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Nonvolatile switching characteristics of laser-ablated Ge₂Sb₂Te₅ nanoparticles for phase-change memory applications

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Electrical characteristics of Ge₂Sb₂Te₅ (GST) nanoparticles have been examined for a phase-change memory applications. The GST nanoparticles were generated by *in situ* pulsed laser ablation and their crystal structure formation was confirmed [H. R. Yoon *et al.*, *J. Non-Cryst. Solids* **351**, 3430 (2005)]. A stacked structure of the GST nanoparticles with 10 nm of average diameter shows reversible nonvolatile switching characteristics between a high resistance state and a low resistance state as in the phase-change memory consisting of bulk GST thin film. Experimental results indicate that it is highly probable to test scaling issues of the phase-change memory with well-defined GST nanoparticles. © 2007 American Institute of Physics. [DOI: 10.1063/1.2430481]

Commercialized nonvolatile memories are facing a trend toward higher density, lower cost, and better performance.¹⁻³ Among nonvolatile memories under development, phase-change random access memory (PRAM) is regarded as one of the most promising candidates on account of high speed, low power, high endurance for repetitive reading and writing and compatibility with conventional Si-based memory processes.⁴ PRAM uses two different structural phases of Ge₂Sb₂Te₅ (GST), amorphous and crystalline, for data storage.^{5,6} In programing, fast and reversible phase transformation is controlled by Joule heating of electrical pulses. High magnitude of current with fast falling edge leads to amorphization through melting followed by quenching processes, while long and moderate magnitude of current induces crystallization by annealing process. Conventionally the former is called reset, and the latter is called set. In sensing, reset and set states are identified by the difference in electrical resistance read using a low magnitude of reading pulse.^{7,8}

Because the cell size reduction of PRAM having one transistor with one resistor (1T-1R) structure is mainly limited by the transistor size which is determined by the maximum operating current, the reset current reduction is one of the most challenging issues for PRAM development. There have been many approaches for the reduction of reset current.⁹⁻¹¹ In most cases, a small size electrical contact between a phase-change material and a conducting electrode increases the current density passing through GST near the contact region, which consequently reduces reset current required for GST melting. From these results, the scaling possibilities of the GST cell size have been proposed.^{4,12}

In such approaches, there is an underlying assumption that there is no physical limitation in phase-change properties of the GST material even in a very small size. However, the validity of this assumption has not been confirmed yet. Moreover, it is very difficult to perform experiments with small sizes of GST directly because an etching damage de-

teriorates the quality of GST during the cell fabrication processes. Instead of the GST cell patterned with lithographic techniques, GST nanoparticles formed without any lithographic techniques can be one of the best examples for the memory operation test in the small size GST. Among the various methods of nanoparticle synthesis,^{13,14} a pulsed laser ablation method has shown a potential for highly pure and composition-controlled GST nanoparticles.¹⁵ Here we report nonvolatile switching characteristics of a phase-change memory cell composed of the GST nanoparticles with 10 nm of average diameter. This is not the final outcome for the prediction of PRAM scaling issues but is an important milestone since the small GST particles show electrical switching phenomena at nanometer-scale level.

The production method of GST nanoparticles by *in situ* pulsed laser ablation was described in the previous work.¹⁵ Nanoparticles fabricated as a phase-change memory test cell mostly have a stoichiometric Ge₂Sb₂Te₅ phase when temperature of heat treatment is close to 200 °C. High-resolution transmission electron microscope (TEM) images demonstrate the parts of fcc GST phase in GST nanoparticles with the lattice constant of ~6 Å similar to that of the bulk value. A test cell has the structure of an aluminum top electrode with a diameter of 20 μm deposited on top of the GST nanoparticles layer, which was grown onto highly *p*-doped Si wafers, as illustrated in Fig. 1(a). The thickness of GST nanoparticles layer is slightly less than 100 nm. For electrical transport measurement, the top electrode was connected to a dc source-measurement unit (Keithley 4200 semiconductor parameter analyzer) for dc sweep or a pulse generator (Agilent 81110A pulse generator) for pulse programing, respectively, in combination with an oscilloscope (Tektronix 7154B digital phosphor oscilloscope) for monitoring of pulse current.

Figure 1(b) shows the dc sweep result for a virgin GST nanoparticles cell. Initially the as-fabricated cell is in a high resistance state of an order of megaohm. It indicates that the as-fabricated cell is in the high resistance state even though the as-deposited GST nanoparticles have parts of a crystal-

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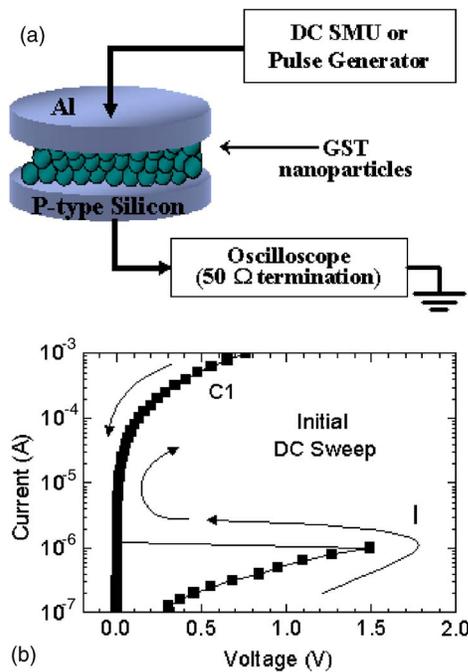


FIG. 1. (Color online) (a) Schematic diagram for the phase-change memory cell consisting of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ nanoparticles and the measurement setup for its electrical transport characterization. (b) Voltage-current characteristics during the initial dc sweep for the as-fabricated cell resulting in the change from initial high resistance state (As-fab.) to low resistance state (C1).

line phase.⁸ Resistive components might come from the contact resistance among the GST nanoparticles in the stacked structure as well as a high surface area of the GST nanoparticles. As the cell current increases, it changes to a low resistance state of 1 k Ω at a threshold voltage of around 1.5 V with a cell current of 1 μA , which is denoted as C1.

Once the test cell is in the low resistance state, reset and set programming can be achieved, as shown in Fig. 2. When a reset programming pulse of 1 V height and 50 ns width is applied, the cell resistance rises up to approximately 1 M Ω . The shape of a current pulse passing through the cell is captured in Fig. 2(a). While the programming pulse is applied, the phases of GST at each time can simply be ascribed to crystalline (C1), melting (M), and amorphous (A) phases. Here the current flowing of roughly 2 mA under 1 V voltage pulse indicates that the melting phase is conducting as in other liquid chalcogenide materials.¹⁶ The amorphous phase (A) is switched to the crystalline phase (C2) again while dc set sweep occurs, as shown in Fig. 2(b).

There are two things noticeable in Fig. 2. One is the peculiar behavior of current at the rising and the falling edges of the programming pulse in Fig. 2(a), showing a hump in the positive and the negative direction of current, respectively. It clearly originates from capacitive component of the test cell because humps occur at the edges of voltage pulse with magnitude proportional to dV/dt . These features do not appear in the normal PRAM cell composed of a GST thin film. Therefore it is the inherent nature of the phase-change memory cell composed of the GST nanoparticles. The other is the two-step set behaviors during dc set observed at around 4 μA in Fig. 2(b). The multiple set behaviors mean crystallization in the various amorphous routes of the conduction paths, indicating that amorphous region is complicated. In successive reset/set programming, the GST nanoparticle cell does show good switching endurance, but it is stuck

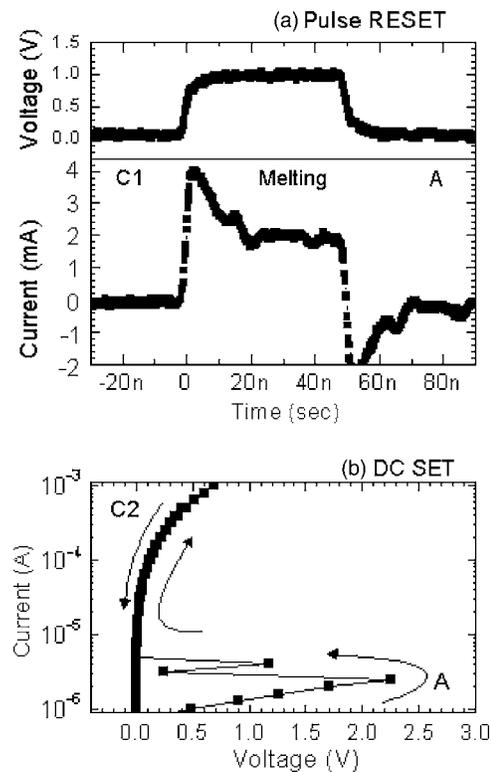


FIG. 2. Memory operation of the phase-change memory cell consisting of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ nanoparticles. (a) Pulse reset: Shape of incident reset pulse (1 V, 50 ns) applied to the cell (up) and output current pulse passing through the cell (down), corresponding to the change from crystalline phase of low resistance (C1) to melting (M) followed by amorphous phase of high resistance (A). (b) dc set: Voltage-current characteristics of dc sweep for set operation following pulse reset in (a), which indicates the change from amorphous phase (A) to crystalline phase (C2).

in the conducting state after several cycles. Because the switching behavior involves transformation of the GST nanoparticles to a melting phase in a certain region, such programming instability originates from the change in the nanoparticle-packed structure due to the fusion of nanoparticles at the particle-particle contact region.

The discussion above may suggest that the present sandwich structure is too early for the direct application of GST nanoparticles to PRAM. However, it is sufficient to clarify the possibility of memory operation characteristics with the GST nanoparticles working as a phase-change memory. For the practical applications, the density of nanoparticles should be higher in the deposition step. Figure 3 shows the TEM image of high-density GST nanoparticles. Compared with nanoparticles formed in the low-density deposition condition, high-density GST nanoparticles seem to be agglomerated with larger particle sizes and lower crystallinity. Search for deposition conditions of higher concentration with smaller particle size is the next research topic toward the practical application.

The magnitude of reset current in Fig. 2(a) can be compared with values in other reports⁹⁻¹¹ where the thin-film GST is employed as a phase-change material. When the electrical contact size between phase-change material and conducting electrode is normalized to a diameter of 50 nm, the reset current of GST nanoparticles is expected to be lower than 1 μA under the assumption that phase-change occurs in the whole area covered by an aluminum electrode. Actually, it is not quite clear how large area shows phase-change be-

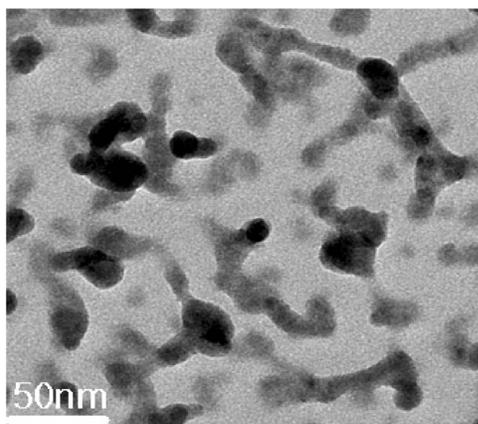


FIG. 3. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ nanoparticles deposited with high concentration condition. Scale bar=50 nm.

havior by electrical programming current. To confirm the idea of low reset current operation, it is required to make the GST cells with different sizes of uniform nanoparticles or further to measure the electrical characteristics of each particle by scanning probes. The present result, however, proposes meaningful perspective in the scaling issues of PRAM because of the successful achievement of Joule-heating driven phase-change in GST nanoparticles.

In summary, the electrical characteristics of the GST nanoparticles as a phase-change material for a higher-density nonvolatile memory were examined. It is confirmed that phase-change properties of GST still exist even in the nanoparticle structure of 10 nm size, indicating that the GST material itself does not limit the PRAM scalability. Further studies for memory applications demand densification, uniformness, and particle-base measurement of the GST nanoparticles.

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