

Metal-Organic Chemical Vapor Deposition (MOCVD) of GeSbTe-based Chalcogenide Thin Films

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Abstract

Chalcogenide Random Access Memory (C-RAM) has shown significant promise in combining the desired attributes of an ideal memory, including: nonvolatility, fast read/write/erase speed, low read/write/erase voltage/power, high endurance, and radiation hardness. Current C-RAM production technology relies on sputtering to deposit the active chalcogenide layer. The sputtering process leads to difficulties in meeting requirements for device conformality (in particular – filling vias), film adherence, compositional control, wafer yield, and surface damage. Ultimately, a viable CVD manufacturing process is needed for high-density products to realize the full potential of C-RAM. In this work, we discuss the Metal-Organic Chemical Vapor Deposition (MOCVD) tool technology used to produce the films and report the materials properties of GeSbTe-based chalcogenide thin films grown in small research scale and in large production scale MOCVD reactors. Films were grown at low pressures at temperatures ranging from 350 C to 600 C. X-Ray Fluorescence (XRF) and Auger Electron Spectroscopy (AES) were performed and determined that the film composition is controllable and uniform.

Introduction

Nonvolatility – the ability to retain data in a memory cell for years when unpowered – is highly desirable for many electronic systems. The dominant nonvolatile memory technology is FLASH memory, so-called because of the ability to write data

individually while erasing them in chunks. FLASH is ubiquitous in today's cell phones, digital cameras, media cards, and PDAs, among others and is projected to be a \$20 billion dollar industry by 2010[1]. But FLASH memory technology suffers from several shortcomings that hamper further device improvement, primarily a lack of scalability beyond the ~65nm node due to increased leakage current through the tunnel oxide. Secondly, FLASH memories can only be reprogrammed a limited number of times, typically on the order of a million. While this may be enough for certain applications, it makes FLASH memory ill-suited for general computing and other applications.

As a consequence a number of different nonvolatile memory technologies are emerging as viable alternatives to replace FLASH; most prominent are: Ferroelectric RAM (FRAM or FeRAM), Magnetoresistive RAM (MRAM) and Chalcogenide RAM (C-

<i>MOCVD Benefits</i>	<i>Sputtering</i>	<i>MOCVD</i>
<i>Conformality</i>	-	++
<i>Composition Tuning</i>	--	++
<i>Purity</i>	+	+
<i>Manufacturability</i>	+	+
<i>Surface Damage</i>	-	+

TABLE I: Benefits of MOCVD for chalcogenide production

RAM, but also called Ovonyx Unified Memory (OUM) or Phase-Change RAM (PRAM)). These devices share in common that they can be reprogrammed nearly unlimited number of times and be programmed in nanoseconds rather than microseconds. While no “ideal” memory device has been developed, C-RAMs have shown the most promise in uniting all the desired attributes of an ideal memory. Development of C-RAM devices is therefore being aggressively pursued by both commercial and military suppliers. Ovonyx – as the manager of the key originating and sustain C-RAM patents [2] – has licensed its technology and established joint R&D programs with several memory manufacturers such as Intel, ST Microelectronics, BAE Systems, Samsung, and Elpida, among others; furthering the potential of this material solution. More recently, others have joined in independent research and development efforts.

C-RAM is a low-power, thermally activated, rapidly reversible phase change memory, which stores digital information as either a crystalline or amorphous structural phase in a thin chalcogenide layer, usually $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Currently, the active, chalcogenide layer is fabricated by sputtering. This process has sufficed to demonstrate first generation C-RAM memory devices, but, ultimately a superior fabrication process is needed to facilitate manufacturability of C-RAM. Metal-Organic Chemical Vapor Deposition (MOCVD) is a mainstay of semiconductor manufacturing and is especially advantageous for fabrication of compound materials such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -based chalcogenide thin films as highlighted in Table I. Specifically, MOCVD offers improved film conformality, film morphology and compositional control, and increased manufacturing throughput without creating surface damage. In addition, MOCVD also has a distinct advantage over sputtering for alloy/dopant tuning in that it offers run-to-run tuning of composition through flow control; as compared to the need to purchase new sputtering targets and to re-qualify the tool for sputtering. Doping and alloying may prove to be key factors in optimizing phase change performance and range of achievable properties. These key advantages of MOCVD over sputtering have the potential to greatly improve C-RAM device performance and cost advantage.

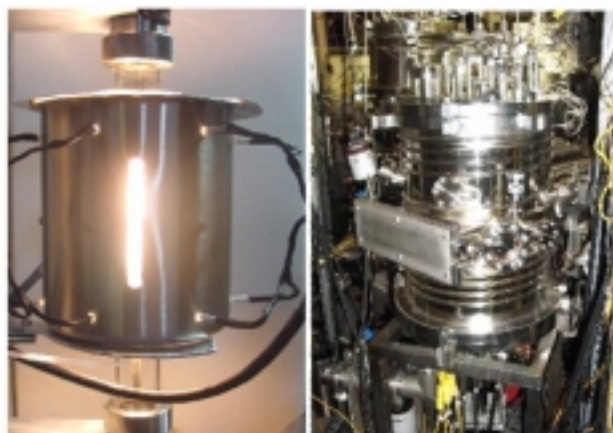


Figure 1. Photograph of two reactors systems used in this investigation; a research *NanoV-CVD™* research reactor (left) and a *SpinCVD™* production reactor (right).

Chamber Pressure	0.005 – 0.1 atm
Chamber Temperature	350 - 600 °C
Deposition Time	Few to 10's of min
Carrier Gas	H ₂ , Inert
Substrates:	
Silicon	Quartz
Sources:	
Ge	Te
Sb	N
Se	S
Ag	Others Optional

Experimental

Until now MOCVD has not generally been applied successfully to Chalcogenide production. Figure 1 shows the two reactors used in this investigation – first a *NanoV-CVD™* research reactor (left) has been used for fundamental materials research and a *SpinCVD™* reactor (right) has been used for large area depositions.

Figure 2 depicts a schematic of an ideal gas panel for depositing GeSbTe-based films. The schematic shows a large cluster tool system with a small SMI *NanoV CVD™* reactor mounted in parallel for research and development work. The system consists of several gas and bubbler type sources, an intervening fast pressure balanced switching manifold for alternating layer and for atomic scale alternating layer deposition (ALD), the parallel reactors, an exhaust system, and a load lock assembly. In SMI's *SpinCVD™* reactor, heating of 6" or 8" wafers is achieved through radiant heating of the wafer carrier by using graphite filaments. The wafers are typically rotated at about 750 rpm. SMI's *Nano V CVD™* reactor can use external resistive, rf or lamp heaters for heating small (<1") stationary samples, and is shown with lamp heaters in place. In each case gases are fed into a vacuum reactor chamber through a showerhead, located at the top of the chamber that contains gas inlets for precursor vapors and a carrier gas.

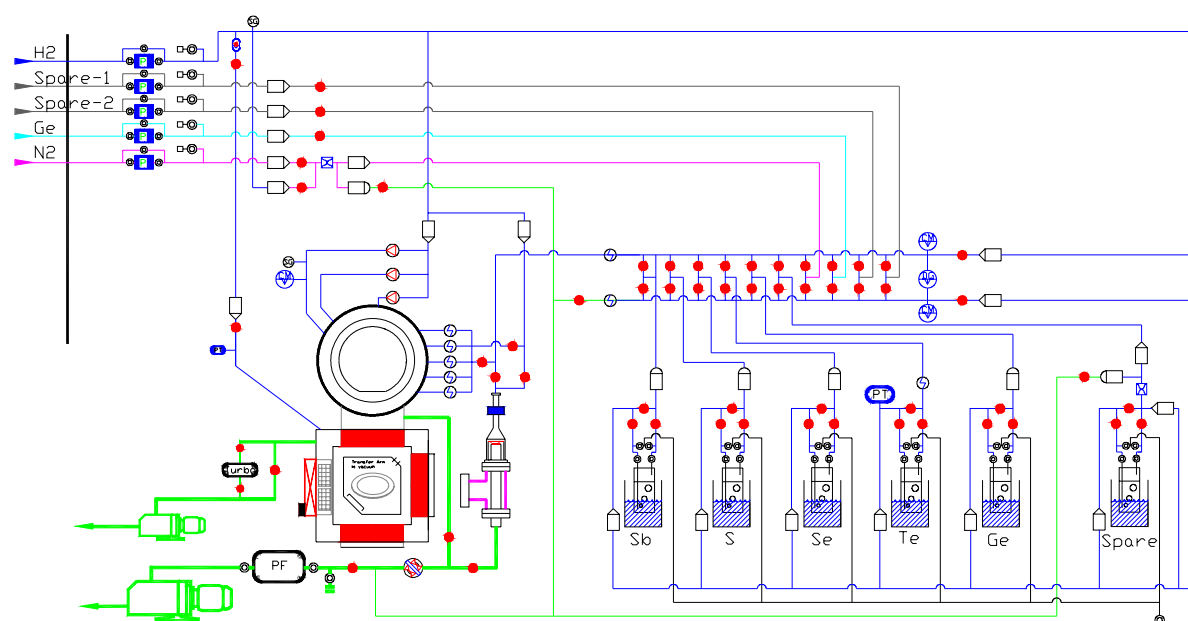


Figure 2. Schematic of an ideal chalcogenide deposition tool – showing, clockwise from top left – the gas inlets, fast switching pressure manifold for ALD, bubbler sources, exhaust, load lock and dual reactors – SMI *NanoV CVD™* reactor for research and SMI *SpinCVD™* for large wafers.

We explored precursors such as tetraethylgermane (C_2H_5)₄Ge, diethylgermane (C_2H_5)₂GeH₂, and trimethylgermane (CH_3)₃GeH. We focused on Germane (GeH_4) as the germanium precursor; however, we also plan to explore the chloride chemistries in the near future. While Trimethylantimony (CH_3)₃Sb [“TMSb”] can be used as the Sb precursor, we focused on Triethylantimony (C_2H_5)₃Sb [“TESb”] as the antimony precursor. Diisopropyltelluride (C_3H_7)₂Te [“DiPTe”] was used as the tellurium precursor; although others could most likely be used to further tune the process chemistry and deposition temperature. Table II reviews the general range of process parameters explored in the effort.

Results

In order to calibrate deposition rates, we began by growing single and binary composition films. First, we established routines deposition process for Ge and Te. Single element Sb films were not deposited due to the relatively low melting point for Sb (630°C) and its tendency not to stick well in deposited films. Thereafter binary calibration films were deposited for GeTe, GeSb, and SbTe; followed by deposition of ternary films. The deposition of films was carried out in both SMI's *SpinCVD™* reactor and in SMI's *Nano V CVD™* reactor; however most depositions were carried out in SMI's *Nano V CVD™* test reactor to lesson material consumption. Films were characterized optically to access their morphology, by X-Ray Diffraction (XRD) to reveal crystalline structure and by X-Ray Fluorescence (XRF) for initial elemental composition analysis. Selected films were also analyzed by scanning and depth profiling Auger spectroscopy to evaluate composition and consistency throughout the film depth.

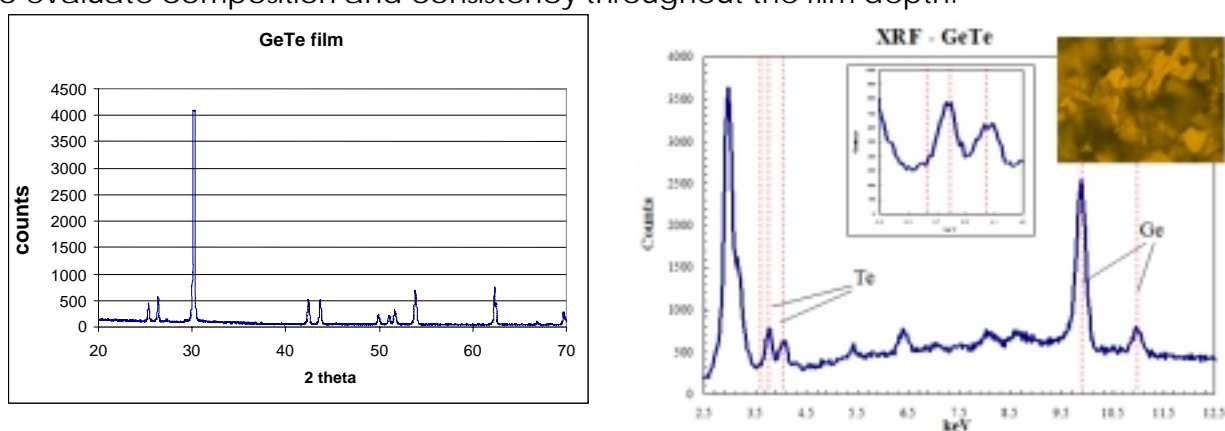


Figure 3. a) XRD pattern for MOCVD GeTe film that well matches that reported in the literature[3] and b) XRF scan of the same; insert in b) shows an image of a textured polycrystalline deposited film.

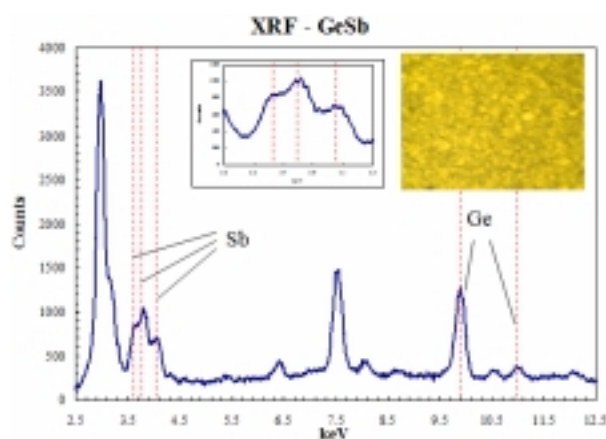


Figure 4. XRF spectra of the GeSb films. The insert shows an optical micrograph of the as-deposited polycrystalline film.

Figures 3 and 4 review some of the measured data. In particular, Figure 3a shows the XRD pattern for GeTe and 3b shows the XRF spectra. Figure 4 shows the XRF spectra for the GeSb films. The insert in each XRF spectra shows the as grown surface. The as grown films are typically polycrystalline and rough. Once the binary film composition and deposition rate were optimized, we began to grow ternary films.

To grow the ternary material, a series of experiments was carried out with all three element precursors, Ge, Sb, and Te, simultaneously introduced into the reactor. Depositions were carried out on both quartz and silicon substrates. Films were generally found to be polycrystalline upon deposition and well adhering to both silicon and quartz. By varying the starting precursor concentration, the resulting film composition can be controlled; however, the conditions for successful deposition of

these films were found to be rather sensitive, with complex chemical interactions often occurring between the precursors, and in some cases, between the precursors and already deposited films. In particular, it appears that the germanium and tellurium precursors can form volatile complexes under some conditions (though there is no literature report of such volatile Ge-Te compounds). However after considerable experimentation we were successful in obtaining films of $\text{Ge}_x\text{Sb}_y\text{Te}_z$ having the desired crystal structure for C-RAM devices using both ternary co-deposition techniques and alternating binary layer deposition. The first ternary films were also rough in morphology, and appeared to have formed rather large crystallites of the 225 phase $\text{Ge}_2\text{Sb}_2\text{Te}_5$. However by optimizing run conditions, particularly deposition rate and temperature, much smoother films were obtained that promise to be suitable for device fabrication.

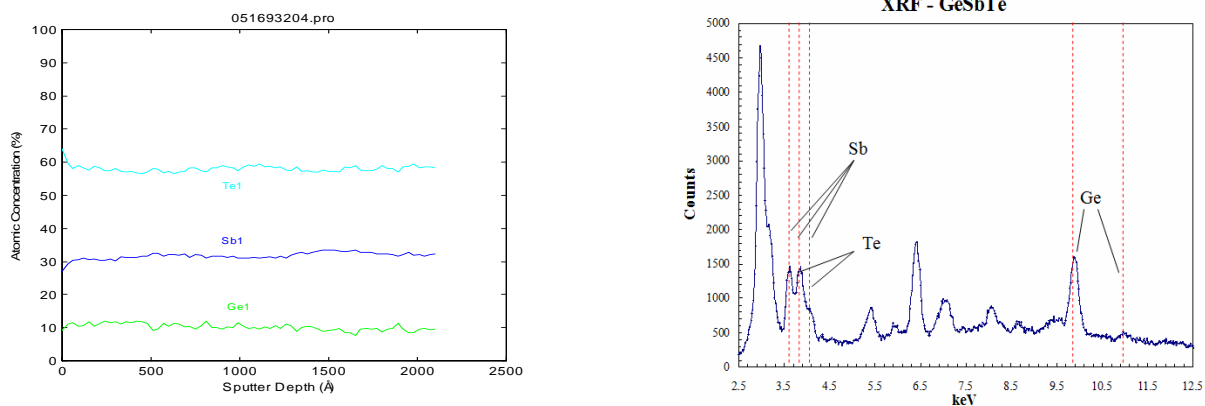


Figure 5. a) Auger depth profile of GeSbTe film deposited by multilayer process and b) XRF of the same; note the Sb and Te XRF peaks overlap.

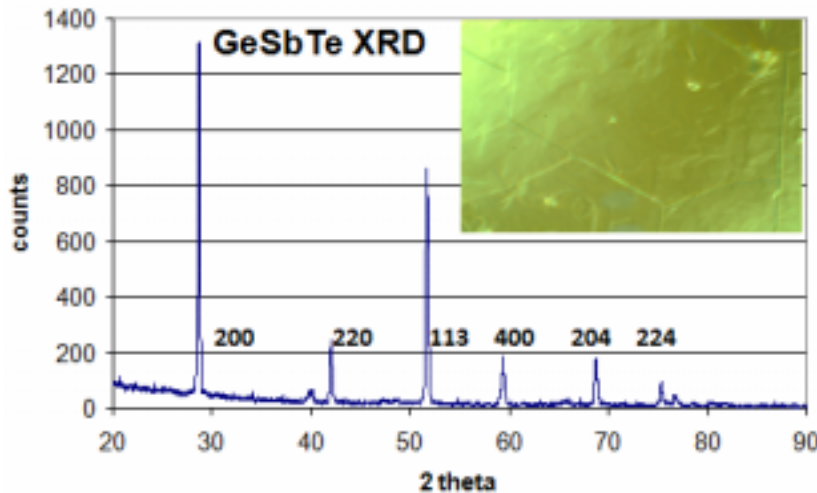


Figure 6. XRD data for MOCVD GeSbTe film, as deposited. The film appears to have the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ low temperature FCC structure – peak indicies are indicated; the insert shows a photomicrograph of a deposited film at about 1500x.

To circumvent the etching effect, further processing was performed in a multilayer fashion. Typically a total of between 10 and 20 layers of – alternately – germanium (Ge) and antimony/tellurium (SbTe) films were deposited. The layers were of 5 to 15 nm thickness. To this extent, germanium precursor was first fed into the chamber. At a specified time the germane gas was turned off, after which both antimony and tellurium precursor vapors were fed into the chamber.

Subsequently, both antimony and tellurium precursors were turned off and germanium precursor was again fed into the chamber. This cycle was repeated a specified number of times. It was found that this multilayer fabrication approach was

advantageous to deposition of GeSbTe-thin films. Additional variations to this process were also found to be advantageous.

The films were generally found to have a large surface roughness as seen in figure 3 and 4; however, some were also made very smooth as shown in figure 5. Further efforts were made to reduce the roughness of the deposited films through process improvements. One improvement in particular, was the use of diethylgermane as a germanium precursor which was found to improve the surface roughness significantly compared to films prepared using germane, when growing in one step. The result of this effort is depicted in Figure 6. This figure shows a microscopic image (magnification 1500x) of a GeSbTe film. Upon visual inspection, the film was found to be smooth.

Summary and Conclusion

The outcome of this work is that we have achieved the main objective of developing an MOCVD process for the deposition of GeSbTe thin films[4]. During the course of the work, we fabricated various samples of GeSb, GeTe, SbTe and GeSbTe thin films and conclusively verified the presence of all three elements (germanium, antimony and tellurium), effectively varying the composition of $Ge_xSb_yTe_z$ over the range x, y, and z between 0 and 1. These results were achieved by overcoming complex chemical interaction issues and establishing a routine of how chemicals are mixed and layers are built up. A number of important aspects of MOCVD technology of GeSbTe-based thin films were established. GeSbTe-based thin films were fabricated by MOCVD in both single layer fashion, i.e. simultaneous feeding of all precursors into the chamber, and multilayer fashion, i.e. germanium (Ge) and antimony/tellurium (Sb/Te) are alternately fed into the chamber. The fabricated films were characterized by X-Ray Fluorescence (XRF) and Auger Electron Spectroscopy (AES) and the desired $Ge_2Sb_2Te_5$ composition and structure achieved. In the future, additional precursors may also be added to the deposition process so as to add a doping or alloying element to the deposited film. Suitable doping/alloying elements include: N, Ga, Si, Ni, V, Se, S, and Sn, among others. We believe that with this work an important milestone has been passed for the future development of C-RAMs.

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References

- 1 <http://www.vnunet.com/vnunet/news/2153180/flash-memory-market-pass-20bn>
- 2 Originating USA patents: 3,271,591, S. R. Ovshinski, 1966 and 3,448,302, D. J. Shanefield, 1969
- 3 Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, and H. Hashimoto, *Thin Solid Films* **370**, 258 (2000)
- 4 PCT/US06/46524, E. M. Dons, G. S. Tompa, C. E. Rice, and J.D. Cuchiaro, 2005 priority.