Control of local ion transport to create unique functional nanodevices based on ionic conductors

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Abstract

The development of nanometer-scale devices operating under a new principle that could overcome the limitations of current semiconductor devices has attracted interest in recent years. We propose that nanoionic devices that operate by controlling the local transport of ions are promising in this regard. It is possible to control the local transport of ions using the solid electrochemical properties of ionic and electronic mixed conductors. As an example of this concept, here, we report a method of controlling the transport of silver ions of the mixed-conductor silver sulfide (Ag$_2$S) crystal and basic research on nanoionic devices based on this mixed conductor. These devices show unique functions such as atom deposition, resistance switching, and quantum point contact switching. The switches operate through the formation and dissolution of an atomic bridge between the electrodes, and the behavior is realized by control of the local solid-state electrochemical reaction. Potential nanoionic devices utilizing the unique functions and characters that do not exist in conventional semiconductor devices are discussed.

Keywords: Nanoionics; Mixed conductor; Atomic switch; Scanning tunneling microscopy; Nanowire

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1. Introduction

Electrical devices exploiting semiconducting properties based on electron transport in silicon (Si) are widely used in information, communication, and industrial equipment.
The further development of such equipment greatly depends on the continuous improvement of semiconductor devices. However, the scale of fine processing will soon reach the atomic scale. It is evident that not only the limits to conventional fine processing technology but also the physical operating limits of semiconductor devices are being reached. Nanometer-scale devices based on new principles that can overcome these limitations in silicon-based microelectronics are actively being sought.

We have developed a nanodevice called an “atomic switch” [1] that operates through the local control of ion transport on (in) an ionic conductor [2]. Such control is possible by utilizing a solid-state electrochemical phenomenon. In a field effect transistor of a conventional semiconductor device used in computers, etc., the switching action between on and off states occurs by changing the electron distribution in the semiconductor materials between the source and drain electrodes by controlling the gate electrode field, and detecting the resulting resistance change in the semiconductor area. In contrast, in the atomic switch made of ionic conductor materials, the switching action is obtained by controlling the formation and dissolution of a metal atom bridge (an electronic conduction path) between the electrodes by utilizing the local transport of metal ions and detecting the resulting resistance change between the electrodes. In spite of the utilization of atoms, which are heavier and larger than electrons, the atomic switch is relatively rapid, since it only has to transfer atoms over a distance of several nanometers.

Furthermore, by utilizing the ion transport of larger masses, new functions and characters that would be impossible to achieve in conventional semiconductor devices become possible.

In this paper, we show that nanoionics based on the local control of ion transport at a heterointerface between an ionic conductor and metallic materials can be used to create new functions and reveal new phenomena. We also discuss potential applications utilizing local ion transport.

![Diagram](image)

Fig. 1. Local solid-state electrochemical process utilizing tunneling electrons for growth of an Ag atom filament at the apex of an Ag₂S tip.
2. Control of local solid-state electrochemical phenomena

2.1. Formation and dissolution of a metal atom cluster on a mixed conductor by scanning tunneling microscopy

The research on nanodevices that operate by exploiting local ion transport originates from an interesting phenomenon in nanoionics in which local control of a solid-state electrochemical reaction in a mixed conductor can be realized by utilizing tunneling electrons [3,4]. As an example, in an experiment we conducted, a needle-like single crystal of a silver (Ag) ionic and electronic mixed conductor, silver sulfide (Ag2S), was used as a scanning tunneling microscope (STM) tip. We found that an Ag nanoscale filament grew at the apex of the Ag2S tip when a negative bias was applied to the platinum (Pt) sample substrate and that the Ag filament dissolved gradually when the substrate bias polarity was switched to positive. It was possible to repeatedly carry out the formation and dissolution of the Ag filament on a nanoscale level. The behavior of the Ag filament observed on the apex of the Ag2S STM tip can be interpreted as being due to a solid-state electrochemical phenomenon concerning mobile Ag ions in the mixed-conductor Ag2S crystal [5,6]. Fig. 1 shows the formation process of the Ag filament. The Ag2S tip was placed facing the platinum (Pt) substrate with a ~1 nm tunnel gap. Electrons could tunnel through the gap between the Ag2S tip and the Pt electrode. When an appropriate negative bias was applied to the Pt substrate, tunneling electrons from the substrate reduced the silver ions (Ag+) in the Ag2S tip to Ag atoms and a cluster of Ag atoms formed on the Ag2S. When the tip’s position was changed during the Ag cluster growth to maintain the distance of the tunnel gap, it became possible to grow an Ag filament of several hundred nanometers, as shown in the scanning electron microscope (SEM) image of Fig. 1. Then, when the polarity of the bias voltage applied to the Pt substrate was changed to positive, the Ag atoms in the filament were oxidized to Ag+ and dissolved back into the Ag2S tip.

2.2. Formation and dissolution of metal filaments inside mixed conductors

We also demonstrated that an Ag atomic filament can be formed and dissolved through a solid-state electrochemical reaction, even inside a mixed-conductor nanostructure. In this experiment, we used the nanostructures of a mixed-conductor (Ag2S or copper sulfide (Cu2S)) thin film [7] and nanowire [8,9] sandwiched between Ag (Cu) and Pt electrodes. Fig. 2 illustrates the formation process of the Ag nanoscale filament inside the Ag2S crystal. In the same manner as shown in Fig. 1, when an appropriate negative bias voltage was applied to the Pt electrode, electrons from the Pt electrode reduced the Ag+ to Ag atoms, which precipitated inside the Ag2S crystal, eventually forming an Ag filament between the Ag and Pt electrodes. On the other hand, when a positive bias was applied to the Pt electrode, the Ag atoms in the filament were oxidized to Ag+ and dissolved in the Ag2S crystal. Compared with the formation of metal filaments on mixed conductors utilizing tunneling electrons through a gap, it is difficult to control the formation position and growth rate of metal filaments inside mixed conductors by utilizing electrons flowing from the electrode via the heterointerface. In addition, it is reasonable to consider that the formation of metal filaments inside crystals induces structural defects in the crystals.

3. Nanostructure fabrication process for elements based on ionic conductors

The development of a nanofabricating process for the elements of nanodevices based on ionic conductors is of great importance. We have fabricated elements by a conventional nanofabricating method using electron-beam lithography and related techniques such as metal deposition and the lift-off of a resist film. For example, the fabrication process for a cross-wire structure (Pt electrode wire/Ag2S-coated Ag electrode wire) with a ~1 nm tunnel gap between the wires [2] and a layered structure (Cu layer/Cu2S layer/Pt layer) [7] was developed to fabricate the elements of new functional nanodevices.

We have also developed a useful template-confined electrochemical process for fabricating nanowires including metal- and ionic-conductor heterojunction segments [8,9]. Nanoscale porous-conductor heterojunction segments [8,9]. Nanoscale porous-alumina membranes are used as the templates for the electrochemical growth of a nanowire array from an electrolytic solution. Controlling the structure of the heterojunction in the nanowires is very important because the interesting solid-state electrochemical phenomena occur there. In addition, the nanowires are promising for use as one-dimensional paths for local ion transport or as building blocks for the elements of...
nanodevices. Fig. 3 illustrates this template-assisted step-electrochemical method for fabricating a nanowire array including the metal- and mixed-conductor heterojunction segments, for example, Ag/Ag$_2$S heterostructures. In fact, we used this method to grow Ag/Ag$_2$S nanowires inside an array of pores (the size of which can be changed from approximately 20 to 200 nm in diameter) of an anodic alumina oxide membrane. First, the Ag nanowires were grown in pores by electroplating using an electrolyte containing Ag ions. Second, Ag$_2$S nanowires confined by the pores of the alumina membrane were grown by the gradual exhaustion of pre-grown Ag nanowires in an anodic electrochemical sulfurization process using an electrolyte containing sulfur ions. Fig. 4(a) shows an SEM image of the surface of the porous alumina membrane including Ag/Ag$_2$S crystals grown in the pores by the step-electrochemical method. An array of pores (the size of which can be changed from approximately 20 to 200 nm in diameter) of an anodic alumina oxide membrane. First, the Ag nanowires were grown in pores by electroplating using an electrolyte containing Ag ions. Second, Ag$_2$S nanowires confined by the pores of the alumina membrane were grown by the gradual exhaustion of pre-grown Ag nanowires in an anodic electrochemical sulfurization process using an electrolyte containing sulfur ions. Fig. 4(a) shows an SEM image of the surface of the porous alumina membrane including Ag/Ag$_2$S crystals grown in the pores by the step-electrochemical method. An array of Ag/Ag$_2$S nanowires densely filling the pores of the alumina template was fabricated. Each nanowire was obtained by removing the alumina membrane using a sodium hydroxide aqueous solution. Fig. 4(b) shows an SEM image of an Ag/Ag$_2$S nanowire, and the inset shows a transmission electron microscope image of the Ag/Ag$_2$S heterojunction part of the nanowire. According to selected-area electron diffraction analysis, the Ag and Ag$_2$S segments in the nanowires exhibited regular diffraction spots that were consistent with those of the single-crystal structures, and the heterojunction interface between these segments had a coherent structure. We have fabricated a number of ionic conductor nanowires with heterojunctions, such as Ag/AgI [10], Ag/AgBr, and Cu/Cu$_2$S [9], by this template-confined electrochemical method.
4. Application research utilizing the local control of ion transport

4.1. Ionic-conductor STM tip as material source and reservoir [11]

An ionic- and electronic-mixed-conductor needle is a promising material for use as a functional STM tip in nanostructure engineering. Electronic conductivity is necessary for STM tip materials, since a tunneling current must flow between the tip and the substrate. Since ions in mixed conductors easily migrate upon the application of an electric field, it is thought that the STM tip can be used as a source of ions and atoms for fabricating nanoscale and even atomic-scale structures, as shown in Fig. 5. The products of this process appear as if the nanostructures had been drawn on a substrate by utilizing a nanoscale pen containing mobile ions as ink. The Ag ionic and electronic mixed-conductor Ag₂S is a promising STM tip material because it is possible to grow a needle-like single crystal. Furthermore, it is easy to handle the sample because the Ag₂S crystal and Ag metal are relatively chemically stable in the atmosphere. We used a needle-like single-crystal Ag₂S as the STM tip material. We confirmed that tunneling current flowed between the Ag₂S tip and the Si substrate, and obtained an image of an Si surface using the Ag₂S tip. As described in Section 2.1 and shown in Fig. 1, the formation and dissolution of the Ag protrusion at the apex of the Ag₂S tip was observed upon applying an appropriate bias voltage. The protrusion behavior can be examined by monitoring the distance over which the Ag₂S tip perpendicular to the substrate moves in constant-current STM mode. We found that by applying an appropriate bias voltage, small numbers of Ag atoms could be continuously deposited on the substrate from the Ag₂S tip using the Ag protrusion. Fig. 6 shows an STM image of the line structure deposited on the Si substrate by scanning the Ag₂S tip. The image was obtained from the Ag₂S tip after deposition under different bias conditions. The line
structure, which was deduced from cross-sectional analysis (Fig. 6(b)) to be made up of two layers of Ag atoms, was fabricated on the Si substrate by scanning the tip. We believe that mixed-conductor materials can be used as a unique functional needle to not only deposit materials and but also absorb materials; thus, we believe it is possible to establish an efficient method for engineering nanostructures composed of inorganic, organic, and biomaterials.

4.2. Nanoswitching devices [2,7,12–14]

After we found that an Ag atom filament between the STM tip and the substrate could be repeatedly formed and dissolved through the local control of the solid-state electrochemical reaction using tunneling electrons, we realized that it may be possible to produce a nanoswitching device using this phenomenon. We subsequently conducted current–voltage measurements between the Ag₂S tip and the Pt substrate to characterize the switching phenomenon (Fig. 7). In this STM experiment, the position of the Ag₂S STM tip was fixed after moving the tip toward the Pt substrate until the tunneling current was detected, and then the current–voltage measurement was started. The bias voltage applied to the Pt sample substrate was swept repeatedly from positive and negative, as indicated by the lines labeled 1–4 in Fig. 7. A sudden increase in current, which corresponds to line 2, indicates the formation of an Ag atom bridge between the Ag₂S tip and the Pt substrate, as illustrated in the schematic diagram in the figure. When the applied bias polarity was switched to positive, the Ag bridge dissolved, which corresponds to line 4, and the current decreased. A switching rate of over 1 MHz was confirmed [15]. Recently, we found that a similar atomic switch could be formed at each point where an Ag₂S wire crossed Pt wires with 1 nm spacing [2]. This cross-bar structure was fabricated by a conventional method used for nanofabricating electronic devices.

4.3. Quantum point contact [2,16]

The local control of ion transport in a mixed conductor has yielded an interesting conductance quantization phenomenon that appears even at room temperature. It occurs when the Ag atom bridge between the Ag₂S tip and the Pt substrate is slowly formed and dissolved by applying a relatively small voltage near the threshold voltage to start the solid-state electrochemical reaction. The experimental setup is the same as that in Fig. 7. Fig. 9 shows the quantized conductance during formation and dissolution of point contact between Ag filament and Pt substrate.

It is possible to obtain the same switching phenomenon by utilizing the formation and dissolution of metal atom filaments inside a mixed conductor [7,8]. For example, Fig. 8 shows the current–voltage characteristics for an Ag/Ag₂S heterojunction nanowire array synthesized by the template-confined electrochemical method using porous alumina. The measurement was conducted using a two-terminal configuration (Pt electrode-Ag/Ag₂S nanowires-W probe electrode). A tungsten (W) tip with a 30 μm diameter was used as the probe electrode. The nanowires showed switching behavior that can be attributed to the Ag conducting filament inside the Ag₂S wire segments. We also confirmed that the elements of layered structures (Cu/Cu₂S/Pt [8] layers and Ag/Ag₂S/Pt) fabricated by a conventional method can switch using the same principle.

Fig. 9. Generation of quantized conductance during formation and dissolution of point contact between Ag filament and Pt substrate.

Fig. 8. (a) Current–voltage characteristics of Ag/Ag₂S heterostructure nanowire array during cyclic formation and dissolution of Ag filament inside Ag₂S segment by sweeping the bias voltage.
$2e^2/h$ (where $e$ is the charge of the electron and $h$ is Planck's constant). Over time, the quantum number decreased from 6 to 1 in steps, and the Ag bridge dissolved. The polarity of the bias voltage was then switched, and as an appropriate voltage was applied, the bridge was reconstructed and the quantum number increased from 1 to 6.

Switching between these quantum numbers can be achieved by applying a pulse bias voltage larger than the threshold bias voltage of the solid-state electrochemical reaction. A bias voltage smaller than the threshold was used to measure the quantum number. We fabricated a 1 × 2 array with a cross-bar structure and a tunneling gap using one Ag/Ag$_2$S wire and two Pt wires. The quantum numbers of the two-point contact in the 1 × 2 array could be switched independently from 0 to 3 using pulsed bias voltages, which suggests that this element acted as an adder circuit or a multistate memory [2].

Furthermore, according to the switching phenomenon characterized by the current–voltage measurement in Fig. 7, the resistance of the point contact between the Ag filament and the Pt substrate markedly decreased from approximately $10^6$–$10^7$Ω, as estimated from line 2 in Fig. 7. This is because the area of the point contact continuously increased from atomic-scale size to over nanoscale size as the Ag atomic bridge grew. The size of the point-contact area and the thickness of the silver bridge can be controlled by applying an appropriate pulsed bias voltage. The growth process of the Ag bridge resembles that by which neurons in the brain grow by learning through the application of a stimulation signal. This shows the possibility of creating unique nanodevices with analogue functionalities, such as a learning function, through the local control of ion transport.

5. Conclusion

We showed that nanoionics based on the local control of ion transport may lead to the creation of unique functions and new types of nanodevices. Ionic and electronic mixed conductors such as Ag$_2$S crystal are promising materials for use in nanodevices, because it is possible to control the ion transport locally using solid-state electrochemical phenomena on the surface or at a heterointerface composed of such materials. We demonstrated that the formation and dissolution of Ag atom filaments on (inside) the mixed-conductor Ag$_2$S can be controlled by using a local solid-state electrochemical reaction to transport Ag$^+$ locally. After that, we described applications to atomic switches and quantum point contacts that can utilize the local ion transport of ionic conductors. We believe that by utilizing the local ion transport of a large mass, it will be possible to obtain unique functions and characters that cannot be implemented within conventional semiconductor devices, and thereby, create novel functional nanoionic devices that can overcome the limitations of silicon-based microelectronics.

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