The First Atomic-scale Observation of a $Ni_2P(0001)$ Single Crystal Surface

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The first clear atomic-scale images of a $Ni_2P(0001)$ surface have been obtained by means of a scanning tunneling (STM) microscope. The STM image shows an ordered hexagonal symmetry of the (0001) face, which can be assigned to phosphorus atoms on Ni_3P_1- and Ni_3P_2-terminated surface. The high temperature annealing is crucial to get a well-ordered atomic structure.

Petroleum is an important source for energy, but sulfur compounds in the crude oil are detrimental to the environment. The hydrodesulfurization catalysts for the petroleum currently employed in the industry are tungsten and molybdenum sulfides promoted by Co and Ni.[1] But more and more strict regulation to limit the sulfur content in transportation fuels has lead to the worldwide research to develop better catalysts.[2–4] Recent work has shown that transition-metal phosphides (e.g., MoP,[5,6] WP,[7,8] Co_2P,[9,10] and Ni_2P[2,11,12]) are a new class of catalysts active for hydrodesulfurization and hydrodenitrogenation for petroleum fuels. Ni_2P shows higher performance for hydro desulfurization than the other phosphides and commercially available hydrodesulfurization catalysts. In order to understand such a high performance of this Ni_2P catalyst, it is necessary to conduct a fundamental surface science research like an atomic scale characterization of the surface. Hitherto a $Ni_2P(0001)$ surface has been studied by LEED and DFT.[13,14] It was concluded that the $Ni_2P(0001)$ surface is composed of two compositionally inequivalent layers with stoichiometry of Ni_3P_1 and Ni_3P_2 which are stacked alternatively along the [0001] direction.[13] The Ni_3P_2-terminated surface was found to be more stable by 2.75 eV/unit cell and the phosphorus atoms have been suggested to play an important role in the adsorption of reactants,[14] but no experimental evidence has been presented. In this paper, we report the first atomic images of the $Ni_2P(0001)$ surface using STM. The images can be rationally interpreted based on the P atoms of the both Ni_3P_1- and Ni_3P_2-terminated surfaces. The atomic scale $Ni_2P(0001)$ studies will be important for revealing the interaction of sulfur compounds with the surface.

The experiments were conducted in an Omicron UHV system, which consists of an STM, an analysis chamber and a fast entry lock. The analysis chamber was equipped with an Ar^+ ion gun (Omicron ISE5), a quadrupole mass spectrometer, an Auger spectrometer, four-grid reverse view LEED optics, and a gas handling system. The base pressure of the chamber was 2×10^{-8} Pa. The STM image was measured at room temperature in a constant current mode. The W tip was electrochemically etched in a 2 M NaOH solution. The piezo scanners in the x–y directions were calibrated using STM images of Si(111)-7 × 7.

A $Ni_2P(0001)$ crystal of 10 mm diameter and 1 mm thickness was prepared by one of the authors (S.O.) and mounted on a sample holder. In the beginning, sputtering was done with a 20 μA beam of 3 keV argon ions for 30 min.[13] After low temperature (723 K) annealing of short duration (5 min) a defective surface was always observed by STM, even though (1 × 1) LEED patterns were obtained with a bright background. Different annealing temperatures (from 723 to 873 K) and durations (from 5 min to ≈2 h) were examined but good STM images were not observed. Finally, the sample was bombarded under much milder conditions (4 μA beam of 500 eV argon ion) for 30 min at $P_{Ar} = 2.5 \times 10^{-3}$ Pa. Again, the surface was examined after high-temperature annealing (up to 970 K) and longer annealing time (up to ≈5 h). The sharp (1 × 1) LEED spots as shown in Figure 1 were obtained, indicating the creation of a flat and smooth surface with a long-range order. The LEED data correspond well to the crystallographical structure ($a_1 = a_2 =$ 0.59 nm).[14]

Figures 2a and 2b show two typical atomic-scale STM images of the $Ni_2P(0001)$ surface. As far as the authors know, these are the first atomic-scale STM measurements of the Ni_2P single crystal surface. Two images were obtained at different places and were observed at a positive bias voltage (in the range of 1.0–2.0 V). It suggests that a net tunneling current flows from the occupied states of the tip to the unoccupied states of the sample. Two different images coincide with an ordered (1 × 1) hexagonal symmetry of the (0001) face. The distances between bright and dark spots in Figures 2a and 2b are 0.59 nm, corresponding well with the crystal data.[15] The crystal data show that

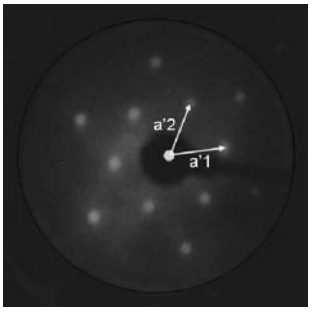

Figure 1. The hexagonal LEED pattern observed at 71 eV beam energy followed by a mild sputtering (4 μA beam of 500 eV Ar^+ ions for 30 min at $P_{Ar} = 2.5 \times 10^{-3}$ Pa) and annealing to 970 K for 5 h.

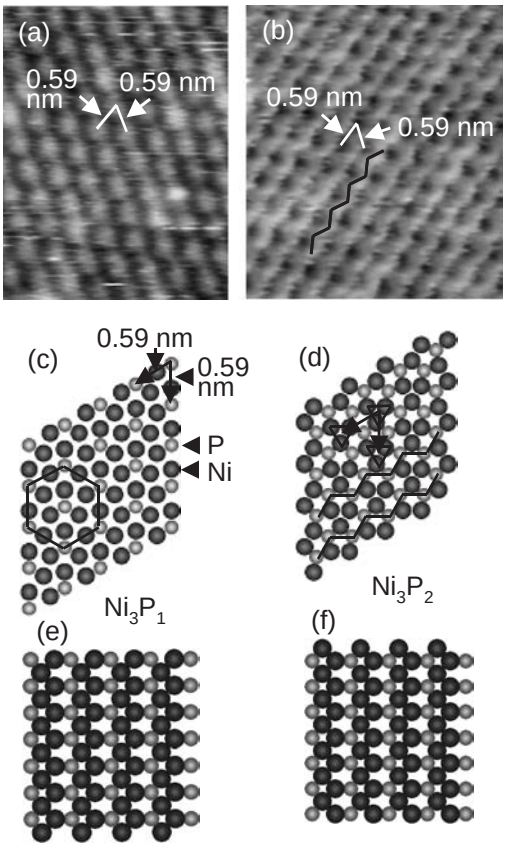

Figure 2. (a) and (b) High-resolution STM images of the $Ni_2P(0001)$ surface at different positions. ($4.6 \times 6.6\,nm^2$, sample bias $= 1.7\,V$ and $5.7 \times 6.5\,nm^2$, sample bias $= 1.2\,V$, respectively), (c) and (d) Top view and (e) and (f) Side view illustrations of Ni_3P- and Ni_3P_2-terminated surfaces of Ni_2P-(0001), respectively.

the P–P distance is 0.59 nm and the Ni–Ni distance is 0.31 nm in Ni_3P_1-terminated surface (Figure 2c). On the other hand, the P–P distance is 0.34 nm and the Ni–Ni distance is 0.26 nm in Ni_3P_2-terminated surface (Figure 2d). The direct comparison with the STM pictures and the atomic positions of the model surface structures as shown in Figures 2c and 2d has suggested that the STM spots in Figure 2a agree well with the P positions on Ni_3P_1-terminated surface. On the other hand, the zigzag structure in Figure 2b corresponds only to the zigzag chain of P on Ni_3P_2-terminated surface. The edge length of the zigzag chain is 0.33 nm, corresponding to the P–P distance on the Ni_3P_2-terminated surface. But great care needs to be taken in the interpretation of STM images because STM visualizes not the geometrical structure but the electronic states. Actually, other interpretations of the image in Figure 2a might be possible. If the Ni triangles in Ni_3P- or Ni_3P_2-termination surface shown in Figures 2c or 2d give one bright spot, it can reproduce the same STM result as shown in Figure 2a. After detail and intensive discussion, we have proposed that the observed bright spots and zigzag structures correspond to P on Ni_3P_1-terminated and Ni_3P_2-terminated surfaces for the following reasons, respectively.

(1) Local density calculations by the DFT method[14] indicated that phosphorus has higher density-of-states in the 1–2 eV regions than Ni, suggesting that P may produce a brighter image than Ni in the STM picture when a positive bias is applied.

(2) A zigzag structure is only a possible arrangement by assuming that the bright structure is P of the Ni_3P_2-terminated surface.

(3) The less-stable Ni_3P_1 surface appeared probably because the surface becomes P-deficient as a result of the ion bombardment which preferentially sputters the lighter element.

In summary, we have successfully observed atomic-scale images of $Ni_2P(0001)$. The bright spots in the STM images are interpreted as phosphorus atoms in Ni_3P_1- or Ni_3P_2-terminated surfaces. This finding is important for further investigation of Ni_2P catalyst from the surface science standpoint to determine the adsorption site and understand the reaction mechanisms for sulfur removal process.

One of the authors (M. G. Moula) thanks to JSPS for their financial support. The work is supported by Grant-in-Aid for Scientific Research Category S (No. 16106010) from JSPS, a NEDO International Grant, and the US Department of Energy.

References

1 F. L. Platenga, R. Cerfontain, S. Eijsbouts, F. van Houtert, G. H. Anderson, S. Miseo, S. Soled, K. Riley, K. Fijita, Y. Inoue, *Surf. Sci. Catal.* **2003**, *145*, 407.
2 S. T. Oyama, *J. Catal.* **2003**, *216*, 343, and the references therein.
3 J. G. Speight, *The Chemistry and Technology of Petroleum*, 2nd ed., Dekker, New York, **1991**.
4 U. S. Environmental Protection Agency, Press Release, December 21, **2000**.
5 W. Li, B. Dhandapani, S. T. Oyama, *Chem. Lett.* **1998**, 207.
6 D. C. Phillips, S. J. Sawhill, R. Self, M. E. Bussel, *J. Catal.* **2002**, *207*, 266.
7 P. Clark, W. Li, S. T. Oyama, *J. Catal.* **2001**, *200*, 140.
8 S. T. Oyama, P. Clark, X. Wang, T. Shido, Y. Iwasawa, S. Hayashi, J. M. Ramallo-López, F. G. Requejo, *J. Phys. Chem.* **2002**, *106*, 1913.
9 W. R. A. M. Robinson, J. N. M. van Gastel, T. I. Korányi, S. Eijsbouts, J. A. R. van Veen, V. H. J. de Beer, *J. Catal.* **1996**, *161*, 539.
10 X. Wang, P. Clark, S. T. Oyama, *J. Catal.* **2002**, *208*, 321.
11 J. A. Rodriguez, J.-Y. Kim, J. C. Hanson, S. J. Sawhill, M. E. Bussell, *J. Phys. Chem. B* **2003**, *107*, 6276.
12 K. A. Layman, M. E. Bussell, *J. Phys. Chem. B* **2004**, *108*, 10930.
13 D. Kanama, S. T. Oyama, S. Otani, D. F. Cox, *Surf. Sci.* **2004**, *552*, 8.
14 P. Liu, J. A. Rodriguez, T. Asakura, J. Gomes, K. Nakamura, *J. Phys. Chem. B* **2005**, *109*, 4575.
15 S. Rundqvist, *Acta. Chem. Scand.* **1962**, *16*, 992.

Published on the web (Advance View) December 10, 2005; DOI 10.1246/cl.2006.90