

Ionic/electronic mixed conductor tip of a scanning tunneling microscope as a metal atom source for nanostructuring

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Silver sulfide (Ag_2S) which has Ag-ionic/electronic mixed conductivity is used for fabricating a tip used for a scanning tunneling microscope. The mixed conductor tip is capable of nanostructuring by depositing Ag atoms continuously on a sample as well as imaging the surface structure. To obtain the surface image, a nanoscale Ag protrusion is formed at an apex of the tip using a local solid electrochemical reaction, working as “a mini-tip.” We fabricate a nanoscale line structure on the sample by scanning the Ag_2S tip with the protrusion under appropriate bias voltages and tunneling currents. The structuring is thought to be made up of two layers of Ag atoms deposited from the protrusion. © 2002 American Institute of Physics. [DOI: 10.1063/1.1480887]

The scanning tunneling microscope (STM) has enabled the fabrication of nanoscale and even atomic scale artificial structures (these are expressed generically as nanostructures) on samples, as well as the imaging of the atomic structures of sample surfaces. Fabrication of nanostructures using the STM^{1–8} has attracted significant attention, since this method makes a variety of novel fundamental and applied research feasible. So far, atomic letters were drawn on a Ni sample by moving individual Xe atoms at a low temperature (4 K) (Ref. 2) and nanostructures on Si samples were fabricated by extracting or redepositing Si atoms using the STM.^{3,5–7} Most of the methods which fabricate nanostructures using a STM have required the physical and chemical effects caused by a bias voltage and tunneling current between the tip and a sample in order to extract, deposit, and displace atoms or molecules. Such ways of manipulating individual atoms are not efficient to produce practical electronic devices. If it were possible to fabricate nanostructures by depositing metal atoms continuously from a STM tip onto sample surfaces,⁸ one could produce nanostructures efficiently using the STM. The products of this process appear as if the nanostructures are drawn on the sample surface using a “nanoscale foundation pen” containing ink of metal atoms or molecules.⁸ However, the method of fabricating nanostructures using such a functional STM tip has not been established yet.

Toward this end, we consider an ionic/electronic mixed conductor for use as the material of the functional STM tip.⁹ Since metal ions in the ionic/electronic mixed conductor are easily moved by an applied electric field, the mixed conductor is expected to be used as a source of metal atoms. Figure 1 shows a schema of nanostructure fabrication using metal atoms transferred from the STM tip of the mixed conductor to a sample surface. If it were possible to supply metal atoms

continuously onto a sample surface from the tip, an efficient method to fabricate nanostructures would become feasible. In the present work, we have found that the STM tip made of a mixed conductor is useful as a source of metal atoms. Furthermore, it is found that a local solid electrochemical reaction at the apex of the tip occurs by applying a bias voltage between the tip and sample, and this interesting phenomenon has also been investigated.

The material of the STM tip to be used as a nanoscale foundation pen is required to have both ionic conductivity and electronic conductivity, since tunneling current must flow between the tip and sample. We have used silver sulfide (Ag_2S) crystal as the material of the STM tip; the crystal is a well-known material of Ag-ionic and electronic mixed conductors.^{9–11} Needlelike single crystal of Ag_2S was prepared by the reaction of a Ag wire with sulfur vapor in an evacuated silica glass ampoule.¹² The Ag_2S crystal grown on the Ag wire was used as the STM tip. In order to examine the performance of the Ag_2S tip, a Si(111) wafer with 7×7 surface structure prepared by repeated flush heating under an UHV was used as a sample. All examinations using the Ag_2S tip were conducted in an UHV.

Using a Ag_2S tip, we examined whether tunneling cur-

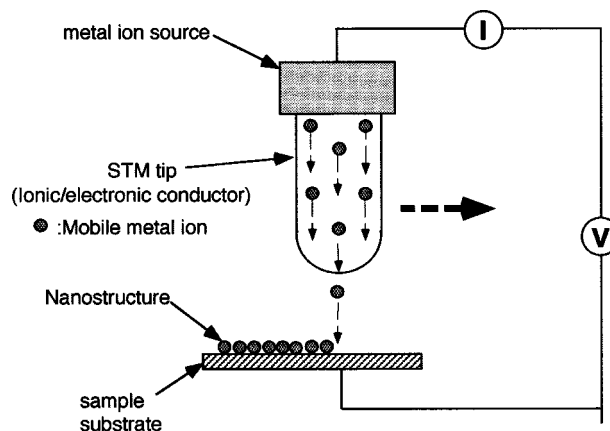


FIG. 1. Schema of nanoscale structure fabrication using metal atoms transferred from an ionic/electronic mixed conductor STM tip.

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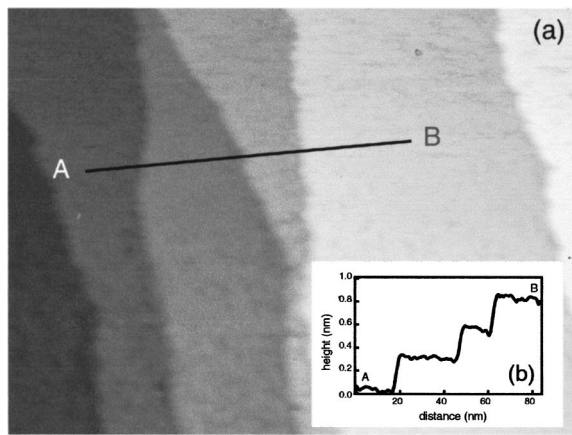


FIG. 2. A constant-current STM image ($150 \times 110 \text{ nm}^2$) of a silicon (111) surface using the Ag_2S tip. (b) The cross-sectional profile along A–B in (a).

rent flows between the tip and Si sample, and whether STM images of the Si(111) surface are obtained. STM operations of tip approaching and surface imaging were performed at a sample bias voltage of $V_s = +2.0 \text{ V}$ and tunneling current of $I_t = 0.05 \text{ nA}$. After the tip approached the sample, the tunneling current between the tip and the sample was detected, but it was not sufficiently stable to image the Si surface structure. It was found that tunneling current became stable and step structure images of Si surfaces were obtained, as shown in Fig. 2(a), if the Ag_2S tip was subjected to a certain condition of V_s and I_t for a while. The step height is about 0.3 nm as shown by the cross-sectional profile in Fig. 2(b). This height corresponds to an actual step height (0.313 nm) of the Si (111) 7×7 surface.¹³ In fact, a nanoscale Ag protrusion was grown at an apex of the Ag_2S tip under certain conditions of V_s and I_t , working as a sharp “mini-tip” to image the structure of the silicon surface. However, the mini-tip was not so stable to resolve the atomic structure of the Si surface. Interestingly, we found the Ag protrusion shrank gradually and disappeared, when the polarity of V_s was switched. The behaviors were revealed by the following examination.

The growth and shrinkage were examined by monitoring the moved distances of the Ag_2S tip perpendicular to the sample surface under a constant-current STM mode. Namely, when the Ag protrusion grows at the apex of the Ag_2S tip, the tunneling current increases because of a decrease in the distance between the tip and the sample. However, under the constant-current STM mode, the tip should be pulled away from the sample so as to keep the tunneling current constant. By monitoring the changes of piezovoltages that control the motions of the tip, the lengths of the growth and the shrinkage of the Ag protrusion can be estimated. The growth and shrinkage of the Ag protrusion under different conditions of V_s and I_t are shown in Fig. 3. No motion of the tip was observed at $V_s = -2.0 \text{ V}$ and $I_t = 0.05 \text{ nA}$. When I_t was, however, increased to $I_t = 1.35 \text{ nA}$ with V_s kept at the same value, rapid motion of the tip by a distance of about 30 nm was observed, and then the tip moved at a rate of about 0.1 nm/s . A direct examination using a scanning electronic microscope revealed that the Ag protrusion was grown at an apex of the Ag_2S tip.¹² As seen in Fig. 3, by switching the polarity of V_s to positive ($V_s = +2.0 \text{ V}$) and by changing I_t

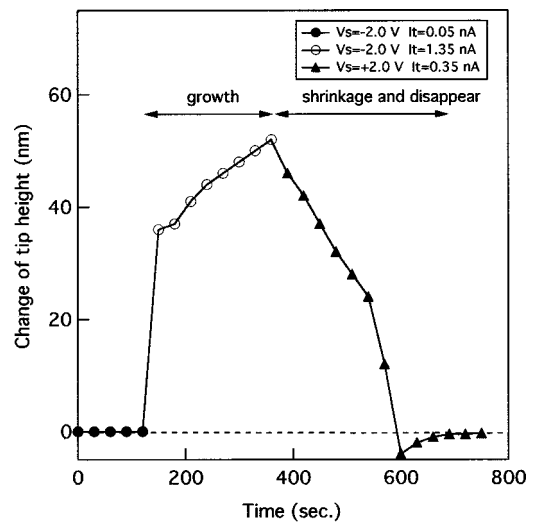


FIG. 3. Growth and shrinkage of the Ag protrusion at the apex of a Ag_2S tip, which were monitored through the change of the tip position.

to 0.35 nA , the Ag protrusion shrank gradually and disappeared. The Ag_2S tip almost returned to the initial position.

It has been reported that millimeter-scale Ag whiskers were grown on the Ag_2S in a galvanic cell: Pt/Ag/AgI/Ag₂S/Pt, when a certain bias voltage was applied between Pt electrodes.^{14,15} Silver iodide used in the cell is a well-known Ag-ionic conductor. The growth mechanism of Ag whiskers was explained based on the solid electrochemical reaction of mobile Ag ions in the cell. The growth and shrinkage of the nanoscale Ag protrusion found in our work can also be interpreted as the local solid electrochemical process of Ag ions in the Ag_2S tip. Figure 4 shows the growth process of the Ag protrusion. When a negative bias voltage is applied to the sample, tunneling electrons from a sample reduce mobile Ag ions in the Ag_2S tip to neutral Ag atoms, and Ag atoms precipitate at the apex of the Ag_2S tip which form the protrusion. At the same time, Ag atoms in a Ag wire on the opposite side are oxidized to Ag ions and are dissolved in the Ag_2S tip so as to keep the Ag ion concentration in the Ag_2S tip constant. On the other hand, when a positive bias is applied to the sample, Ag atoms in the Ag protrusion are oxidized to Ag ions, and the Ag ions are redissolved in the Ag_2S tip which results in the shrinkage of the protrusion.

The rates of the growth and shrinkage of the Ag protrusion increased with an increase of I_t , but hardly by that of V_s . The reason for this is thought to be that energy barriers for solid electrochemical reactions of Ag ions exist at the

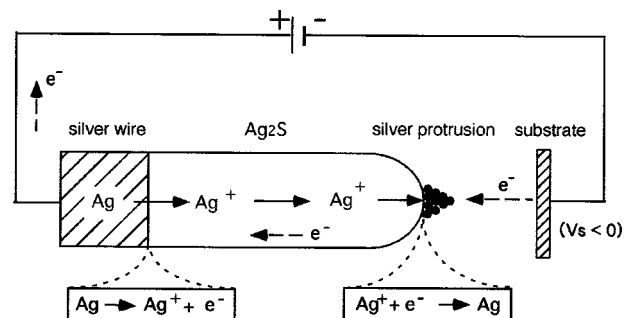


FIG. 4. Solid electrochemical processes for the growth of a Ag protrusion at the apex of Ag_2S tip.

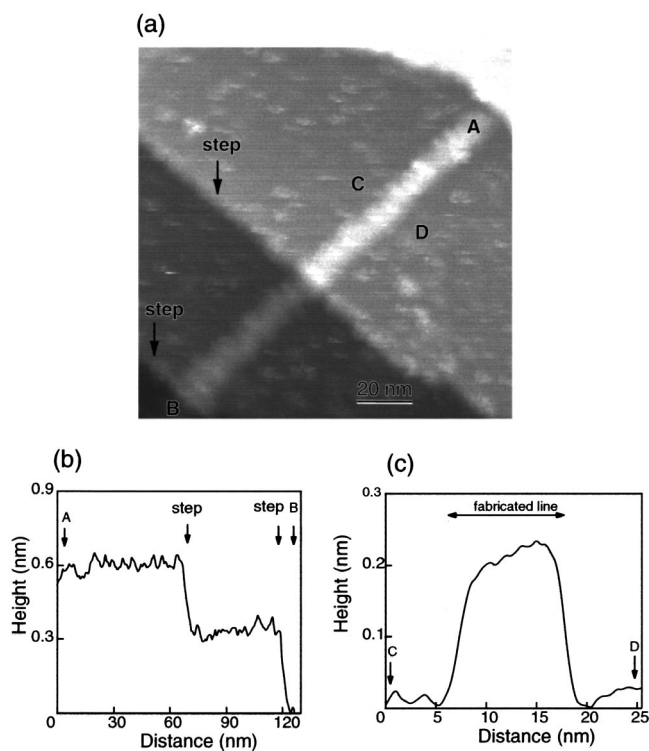


FIG. 5. (a) A line structure fabricated by scanning the Ag_2S tip along A–B at a speed of 1 nm/s at $V_s = -2.0$ V and $I_t = 1.35$ nA. (b) and (c) The cross section along A–B and C–D in (a), respectively.

growth and shrinkage of the protrusion. When I_t increases, the energy barriers are surmounted and the rates increase. According to solid electrochemical treatment, the applied bias voltages change the height of energy barriers, namely, they control the rates of the reactions. However, the rates were changed by I_t , not V_s , in our study. This reason for this is explained as follows. The actual bias voltage, which changes the energy barrier, is $V_{\text{Ag}_2\text{S}}$, not V_s , applied to the Ag_2S tip. Here, the relation between V_s and $V_{\text{Ag}_2\text{S}}$ is represented as $V_s = V_{\text{Ag}_2\text{S}} + V_{\text{tunneling space}}$, where $V_{\text{tunneling space}}$ is the applied bias voltage between the tip and the sample. Thus, even if V_s is constant, $V_{\text{Ag}_2\text{S}}$ increases with increasing I_t under the condition that the resistance ($R_{\text{Ag}_2\text{S}}$) of Ag_2S tip is constant, because of $V_{\text{Ag}_2\text{S}} = I_t \times R_{\text{Ag}_2\text{S}}$. It means that the rates of growth and shrinkage depended on the magnitude of I_t .

We found that small amounts of materials are deposited continuously on the sample from the Ag_2S tip with the Ag protrusion. Thus, by scanning the Ag_2S parallel to the sample surface under certain conditions of V_s and I_t , nanoscale line structures were obtained on the surface. An example is shown in Fig. 5(a). The line structure was fabricated by scanning the Ag_2S tip back and forth at a speed of 1 nm/s at $V_s = -2.0$ V and $I_t = 1.35$ nA. This condition corresponded to that for further growing the Ag protrusion. Figures 5(b) and 5(c) show the cross sections along A–B and C–D in Fig. 5(a), respectively. These cross sections reveal that the line structure has a width of about 10 nm and a height of about

0.2 nm, and that the roughness in height is as small as 0.1 nm, suggesting that the structure is made of two layers of atoms. Depositions from the Ag_2S tip with the protrusion were also obtained by scanning under conditions of $V_s = -2.0$ V and $I_t < 0.50$ nA; no further growth of the protrusion was observed under such conditions. We consider that the depositions are caused by the field evaporation¹⁶ of Ag atoms from the Ag protrusion. High-field condition required for evaporating the Ag atoms is achieved by the high-speed vibration of the protrusion. According to electrochemical treatment, an interchange between Ag ions in Ag_2S and Ag atoms forming the Ag protrusion occurs at the interface even at equilibrium state. The interchange accompanies a high-speed change of the height position of the protrusion at an atomic scale. The high-field condition is instantly achieved by decreasing the distance between the protrusion and sample due to the change of the height position. Furthermore, the reason, why the atomic structure of the Si surface could not be imaged in Fig. 2, is that the interchange with the vibration of the protrusion disturbs the atomic-scale imaging.

In conclusion, a mixed conductor of Ag_2S was used as the tip material of STM. After the Ag_2S tip was subjected to a certain condition of V_s and I_t , the step image of Si surface was obtained using the tip. It was found that the nanoscale Ag protrusion was grown on the apex of the Ag_2S tip by this treatment, working as a mini-tip to image the surface structure. The protrusion growth is explained by the solid electrochemical reaction of Ag ions in Ag_2S . A line nanostructure on a sample surface could be fabricated by scanning the Ag_2S tip with the protrusion. The structure is thought to be made up of two layers of Ag atoms deposited continuously from the protrusion. We believe that it is possible to establish an efficient method for nanostructuring, if a mixed conductor is used as a material of the STM tip.

- ¹R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, *Nature (London)* **325**, 419 (1987).
- ²D. M. Eiger and E. K. Schweizer, *Nature (London)* **344**, 524 (1990).
- ³I. W. Lyo and Ph. Avouris, *Science* **253**, 173 (1991).
- ⁴S. Hosoki, S. Hosaka, and T. Hasegawa, *Appl. Surf. Sci.* **60**, 2418 (1992).
- ⁵H. Uchida, D. H. Huang, F. Grey, and M. Aono, *Phys. Rev. Lett.* **70**, 2040 (1993).
- ⁶A. Kobayashi, F. Grey, S. Williams, and M. Aono, *Science* **259**, 1724 (1993).
- ⁷D. H. Huang, H. Uchida, and M. Aono, *J. Vac. Sci. Technol. B* **12**, 2429 (1994).
- ⁸T. Nakayama, D. H. Huang, and M. Aono, *Microelectron. Eng.* **32**, 191 (1996).
- ⁹T. Takahashi, *High Conductivity Solid Conductors* (World Scientific, Singapore, 1989).
- ¹⁰S. Miyatani, *J. Phys. Soc. Jpn.* **15**, 1586 (1960).
- ¹¹H. Rickert, *Electrochemistry of Solids; An Introduction* (Springer, Berlin, 1982).
- ¹²K. Terabe, T. Nakayama, and M. Aono, *Proceedings of the Ninth International Conference on Production Engineering, Precision Science and Technology for Perfect Surface*, Osaka, Japan (JSPE Publication Series, Tokyo, Japan, 1999), Vol. 3, p. 117.
- ¹³R. S. Becker, J. A. Golovchenko, E. G. McRae, and B. S. Swartzentruber, *Phys. Rev. Lett.* **55**, 2028 (1985).
- ¹⁴J. Corish and C. D. O'Braian, *J. Cryst. Growth* **13**, 62 (1972).
- ¹⁵T. Ohachi and I. Taniguchi, *J. Cryst. Growth* **13**, 191 (1972).
- ¹⁶F. Grey, A. Kobayashi, H. Uchida, D. H. Huang, and M. Aono, *Technology of Proximal Probe Lithography* (SPIE, Bellingham, WA, 1993), Vol. 10, p. 74.