Sequential Phase Transition during Fabricating $\beta$-Ag$_2$S Film on Ag Electrode by Wet Chemical Process*

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A wet chemical process was used for low-cost fabrication of Ag$_2$S flat thin films on the Ag electrodes utilized for an atomic switch. By precisely controlling the dipping condition, a flat thin film of $\beta$-Ag$_2$S (cubic) was successfully fabricated. When a Ag thin film was dipped into a 0.01%-Na$_2$S aqueous solution, $\alpha$-Ag$_2$S (monoclinic) was first precipitated, and then $\beta$-Ag$_2$S, a Ag(I) ion conductor, was precipitated on the surface after dipping for 12 h. Because the ion-conduction in $\beta$-Ag$_2$S is much larger than that in $\alpha$-Ag$_2$S with negligibly small, the results are important information for utilization of Ag$_2$S for electric devices such as atomic switch. By combining the fabricated $\beta$-Ag$_2$S electrodes with an organic field effect transistor structure, a Ag wire was grown on the surface of the $\beta$-Ag$_2$S electrode only when the FET was in the “on” state. [DOI: 10.1380/ejssnt.2014.185]

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I. INTRODUCTION

Because of the recent rapid development of atomic switches utilizing solid ion conductors [1–5], the application of nonvolatile devices in complementary metal oxide semiconductor (CMOS) devices is becoming possible. A gap-type atomic switch, which is one of the most desirable nonvolatile nanodevices, is a new style of switching device that has a structure consisting of $\beta$-Ag$_2$S and Pt counter electrodes with a 1-nm gap. The switching mechanism is as follows: when a negative bias is applied to the Pt electrode, the Ag(I) ions conduct in the Ag$_2$S, the solid ion conductor, and Ag is precipitated from the surface of the Ag$_2$S electrode by the reduction of the Ag(I) ions. When the grown Ag wire contacts the Pt counter electrode, the switch is turned on with a high current. In contrast, when a positive bias is applied to the Pt electrode, Ag is oxidized to become Ag(I) ions, which disperse into the Ag$_2$S, and the Ag wire shrinks to cut the bridge and turn the switch off with a low current. One of the weak points of a gap-type atomic switch is that precise fabrication is required for the 1-nm gap, with no error, in order to use it in a CMOS device. To avoid problems, we attempted to make the gap wider in a previous study. We succeeded in operating an atomic switch only when light was irradiated by placing photococonductive organic molecules in the gap between the counter electrodes [4, 5]. To commercialize this wider-gap atomic switch, it is necessary to stably mass produce flatter Ag$_2$S electrodes.

Until today, Ag was usually sulfurized to obtain Ag$_2$S using sulfur evaporation gas under air [1, 2], CVD [6], and assisted in the Ag nanowire growth only when the

process [7] and some other processes [8]. It was, however, difficult to control the phase of Ag$_2$S of the film. If it were possible to control the phase more precisely, these methods could be commercially utilized for the continual fabrication of devices. Thus, we attempted to use a wet process with a Na$_2$S aqueous solution to realize a convenient and mild method [9] and succeeded in fabricating a flat Ag$_2$S surface. At the beginning of the dipping in the 0.01%-Na$_2$S water solution, $\alpha$-Ag$_2$S (monoclinic) was precipitated. Finally, $\beta$-Ag$_2$S (cubic), a Ag(I) ion conductor, was precipitated on the surface after 12 h of dipping. Because the ion-conduction in $\beta$-Ag$_2$S is much larger than that in $\alpha$-Ag$_2$S with negligibly small, the results are important information for utilization of Ag$_2$S to construct the atomic switch. Although fabrication and structure of $\beta$-Ag$_2$S by wet chemical method was reported a lot, this is the first report about sequential phase transition of Ag$_2$S at the surface of Ag during chemical wet process, because the previous report on wet chemical method just focused only on $\alpha$-Ag$_2$S phase [7].

Then, an organic field effect transistor (OFET) structure was fabricated with the obtained sulfurized Ag and counter Pt electrodes. Because the on and off states of an OFET can be controlled by the gate bias, the current passed between source and drain electrodes became larger and assisted in the Ag nanowire growth only when the

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FIG. 1: Procedure for fabricating Ag$_2$S on Ag surface. (a) Prepare Ag thin film on SiO$_2$. (b) Dip the substrate into 0.01%-Na$_2$S aqueous solution. (c) Ag$_2$S is precipitated from the Ag surface.
OFET device was in the “on” state. The results showed that an intrinsic memory could be added to the OFET by combining it with an atomic switch structure.

II. EXPERIMENTAL

A counter electrode made of Ag with a gap of approximately 1 μm was fabricated using conventional UV-lithography (Cr:10 nm, Ag:100 nm) on a Si substrate. The Ag was sulfurized by following a modified version of a reported technique [9]. The substrate was dipped into an aqueous solution of 0.01%-Na$_2$S for sulfurization (Fig. 1). The surface structure of the obtained sample was analyzed using grazing-incident X-ray diffractometry (GIXRD, Rigaku Smart Lab) with CuKα. The GIXRD measurements were carried out at $\alpha = 0^\circ$.

The roughness of the surface was measured using tapping mode atomic force microscopy (AFM) (JEOL JSPM-4200). Scanning electron microscope (SEM) images were used to compare the surface structures of samples fabricated by sulfurization in the aqueous solution with different dipping times. The Ag growth was examined under electron beam irradiation in SEM to verify the existence of Ag(I) ion conduction. Finally, the quality of the obtained Ag$_2$S electrode was proved by using the electrodes for an atomic switch with a hybrid structure in an OFET. The OFET layer was placed in the gap of the counter electrodes of Ag$_2$S/Ag. A gate bias was applied from the back side of the SiO$_2$ substrate (back gate). The structure of the device was made as the same as the photo-assisted atomic switch previously reported [10] by replacing photoconductive molecules with OFET molecules.

III. RESULTS AND DISCUSSION

AFM was utilized to check the surface condition of the Ag sulfurized by the aqueous solution of 0.01%-Na$_2$S. As shown in Fig. 2, the roughness was proportional to the dipping time in the aqueous solution. Because a flatter electrode is more suitable for precise atomic switch devices, it is better to use a shorter dipping time to grow the Ag$_2$S layer.

Analyzing the GIXRD results showed that the surface diffraction peaks from Ag gradually decreased as the dipping time increased, and then disappeared at 24 h, as shown in Fig. 3(a). New peaks appeared in the GIXRD spectrum just after the dipping began, and the intensity increased with the dipping time. All the new peaks could be assigned to monoclinic Ag$_2$S (the solid lines in Fig. 3(a) and the black lines in (b), monoclinic $P2_1/n$, $a = 4.226\ \text{Å}$, $b = 6.928\ \text{Å}$, $c = 7.858\ \text{Å}$, $\beta = 99.610^\circ$, JCPDS #14-0072) [11].

After dipping for approximately 12 h, peaks from cubic beta-Ag$_2$S started to be appeared (indicated by blue circle).

After dipping for 3 h, the sample did not show the growth of the Ag wire by the electron irradiation, which confirmed that the Ag$_2$S was the phase. In contrast, the sample dipped for 12 h showed the growth, which confirmed that the beta-Ag$_2$S phase was precipitated. These phenomena do not contradict the data obtained from GIXRD.

Because the sample dipped for 12 h was considered to
FIG. 4: (a) Ag surface dipped in 0.01%-Na$_2$S aqueous solution for 3 h. (b) Electron beam was irradiated to the same area of (a). No Ag wires were grown. (c) Ag surface dipped in 0.01%-Na$_2$S aqueous solution for 12 h. (d) Electron beam was irradiated to the same area of (c). Ag wires were grown by the reduction of Ag$_2$S. The electron beam was irradiated to (a) and (c) under the same condition.

have the best structure for an atomic switch, a test was performed using the Ag$_2$S electrode obtained using this dipping time. For the demonstration, the previously reported condition was modified [4] and pentacene, the OFET material shown in Fig. 5(a), was placed between the counter electrodes. Because the atomic switch could be controlled by the current density [4] we attempted to control the Ag growth by controlling the current density using the OFET. As shown in Fig. 5, at the beginning, when no gate bias was applied, the Ag wire did not grow at all. Then, after 5 V was applied to the gate electrode, the current was rapidly increased after 2000 s. This occurred because the grown Ag wire contacted the counter electrode, and the resistance suddenly decreased. Figure 6 shows SEM images before and after the Ag bridge formation. The observation shown in Fig. 6(b) was performed after removing the pentacene. Ag was grown from the upper Ag$_2$S electrode and attached to the counter electrode 820 nm away by the bridge formation. This experiment also proved that a memory function could be added to an OFET device.

IV. CONCLUSION

Sequential phase transition of Ag$_2$S during dipping time in a 0.01%-Na$_2$S aqueous solution was controlled. As shown by electron beam irradiation, a Ag wire grew on the surface of the Ag$_2$S when it was dipped longer than 12 h. The GIXRD results confirmed that α-Ag$_2$S was precipitated for dipping times shorter than 12 h, and β-Ag$_2$S was precipitated for dipping times longer than 12 h. The surface flatness of Ag$_2$S was also changed by dipping time. A longer dipping time made the surface rougher by sulfurization. By combining the sequential phase transition of Ag$_2$S with the surface roughness results, a 12-h dipping time was the best condition for the atomic switch.

The β-Ag$_2$S electrode obtained by 12 h of dipping was used for an OFET. A Ag wire could be grown in the SD electrode gap by controlling the gate bias. This device could replace to present semiconductor devices because gate bias control is available.

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