

Development of Deposition Technologies and Processes for Phase Change Memory

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Phase change random access memory (PCRAM) is a type of non-volatile memory that is embedded in semiconductor devices and has been put to practical use as storage class memory (SCM) with high speed and large capacity at a lower cost than DRAM. It is also expected to be applied to neural computing, which mimics the neural circuits of the human brain.

In order to realize PCRAM, it is essential to develop film deposition technologies and processes to realize appropriate film properties and mass productivity for memory elements, selector elements, and electrode materials (carbon is widely used). In this paper, we will explain the status of technology development for depositing each of these elements, and also present the evaluation results of a prototype AI device using CVD technology for applications in neural computing.

1. Introduction

In recent years, there has been remarkable progress in the spread of the IoT (Internet of things; a system that connects all things via the Internet), the full-scale implementation of 5G (5th generation mobile communication system), and the introduction of autonomous driving control systems based on these advances. In order to realize these infrastructures, a variety of technologies are required, including highly integrated and high-speed mobile devices, data centers using cloud computing to connect these devices and perform high-speed data processing, and edge computing to process large amounts of real-time data such as images and video. Semiconductors are an indispensable technology to support these fundamental technologies, and technological development is advancing on a daily basis.

In this paper, we introduce phase change random access memory (PCRAM), a type of non-volatile memory that is embedded in semiconductor devices. We expect that ULVAC semiconductor manufacturing equipment will contribute significantly to the mass production of PCRAM in order to meet the increasing demand that is anticipated.

2. Background

2.1 Necessity of PCRAM

Non-volatile memory is memory whose electrical characteristics (resistivity, amount of charge, etc.) are maintained even when the power is turned off. NAND flash memory, which has become a mainstream high-capacity storage technology for today's notebook computers and mobile devices, is classified in this category. DRAM, in

contrast, requires periodic activity to maintain the values in the memory. However, because DRAM enables high-speed, high-capacity storage, it is widely used as the primary internal storage for computers. However, when higher speed and larger capacity data processing is required, as described above, a bottleneck occurs due to the difference in processing speeds (3 to 6 orders of magnitude) between DRAM, which operates at high speeds (1 ns to 100 ns), and NAND, which operates at low speeds (10 μ s to 1 ms). To bridge this gap in speed, IBM devised a type of memory called "storage class memory" (SCM)¹ that has non-volatile storage characteristics and is much faster than NAND yet cheaper than DRAM in terms of cost.

PCRAM is a type of memory that can switch between the crystalline phase and the amorphous phase at high speed by the Joule heat generated when an electric current is passed through a certain chalcogenide material, and then utilize differences in resistance to store data. PCRAM operates at a higher speed and lower power consumption than NAND flash memory, and has non-volatile memory characteristics as opposed to the volatile DRAM. Furthermore, the phase change materials used in PCRAM have already been put into practical use in recordable DVDs and Blu-ray discsTM, and are highly reliable. For these reasons, PCRAM has attracted attention from early on as a leading candidate for SCM, and device manufacturers have been developing it for mass production.

2.2 Applications using PCRAM

Applications of PCRAM are expected to include not only SCM, but also neural computing, which mimics the neural circuits of the human brain and is positioned as a key technology for the deployment of artificial intelligence (AI). As mentioned above, the phase change materials move back

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and forth between crystalline and amorphous states due to Joule heat. By controlling the generation of Joule heat in a pulsed manner, crystallization can be advanced gradually. This makes it possible to linearly control the ease of current flow (conductance) of the element. This process is similar to the way in which people connect neural circuits through learning. These characteristics of phase change elements are being exploited for computing applications worldwide. The film performance and deposition technology required for phase change materials are explained in section 6.

2.3 3D crosspoint devices and required materials

PCRAM is a promising material for the future, but how to achieve a large capacity is a very important issue when mass-producing PCRAM for devices. At IEDM in 2009, Intel/Numonyx reported on the operation of a device that uses PCM as a storage element and an Ovonic Threshold Switch (OTS) as a selector element in a structure (PCMS) in which they are sandwiched between electrode materials (Fig. 1)², thereby demonstrating the possibility of increasing the capacity by using a more compact cell structure. Then, in 2015, Intel/Micron announced a 3D crosspoint device that combines a resistance change element and a selector element in this way (Fig. 2)^{3,4}. This structure, released under the trade name 3D XPoint™ memory, contains a storage element located at the point where orthogonal word lines and bit lines are connected, paving the way for the mass production of high-capacity resistance change type devices.

2.4 Required film properties and deposition technology

We have been working on the development of sputtering deposition processes for PCRAM materials for more than 15 years. In order to create PCRAM memory elements,

appropriate film characteristics and mass productivity must be achieved for the phase change elements, selector elements, and electrodes (carbon is widely used) mentioned above. A typical membrane structure is the PCMS structure (Fig. 3), which is introduced in the Japanese translation of a PCT International Application Publication (JP2018-502444)⁴ by Intel.

- Phase change element: A multi-component system comprising a chalcogenide material, with Ge, Sb, and Te as the main components. As mentioned above, when a voltage is applied to the element, it enters either a low-resistance alloy state or a high-resistance amorphous state, which is maintained even when the voltage application is stopped. Films deposited at low temperatures are amorphous, while films deposited at or above the crystallization temperature are in an alloy state. In order to realize more stable discharge, deposition is performed by RF sputtering or pulsed DC sputtering. The crystallization temperature varies depending on the application and required specifications of the device, and is controlled by adjusting the target composition and deposition conditions.
- Selector element: The material is the same chalcogenide material as the phase change element, with the addition of As and Se. Unlike the phase change element, it enters a high-resistance amorphous state at room temperature. The target material is brittle and fragile, so low-power RF sputtering is used. Since arsenic, selenium, and

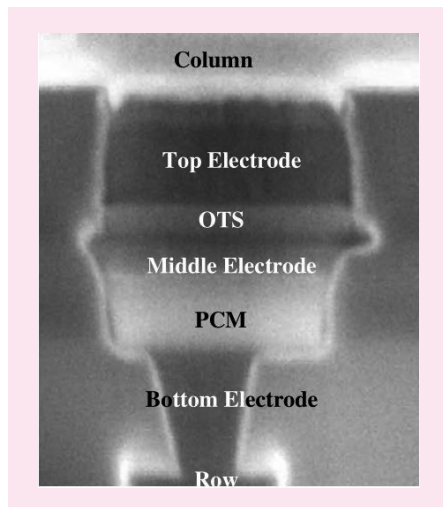


Fig. 1 Device structure with phase change element and selector element. ©2009 IEEE. Reprinted, with permission, from Ref. 1

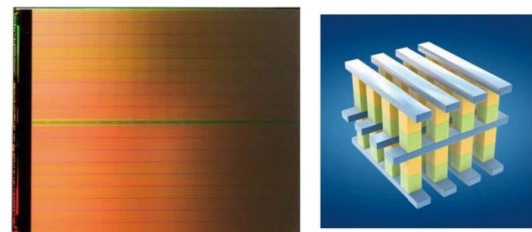


Fig. 2 128 GB 3D XPoint™ die and structure. ©2015 IEEE. Reprinted, with permission, from Ref. 3

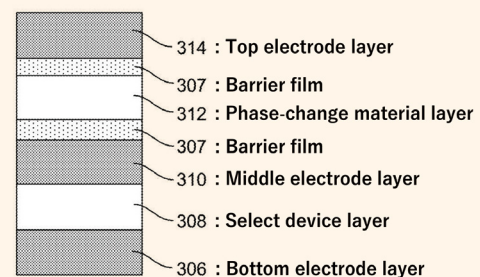


Fig. 3 PCMS structure in Intel's patent

compounds thereof contained in this material are designated as toxins, it is necessary to take sufficient safety measures for maintenance and handling of the substrate after deposition.

- **Electrode materials (carbon, etc.):** Electrode materials are required to have controlled resistivity (1 to 100 mΩcm), smoothness, and adhesiveness. Reference document 4 lists carbon and other materials as electrode materials. In the case of sputter deposition of carbon, particles are also a significant problem in terms of productivity, in addition to the above. It is necessary to consider the target materials as well. It is known that some of the constituent elements of chalcogenides easily diffuse into the electrode material with which they come into contact when heated, so a barrier film is necessary to prevent this diffusion.

At ULVAC, we are developing devices to enable in-situ processing of these multilayer films, and connecting them as modules to our ENTRON™-EX W300 multi-chamber sputtering system (Fig. 4). The next section describes the results of our technical development of the phase change elements, cell selector elements, and electrode materials.



Fig. 4 ENTRON™-EX W300

3. Development of Phase Change Element Deposition Technology

In order to utilize phase change elements as non-volatile memory, there are several performance requirements that must be met. Table 1 shows these requirements and the material properties required to achieve them. In a phase change element, a phase change is generated by Joule heat from the current flowing through the element. Effective ways to lower power consumption are to use a material with a low melting point to reduce the amount of current, to build materials and structures that prevent more heat than necessary from escaping from around the element, and to increase the resistance of the crystalline state. In terms of long-term data retention, it is important that there is no phase change, i.e., crystallization, in the storage environment. This can be accomplished by selecting materials with high crystallization temperatures. Data is written in the process of raising the temperature above the melting point and then cooling it. Crystallization depends on the material, and high-speed operation can be achieved by selecting a material with fast crystallization speed. The ability to tolerate repeated rewriting can be attributed to a number of factors, including material and structure, but the main factor is material-related, with the occurrence of phase separation being a particular issue⁶.

The phase change element uses Ge-Sb-Te material (GST), which is the same material system used in the phase-change optical discs that preceded non-volatile memory in practical use. In the phase-change optical discs, a phase change of the GST thin film is induced by a laser. However, in the phase change element, this phase change is induced by the current flowing through the stacked structure sandwiched between the electrode materials. Because this structure consists of a stacked structure including electrodes, a production technology different from that of optical discs is required. The deposition technology and the characteristics of GST are described below.

3.1 GST thin film deposition technology

Parallel flat-plate sputtering is employed as the deposition technology for GST thin films, especially for mass production, using GST targets configured from a desired composition ratio. This is because this deposition

Table 1 Requirement specification for phase change element, and process and material properties for device performance

Performance requirements	Material properties
1) Low power consumption	Low melting point
	Low thermal-conductivity material and element structure
	Higher resistance for crystalline state
2) Long retention	Crystallization at high temperature
3) High speed operation	High crystallization speed
4) High endurance	Less segregation

technology is able to simultaneously achieve the large-area uniformity, high deposition speed, and long-term deposition stability required for production. Although GST is electrically conductive, it is a high-resistance material (from several mΩcm in the crystalline phase to hundreds of Ωcm in the amorphous phase), so pulsed direct current (DC) sputtering is used. Certain factors can cause a change in resistance in the discharge surface on the target, but the abnormal discharge generated at this time can be suppressed by pulsing, making it possible to maintain long-term production stability. In addition, in order to obtain the desired film quality and properties, the composition of the target is changed, additives are added, and the process conditions are adjusted.

3.2 Controlling the crystallization temperature of the resistance change material

This section presents the properties of sample GST thin films that we actually produced. Fig. 5 (a) shows specific examples of the phase changes, i.e., resistivity changes, in GST films we prepared. The crystallization temperature can be controlled by adding certain elements to the GST. The figure shows examples from this experiment where oxygen and nitrogen are the added elements. It can be seen that in all the films, the resistivity decreased as the temperature rose from the high resistance state. The figure also shows that it is possible to raise the phase change temperature by adding oxygen and nitrogen. Fig. 5 (b) shows the results of our investigation of the crystal state of these films by the X-ray diffraction method (XRD). The results demonstrate that there was a change in resistivity and phase change temperature corresponding to the phase change from amorphous to cubic crystal (fcc) and then to hexagonal crystal (hcp).

4. Development of OTS Deposition Technology

Like the phase change material GST, OTS is a type of chalcogenide glass, but because it is an insulator and the current mainstream material systems contain toxic substances such as arsenic, there are a number of issues to be solved in the development of OTS film deposition technology. Fortunately, we have accumulated many years of experience in the sputtering of insulating materials, and we were able to make effective use of this expertise, as described in detail below. We have installed a dedicated development machine for the handling of OTS materials and, through repeated investigation and verification, have been able to establish techniques for safe handling.

4.1 Insulator sputtering technology

As mentioned above, OTS is an insulator. OTS films are deposited by using parallel plate type high frequency (RF) sputtering with an OTS target composed of the desired materials and composition. The reason for this is the same as noted for GST: to achieve uniform deposition on a large area substrate and long-term stability of the film. Since RF sputtering is not a power-efficient method, much of the power is consumed as heat. Furthermore, chalcogenide materials have a low thermal conductivity but a high thermal expansion coefficient, which can lead to target failure due to heat generation during sputtering. Stable operation that can withstand mass production is difficult with conventional RF sputtering technology alone. We are developing a deposition technology that supports OTS, but further improvements are needed to achieve high-speed performance.

Although there are still some elements to be developed in terms of high-speed deposition, the RF sputtering

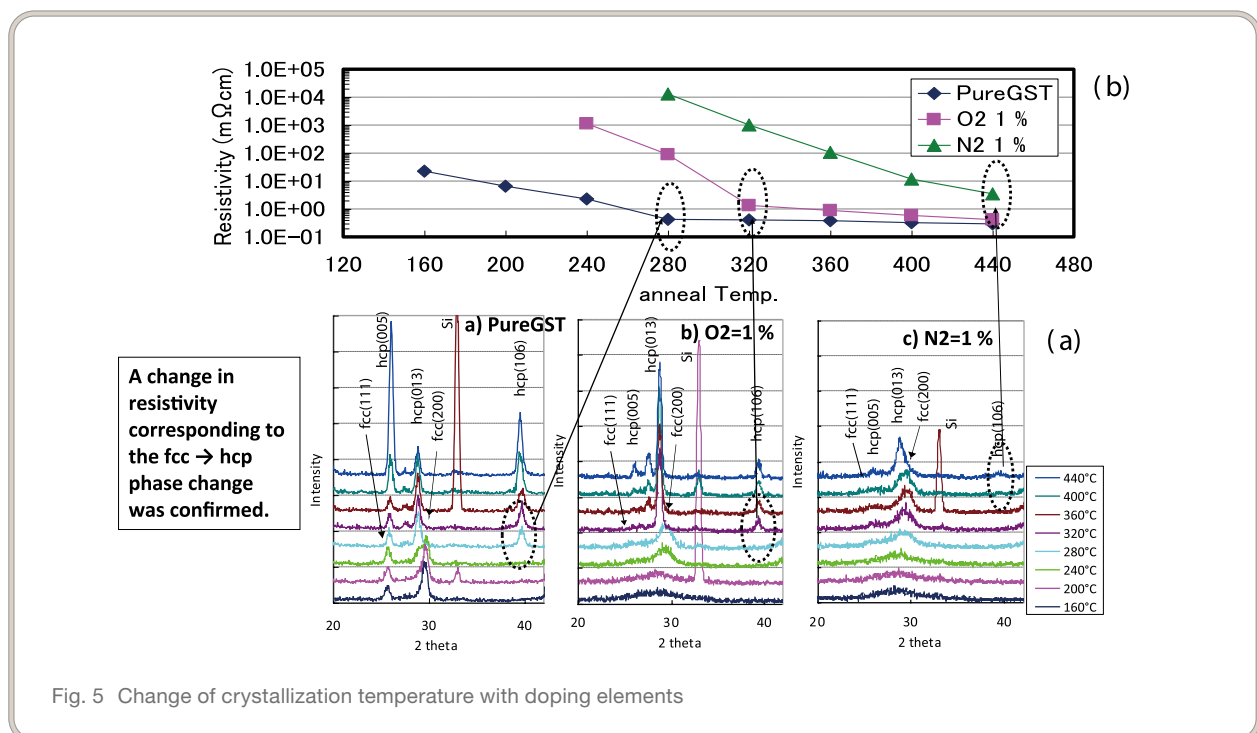


Fig. 5 Change of crystallization temperature with doping elements

technology we have devised enables stable production of OTS thin films. An example of the quality of the OTS thin film we prepared is shown in Fig. 6, where a thickness distribution of no more than 5% (1σ) was achieved. In addition, we were able to achieve a composition distribution of no more than 5% (1σ), a surface roughness (Rms) of no more than 1 nm, and a particle count of no more than 50 particles (80 nmUP) (Table 2).

4.2 Building a system that is environmentally and human-friendly

OTS contains arsenic and other toxic substances, so it is necessary to construct a system that takes the environment and human health into consideration when handling OTS. A lot of expertise has been put into the development of the system, including the equipment. Although the details are omitted, the following is a list of the areas we have investigated and improved.

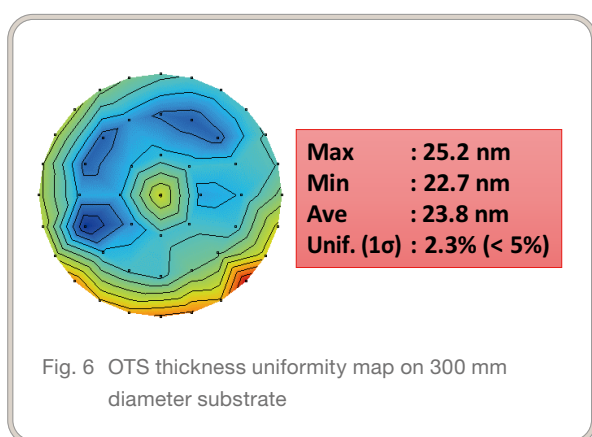


Fig. 6 OTS thickness uniformity map on 300 mm diameter substrate

Table 2 Performance requirements in OTS deposition process

Item	Specification
THK uniformity (1σ)	< 5.0%
Comp. uniformity (1σ)	< 5.0%
Surface roughness (Rms)	1.0 nm or less
Particle (80 nm or greater)	< 50 pcs.

- 1) General equipment and utility-related technologies
 - (a) Safe handling of toxic substances including arsenic
 - (b) Methods to control toxic gases generated during maintenance
 - (c) What to do when the OTS target or the substrate to which the OTS film is attached is damaged

- 2) Deposition device and processing technologies
 - (a) Investigation of sputtering methods and equipment (to achieve a stable process)
 - (b) How to check the quality of the OTS target
 - (c) Examination of process conditions for safe operation

5. Development of Electrode Material Deposition Technology

Diamond-like carbon (DLC) is used as the main electrode material. DLC has characteristics between those of graphite and diamond, and has excellent performance in terms of conductivity, barrier properties, and stability. The requirements for non-volatile memory, especially electrodes for memory having a three-dimensional structure, fall under three categories: (1) film quality distribution, (2) surface roughness, and (3) particles.

5.1 Determinants of film quality and how to control them

The factor that determines the film quality of DLC is the chemical bonding between carbon atoms, specifically the ratio of sp^2 to sp^3 . The larger the ratio of sp^2 , the more graphite-like the material becomes, and although the conductivity improves, the barrier properties and stability tend to decrease. When the ratio of sp^3 is large, the opposite tendency is observed. The film quality and the optimal deposition process to achieve it are selected depending on where and for what DLC is being used. The film quality, its distribution, and the surface roughness vary depending on the deposition conditions.

The reduction of particles is a major issue in the deposition of DLC. Factors affecting the generation of particles include the quality of the sputtering target and the deposition method, and care must be taken in the selection of these factors.

5.2 Specific examples of film quality control

As a specific example of film quality control, consider the effect of stage bias, in which an electrical bias is applied to the stage on which the substrate is placed. In sputtering, it is known that the film quality can be controlled through the application of stage bias⁷. Here we show an example of the use of RF as a stage bias in DLC deposition. Fig. 7 (a) shows resistivity as a function of bias and Fig. 7 (b) shows surface roughness as a function of bias. It can be seen that both characteristics are improved by applying stage bias and increasing its applied power. It is thought that the attraction of active species (positive ions) promotes the densification of the film and the smoothing of the surface.

5.3 Typical properties of DLC films

As mentioned above, we adjusted the combination of the sputtering target, deposition method, and processes to achieve the optimum film quality for DLC deposition. Table 3 shows the typical characteristics of a DLC film

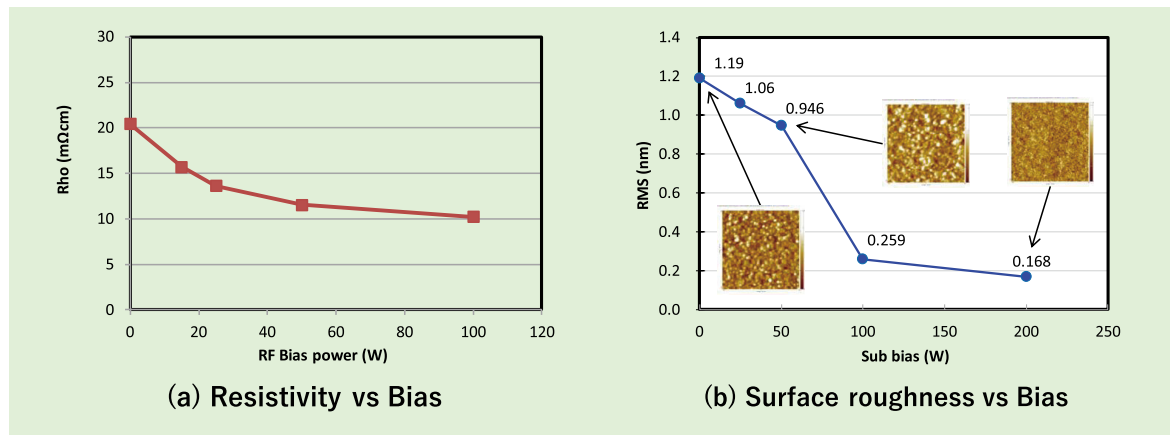


Fig. 7 Resistivity and surface roughness as functions of RF bias power

Table 3 Standard process requirements of DLC film

Item	Specification
THK uniformity (1σ)	< 3.0%
Surface roughness (Rms)	< 1.0 nm
Resistivity	< 30 mΩcm
Particle (50 nm or greater)	< 100 pcs.

(15 nm thickness) under standard deposition conditions. It is noteworthy that the surface roughness (Rms) is less than 1 nm and the number of particles is no more than 100 with a particle diameter of 50 nmUP.

6. Application in AI Devices

As noted in section 2, PCRAM can be used as an element for neural computing to the extent that it can mimic changes in the resistance values of elements equivalent to neural circuits. In this section, we will discuss what specific technologies are needed, and then introduce the results of our development to date.

6.1 Required device characteristics

When PCRAM is applied as a non-volatile memory element in neural computing, it is important to reduce resistance drift and power consumption.

- 1) Resistance drift: When the material is in the amorphous state and in principle has high resistance, resistance drift causes the resistance to increase slowly over time

in accordance with a power law ($\propto t^{0.1}$). This is a serious issue in AI devices, where the analog resistance value itself directly affects computing. IBM has proposed a metallic liner that provides a current bypass when a high-resistance amorphous state is reached⁷.

- 2) Power consumption: Experiments have shown that current AI devices consume thousands to tens of thousands of times more power than the human brain. It is necessary to reduce the current consumption of each parallel process, and for this purpose, it is necessary to increase the resistance of the material used as the resistive element. Specifically, it is necessary to develop a new process to dope oxygen or the like into the phase change material. Alternatively, a higher resistance could be achieved by minimizing the path of the current as much as possible.

6.2 Demonstration of analog computing using CVD-GST film technology

For the aforementioned application of PCRAM in neural computing, we conducted machine learning using a fill-in confined PCRAM element produced using PCM-CVD technology and evaluated the accuracy of the results with MNIST.

First, Fig. 8 shows the integration scheme of the PCRAM element used in this experiment⁹. One of its distinctive features is its structure in which the thin film plays the role of a current bypass when the GST element sandwiched between the upper and lower electrodes undergoes a phase change to a high-resistance amorphous state. This is achieved by laying a metallic thin film before implanting the GST in a confined cell. During analog operation using this structure, the resistance values could be controlled to between 40 kΩ and 500 kΩ, and the resistance drift was

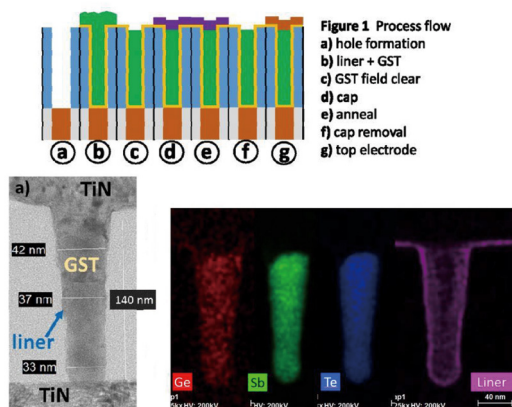


Fig. 8 Integration scheme of fill-in confined PCRAM and results of GST filling. ©2015 IEEE. Reprinted, with permission, from Ref. 8

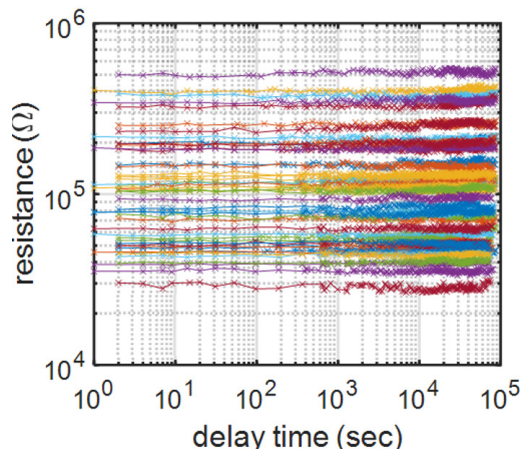


Fig. 9 Control of GST resistance with performance of low resistance drift. ©2019 VLSI. Reprinted, with permission, from Ref. 9

suppressed to a drift factor of 0.005, which is low enough to maintain constant resistance (Fig. 9)¹⁰.

When this device is used for machine learning, the resistance values need to be raised and lowered. In this study, we were able to raise and lower the output value by combining two phase change elements as shown in Fig. 10 to create a 2T2R circuit and outputting the difference, as

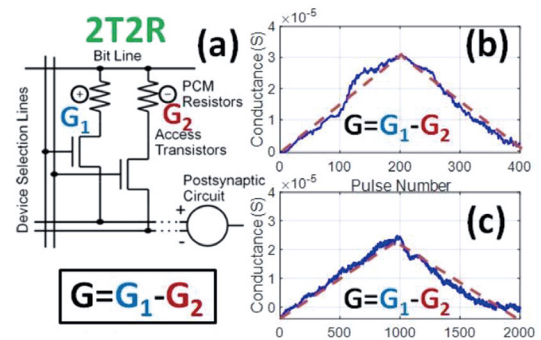


Fig. 10 Linear Controllability of GST resistance with 2T2R circuit. ©2019 VLSI. Reprinted, with permission, from Ref. 9

shown in Fig. 10. We further combined this with another 2T2R circuit that complements the device to create a 4T4R circuit, and then used the 4T4R circuit to train the machine, resulting in a 97.4% correct response rate in MNIST. This indicates that phase change materials can be applied to AI devices in the future¹⁰.

7. Summary

In this paper, we described our deposition technology and process development for phase change memory. Our years of continuous development of nonvolatile memory have borne fruit, and now the range of applications thereof is expanding to include SCM and AI devices. Based on our PCRAM device and process technology suitable for unique chalcogenide materials, we are continuing development to improve mass productivity and to achieve higher performance and higher integration. In the future, we hope that our technology will be useful for common tasks such as high-speed data processing and edge computing.

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