

MOCVD of Chalcogenide Films for Phase Change Memory Applications

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1. CRAM Background

Nonvolatility, the ability to retain data in a memory cell for years when unpowered, is crucial for many instrument applications. Most nonvolatile memory devices are Flash memory chips, so-called because of the ability to write them individually while erasing them in chunks. This type of device is ubiquitous in today's cell phones, digital cameras, media cards, etc. But Flash memory suffers from several shortcomings that limit its market potential. Primarily, writing data to a Flash memory is too slow for Flash to rival its DRAM cousins. 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, programming limitations make Flash memory ill-suited for general computing or intense data manipulation applications.

Perhaps most importantly, the nonvolatile memory industry recognizes that current flash memory technology will soon face a crisis: along with the rest of computer technology, flash chips must shrink to remain profitable, but the physics of the barrier oxide used in current flash technology prevents memory cells from being shrunk much further [1].

As a consequence, a number of different nonvolatile memory technologies are emerging as potential alternatives to replace Flash, most prominently Ferro-electric RAM (FRAM or FeRAM), Magneto-resistive RAM (MRAM), Chalcogenide RAM (CRAM, but also called Ovonic Unified Memory (OUM), or Phase-Change RAM (PRAM) and Chemical Bridge RAM (CBRAM). These devices have little in common, except that they can be reprogrammed a near unlimited number of times and be programmed in nanoseconds rather than microseconds. Table 1 summarily compares the different nonvolatile memory technologies. The term chalcogenide refers to the Group VI elements of the periodic table. "Chalcogenide" refers to alloys containing at least one of these elements such as the alloy of germanium, antimony, and tellurium as discussed here.

Development of CRAM devices is being aggressively pursued by both commercial and military suppliers (Table 2). Ovonyx – as the owner of the key CRAM and related patents – has licensed its technology and established joint R&D programs with several memory manufacturers such as Intel, ST Microelectronics, BAE Systems, Samsung, and Elpida. More recently, they have been joined in pursuing CRAM memory technology by Qimonda and by a joint development team of IBM and Macronix. Yet others, such as Micron, Philips and Silicon Storage Technology are pursuing CRAM more independently.

From Table 1 it is clear that CRAM, in addition to having a small cell size and large endurance, is a low-power memory. Since the binary information is represented by two different phases of the material it is inherently nonvolatile, requiring no energy to keep the material in either of its two stable structural states. Further, since the data in a chalcogenide memory element is stored as a structural phase rather than an electrical

charge or state, it is largely immune to EMF disruption and it is expected to be impervious to ionizing radiation effects [1, 2]. This makes CRAM ideally suited for terrestrial, space-based and military applications. In addition, CRAM memory devices can be operated at low voltages and offer fast write/erase speeds. Furthermore, the ease with which CRAM memory can be scaled to smaller sizes offers the opportunity to develop high density memories that are radiation hard.

Chalcogenide films for CRAM devices are currently produced by sputtering; however, there is strong interest in developing a MOCVD process. Sputtering limits further device improvements because of difficulties in meeting device conformality requirements for increased endurance, reliability and higher density components. Furthermore, sputtering has limited flexibility in varying the composition of the chalcogenide alloy. MOCVD overcomes these and other sputter-related limitations. Our team has demonstrated, for the first time, key proof-of-concept films that MOCVD can be employed to grow the required thin films.

MOCVD is a well-established manufacturing technology that has a demonstrated capability of uniformly fabricating thin films of high quality and excellent conformality at a high throughput rate. However, until now MOCVD has not been applied successfully to CRAM fabrication. Importantly, MOCVD also offers the opportunity to easily vary the alloy composition of the chalcogenide layer which should further improve endurance and other device characteristics. In addition, MOCVD has advantages 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-setup and qualifying the tool for sputtering; thus greatly speeding the development process and reducing the cost. In this article, we review basic research results on the MOCVD growth of phase change memory materials using a new, small research MOCVD designed to be both economical and highly flexible to allow researchers the ability to address many different material systems easily, economically and swiftly. We call our new tool the NanoCVD™ tool.

2 CRAM Memory Principle

Most commercial research on phase-change nonvolatile memories is focused on the chalcogenide material $\text{Ge}_2\text{Sb}_2\text{Te}_5$ used for rewriteable optical media (CD-RW and DVD-RW) [4-6]. This phase-change technology uses a thermally activated, rapid, reversible change in the structure of the alloy to store data. The two structural states of the chalcogenide alloy, as grown at SMI and shown in Figure 1, are an amorphous state and a polycrystalline state [7]. Relative to the amorphous state, the polycrystalline state shows a dramatic increase in free electron density, similar to a metal. This difference in free electron density gives rise to a difference in reflectivity and resistivity. In the case of the re-writeable CD and DVD disk technology, a laser is used to heat the material to change states. The state of the memory is read by directing a low-power laser at the material and detecting the difference in reflectivity between the two phases.

A memory cell consists of a top electrode, a layer of chalcogenide, and a bottom electrode that at the base is connected to a transistor (see Figure 2). Reading the cell is done by measuring the resistance. Resistive heating is used to change the phase of the chalcogenide layer. To write data into the cell, the chalcogenide is heated past its melting

point T_m and then rapidly cooled to make it amorphous. To make it crystalline, it is heated just below its melting point and held there for approximately 50 ns, giving the atoms time to position themselves in their crystal locations. This process is depicted in Figure 3.

Development of CRAM is taking place in three areas: device physics, programming current reduction and manufacturing. Single cells have been studied in detail [8.9] with reported cycling endurance up to one trillion and write/erase speeds in the tens of nanoseconds. Cycling endurance is observed to be dependent on the magnitude of the reset current. Overheating the cell with a large programming current causes failed cells to get stuck at low resistance states. Programming currents are typically on the order of 1 mA, but for practical reasons are desirable to be reduced to 0.2 mA to 0.4 mA. One way to achieve this is to dope the chalcogenide material with nitrogen [10]. Doped chalcogenides have a higher resistance and therefore a lower programming current. Similarly alloying the chalcogenide with Sn or Se may have the same effect on programming current [11]. Consideration of these doping and alloying needs is a strong part of our NanoCVD™ research tool and material demonstration efforts.

3. MOCVD an Enabling Technology for CRAM [1]

Metal-organic chemical vapor deposition (MOCVD) is a mainstay process for thin film manufacturing, as MOCVD is presently the process of choice for capacitor production in semiconductor fabs as well as for compound semiconductor manufacturing. High purity metal-bearing, gaseous metal-organic precursor chemicals are mixed into a carrier gas such as hydrogen. This mixture flows into a controlled atmosphere reaction chamber that is under vacuum or, less often, at atmospheric pressure. Substrate wafers are placed in the chamber and heated. The high temperature causes the precursor molecules that impinge the substrate surface to decompose (or pyrolyze), resulting in the deposition of metal. Oxidizing, inert or reducing gas may be introduced into the chamber to oxidize or reduce the growing film. Several precursor chemicals may be mixed into the carrier gas flow in the proper ratio in order to form compounds. MOCVD is a mainstay of semiconductor wafer processing because it can be readily controlled and scaled for large wafers. Key process parameters include tight control of substrate and reactor temperature, control of precursor flow, and the gas-dynamics of the reactant flow to achieve uniform and repeatable deposition of films over large diameter wafers. The deposition of chalcogenide compound films on a production basis will be new. SMI has been involved in the development of MOCVD derived oxide and semiconductor films for years and has emerged as the industry's leader in complex oxide technology area. It is from this platform that we will address chalcogenides.

Aside from its production-proven track record, MOCVD has several advantages specific to deposition of high quality chalcogenide thin films for integration with the memory design, which as seen in Figures 2 and 3 require via (hole) filling technology. First, MOCVD will provide the conformality, uniformity and thickness control required to ensure consistent performance of every cell in the device, which is necessary for high quality. Additionally, MOCVD offers the flexibility to improve the materials through doping of the chalcogenides, the fabrication of multilayered active regions, and the integration of contact or cladding layers. Doping of the material with very low concentrations of other elements has shown promise to enhance device performance. With MOCVD, the addition of dopants

is easily accomplished. The fabrication of multilayers of materials is also an option that can be easily produced using MOCVD.

Structured Materials Industries, Inc. (SMI) has adapted its MOCVD thin film processing reactor technology to address the need for low cost production of chalcogenide based memory devices both at the large scale and at the research scale as focused upon in this document [12]. SMI's MOCVD process technology has been successfully introduced commercially, with more than a dozen systems produced and installed across the world. We offer tools from research and development to systems fully compatible with state-of-the-art cluster-tool process automation architecture.

Using an SMI NanoV CVD™ research reactor that allows us to carry out many runs in rapid succession while consuming a small amount of precursor and hence generating small amounts of toxic process exposure and waste, we achieved significant results, as will be reviewed in the results below. Figure 4 shows a photograph of the NanoV CVD™ test reactor. The small reactor consists of a 1.5" diameter quartz tube with the substrate being heated by any of quartz lamps; rf induction coils, other heating configurations, including radiant heat furnace, and internal filament heaters are also possible. With this configuration we have been able to easily reach 1" diameter substrate temperatures in excess of 800 to 900°C in a few minutes. Our large reactor has also been demonstrated to cover the same process parameter ranges and grow uniform films on 6" and 8" wafers¹.

We developed the MOCVD process in multiple modes using the precursors shown in Table 5 after installing a special wet scrubber to neutralize the Te and S precursors, whose exceptionally offensive odor can be detected by humans at the parts per billion level, we developed a series of recipes wherein we either used sequential multi-layer multi-component film deposition or conventionally enhanced deposition.

Our initial experiments to deposit GeSbTe were carried out at > 500 °C. However, based on the Ge-Te, Ge-Sb and Sb-Te binary phase diagrams, there is a high probability that one of two low melting point eutectic compositions combined with the high vapor pressure of tellurium can result in re-evaporation above 400 °C. Therefore, we focused on depositions at ≤400 °C. We first modified the test reactor to operate with or without an rf generator to create plasma in the system. We carefully selected the frequency and design to allow plasma activation, yet minimize the generation of detrimental precursor species that could contaminate the growing film. Films, as deposited, were amorphous under most conditions. Roughly, the best deposition temperature is ~300 °C to produce amorphous films with all precursors. Data suggests that deposition temperature is critical since there are known phase transformations (crystallization of amorphous sputtered films) above 380 °C. However, when depositing GeS alone, we have evolved a very clean process that works through <100C¹ – this will be important in future considerations first because GeS is a cornerstone of the GeSAG material as needed for CBRAM devices and where we wish to deposit memory materials on flexible foil or polymer substrates.

It has been reported that GeSbTe films occasionally show poor adhesion to silicon. It should be noted that in addition to having the ability to deposit amorphous films, the plasma assisted process developed here has the ability to a) clean the substrate and b) deposit a few mono-layers of Ge which appears to be an excellent adhesion layer for

¹ G. S. Tompa, S. Sun, C. E. Rice, J. Cuchiaro, and E. M. Dons, Proceedings of the Spring 2007 MRS meeting.

silicon – a step we are adding to our existing patent application as a continuation in part. Additionally, we have deposited films on Pt electrodes on Si substrates. Our initial runs appear to be very reproducible.

We now review results obtained with our new NanoCVD™ system. Analysis included XRF, optical microscopy, XRD, SIMS, and electrical measurements. First, we subjected films to thermal cycling. We used XRF to again confirm material deposition. The two produced phases are shown optically in Figure 1a and 1b, which are magnified images of amorphous (which is also how films were grown) and polycrystalline after phase change heating and proper cooling. Sheet resistance of as-deposited amorphous films were “Over Range,” i.e. too high to measure with our 4-point probe; whereas sheet resistance of annealed GeSbTe films were less than 5 Ω/\square - Figure 5 depicts this range. This is an order of lower than some of the other as-deposited amorphous and partially crystalline films and may in fact relate to how the film was grown. The total range of change of resistance is in line with reported results. Lastly, we also confirmed phase change by examining the films crystallinity as shown in Figure 6. SIMS has also been used to confirm the presence of GeSbTe in the phase changing film compositions, as shown in Figure 7. While not fully revealed in this summary of results, by changing the parameters and using the plasma, we have been able to far exceed the range of desired composition and crystalline/amorphous specifications needed to produce CRAM devices far easier than without the plasma.

4. Conclusions

We have developed both tooling and processes for the MOCVD of phase change materials – in particular: GeSbTe. This is a milestone in the enablement of phase change random access memories (PRAMs (also known as CRAMs)). The process is scalable to production needs, i.e. deposition on 200mm or 300mm wafers. Of significant note is that the processes developed are also applicable to the related CBRAM system; especially at low temperature for flexible memory systems. SMI is presently seeking development and investment partners for this technology.

5. Acknowledgements

SMI wishes to thank the following organizations whose funding has led to our efforts success: Ken Hunt of the AFRL, The Missile Defense Agency – Contract Number HQ0006-07-C-7769, Laura Burcin of BAE, and most recently the support of The National Science Foundation – Contract number: 0637775 ; as well as Ed Spall and John Maimon of Ovonyx and Michael Kozicki of Arizona State University, among others.

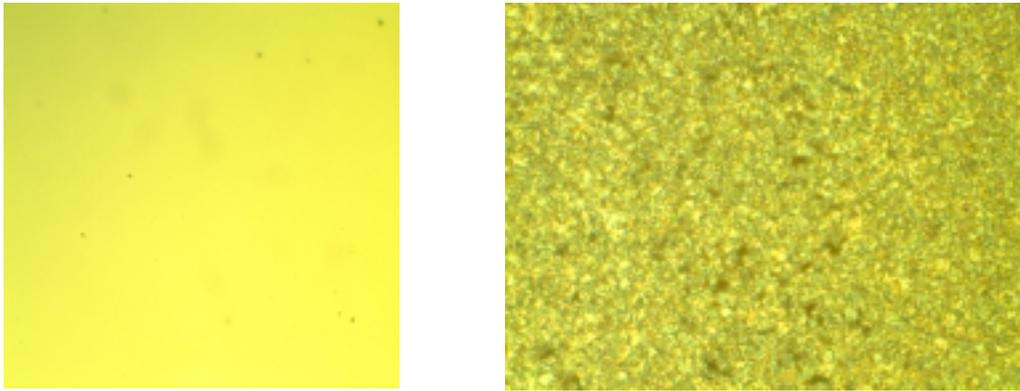


Figure 1: SMI grown chalcogenide film: (left) smooth amorphous GeSbTe at 1500X and same film (right) crystalline with granular texture at 1000X after phase change (heating). “Textbook” results [7].

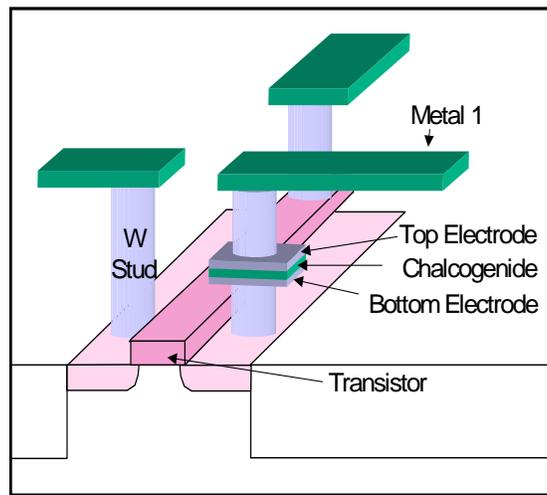


Figure 2: Chalcogenide Memory Element Integrated with Transistor [7].

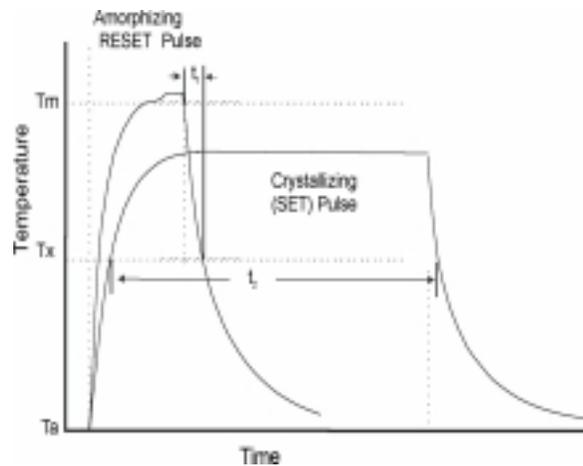


Figure 3: Example of Chalcogenide Programming [7].

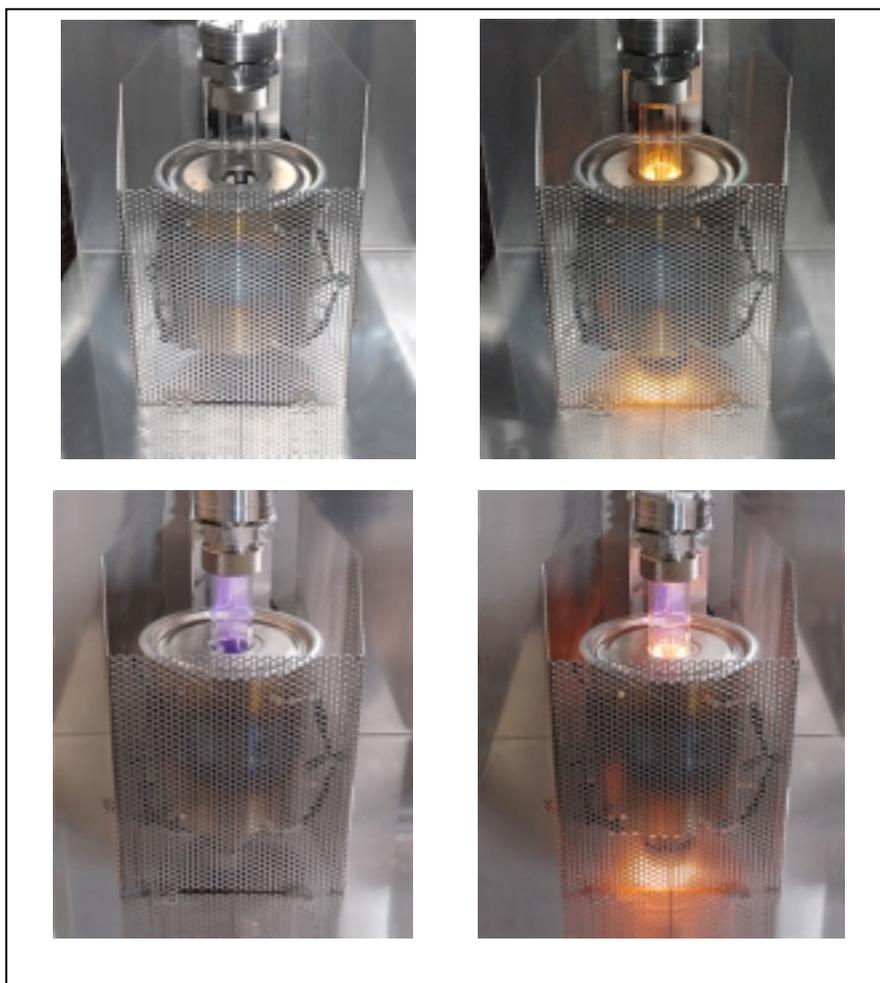


Figure 4. NanoV CVD™ system used in this work – clockwise from top left – system cool with no plasma, system heated with lamp heaters, system with just plasma activated, and system with both plasma and heating activate. SMI has also used it large scale rotating disc reactors to produce switching

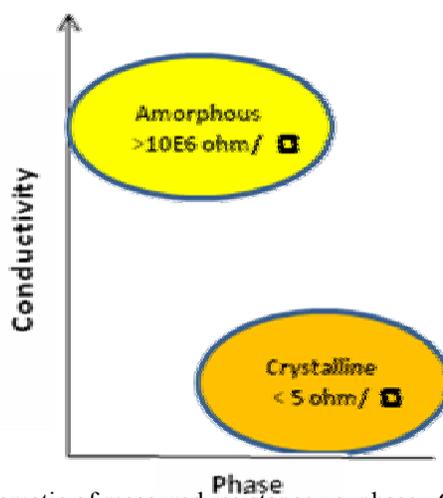


Figure 5: Representative schematic of measured resistance vs. phase. Our amorphous films were $>10^6$ Ohm/sq. and our conductive films were less than 5 Ohm/sq.; confirming a significant phase change effect.

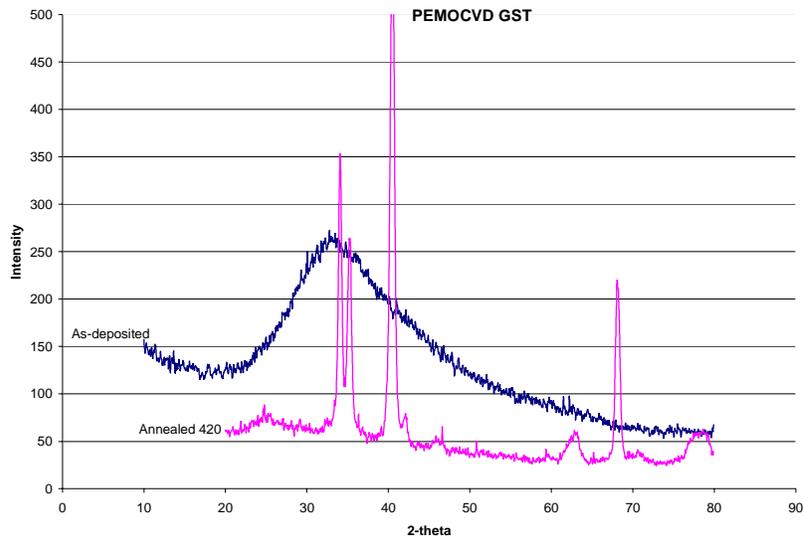


Figure 6: XRD confirmatory evidence of phase change of films: as-deposited amorphous (blue), and heat processed for crystallization (purple).

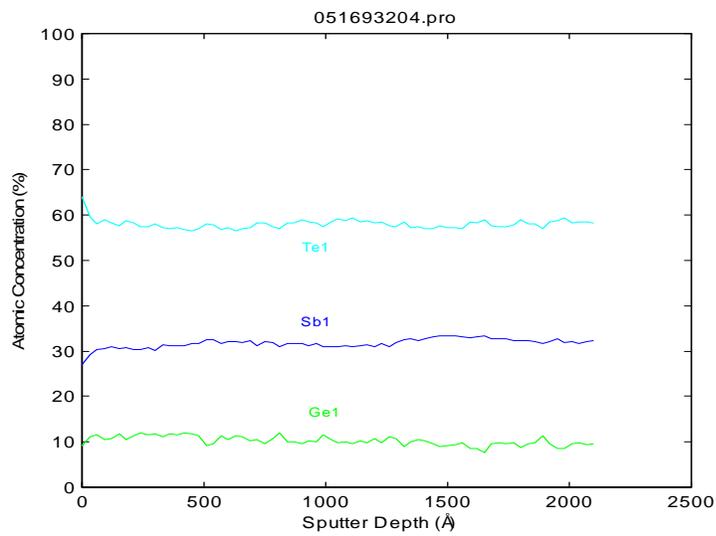


Figure 7. SIMS depth profiling of a sample of GeSbTe, the composition is uncalibrated due to lack of standards.

	SRAM*	FLASH	FRAM**	MRAM***	CRAM#
Nonvolatile	No	Yes	Yes	Yes	Yes
Cell size factor	8	8	18	10-20	6
Endurance, cycles	Infinite	10 ⁶	10 ¹⁶	10 ¹⁴	>10 ⁸
Read/write Voltage	Low	High	Low	Moderate	Low
Read/write Speed (ns)	25/25	20/1000	40/40	20/30	<50/<50
Radiation Hard	Yes	No	Yes	No	Yes
* BAE Systems Millenium 4 Mb Radiation Hardened SRAM, ** Ramtron FM20L08 1MbByte-wide FRAM, *** Freescale MR2A16A 4Mb MRAM # BAE Systems 512Kb Radiation Hardened C-RAM					

Table 1: Comparison of commercially available memories.

<i>Company Name</i>	<i>Products</i>	<i>Patents</i>	<i>Notes</i>
<i>ECD</i>	No	Few	Original inventor of technology
<i>Ovonyx</i>	No	Few	Licensing of GeSbTe-based technology
<i>BAE SYSTEMS</i>	YES	Few	Only company offering a product
<i>Intel</i>	No	Many	Joint R&D with Ovonyx
<i>ST Microelectronics</i>	No	Many	Joint R&D with Ovonyx
<i>Samsung</i>	No	Few	Joint R&D with Ovonyx
<i>Elpida</i>	No	Many	Joint R&D with Ovonyx
<i>Macronix</i>	No	Many	Joint R&D with Infineon and IBM
<i>IBM</i>	No	Few	Joint R&D with Infineon and Macronix
<i>Hynix</i>	No	TBD	Joint R&D with Ovonyx
<i>Infineon/Qimonda</i>	No	Few	Joint R&D with Macronix and IBM
<i>Micron</i>	No	Few	No joint R&D; some patents
<i>Philips</i>	No	Few	No joint R&D; some patents
<i>Silicon Storage</i>	No	Few	No joint R&D: some patents

Table 2: Companies currently developing CRAM technology

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