Fabrication of an Array of Ni/NiO Nanowire-ReRAM Using AAO Template on Si*

Tomohiro Shimizu,[†] Yuzuru Sumita, Fumihiro Inoue, Tetsuji Minokuchi, and Shoso Shingubara
Graduate School of Science and Technology, Kansai University, Yamate-cho 3-3-35, Suita564-8680, Japan

Shintaro Otsuka and Koichi Takase

College of Science and Technology, Nihon University, Kanda-surugadai 1-8, Chiyoda 101-8308, Japan

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The resistive switching random access memory (ReRAM) device using Ni/NiO nanowire as a building block was demonstrated; this is prepared by a combination of top-down and bottom-up techniques. The Ni nanowire arrays on Si substrates were prepared by electroplating of Ni into the anodic aluminum oxide (AAO) template, and the surface of the nanowires were oxidized by O₂ plasma treatment at room temperature. We observed an improvement of stability of the switching properties in the nanowire device compared with the device using nickel oxide thin film. [DOI: 10.1380/ejssnt.2012.476]

Keywords: Nano-wires; Nano-electronics and related devices; Nickel oxides

I. INTRODUCTION

The resistive random access memory (ReRAM) is a promising candidate for the next-generation high-density nonvolatile memories as post-flash memories, due to their advantages for structural simplicity and memory characteristics such as high-speed switching and high on-off signal ratio [1–4]. Various metal oxides and perovskites have been actively studied as a material for ReRAM [1–9]. A metal oxide or perovskite layer, which exhibits resistive switching (RS) phenomenon, is sandwiched between two metal electrodes. Therefore, to achieve a high density ReRAM, it is important to reduce the size of RS cells. Using self-organized nanowires as an element of RS cell, it would be one of the solutions to realize a high density ReRAM. There have already been several studies of metal oxide nanowire devices using self-organization technique [5–12]. Most of the previous studies used the individual metal nanowires laid on the substrate, and employed thermal oxidation in forming metal oxide in the metallic nanowires. Such a high temperature process would cause metal diffusion problems into adjacent semiconductor materials. In this study, we studied to fabricate vertically aligned NiO_x nanowire array, which has advantages for reduction of device dimensions, with a low temperature processing using O₂ plasma treatment at room temperature for oxidation of nanowire of RS cell.

II. EXPERIMENTAL

Figure 1 shows schematics of the sample preparation. The AAO (anodic aluminum oxide) templates were prepared on Si substrates to fabricate Ni nanowire arrays for nanowire ReRAM. 50 nm-Ti, 50 nm-Au and 500 nm-Al films were successively sputtered on H-terminated *n*-Si(100) substrates. Usually, an amorphous alumina layer called the barrier layer exists at the bottom of AAO pores

FIG. 1: Schematics of the sample preparation of Ni/NiO nanowire ReRAM device.

on the Si substrate, which hinders homogeneous electrodeposition in each pore. The barrier layer can be removed by wet chemical thinning process of aluminum oxide after completion of anodization of Al [13–15]. Moreover, the Au functions as the protective layer for oxidation of the Si substrate during anodization. The Ti layer was introduced to improve adhesion strength between the Au film and Si substrate.

The Al films on the Si substrates were anodized in 0.3 M oxalic acid under constant voltage conditions of 40 V. Then, the AAO nanopore array with the diameter of about 30 nm and the density of 80 G pores/inch² was obtained [16]. During anodization, the electrical contact to the Al film was formed from the back surface of the Si substrate, which was tightly contacted with a Cu anode plate. The temperature during anodization process was controlled at 5°C. Subsequently, the AAO films were slightly etched in 5 wt% phosphoric acid solution to remove the amorphous alumina barrier layer that existed at the bottom of the nanohole. At this process, the pores are widened from 30 nm to 70 nm. Although the diameter of the pores was increased, we were able to obtain the AAO templates without the barrier layer on the Au/Ti/Si substrates.

Ni nanowire arrays were formed in the AAO templates

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[†]Corresponding author: shimi@kansai-u.ac.jp

FIG. 2: XPS spectra of (a) oxygen 1s and (b) nickel 2p for as-deposited and O₂ plasma treated Ni films.

by pulsed electroplating, and the bottom Au layer acted as working electrode during Ni deposition. The Ni electroplating was continued until complete filling of AAO pore with Ni.

On the other hand, Ni film with thickness of 50 nm was prepared for X-ray photoelectron spectroscopy (XPS) measurement, and both the film and the nanowire sample were treated with 200 W oxygen RF plasma for 10 min. The Au/Ti layer was sputtered on the nanowire samples as a top electrode, and the electrode of $10 \times 10 \mu\text{m}^2$ were patterned by photolithography and lift-off process on nanowire samples.

The crystalline quality and morphology of the nanowires were investigated by transmission electron microscope (TEM) and scanning electron microscope (SEM). A cross-sectional TEM specimen was prepared using a focused ion beam (FIB) system.

The thickness of the TEM specimen was about 80 nm. The electrical properties were measured using a semiconductor analyzer (HP 4510B) at room temperature. In these measurements, top electrode was connected to the cathode. The composition analysis of the samples was performed by XPS and energy dispersive X-ray analysis (EDX) with scanning TEM. The diameter of electron beam for EDX was 0.1 nm and the diameter of detection area was less than 10 nm, considering the diffusion of the beam in the sample.

FIG. 3: Cross sectional TEM image of Ni/NiO nanowire device in AAO template. The inset shows enlarged view of dashed box at the interface between top electrode and surface of nanowire.

III. RESULTS AND DISCUSSIONS

To confirm O₂ plasma treatment clearly, we prepared sputtered Ni film on Si substrate without AAO template. Figure 2 shows the XPS spectra of (a) oxygen and (b) nickel for as-deposited and O₂ plasma treated Ni films. The XPS spectra of nickel oxide systems in O 1s and Ni 2p regions have been described elsewhere [17–19]. The possible nickel oxide phases in this case are NiO, Ni₂O₃ and oxygen absorbed on surface of metal Ni. Figure 2(a) shows the spectra range from 520 to 545 eV corresponding to the O 1s region. In the as-deposited sample, only one peak arising from adsorbed oxygen or Ni₂O₃ was observed at 532.1 eV, which indicated existence of the native oxide on as-grown film. After O₂ plasma treatment, the NiO peak at 529.7 eV was observed besides the as-grown peak. The XPS spectra of Ni 2p_{3/2} and 2p_{1/2} are shown in Fig. 2(b). The metal Ni 2p_{3/2} peak at 852.8 eV and the Ni oxide 2p_{3/2} peak at 855.7 eV were observed in the as-grown sample. In the O₂ plasma treated sample, the Ni oxide 2p peaks dominated. These results indicate the Ni surface was almost oxidized after O₂ plasma treatment for 10 min, and the oxide layer consisted of NiO and Ni₂O₃, which well agreed with the previous XPS of O₂ plasma treated Ni surface [17, 19].

Figure 3 shows cross-sectional TEM image of Ni/NiO nanowire device in AAO template, and inset shows enlarged view of the interface between top electrode and the nanowire indicated in the dashed box in Fig. 3. The nanowire grew in AAO pore, which connected to the top and bottom electrode. The diameter and length of the wire are 65 and 500 nm respectively, which well agreed with the original AAO pore size. The polycrystalline structure was observed in the nanowire, and the grain size of Ni was larger than the nanopore diameter. Therefore, individual grain looked like cylindrical shape, and the nanowire consisted of the stacked cylinders along the pore. The region of mixture of amorphous and nanoparticles was observed at the surface of the nanowire indicated as dashed line in the inset of Fig. 3. The thickness of the area was 6–10 nm, which was difficult to decide because

FIG. 4: I-V curve of the Ni/NiO device. The red line shows reset process, and the blue line shows set process with a compliance of 50 μA .

FIG. 5: (a) Reset-current and (b) set-voltage for nanowire and film device.

of the unclear contrast and the surface roughness of sample itself. Moreover, high content of oxygen was observed at the surface of Ni nanowire compared with other area by EDX with TEM. Therefore, we conclude the thickness of the nickel oxide was less than 10 nm at the surface of nanowire.

Typical I-V characteristics of the Ni/NiO nanowire device are shown in Fig. 4. The O_2 plasma treated nanowire devices shows RS behavior. The blue line shows so-called “set-process”. The voltage was applied with current compliance of 50 μA . Initially, the device was in high resistance with 20 $\text{M}\Omega$ at 1 V. After application of 3 V to the device, the resistance decreased down to 0.1 $\text{M}\Omega$ at 1 V. Then, the conductive filaments are formed in the nickel oxide layer. We defined the voltage at which set-

process occurred as set-voltage. The red line shows “reset-process”. At 4.6 V and the current 180 μA , the resistance suddenly increased again. At this time, the conduction filaments were disconnected. The current value at this moment was defined as reset-current. The switching effect was repetitive, and it was regarded as a memory device. Moreover, we also prepared other kinds of devices with top and bottom electrode, in particular the Ni nanowires without O_2 plasma treatment, only the AAO membrane device, and Ni sputtered films with O_2 plasma treatment. There was no switching property in the Ni nanowire device, and the I-V characteristics showed metallic behavior. In both of the AAO membrane and the sputtered Ni film device, the switching effect was observed, although set-voltage in AAO membrane was about 30 V, which was higher voltage compared with Ni/NiO nanowire device. These results indicated that the switching phenomena occurred in the Ni oxide layer at the surface of the nanowires.

Figures 5(a) and (b) show the reset-current and the set-voltage for each number of cycles. Compared with the film and the nanowire devices, distributions of the nanowire device in both of reset current and set-voltage were smaller than the film device, indicating the switching stability of nanowire was better than the film device. The origin of improvement of stability of the switching properties has not cleared yet, but we believe that the shape of nanowire contributed a limitation of the dimension of conduction filament in the oxide in the nanowire. To discuss further details, the TEM observation of the conduction filament in the nanowire would be necessary.

IV. CONCLUSIONS

We fabricated Ni/NiO nanowire ReRAM device using a combination of electroplating of Ni into AAO pore and plasma oxidation, and observed RS memory effect. Improvement of stability of the switching properties was observed in the nanowire device compared with the film device. To improve the switching properties, further optimization of oxidation condition, control of size of nanowire, and choice of appropriate electrodes are required.

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