Memristor property of an amorphous Sn–Ga–O thin-film device deposited using mist chemical-vapor-deposition method

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ABSTRACT
A memristor property of an amorphous Sn–Ga–O (α-TGO) thin-film device deposited using a mist chemical-vapor-deposition (mist-CVD) method has been found. The α-TGO device can be manufactured at a low cost because it does not include rare metals such as In. Moreover, it is expected that the α-TGO device can be manufactured at an even lower cost because the mist-CVD method is performed at atmospheric pressure. Here, the α-TGO layer was deposited using a hot-wall-type mist-CVD method. The hysteresis curve of the memristor characteristic was certainly obtained, and the electric resistances for the high- and low-resistance states were stably repeated at least 20 times. Although the switching ratio and repeatability are not sufficient in the case that it is applied to resistive random access memories, they are acceptable for some applications such as synapse elements in neuromorphic systems.

I. INTRODUCTION
A memristor is one of the passive devices in circuit elements, whose electric conductance depends on the past history of the flowing current. Recently, they are mainly applied to resistive random access memory (ReRAM) and neural computing. However, the conventional memristors require expensive composition materials, device structures, and manufacturing processes.

On the other hand, amorphous metal-oxide semiconductor (AOS) thin-film devices are generally applied to thin-film transistors (TFTs) for flat-panel displays (FPDs) such as liquid-crystal displays (LCDs) and light-emitting diode displays (OLEDs) because the device characteristic is excellent, the operation stability is superior, and the manufacturing process is simple. AOS thin-film devices are also promising for various applications such as arithmetic processors, power devices, and thermoelectric devices because special properties can be added on each demand by optimizing the composition materials, device structures, and manufacturing processes, and they can be manufactured at a low temperature on a large area at a low cost. In particular, the authors are focusing on amorphous Sn–Ga–O (α-TGO) thin-film devices for TFTs, thermoelectric devices, and neuromorphic systems because they do not include rare metals such as In, and industrial issues on supply shortage and resource depletion can be resolved. Recently, the authors reported a memristor property of an α-TGO thin-film device, and the above-mentioned problems of the memristors may be resolved in the future.

In addition, a mist chemical-vapor-deposition (mist-CVD) method is one of the deposition methods, where various kinds of thin films can be deposited without vacuum environment, and AOS devices were also manufactured using the mist-CVD method. It is expected that they can be manufactured at an extremely low cost.

In this research, a memristor property of an α-TGO thin-film device deposited using a mist-CVD method has been found.
The α-TGO thin-film device can be manufactured at a low cost because it does not include rare metals such as In. Moreover, it is expected that the α-TGO thin-film device can be manufactured at an even lower cost because the mist-CVD method is performed at atmospheric pressure. In this paper, the device structure, manufacturing process, memristor characteristic, and repeating characteristic of the α-TGO thin film device will be presented, and the operating mechanism of the memristor property will be discussed.

II. EXPERIMENT

Figure 1 shows the device structure of the α-TGO thin-film device deposited using the mist CVD method and the deposition system of the mist-CVD method. First, a quartz glass was used as a substrate, and an Al thin-film electrode was deposited by vacuum evaporation through a cover mask to form a bottom terminal. Next, an α-TGO thin-film layer was deposited by a hot-wall-type mist-CVD method to form a variable conductance layer. Sn acetylacetonate [Sn(acac)] of 243 mg and Ga acetylacetonate [Ga(acac)] of 160 mg were dissolved in HCl of 450 mg and H$_2$O of 40 ml. A mist of the solution was generated by an ultrasonic generator, carried by a carrier gas of air of the flow rate =1 l/min, diluted by a dilution gas of air of the flow rate =1 l/min, and injected into a quartz tube. The quartz tube was heated to the inside temperature of 400 °C by a heater, and the α-TGO thin-film layer was deposited on the substrate, whose thickness was 80 nm. Next, a Au thin-film electrode was also deposited by the same vacuum evaporation through another cover mask to form a top terminal. Finally, the α-TGO thin-film device had a device structure that the α-TGO thin-film layer as the variable conductance layer was sandwiched between the Al thin-film electrode as the bottom terminal and the Au thin-film electrode as the top electrode, whose area was 600 μm × 600 μm, which corresponded to an overlap area of the top terminal and the bottom terminal.

III. RESULTS

Figure 2 shows the X-ray diffraction (XRD) pattern of the α-TGO thin-film layer deposited using the mist CVD method. It was shown that no clear peak was observed, which indicated that the α-TGO thin-film layer was surely in an amorphous phase.

Figure 3 shows the X-ray photoelectron spectroscopy (XPS) spectrum of the O1s peak of the α-TGO thin-film layer deposited using the mist CVD method.
using the mist CVD method. It was shown that the O1s peak was separated to the metal-oxygen (M-O) and oxygen-vacancy (Vo) peaks. It should be noted that the α-TGO thin-film layer contained relatively many oxygen vacancies.

Figure 4 shows the memristor characteristic of the α-TGO thin-film device deposited using the mist CVD method. The applied voltage (V) between the top and bottom terminals was scanned from −5 V to +5 V, and the flowing current (I) through the α-TGO thin-film device was evaluated. It was found that the hysteresis curve of the memristor characteristic was certainly obtained. As V increased from V = 0 V to V = +5 V, I also increased. As V decreased from V = +5 V, I was larger in comparison with the previous I, which was called a “set transition.” On the other hand, as |V| increased from V = 0 V to V = −5 V, |I| also increased. As |V| decreased from V = −5 V, |I| was smaller in comparison with the previous |I|, which was called a “reset transition.” It should be noted that the memristor characteristic was stable even at the first hysteresis and completely overlapped at least 20 times.

Figure 5 shows the repeating characteristic of the α-TGO thin-film device deposited using the mist CVD method. The high-resistance state (HRS) was defined as a nonvolatile state after the reset transition, while the low-resistance state (LRS) was defined as another nonvolatile state after the set transition, and the electric resistances for V = +1 V for the HRS and LRS were plotted. It was found that the electric resistances for the HRS and LRS were clearly distinguished and stably repeated at least 20 times. The switching ratio was defined as the resistance ratio between the HRS and LRS and was roughly 11.7.

IV. DISCUSSION

Figure 6 shows the operating mechanism of the memristor property of the α-TGO thin-film device deposited using the mist CVD method. As aforementioned, because the α-TGO thin-film layer contains relatively many oxygen vacancies, it is strongly suggested that the oxygen vacancies play an important role. It is...
assumed that the Al thin-film electrode is oxidized during the mist-CVD method, an AlO$_x$ layer is formed at the film surface of the bottom terminal, and the AlO$_x$ layer blocks the drift and diffusion of the oxygen ions. The memristor property can be explained using the drift of the oxygen ions in the α-TGO thin-film layer. For the set transition, for $V = +5$ V, the oxygen ions are attracted to the top part of the α-TGO thin-film layer and partially injected into the Au thin-film electrode. The region with many oxygen vacancies becomes thicker at the bottom part of the α-TGO thin-film layer, and I becomes larger because the region has a high electric conductivity. On the other hand, for the reset transition, for $V = −5$ V, the oxygen ions are attracted to the bottom part but blocked by the AlO$_x$ layer at the film surface of the bottom electrode. The region with many oxygen vacancies becomes thinner or disappears, and I becomes smaller. This operating mechanism is consistent with the previous one. Moreover, because the above-mentioned behavior is the same from the first hysteresis to the steady state, the hysteresis curve is stably repeated.

**V. CONCLUSION**

A memristor property of an α-TGO thin-film device deposited using a mist-CVD method has been found. The α-TGO device can be manufactured at a low cost because the α-TGO device does not include rare metals such as In. Moreover, it is expected that the α-TGO device can be manufactured at an even lower cost because the mist-CVD method is performed at atmospheric pressure. Here, the α-TGO layer was deposited using a hot-wall-type mist-CVD method. The hysteresis curve of the memristor property was certainly obtained, and the electric resistances for the HRS and LRS were stably repeated 20 times.

In this paper, the area of the α-TGO thin-film device is as large as 600 μm × 600 μm because the top and bottom terminals are formed through rough cover masks. However, based on the aforementioned operating mechanism, the switching behavior is not caused by the filaments but uniformly distributed throughout the device area. Therefore, even if the device area is scaled down, the hysteresis shape of the memristor characteristic remains the same, and only the current value decreases in proportion to the device size. Moreover, it is believed that there is no unavoidable barrier to introduce the most advanced miniaturization technology to the α-TGO thin-film device. In conclusion, high integration and power reduction are simultaneously achieved, and the memristor property of the α-TGO thin-film device can be practically utilized.

Although the switching ratio and repeatability are not sufficient in the case that it is applied to ReRAMs, they are acceptable for some applications such as synapse elements in neuromorphic systems. This is because the neuromorphic systems are probabilistic systems, and it has been confirmed that some systems are robust against characteristic variations of synapse elements. In this paper, the electric resistances for the HRS and LRS are confirmed to repeat only 20 times. However, even if they cannot be repeated more times, it can still be applied to some types of neuromorphic systems because some systems require only a few writes after the simulation of learning outside the system. In the future, we will continue our efforts to enhance the analog tunability and characteristic linearity to implement the α-TGO thin-film device in various neuromorphic systems.

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