Electrical phase change of CVD-grown Ge-Sb-Te thin film device

C.C. Huang, B. Gholipour, J.Y. Ou, K. Knight and D.W. Hewak

Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, United Kingdom

Abstract

A prototype Ge-Sb-Te thin film phase-change memory device has been fabricated and reversible threshold and phase change switching demonstrated electrically, with a threshold voltage of 1.5 – 1.7 V. The Ge-Sb-Te thin film was fabricated by chemical vapour deposition (CVD) at atmospheric pressure using $GeCl_4$, $SbCl_5$, and Te precursors with reactive gas H_2 at reaction temperature 780 °C and substrate temperature 250 °C. The surface morphology and composition of the CVD-grown Ge-Sb-Te thin film has been characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The CVD-grown Ge-Sb-Te thin film shows promise for the phase change memory applications.

Keywords

Ge-Sb-Te, thin films, chemical vapour deposition, phase-change memory

Introduction

Phase change random access memory (PCRAM) has attracted considerable interest as a candidate for the next generation of non-volatile devices which will meet current and future needs of higher density and operation speed [1, 2]. Ternary $Ge_2Sb_2Te_5$ (GST) compounds are widely regarded as the most commercially viable and practical phase change family of materials for this application. These materials are currently being trialled commercially and processes which deposit GST films by RF sputtering are being implemented into production lines [3]. CVD techniques are expected to play a role in device fabrication and recently metal organic CVD process has been

applied to deposit GST materials in sub micron cell pores [4]. There remain however many challenges [5] which include the need to control device to device variability and undesirable changes in the phase change material that can be induced by the fabrication procedure. A confined cell structure where the phase change material is formed inside a contact via is expected to be essential for the next generation PCRAM device because it requires lower switching power [6]. This structure however requires more complex deposition of the active chalcogenide into a cell pore. We believe that CVD techniques could provide better performance and enable the production of thin films with superior quality compared to those obtained by sputtering, especially in terms of conformality, coverage, and stoichiometry control, and allows implementation of phase-change films in nanoelectronic devices. In addition, CVD deposition is well known to provide higher purity materials and provides the scope for new phase change materials with optimized properties to be deposited.

For the past eight years, we have been developing a CVD technique based on metal halide precursors for the deposition of chalcogenide thin films [7]. In this paper, we report on the deposition of Ge-Sb-Te thin film using atmospheric pressure CVD processes with metal chloride and Te precursors. The Ge-Sb-Te thin film has also been characterized by SEM and EDX techniques. In addition, electrical characterization of a prototype Ge-Sb-Te thin film phase change memory device has been carried out and reversible threshold and phase change switching demonstrated.

Apparatus and experimental methods

The CVD apparatus for Ge-Sb-Te thin film deposition is shown schematically in Figure 1a. A specially designed tube furnace with two individually controlled heating zones was used to produce a tailored gradient hot zone within a horizontal quartz tube which formed the reactor. The first heating zone (zone 1) upstream of the sample provided a region of sufficient temperature for the reaction of precursors to

take place efficiently. The second heating zone (zone 2) was designed to keep the substrate at suitable temperature for deposition. The entire process took place at atmospheric pressure.

The reaction temperature at zone one was set at 780°C where the Te precursor within a quartz crucible injection tube was located. The reactive gas, 6% H_2 balanced with argon gas (6%H_2/Ar), and the carrier argon gases for $GeCl_4$,$SbCl_5$ and Te vapours were delivered through mass flow controllers (MFCs). The substrates, located in zone two, were kept at 250°C inside the gradient tube furnace throughout the deposition process. For the initial trials of Ge-Sb-Te thin film depositions by our CVD reaction, we used fixed gas flow rates of 50ml/min, 200ml/min, 50ml/min, and 300ml/min for $GeCl_4$, $SbCl_5$, Te and 6%H_2 /Ar respectively. The temperatures selections were based on our previous work on Ge-Sb thin films fabricated by a similar CVD technique [8]. A prototype Ge-Sb-Te thin film phase-change memory device, as shown in Figure 2a has been fabricated for our preliminary electrical characterization. The Ge-Sb-Te thin film grown by CVD technique with a thickness of about 20nm was deposited on the SiO_2/Si substrate pre-sputtered with a Mo bottom electrode slab about 500nm thick. This was followed by the top molybdenum (Mo) electrode strips with the dimensions of 1.5mm wide and 150nm thick which were deposited on top of the CVD-grown Ge-Sb-Te thin film. The device was then completed with a sputtered 140nm ZnS-SiO_2 capping layer. Among several of the devices fabricated, one was sacrificed with a diamond pen and cleaved to show the multilayer structure of the edge profile as shown in Figure 2b. This SEM image revealed the Ge-Sb-Te thin film phase-change memory device fabricated was in good agreement with the design in Figure 2a.

Results and Discussion

Ge-Sb-Te thin films have been successfully deposited on SiO_2/Si substrates. Scanning electron microscopy (SEM) technique has been applied to study the

morphology of the Ge-Sb-Te thin films. A typical SEM micrograph of the Ge-Sb-Te thin film on SiO_2/Si is shown in Figure 1b. As shown in Figure 1b, homogeneous crystallized Ge-Sb-Te thin film has been successfully fabricated by this CVD technique. The thickness of the film determined by the edge profile of cleaved sample (Figure 1c) revealed that the deposition rate was about 3 nm/min. The grain sizes of the 450nm thick crystallized Ge-Sb-Te thin film were in the range of 30-40nm. Energy dispersive X-ray (EDX) analysis has been applied to determine the composition of Ge-Sb-Te thin films. In the result shown, a composition with 32.1 ± 0.7 % Ge, 8.8 ± 0.3 % Sb and 59.1 ± 0.8 %Te was obtained in the 450nm thick Ge-Sb-Te thin film.

The CVD technique potentially offers improved film conformality, morphology, and compositional control, and increased manufacturing throughput without creating surface damage. From the SEM images shown in Figure 1b and 1c, we have demonstrated the good surface morphology of Ge-Sb thin films with our CVD process using metal chloride precursors. Ge-Sb-Te materials have been intensively studied in the phase change switching memory application therefore we have designed and fabricated a prototype phase change device based on our CVD deposited film for further electrical characterization.

The electrical characterization of the above Ge-Sb-Te thin film device was carried out with the Cascade probe station and Agilent 4155C semiconductor parameter analyzer shown in Figure 2c. By introducing a voltage sweep between 0 – 4.5 volts, the current across the fabricated cell was measured using the source measure unit within the semiconductor parameter analyzer. It should be noted that an internal load resistance within the instrument provides current limitation in order to protect the device. The I-V characteristics of the CVD grown Ge-Sb-Te thin film device are shown in Figure 3a and 3b. These were obtained both using a voltage sweep whilst measuring the current as well as using a current sweep whilst measuring the voltage. This revealed three states of the film with a threshold of around 1.5 -1.7 Volts.

Starting at a high resistance state and applying the sweep, which at the threshold gives way to the stable phase change (memory switching) by virtue of the Joule heating to above the crystallization point of the material. Subsequent sweeps reveal that the low resistance crystalline state is stable unless switched back to the high resistance through electrically melt quenching the layer. This electrical switching between amorphous and crystalline phases, is reproducible at least ten times. The resistance contrast between the two phases is in the order of $10^2\,\Omega$ making this result very promising for PCRAM application.

Conclusion

A prototype Ge-Sb-Te thin film phase-change memory device has been fabricated and reversible threshold and phase change switching demonstrated electrically, with a threshold voltage of 1.5 – 1.7 V. Ge-Sb-Te thin films deposited on SiO_2/Si substrates have been successfully fabricated by CVD using metal chloride precursors. The Ge-Sb-Te films have been characterized by the SEM and EDX techniques. Currently, we are working on composition optimization, further characterization and nano-scale device fabrication based on these Ge-Sb-Te thin films. The growth of phase-change materials into nanoelectronic devices is very essential and our CVD process has demonstrated a potential solution for this application.

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List of figure captions

Fig. 1 *(a) Schematic diagram of CVD system used for Ge-Sb-Te thin film deposition (b) SEM top-view image of Ge-Sb-Te thin films deposited SiO_2/Si substrate (c) SEM cross-sectional image of 450nm thick Ge-Sb-Te thin film deposited on SiO_2/Si substrate*

Fig. 2 *(a)A designed Ge-Sb-Te thin film phase-change memory device (b) SEM image of the fabricated Ge-Sb-Te thin film device (c) setup for electrical characterization of Ge-Sb-Te thin film device*

Fig. 3 *(a)I-V characteristics of the Ge-Sb-Te thin film phase-change memory device using a voltage sweeps whilst measuring the current.(b) I-V characteristics of the Ge-Sb-Te thin film phase-change memory device using a current sweep whilst measuring the voltage.*

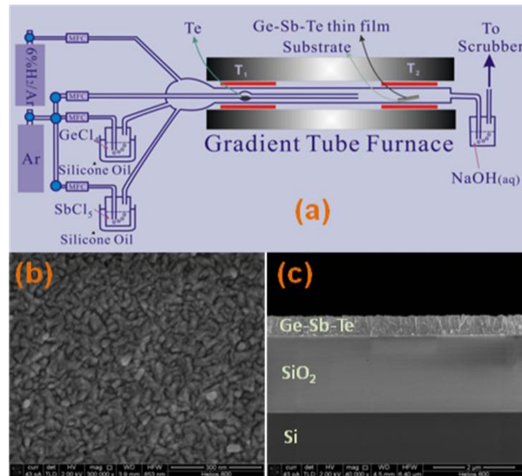

Fig. 1

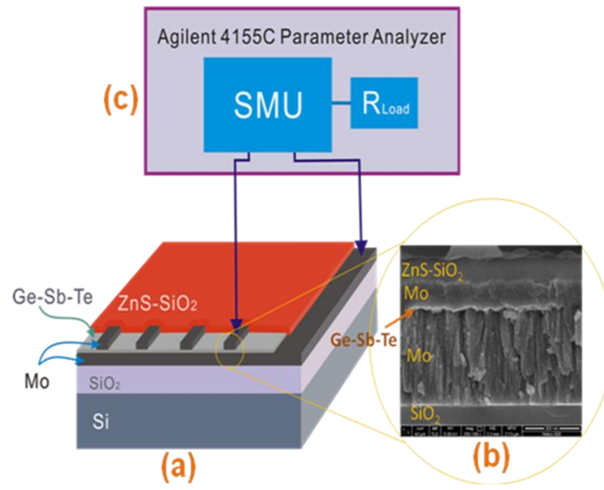

Fig. 2

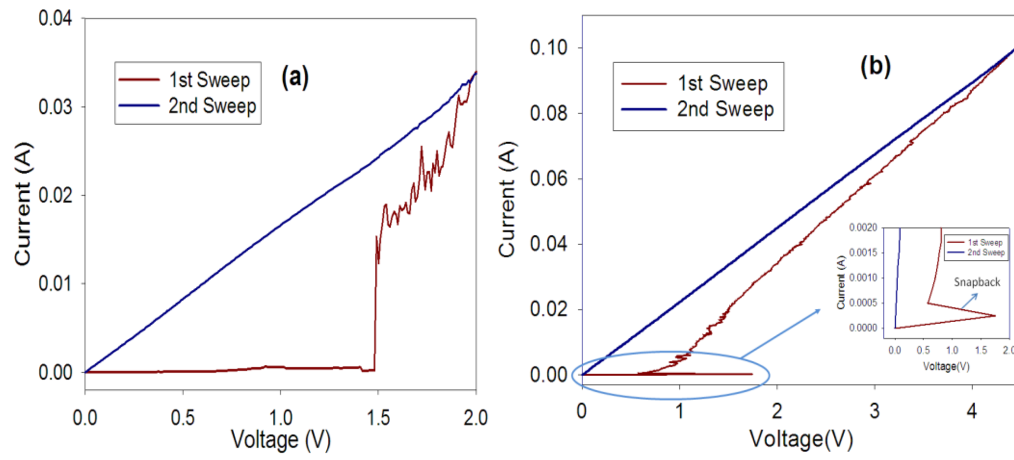

Fig. 3