerals.

We are grateful to Huang Gui-zhen, Gu Jian-guo, Dai Chang-chun and other researchers of the STM Laboratory of the Institute of Chemistry, Academia Sinica.

REFERENCES

- [1] Binnig, G. & Rohrer, H.. *Surface Sci.*, 126 (1983), 236.
- [2] Zheng N. J. et al.. *Physical Review B*, 38 (1988), 1207.
- [3] Michael, F. et al.. *American Mineralogist*, 1989, Vol. 74.
- [4] Weimer, M. et al.. *Phys. Rev. B. Rapid Commun.*, 37 (1988), 4292.