

Formation and disappearance of a nanoscale silver cluster realized by solid electrochemical reaction

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We have developed a nanostructuring method using the solid electrochemical reaction induced by a scanning tunneling microscope (STM). This method has some distinctive features that have not previously been obtained by conventional nanostructuring STM methods. The formation and disappearance of the nanostructure are reversible, and the rates can be controlled using STM. These features are realized via a local oxidation/reduction reaction of mobile metal ions in an ionic/electronic mixed conductor. In this study, a crystal of silver sulfide (Ag_2S), a mixed conductor, was used as the material for the STM tip. A nanoscale Ag cluster was formed at the apex of the Ag_2S tip when a negative bias voltage was applied to the sample. The Ag ions in the Ag_2S tip are reduced to Ag atoms by the tunneling electrons from the sample, and the Ag cluster is formed by the precipitation of the Ag atoms at the apex of the tip. The Ag cluster shrank gradually and disappeared when the polarity of the sample bias voltage was switched to positive. Ag atoms in the Ag cluster are oxidized to Ag ions, and the Ag ions redissolve into the Ag_2S tip. The formation and disappearance rates of the cluster were controlled by regulating the tunneling current. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481775]

I. INTRODUCTION

Fabrication of nanoscale structures has attracted significant attention not only due to novel fundamental research but also due to the potential applications in new electronic devices. The scanning tunneling microscope (STM) is a promising tool for fabricating nanoscale and even atomic scale artificial structures (these are referred to generically as nanostructures) on samples, as well as imaging nanostructures of sample surfaces.¹⁻⁹ To date, atomic letters have been written on a Ni sample by moving individual Xe atoms at low temperature (4 K)² and nanostructures on Si samples have been fabricated by extracting or redepositing Si atoms using the STM.^{3,5-8} For these types of nanostructuring using the STM, physical effects caused by bias voltage and tunneling current between the tip and the sample have been used to extract, deposit, and displace atoms or molecules on the samples.

We have developed a nanostructuring method using the solid electrochemical effects induced by the STM. For this method, an ionic/electronic mixed conductor¹⁰ is used as the material for the STM tip or a sample, and an oxidation/reduction reaction of mobile metal ions in the mixed conductor tip is employed to fabricate the nanostructures. This method has some distinctive features which have not previously been obtained by the conventional STM method of fabricating nanostructures using physical effects. The forma-

tion and disappearance of the nanostructures are reversible; furthermore, the rates can be controlled by regulation of the applied tunneling current. In this article, we realized the nanostructuring using the STM. A crystal of silver sulfide (Ag_2S),¹⁰⁻¹³ a silver (Ag)-ionic/electronic conductor, was used as the material for the STM tip. The nanoscale Ag cluster was formed by the reduction of the Ag ions in the Ag_2S at the apex of the tip when a negative bias voltage was applied to the sample. The Ag cluster shrank and disappeared due to the oxidation of the Ag atoms in the cluster when the polarity of the bias voltage was switched. We discuss mechanisms of the formation and disappearance of the Ag cluster.

II. EXPERIMENT

We have used a crystal of Ag_2S , an ionic/electronic conductor, as the material for the STM tip; the crystal is a well-known material among ionic and electronic mixed conductors.¹⁰⁻¹³ Needlelike single crystals of Ag_2S on a Ag wire were grown by reaction of the Ag wire with sulfur vapor in an evacuated silica glass ampoule. The Ag_2S crystal on the Ag wire was used as the STM tip. Preparation of the Ag_2S tip has been described elsewhere in detail.¹⁴ In order to examine the performance of the Ag_2S single crystal as a STM tip, a platinum (Pt) plate treated by flash heating under UHV was used as a sample. All examinations using the Ag_2S tip were conducted in UHV.

The formation and disappearance behaviors of the nanoscale Ag cluster were examined by monitoring the distance of the displacement of the Ag_2S tip in the direction perpendicular to the Pt sample surface under a constant-current STM mode. Namely, when the Ag cluster forms at the apex of the Ag_2S tip, the tunneling current increases

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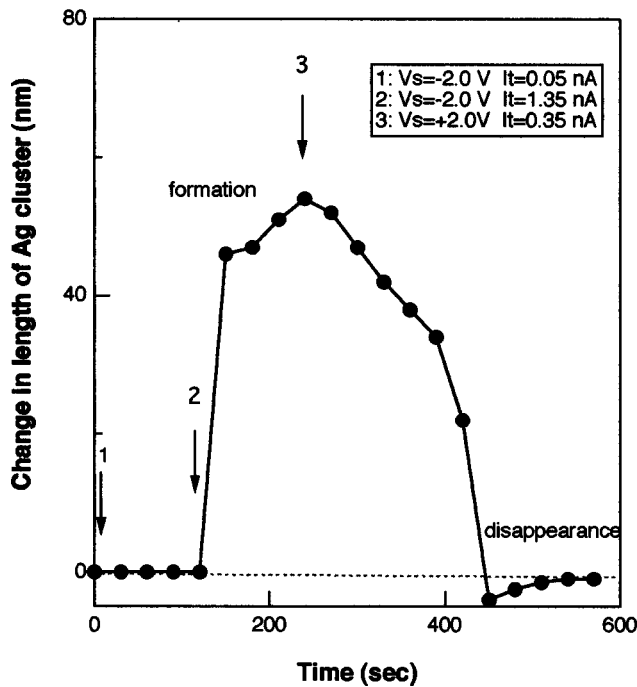


FIG. 1. Formation and disappearance behaviors of the nanoscale Ag cluster at an apex of the Ag_2S STM tip, which were monitored through the change of the tip position.

because of a decrease in the distance between the tip and Pt sample. However, under the constant-current STM mode, the tip should be pulled away from the sample in order to keep the tunneling current constant. In the case where the Ag cluster shrinks, the tip motion is reversed. By monitoring the changes of piezovoltages that control the motion of the tip, changes in length of the Ag cluster at the apex of the Ag_2S tip were estimated during the growth and shrinkage processes.

III. RESULTS AND DISCUSSION

A. Formation and disappearance of Ag cluster

An Ag_2S tip was made to approach a Pt sample at a sample bias voltage of $V_s = 2.0 \text{ V}$ and tunneling current of $I_t = 0.05 \text{ nA}$. Subsequently, the formation and disappearance of the Ag cluster at the apex of Ag_2S tip were observed when the tip was exposed to certain conditions of V_s and I_t . This is shown in Fig. 1, in which numbered arrows (1–3) indicate the starting points of three different conditions in the inset. No formation of Ag clusters was observed at $V_s = -2.0 \text{ V}$ and $I_t = 0.05 \text{ nA}$ (condition 1). However, when I_t was increased to $I_t = 1.35 \text{ nA}$ with V_s kept constant (condition 2), a Ag cluster with a size of approximately 40 nm was formed rapidly. As seen in Fig. 1, by switching the polarity of V_s to positive ($V_s = 2.0 \text{ V}$) and by changing I_t to 0.35 nA (condition 3), the Ag cluster shrank gradually and disappeared. In other words, the position of the Ag_2S tip almost returned to its initial state.

The formation and growth behaviors of the Ag cluster were investigated as the Ag_2S tip was subjected to the formation conditions of the cluster for period of time. As we can see in Fig. 2, no formation of the clusters was observed

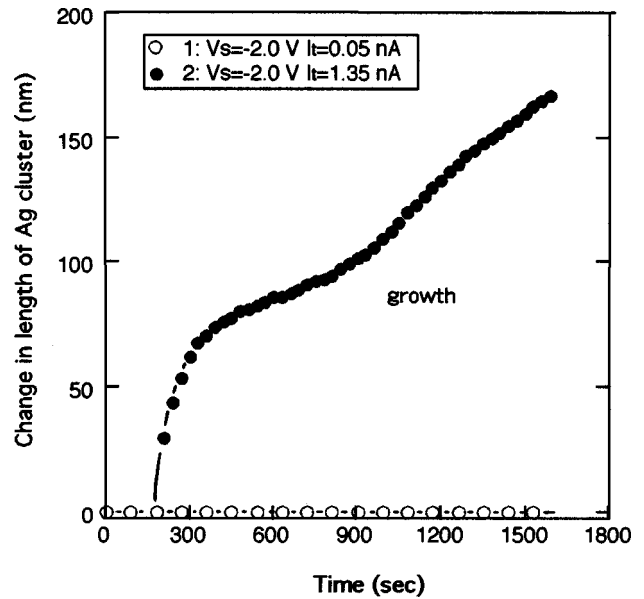


FIG. 2. Formation and growth behaviors of the Ag cluster.

when the condition of $V_s = -2.0 \text{ V}$ and $I_t = 0.05 \text{ nA}$ (condition 1) was maintained for 1550 s. However, when the condition of $V_s = -2.0 \text{ V}$ and $I_t = 1.35 \text{ nA}$ (condition 2) was maintained for 2000 s, a cluster of approximately 40 nm in size was formed and grew to a length of 200 nm at a rate of approximately 0.1 nm/s. Figure 3 shows a scanning electron microscope (SEM) image of a Ag cluster at the apex of the Ag_2S tip, which was grown under the condition of $V_s = -2.0 \text{ V}$ and $I_t = 1.35 \text{ nA}$ maintained for 2000 s. The grown cluster has a filamentary shape; the length measured from the SEM image was about 200 nm and the diameter was about 70 nm. The length of the Ag protrusion agrees with that estimated from measurement of an Ag_2S tip displacement.

B. Reversible growth and shrinkage of Ag cluster

The Ag cluster at the apex of the Ag_2S tip grew and shrank reversibly when the polarity of V_s and magnitude of I_t were changed. This behavior is shown in Fig. 4. The conditions of V_s and I_t were changed in the order of 1, 2, 1, 4, 3,

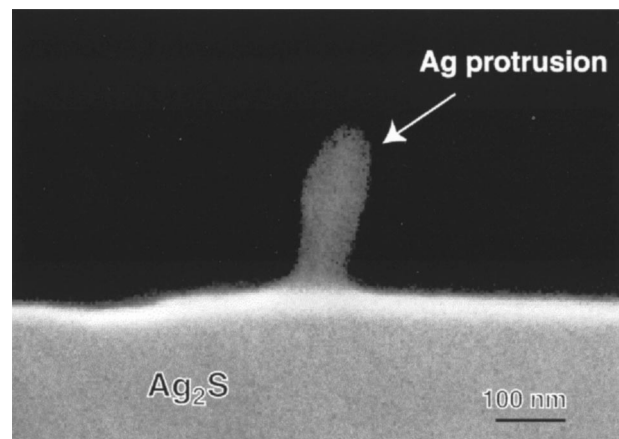


FIG. 3. SEM image of the filamentary Ag cluster.

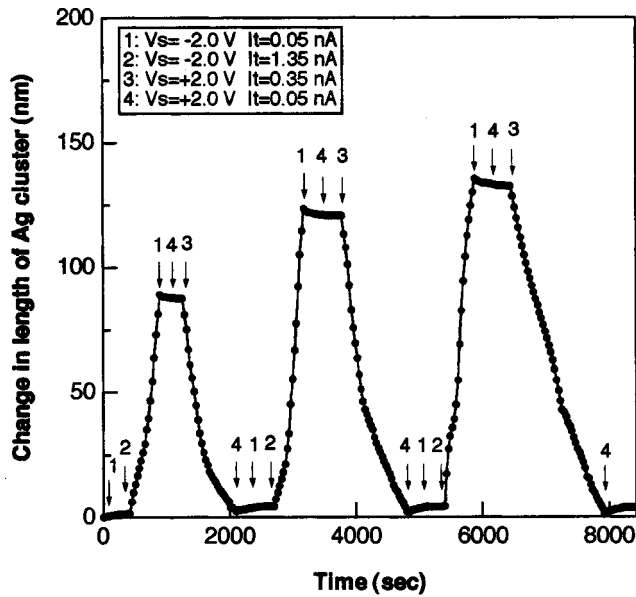
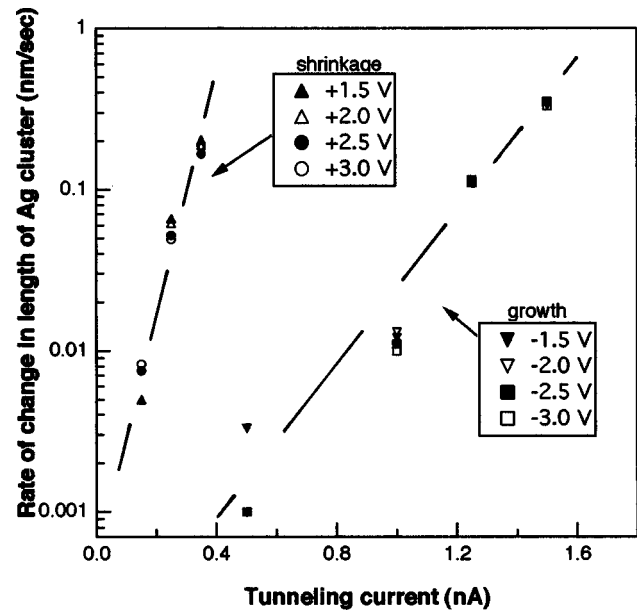


FIG. 4. Reversible growth and shrinkage of the Ag cluster.

and 4; and this sequence was repeated three times. At $V_s = -2.0$ V and $I_t = 0.05$ nA (condition 1), no Ag cluster growth occurred. However, when I_t was increased to $I_t = 1.35$ nA with V_s kept constant (condition 2), the Ag cluster grew at the apex of the Ag_2S tip at a growth rate of about 0.1–0.2 nm/s. The growth stopped when I_t was decreased again to $I_t = 0.05$ nA (condition 1). Keeping I_t at the same value, V_s was changed to $V_s = 2.0$ V (condition 4). With this polarity switching of V_s , no change was observed to occur in the Ag cluster. However, when I_t was increased to $I_t = 0.35$ nA (condition 3), the cluster shrank at a rate of about 0.1 nm/s. The shrinkage stopped when I_t was decreased again to $I_t = 0.05$ nA (condition 4). It was possible to observe the growth and shrinkage of the Ag cluster repeatedly, as shown in Fig. 4. Rates of the change in length of the Ag cluster during the growth and shrinkage depended significantly on the magnitude of I_t but negligibly on that of V_s . As seen in Fig. 5, the rates increased almost exponentially with increasing I_t .

C. Effect of an Ag wire on the growth of the Ag cluster

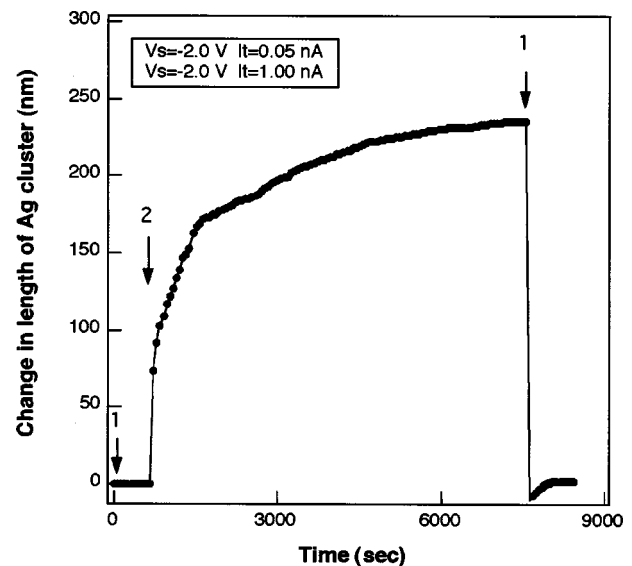
The growth behavior of the Ag cluster was investigated when the Ag_2S crystal, which was detached from the Ag wire, was used as the STM tip. For this experiment, the Ag_2S crystal grown on the Ag wire was detached from the wire. The Ag_2S crystal was fixed on a STM tip holder using carbon paste to fabricate the STM tip. Formation and growth behaviors of the Ag cluster on the Ag_2S tip detached from the Ag wire are shown in Fig. 6. At $V_s = -2.0$ V and $I_t = 0.05$ nA (condition 1), no formation of the Ag clusters occurred. This behavior agrees with that observed in the case of using the Ag_2S tip on the Ag wire (Fig. 2). When I_t was increased to $I_t = 1.00$ nA with V_s kept constant, formation of the Ag cluster was observed. The rate decreased as the length of the cluster increased, and the growth almost stopped at a length of approximately 230 nm. On the other hand, the rate

FIG. 5. Dependence on V_s and I_t of the growth and shrinkage rates of the Ag cluster.

was almost constant when the Ag_2S crystal on the Ag wire was used as the tip (Fig. 2). The cluster shrank rapidly and disappeared on the Ag_2S tip detached from the Ag wire, as shown in Fig. 6, when I_t was decreased to $I_t = 0.05$ nA and V_s was maintained at the same value of $V_s = -2.0$ V. The maximum lengths of the cluster were measured when the Ag_2S tip detached from the Ag wire was subjected to various conditions of V_s and I_t . As we can see in Fig. 7, the maximum length of the Ag cluster depended on the magnitude of I_t , but negligibly on that of V_s .

D. Mechanism of formation and disappearance of the Ag cluster

The formation and disappearance behaviors of the nanoscale Ag cluster observed in the present study can be

FIG. 6. Growth of the Ag cluster on the apex of the Ag_2S tip, which was detached from the Ag wire.

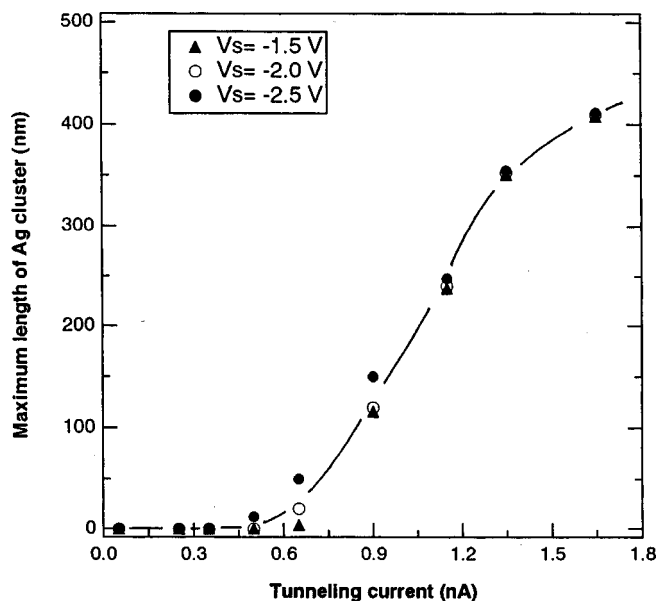


FIG. 7. Maximum lengths of the Ag cluster on the Ag_2S tip detached from the Ag wire, when the tip was subjected to various conditions of V_s and I_t .

interpreted as being due to a solid-state electrochemical process^{15,16} of mobile Ag ions in the crystal of Ag_2S . Figures 8(a) and 8(b) show the formation and disappearance processes of the Ag cluster. When a negative bias voltage is applied to the Pt sample, tunneling electrons from the sample reduce the mobile Ag ions in the Ag_2S tip to neutral Ag

atoms and Ag atoms precipitate at the apex of the Ag_2S tip, forming the Ag cluster. With the growth of the Ag cluster, the electrochemical potential of the Ag ion decreases in the Ag_2S tip. Thus, Ag atoms in a Ag wire on the opposite side are oxidized to Ag ions and are dissolved in the Ag_2S tip in order to compensate the decrease of Ag ions in the Ag_2S tip. On the other hand, when a positive bias is applied to the sample, Ag atoms in the Ag cluster are oxidized to Ag ions and the Ag ions are redissolved in the Ag_2S tip, resulting in the shrinkage and disappearance of the Ag cluster. Utsugi found that the local accumulation of mobile silver ions in a mixed conductor consisting of a silver-selenide film could be realized by applying a bias voltage using the STM tip.¹⁷

When the Ag_2S crystal detached from the Ag wire is used as the tip, the concentration (electrochemical potential) of Ag ions in the Ag_2S tip gradually decreases as the Ag cluster grows on the tip due to a lack of compensation of the Ag ions. Thus, the growth of the Ag cluster is stopped because the oxidation/reduction reaction between the Ag ions in the Ag_2S tip and the Ag atoms in the Ag cluster ($Ag_{(Ag_2S)}^+ + e^- \rightleftharpoons Ag_{(cluster)}$) reaches the equilibrium state. In the equilibrium state, the Ag cluster shrinks rapidly and disappears when I_t is decreased, as we can see in Fig. 6. The decrease of I_t indicates a decrease of the actual voltage applied to the Ag_2S tip (the relation between I_t and the voltage applied to the Ag_2S tip is discussed in the following paragraph). The equilibrium state between the Ag_2S tip and the Ag cluster is disrupted due to the decrease of the voltage applied to the Ag_2S tip. Thus, the dissolution reaction of the Ag atoms into the Ag_2S tip ($Ag_{(cluster)} + e^- \leftarrow Ag_{(Ag_2S)}^+$) becomes predominant, and the Ag cluster on the Ag_2S tip disappears.

The formation and growth of the Ag cluster on the Ag_2S tip could be also understood in the light of the knowledge of photographic science.^{18,19} When a negative bias voltage is applied to the Pt sample, a tunneling electron from the sample is trapped by one of the electron traps around the Ag_2S surface. The trapped electron attracts and reacts with a mobile Ag ion in the Ag_2S tip to form an Ag atom. The silver cluster formation on the Ag_2S takes place through the capture of the tunneling electron and the Ag ion one after the other. It is recognized that the efficiency of its nucleation stage is usually very low, while that of its growth is high because a deep electron trap is made by the cluster formation. Namely, a silver cluster itself enhances its growth by effectively capturing the tunneling electron. It is considered that this is reason why the Ag cluster is formed and grown on the Ag_2S tip by applying an bias voltage between the tip and the sample.

A growth mechanism of the filamentary silver, which are produced from a silver halide crystal (silver-ionic/electronic conductor) in photographic development, has been proposed.²⁰ According to this model, silver atoms are formed at point; the surface tension causes them to pack into a sphere. However, when the particle attains a certain size, the new silver atoms produced from the silver halide can not diffuse around the whole particle in time, and the shape becomes elongated. The required growth rate of at least 10–100 nm/s to form the filamentary silver was estimated. How-

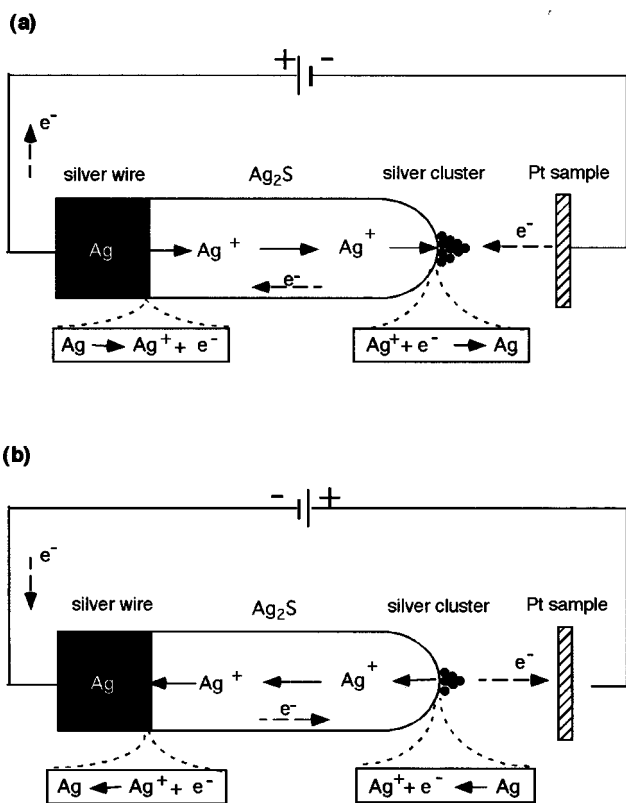


FIG. 8. Solid electrochemical process in (a) the growth of the Ag cluster on the Ag_2S tip at a negative sample bias, and (b) the shrinkage of the Ag cluster at a positive sample bias.

ever, in our study, the growth rate of the filamentary silver cluster on the Ag₂S tip is 0.1 nm/s, which is very small compared to the aforementioned value (10–100 nm/s). It is plausible to think that the filamentary silver growth on the Ag₂S tip results from not only a limited rate of surface diffusion of the silver atom but also electrical effects caused by the bias voltage and tunneling current between the tip and the sample.

According to the growth experiments on the Ag cluster shown in Figs. 2 and 3, one in every 10⁵ electrons tunneling from the Pt sample to the Ag₂S tip is estimated to be used for the reduction of Ag ions into Ag atoms in the Ag₂S tip. The transport number [$t_{(\text{Ag ion})}$] of the Ag ions in the Ag₂S is defined by $t_{(\text{Ag ion})} = \sigma_{(\text{Ag ion})} / (\sigma_{(\text{Ag ion})} + \sigma_{(\text{el})})$, which represents the ratio of the current due to the flow of Ag ions to the total current, where $\sigma_{(\text{Ag ion})}$ and $\sigma_{(\text{el})}$ are Ag-ionic and electronic conductivities of the Ag₂S, respectively. Using the reported values²¹ of $\sigma_{(\text{Ag ion})}$ and $\sigma_{(\text{el})}$, $t_{(\text{Ag ion})}$ is calculated to be 10⁻³. Thus, if the reduction process of the Ag ions in the Ag₂S tip proceeds without a reaction barrier, the ratio of the electrons used for the reduction of the Ag ions to all of the electrons tunneling from the sample to the tip is considered to be 10⁻³. This value is larger than the value of 10⁻⁵ estimated from the results of the growth experiments of the Ag cluster. This is because the reduction process of the Ag ions is actually accompanied by some reaction barriers, such as the activation processes of the charge transfer.

The rates of the growth and shrinkage of the Ag cluster are defined by the solid electrochemical reaction of the Ag ions in the Ag₂S tip. The barrier energy in the activation process of the charge transfer most likely affects the reaction rate. The barrier energy can be controlled via the bias voltage (overvoltage) applied to the Ag₂S tip. When a pure Ag-ionic conductor is used as the tip and the charge-transfer process is a rate-determining step, the solid electrochemical reaction involving the Ag ions obeys the Tafel equation ($\eta = a + b \log(I)$), where η is overvoltage, I is current, and a and b are constants.²² Because the current of I represents the flow of electrons in the reaction, the equation indicates that the rates of the electrochemical reaction increase exponentially as the overvoltage of η increases. In our study, because Ag₂S is used as the ionic and electronic mixed conductor, the current is the sum of the flows of individual electrons in the reaction and electrons merely migrating in the Ag₂S. Thus, it is impossible to examine the rates of the solid electrochemical reactions from the value of I_t . We estimate the reaction rates from the rates of growth and shrinkage of the cluster. The rates of growth and shrinkage are proportional to the changes in length of the cluster, because the shape of the grown cluster was almost columnar. As we can see in Fig. 5, the rates of change in length increased exponentially with increasing I_t , namely the rates of solid electrochemical reaction increase exponentially by increase of I_t . Under the condition that the electric resistance of the Ag₂S tip is constant, the actual voltage applied to the Ag₂S tip increases

with increasing I_t (even if V_s is constant). These results show that the rates of the solid electrochemical reaction increase exponentially with increasing actual voltage applied to the Ag₂S tip. This relationship agrees with the Tafel equation.

IV. CONCLUSION

We have developed a nanostructuring method using the solid electrochemical reaction induced by a STM. In this method, the formation and disappearance of the nanostructures were reversible, furthermore, the rates could be controlled. In this study, a mixed conductor, Ag₂S, which shows Ag-ionic and electronic conductivities, was used as a STM tip, and a nanoscale Ag cluster was formed at the apex of the Ag₂S tip by subjecting the tip to certain bias voltage and tunneling current conditions. The cluster could, then, be made to disappear by changing the polarity of the bias voltage. The rates of the growth and shrinkage could be controlled via the tunneling current. These phenomena are explained by the solid-state electrochemical reaction of Ag ions in the Ag₂S. We believe that the nanostructuring method developed in this study, which reveals interesting phenomena such as the formation and disappearance of Ag cluster, is a potential means of creating functional electronic devices.

- 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 P. Avouris, *Science* **253**, 173 (1991).
- ⁴S. Hosoki, S. Hosaka, and T. Hasegawa, *Appl. Surf. Sci.* **60**, 2418 (1992).
- ⁵D. H. Huang, H. Uchida, and M. Aono, *Jpn. J. Appl. Phys., Part 1* **31**, 4501 (1992).
- ⁶H. Uchida, D. H. Huang, F. Grey, and M. Aono, *Phys. Rev. Lett.* **70**, 2040 (1993).
- ⁷A. Kobayashi, F. Grey, S. Williams, and M. Aono, *Science* **259**, 1724 (1993).
- ⁸D. H. Huang, H. Uchida, and M. Aono, *J. Vac. Sci. Technol. B* **12**, 2429 (1994).
- ⁹R. Wiesendanger, *Scanning Probe Microscopy and Spectroscopy* (Cambridge University Press, Cambridge, UK, 1994).
- ¹⁰T. Takahashi, *High Conductivity Solid Conductors* (World Scientific, Singapore, 1989).
- ¹¹S. Miyatani, *J. Phys. Soc. Jpn.* **15**, 1586 (1960).
- ¹²S. Miyatani, *J. Phys. Soc. Jpn.* **24**, 328 (1968).
- ¹³H. Rickert, *Electrochemistry of Solids: An Introduction* (Springer, Berlin, New York, 1982).
- ¹⁴K. Terabe, T. Nakayama, N. Iyi, and M. Aono, *Proceedings of the Ninth International Conference on Production Engineering*, Osaka, 1999 (JSPE Publication Series No. 3). (JSPE, Tokyo, 1999), p. 117.
- ¹⁵J. Corish and C. D. O'Braian, *J. Cryst. Growth* **13**, 62 (1972).
- ¹⁶T. Ohachi and I. Taniguchi, *J. Cryst. Growth* **13**, 191 (1972).
- ¹⁷Y. Utsugi, *Jpn. J. Appl. Phys., Part 1* **32**, 2969 (1993).
- ¹⁸T. Tani, *Photographic Sensitivity: Theory and Mechanisms* (Oxford University, New York, 1995).
- ¹⁹*The Theory of the Photographic Process*, 4th Edition, edited by T. H. James (Macmillan, New York, 1977).
- ²⁰C. R. Berry, *Photograph. Sci. Eng.* **13**, 65 (1969).
- ²¹Y. Y. Gurevich and A. K. Ivanov-Shits, *Semiconductors and Semimetals* (Academic, New York, 1988).
- ²²R. D. Armstrong and M. Todd, *Solid State Electrochemistry*, edited by P. G. Bruce (Cambridge University Press, Cambridge, UK, 1995).