

# Germanium antimony sulphide nano wires fabricated by chemical vapour deposition and e-beam lithography

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## ABSTRACT

Germanium antimony sulphide (Ge-Sb-S) amorphous thin films have been deposited directly onto SiO<sub>2</sub>-on-silicon substrates by means of chemical vapour deposition. The Ge-Sb-S films have been characterized by micro-Raman, scanning electron microscopy, energy dispersive X-ray analysis and static tester techniques. Ge-Sb-S nano wires have been patterned and fabricated by e-beam lithography and dry etching techniques. Modeling results show the potential for fast switching of these Ge-Sb-S nano wire structures, making it a possible candidate for the phase-change memory applications.

**Keywords:** germanium antimony sulphide, nano wires, chemical vapour deposition, e-beam lithography, phase-change memory

## 1 INTRODUCTION

Chalcogenide materials (which contain sulphur, selenium or tellurium) have been studied since the 1960s. Chalcogenide thin films are very interesting materials because their properties allow a diverse range of applications in the field of optoelectronics [1-3]. However, it was only recently that their special properties generated attention in electronic memory [4]. There is currently a worldwide interest in the development of the next generation computer memory, fuelling research in new materials which can be used to store vast amounts of information.

The preparation of chalcogenide thin films can be performed by techniques which include thermal evaporation [5], sputtering [6], laser ablation [7], sol-gel [8], spin coating [9], and chemical vapour deposition (CVD) [10-13]. Phase-change thin films are predominately grown by thermal evaporation or sputtering techniques, which to date have yielded demonstrator chips for high-density memories but have yet to enter the commercial domain. To do this, and at the same time meet the continued down-scaling of nanoelectronic devices, better control of film deposition and conformal coatings over non-planar structures is necessary. At the same time, reductions in feature size are essential and would allow lower

programming currents, leading to improved performance and lower costs [14]. We believe that the CVD technique could provide better yield and device performance, in part from its ability to provide high throughput deposition over irregular surfaces. In addition, CVD technique could also enable the production of thin films with superior quality compared to those obtained by sputtering, especially in terms of purity, conformality, coverage, and stoichiometry control thus allowing the implementation of phase-change films in nanoelectronic devices.

## 2 APPARATUS AND EXPERIMENTAL METHOD

For the past seven years we have been developing new CVD techniques specially targeted at the deposition of chalcogenide materials, in particular glassy and crystalline thin films and high purity bulk materials. The CVD apparatus we have constructed for Ge-Sb-S amorphous thin film deposition is shown in figure 1. In the process we exploit, Ge-Sb-S amorphous thin films are deposited on SiO<sub>2</sub>-on-silicon substrates placed in the quartz tube reactor (25mm O.D. x 500mm long) and heated by an electrical resistance furnace to a temperature of 300°C. The reactive gas, H<sub>2</sub>S, and the carrier argon gas for GeCl<sub>4</sub> and SbCl<sub>5</sub> are delivered through the mass flow controllers (MFC) at a flow rate in the range of 50 ml/min-150 ml/min.

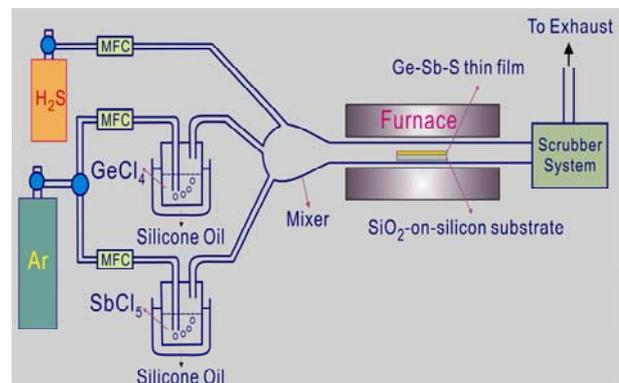


Figure 1: Schematic diagram of CVD system used for Ge-Sb-S thin film deposition.

The Ge-Sb-S thin films were formed at a deposition rate of approximately 10nm/min at a temperature of 300°C. In this way, Ge-Sb-S thin films with 100nm in depth were achieved in approximately 10 minutes. The compositions of Ge-Sb-S thin films were characterized by micro-Raman and energy dispersive X-ray analysis (EDX) techniques whilst a static tester system [15, 16] has been employed to measure the crystallization time. A 658nm laser diode was focused to a diffraction limited spot through a 0.65NA lens on to the samples surface. The change in reflectivity was measure with a second 635nm diode laser. Its optical power at the sample was controlled at 100 $\mu$ W. The percentage increase in reflectivity was collected for pulse times increasing from 5 to 110mW in steps of 5mW whilst the pulse time was increased from 20ns to 500ns. The resultant power, time, reflectivity matrix has been plotted as an intensity map in figure 2. The lighter areas denote an increase in reflection due to crystallization.

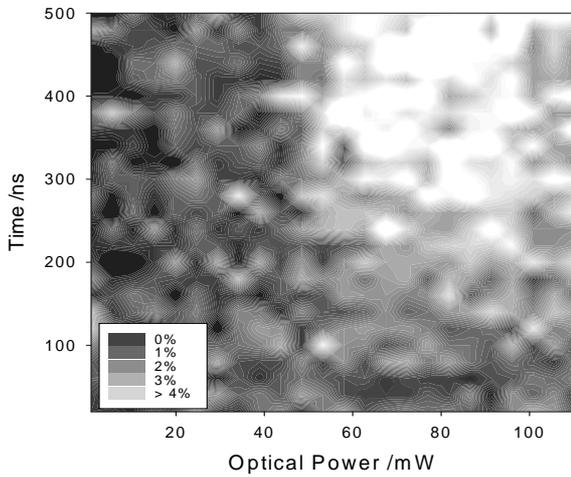


Figure 2: Phase change time as a function of power, as measured directly on a static tester for Ge-Sb-S thin films fabricated by CVD.

### 3 DEVICE FABRICATION

As part of this work, a prototype adopting the so-called phase-change line memory structure [14] was fabricated by electron beam (e-beam) lithography and reactive ion etching techniques. Prior to the fabrication of the nano wire, electrodes were photolithographically defined in a Ti-W film, which was evaporated by E-gun on the CVD grown Ge-Sb-S thin film. The electro-resist (ZEP520A) was then spin-coated on the sample at 4000 rpm for 35 seconds, obtaining a masking film with thickness of 100nm. After curing of the resist at 180°C for 3 min, the nano-wire was patterned with an e-beam writer (Elionix ELS-7000) operating at 10 keV. With the irradiation dosage keeping at 640 Coulomb/cm<sup>2</sup>, the nano-wire pattern was directly

created in a dot-by-dot fashion. The electro-resist was then developed and the unwritten regions were used as mask for the subsequent etching process.

Upon etching, SF<sub>6</sub>, CH<sub>4</sub>, and He were injected into the chamber with gas flow rate controlled at 16 sccm, 4 sccm, and 10 sccm, respectively. The radio frequency (rf) power of 150 W was used in conjunction with a low chamber pressure of 8 mTorr to efficiently generate high density corrosive plasma, resulting in an etch rate of 20nm/min for Ge-Sb-S thin film. Finally, after stripping off the residual resist, a phase-change memory in form of a line cell was constructed. It should be noted that the fabrication process of the present memory cell is completely compatible with current standard Si-CMOS technology.

### 4 RESULTS AND DISCUSSION

High quality amorphous Ge-Sb-S thin films have been successfully deposited on 2 micron SiO<sub>2</sub>-on-silicon substrate at a temperature of 300°C. Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) technique has been applied to study the morphology and composition of Ge-Sb-S thin films, from which a composition with a Ge:Sb:S molar ratio of 12.2: 27.5: 60.3, respectively, was obtained.

In addition, a micro-Raman was used to characterize the composition and phase structure of Ge-Sb-S thin films deposited by the CVD process. A RENISHAW Ramascope equipped with a CCD camera was used to perform the micro-Raman analysis of Ge-Sb-S thin films. A 633nm He-Ne laser was used to excite the sample and the Raman shift spectrum was measured from 1200cm<sup>-1</sup> to 100cm<sup>-1</sup> with a resolution of 1cm<sup>-1</sup>. The Raman spectrum is shown in figure 3 which also agrees with that in the reference [17]. From the Raman spectrum, the Raman shift peaks of Si, SiO<sub>2</sub>, and Ge-Sb-S are found at 520cm<sup>-1</sup>, 940cm<sup>-1</sup> and 298cm<sup>-1</sup>, respectively. In addition the band width of the peak revealed that a stable amorphous phase of the Ge-Sb-S thin film has been demonstrated.

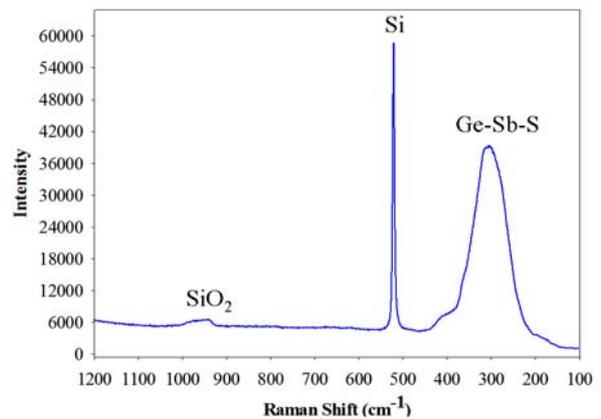


Figure 3: Raman spectrum of Ge-Sb-S thin film deposited on SiO<sub>2</sub>-on-silicon substrate at the temperature of 300°C.

The SEM image of the fabricated Ge-Sb-S nano wire phase-change device is shown in figure 4. From the image, a Ge-Sb-S nano wire with the dimensions of 24nm x 100nm x 100nm thickness has been demonstrated.

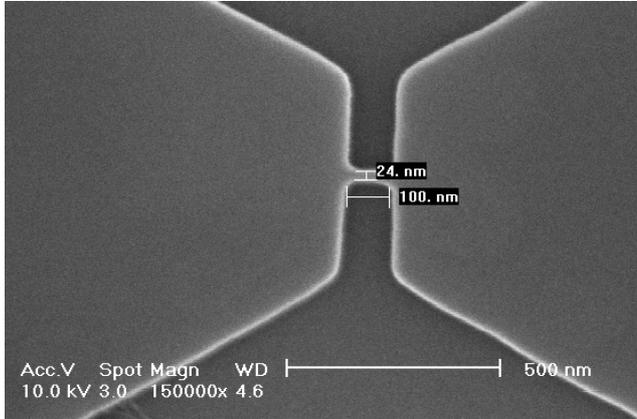


Figure 4: Scanning electron microscope image of Ge-Sb-S nano wire fabricated by CVD, e-beam lithography and dry-etching techniques.

The crystallization time of Ge-Sb-S thin films have been measured with a static tester system. The results in figure 2 show a clear crystallization region for pulse duration greater than 300ns. To invoke the crystallization high optical powers were required. This is partly due to the relatively high crystallization temperature of these materials but also due to the inefficient absorption of the below bandgap laser radiation. The poor optical absorption in the crystalline phase prevented amorphization of written crystalline marks. It is also thought that the small change in optical reflectivity after crystallization is due to the long wavelength of the probe laser.

The thermal properties of a Ge-Sb-S nano wire device have been simulated using a finite-element approach to solve the heat diffusion equation for a structure similar to that shown in figure 4. Figure 5 shows the heating and cooling curves for a device comprising of a Ge-Sb-S cell in its crystalline state. For the results shown in figure 5, the nanowire is contacted by Ti9W1 tapered electrodes with a final width of 300nm reduced from 2.5 $\mu$ m in a length of 1 $\mu$ m. The heating and cooling curves for an input current of 6.3  $\mu$ A are shown for a cell of increasing length but a constant width of 20nm. The model assumed that the whole arrangement was deposited on a SiO<sub>2</sub> substrate. The electrical conductivity and thermal conductivities were assumed to be 5x10<sup>-3</sup>  $\Omega$ .m [18] and 0.77 J.m<sup>-1</sup>.s<sup>-1</sup>[19] respectively.

Due to the lack of published data the specific heat was assumed to be similar to that of Ge-As-S, approximately 1000J.kg<sup>-1</sup>[20]. To simplify the model, the thermal and electrical properties of the materials were assumed to be independent of temperature. It can be seen that even with a current of 6.3  $\mu$ A the melting temperature of this material can be achieved efficiently. In order to compare the

material, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, has also been simulated in a similar device. The relatively high electrical conductivity of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> had a significant influence on its heating efficiency and a 2.5mA current was necessary in order to achieve its melting temperature, this is in agreement with other results [14] on other Tellurium based films. The results show the importance of scaling on the heat diffusion for such a device. Ge-Sb-S has an order of magnitude lower thermal diffusivity than that of its tellurium based counterpart [21] and consequently smaller volumes of material are required to achieve the amorphous state. In order to realize comparable quench rates in Ge-Sb-S materials to Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, the active phase change area should be less than 50nm by 20nm as can be seen in figure 5.

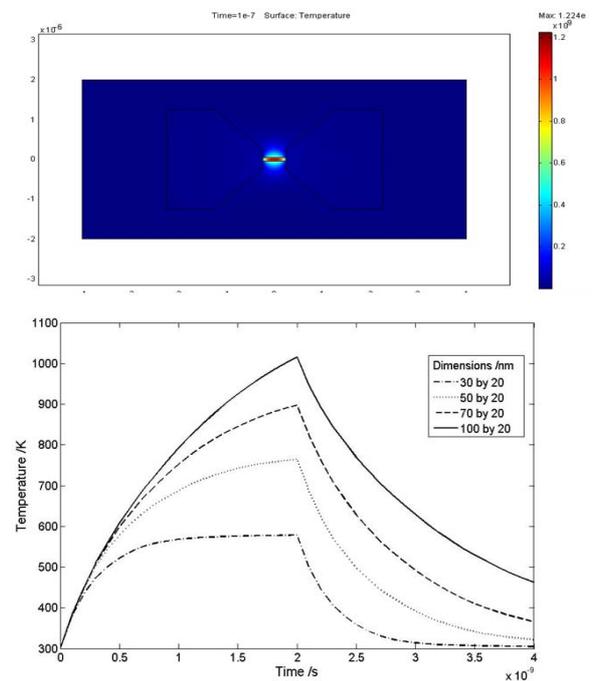


Figure 5: Simulation of temperature at centre of nano wires as a function of time.

## 5 CONCLUSION

Amorphous Ge-Sb-S thin-films deposited on SiO<sub>2</sub>-on-silicon substrate have been successfully fabricated by chemical vapour deposition (CVD) at a temperature of 300°C. The resulting thin films have a composition of Ge<sub>12.2</sub>Sb<sub>27.5</sub>S<sub>60.3</sub>, which has been characterized by micro-Raman, SEM and EDX techniques. Single Cell Ge-Sb-S nano-wire phase-change line memory devices have been fabricated on the CVD grown Ge-Sb-S thin film by e-beam lithography followed by reactive ion etching techniques.

The finite element simulations have shown that the high electrical resistivity of these sulphide based films allow a

significant increase in the heating efficiency in comparison to  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films.

An attempt to measure the crystallization time of the as deposited films has been made with a static tester. The crystallization time for the Ge-Sb-S film was found to occur after 300ns. This is three times slower than that of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  [22] however the significant increase in heating efficiency and the opportunity to optimize the crystallization rate through changes in the device structure or the active material composition through the use of dopants should be considered. This is the focus of our current research. Finally, the potential for fast switching (<4ns) of Ge-Sb-S nano wire structures makes it a possible candidate for the phase-change memory applications.

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