

OVONICS: FROM SCIENCE TO PRODUCTS

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Ovshinsky's pioneering work and inventions in amorphous chalcogenide semiconductor materials in the 1960s invigorated an entire field of physics. The electronic switching he first demonstrated has led to many things, including what many refer to generically as phase change technology. These Ovonic chalcogenide materials are now used in several kinds of devices, primarily optical and electrical storage. The applications are growing, fueled in part by the successes gained in the first applications and also by market opportunities and demands. The remarkable properties of these materials and the underlying physics opened up these commercialization possibilities, but significant engineering including the materials themselves, but more so of the device structures, has provided for the consistent properties of the products. We present a review of the many device and engineering aspects which have led to so many applications.

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1. Introduction

The vision of Ovshinsky has led to new industries and will continue to spawn additional materials, devices, products, manufacturing technology and manufacturing machines. His ability to visualize things ranging from electronic orbitals and their interactions to high-speed low-cost manufacturing systems is unparalleled. It is my pleasure to discuss the progression of his ideas from scientific principle to important commonplace products of today and progressing into the future. Ovshinsky's inventions and other contributions range from semiconductor circuits through optical storage, photovoltaics, batteries, fuel cells, hydrogen storage and other applications. In this paper the description is of the chalcogenide-based devices.

By 1955 Ovshinsky's proposals for the mechanisms present in the mammalian brain were received and encouraged by the chairman of the medical college at Wayne State University in Detroit. His subsequent work with doctors and professors from various universities led to multiple publications including a study on the functional aspects of cerebellar afferent systems and of cortico-cerebellar relationships [1] which is still used in medical instruction at Cambridge University and others.

His considerations of the electronic properties of amorphous semiconducting materials convinced him that electronic devices and circuits could be made that would in part have analogous function to the processes in the brain he had studied and elucidated. And so was born the field of Ovonics.

Dictionaries define Ovonics as the combination of Ovshinsky and electronics, introducing new substance based on the new physics that his devices entailed. The Ovshinsky switch was revolutionary, and its function has been the subject of scientific study for years since.

As we know, the Ovshinsky switch [2] involves an amorphous chalcogenide alloy that when in its quiescent state has very low conductivity. The device has negative differential conductivity so when a voltage field of about 3×10^5 V/cm is exceeded, rapid switching to a highly conductive state

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ensues and a solid state plasma is created. The switching speed at threshold is subpicosecond; equipment limitations have prevented ultimate measurement of the switching time.

Ovshinsky also recognized that the highly cross-linked bonding configurations that gave the stability of the amorphous phase could be re-designed to provide meta-stability and so the field of phase change memories was born [3]. Chalcogenide alloys with fewer cross-links could be switched just as the threshold materials, but reconfigurations in the atomic bonds while in the dynamic state and during extinguishing of the plasma led to different degrees of crystallization as a consequence. Since the crystalline material has marked differences in electrical and optical properties from those of the material in the amorphous state, new optical and semiconductor devices are enabled.

The first commercial devices were semiconductor memories. Here the changes in electrical conductivity of up to six orders of magnitude result in a device that is essentially a programmable resistor. In the early 1970s Ovonic provided non-volatile memory switches that could be programmed fast, with low voltage and that could be programmed very many times.

Two-dimensional arrays of devices could be fabricated that were programmable by simple delivery of electrical pulses. This was in contrast to EPROM devices based on silicon that relied on lengthy exposure to ultraviolet light that led to drain of storage charge. Arrays of 1024 Ovonic devices could be fully reprogrammed in a few seconds, whereas the UV exposure for EPROMs required twenty minutes.

The first products were developed in cooperation with the American semiconductor company Burroughs. Workers at ECD developed the materials and device structures, and both were easily made using conventional sputtering and wet etching techniques. Lithographic dimensions of several microns tolerated the undercutting that wet etching leads to, and since all semiconductor circuits were new at that time there were no cautions about bringing new materials into the fabrication facilities. The first commercialization proceeded smoothly.

Although memory devices were sold and applied in electronic systems in the 70's, the widespread commercialization of Ovonic memory devices, such as the Ovonic Universal Memory, is now reaching the market. The contemporary devices have far faster programming rates, and can be reprogrammed in the nanosecond range, as opposed to the millisecond range of the earlier devices. This enormous improvement in speed came through new materials that were initially developed for application as optical storage media.

2. Phase change optical storage

Ovshinsky invented phase change optical storage devices in the early 1970s, and in fact Energy Conversion Devices, Inc. in 1974 built a 4 gigabyte optical disk storage system. It was ahead of its time, both in terms of capacity and productization. It used a water cooled argon ion laser, and was contained in a box two by two by 1.5 meters, compared to optical DVD drives today that have similar capacity in a package that is more like 2×14×20cm.

The early Ovonic phase change materials used in optical storage were comprised of simple alloys based primarily on compositions in the vicinity of the tellurium-germanium eutectic. With just these two elements there is a tradeoff between crystallization speed and thermal stability of the amorphous phase, so the principles of atomic engineering that Ovshinsky introduced for the threshold devices were used to formulate alloys that could have both speed and stability.

Antimony was primarily used, although other elements including selenium, arsenic and bismuth all were shown to have beneficial effect. Ovshinsky reported the first use of germaniumantimony-tellurium materials in 1971 [4]. These materials opened the possibility for direct overwrite in phase change rewritable optical disks. The final desired state could be achieved regardless of the starting state, so there is no requirement for an erase step before a new recording is made.

By the 1980's semiconductor lasers had been developed to the point where drives of practical size could be made, and optical storage began to blossom. The first major product was the familiar CD format, initially introduced to store audio information. The enjoyment of music was forever changed when CDs were used to store and play back pre-recorded music. The physical size of the disk is much more convenient than the predecessor 12 inch vinyl records, and the quality of the digitally represented music is incomparably better than the earlier records and magnetic tapes,

particularly as those media were used over and over. They degraded, and the CD music does not. Within a few short years the vinyl record which we had used for over fifty years was completely replaced.

Once read-only disks were common place, the attention turned to recordable disks. At the time there were two technologies contending for the rewritable market: Ovonic phase change and magneto-optical. The magneto-optical at that time had greater record speed and longer life, but phase change was adopted for the CD format because the large change in its optical properties led to wider margins in the products, and since standardization is a fundamental requirement of removable storage media, this was essential.

However, compatibility with the read-only disks requires the same rotation rate in both types of disks, and the earlier alloys were not fast enough in their crystallization speed. This led to the development of the family of materials now referred to as GST [5], namely the compounds of germanium, antimony and tellurium found along the pseudo-binary tie line between antimony telluride and germanium telluride in their ternary diagram. These alloys have switching speed in the nanosecond regime (Fig. 1), and so could be transformed to either the amorphous or the crystalline structures easily within the time afforded by the dwell of a focused laser beam on a spinning disk.

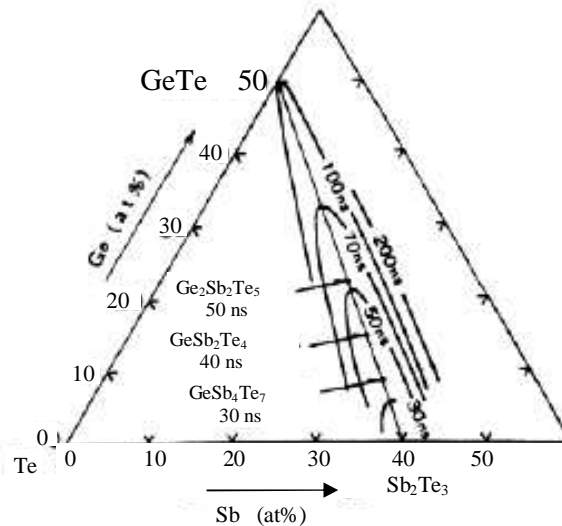


Fig. 1. Crystallization times of GST alloys along the $\text{Sb}_2\text{Te}_3/\text{GeTe}$ pseudo binary tie line.

The second family of rewritable phase change materials was introduced by workers at Ricoh [6].

This family is based on the SbTe eutectic ($\text{Sb}_{69}\text{Te}_{31}$), modified with various elements, the first being indium and silver, to optimize for the various product requirements. The SbTe eutectic family is clearly different from the GST family in the crystallization process. GST nucleates fairly uniformly and growth proceeds from many nucleation centers. An erased mark on a GST disk is comprised of many small crystallites. The SbTe eutectics do not readily nucleate, and so an erased mark is formed of fewer, larger crystallites that grow from the edge of an amorphous mark towards the middle. Slight differences in crystal morphology between the erased mark and the background field in GST media lead to very small differences in reflectivity, and so when using the logarithmic dB scale for signal characterization residual signals can be seen. The SbTe eutectics have more uniformity in the crystallite reflectivity, and so the erasure is more complete.

Both, however, function well as rewritable phase change media. This said, it understates the technological advances that went into developing the products. There are several considerations in making a phase change rewritable optical disk. These include record sensitivity, readback reflectivities of both structural states, encapsulation to prevent oxidation, and precise control of the shape and size of the recorded mark. Although the record process of a phase change optical disk is initiated by the electronic excitation accompanying the absorption of the photons, these excited carriers rapidly thermalize and significant heat is generated. Developing an optimized thermal structure of the disk was a key challenge. While cooling from the energized state, the rate of cooling, or the quench rate, plays a significant role in the determination of the final structure. Since each recording of a spot is immediately followed by the next spot, lateral heat conduction plays a role in

the final shape of the mark as well. Finally, since the cost of the product must be low, the product must be based on inexpensive injection molded plastic substrates, which easily soften at the temperatures encountered in the recording process. Fortunately, all of these issues have been successfully addressed. Further, the solutions are robust enough to position Ovonic phase change to be selected not only for CD, but also the more demanding successor generations of DVD and disks for high definition TV.

Thermal structure optimization alone does not give good enough shape and reproducibility in the recorded marks. At the beginning of the mark the exposed region starts at ambient temperature, but as the process continues heat builds up and by the time the end of the mark is reached this heat energy alters the mark shape. Interestingly, in GST media the marks become wider, whereas the fast growth of the SbTe eutectics leads to recrystallization during the recording process, and the mark becomes smaller. Both of these materials require dividing the laser pulse into individual smaller pulses which prevent heat buildup [7]. The characteristic pulse profile is shown in Fig. 2. In addition to forming amorphous marks using high laser powers, the profile also includes intermediate power levels that ensure that the previously recorded marks are crystallized so that the process is direct-overwrite.

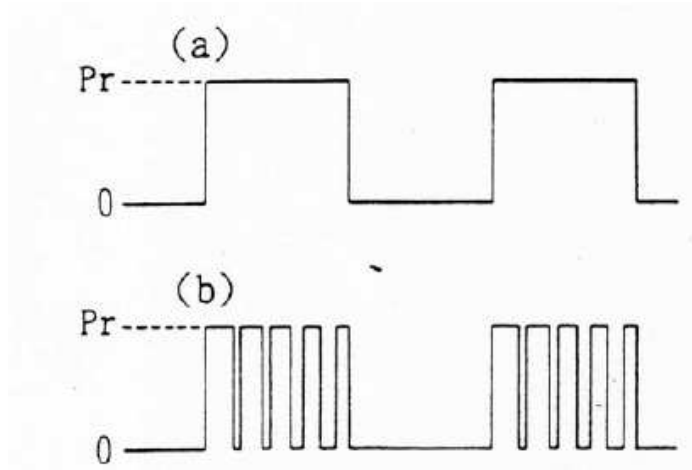


Fig. 2. Basic Phase Change Rewritable Media Write Strategy. The total laser on time is divided into multiple pulses to control the shape of the recorded mark.

The GST compounds show remarkable crystallization speed combined with good stability and using these compounds, disks spinning at rates enabling transfer of data at 1MB per second is possible. Early workers made media by sandwiching the chalcogenide material between two layers of ZnS, and added a metal reflective layer for optical properties and thermal conduction (Fig. 3).

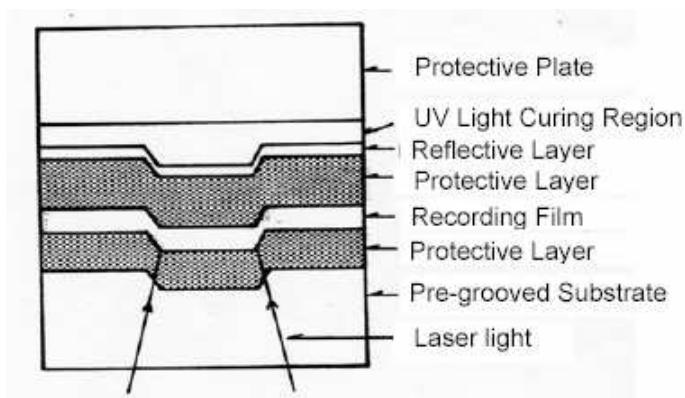


Fig. 3. Basic four-layer phase change rewritable optical disk structure.

Although the high index and relatively low thermal conductivity of ZnS were favored for both thermal and optical structures, it gradually crystallizes during the recording process, which eventually leads to non-homogeneities on the scale of the recorded marks, and the uniformity of reflectivity from each mark suffers. In 1990 [8] the noise level of the disks was improved by adding SiO₂ to the ZnS layers. The grain size of ZnS-SiO₂ films is very small, at around 2 nm. The new ZnS-SiO₂ dielectric layer is thermally stable and does not show grain growth even after annealing at 700C for 5 minutes. Complex bonding structures among the four elements in ZnS/SiO₂ mixtures [9] stabilize against crystallization, and cycle lifetime increases.

Cycle life of phase change media was extended past the milestone of a million cycles when Takeo Ohta refined the disk structure in 1989[10] to lessen perturbations initiated by the thermal expansions of the various layers. Deformation occurs by thermal expansion of the layers accompanying the thermal diffusion process. The deformation is generally asymmetrical along the laser scanning direction, toward the forward edge and the backward edge of the mark. By adding an additional SiO₂ layer, the thermal deformation of the space between the bottom and upper dielectric layer is reduced. Fig. 4 shows more than 2-million cycle characteristics of the phase-change optical disk with the additional SiO₂ layer.

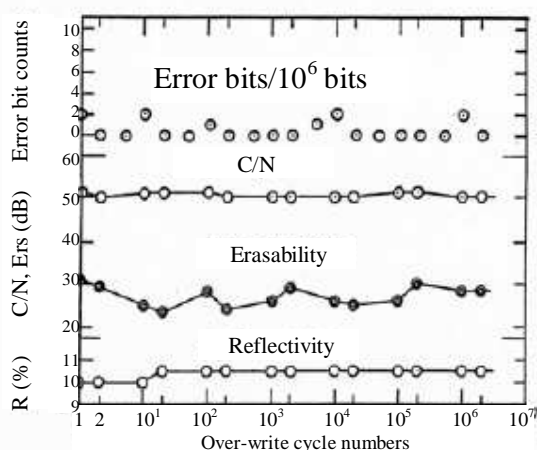


Fig. 4. Two million overwrite cycle life of GST phase change optical media.

Based on this improvement Matsushita/Panasonic was in 1990 the first to ship rewritable phase change optical disk products [11].

A general method for increasing the storage capacity of optical disks is to use shorter wavelength lasers. Larger numerical aperture (NA) lens also form smaller laser spots, since the diffraction limited spot size of a system is related to the wavelength and inversely related to the NA.

However, as the numerical aperture is increased, there is also an increase aberration of the beam related to tilt in beam path through the substrate. I. Satoh and T. Ohta first showed that the disk tilt problem can effectively be resolved using a thin disk substrate [12]. The CD capacity of 0.65GB was increased to 4.7GB in DVD by using a shorter wavelength laser (650 nm vs. 780 nm), a higher numerical aperture (0.65 vs. 0.45) and practical development of substrates half the thickness of those used in CDs (0.6mm vs. 1.2mm). In 1998 the BluRay disk structure was introduced, using a 0.85 NA lens and a 405nm laser [13]. This increased capacity to 25GB on a 120mm diameter disk.

There are other ways storage capacity is being increased. Even higher numerical apertures, dual layer disks, and multi-level recording are all being developed. Nagata et.al. first proposed a dual layer phase change optical disk [14] It has a transmittance balanced structure so that the recording performance of the second layer is the same, regardless of whether the first layer L0 is recorded or not. Both layers were designed as optical "high-to low-structures", meaning that they have higher reflectivity in the crystalline state than the amorphous state. Typically the amorphous layer has lower reflectivity. The transmittance difference between the crystalline and amorphous state in the first layer is as small as 2%.

Multi-level recording can also increase storage capacity. Multi-level recording was first announced in a phase-change electrical switching memory (Ovonic memory) device in 1997, which showed 16 switching levels [15]. M. P. O'Neil showed 8-level phase-change recording technology in 2000 which enabled 2GB of capacity on a CD-RW disk [16]. Near field systems have been proposed to increase storage density, including solid immersion lenses) which have numerical apertures larger than 1.0, and super-hemispherical solid immersion lenses. (17) The air gap between a rotating disk and a near field optical head is only 50 nm. This led to development of other types of near field systems, such as super-RENS (super-resolution near-field structure) which realizes recording and readout of marks beyond the diffraction limit. (18) Super-RENS is unique in that the near-field aperture is fabricated in the optical disk itself with, for example, a Sb thin film. At the recording process, the laser spot heats up the Sb layer, which forms an aperture smaller than the diffraction limit size when heated by the laser beam and marks are recorded through an underlying dielectric layer. Much work has been done on the Super RENS effect, and the mechanism is still being elucidated.

High-speed recording is very important. T. Kato et al. announced data recording at 140 Mbps rate [19]. The disk structure uses a rapid cooling layer including Al_2O_3 . The recording material is modified SbTe eutectic which has Ge added. No inherent speed limitation of amorphous mark formation has yet been observed. T. Ohta first reported using 120 femto second laser pulses [20] to record amorphous marks in phase-change media

3. Ovonic Universal Memory

Ovonic Universal Memory (OUM) semiconductor devices based on Ovonic phase change materials are now reaching the marketplace. Whereas optical disks are fabricated by first patterning the substrate with the format information, followed by deposition of blanket films to form the optical stack, semiconductor memories are formed on a smooth silicon wafer, and successive layers are individually patterned to form electrical circuits. This introduces completely different considerations for the fabrication and optimization of devices.

The data storage function starts with the Ovonic switching event (Fig. 5). When a voltage is applied to a device whose memory material is in the amorphous structure, the device starts in a high resistance state, and when the threshold voltage is reached it switches into a dynamic state. In the dynamic state the current-voltage characteristics show the resistance of the contact materials. The Ovonic material itself shows almost zero dynamic resistance, as the current flow increases dramatically with very small changes in applied voltage (Fig. 5). This behavior is made possible by the formation of a solid state plasma. The plasma follows from electronic transitions that overcome the energy of the inter-atomic bonding. It is during the quenching of the plasma to the ground state that the formation of the final structure is initiated.

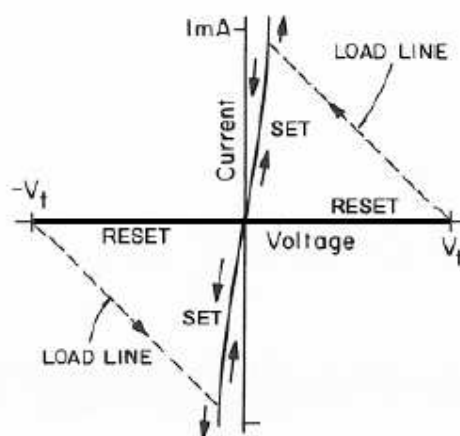


Fig. 5. IV Characteristics of an OUM device.

As in the case of the optical storage device, once again the thermalization of the excitation energy induces heating of the chalcogenide material. The final structure is determined by the amount of energy applied and the thermal structure of the local environment. Of course in a single device design the environment remains constant, so it is the amount of energy applied that determines the final structure. Lower amounts of energy lead to temperatures that will crystallize the material, and higher amounts of energy lead to temperatures that will amorphize the material (Fig. 6). Since the crystallization process is inherently slower than the quenching, longer pulse duration tend to favor crystallization, and shorter pulse durations tend to favor formation of the amorphous structure. However, a single pulse width can be used to program both states.

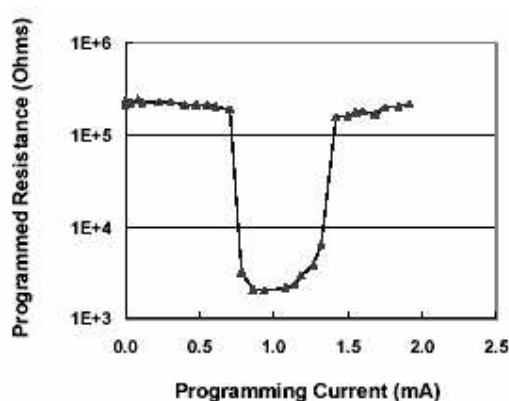


Fig. 6. Characteristic programming curve of an OUM device.

The engineering challenges in making repeatable and reliable devices start with creating a device structure that strives to allow the Ovonic material to maintain its compositional integrity. Particularly since temperatures over 600 °C are reached during the amorphization step, materials that chemically react with the chalcogenide material must be avoided. There are a number of refractory metals and non-reactive alloys that can be used to make suitable contacts. Even though oxygen is a particular concern, oxygen in silicon dioxide is bound strongly enough that it can be used in direct contact with the chalcogenide memory material. Silicon nitride also can be used in direct contact with the memory material, and so the two major dielectric materials used in semiconductor fabrication are both acceptable candidates. The ZnS/SiO₂ dielectric material used in almost every optical disk certainly has been demonstrated to be acceptable in contact with the chalcogenide material, but since zinc is considered as a contaminant in semiconductor fabrication facilities, and since it doesn't form a volatile species for reactive ion etching, it isn't yet used in phase change semiconductor memories.

Two things go forward in parallel in these circuits. First, successive generations of lithography form smaller and smaller device dimensions. Second, the Ovonic devices require lesser amounts of programming current as the device size decreases. So smaller devices are both required and preferred. Additionally, the phase change devices can be made at smaller and smaller dimensions. Using an electron beam ECD has demonstrated that regions as small as 10 nm can be crystallized.

Low programming currents are very important in OUM. The size of a transistor capable of sourcing sufficient current to program an OUM device is much larger than the device [21] Several clever techniques can be used to decrease the effective size of the OUM device. Further, heat can be generated not only by the thermalization in the memory material itself, but by use of resistive contact materials. Fig. 7 shows a basic OUM cell structure. The region within the chalcogenide film that is programmed is where the current is at its highest density, where the bottom contact forms the smallest area. The heater can be formed at smaller dimensions than the current source transistor using the same lithographic techniques, and so the overall device area can be decreased.

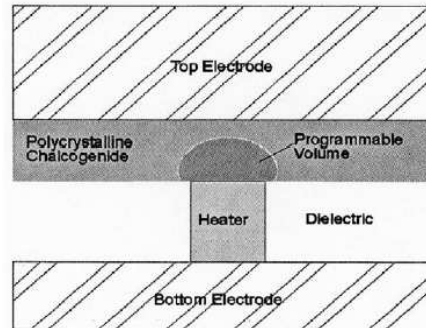


Fig. 7. Basic OUM device structure.

Device lifetimes have been shown to exceed 10^{13} cycles [22]. In principle, lifetime is infinite as it is when water is frozen and re-melted. Mechanical limitations in actual device structures can limit lifetime, and they are being successfully addressed. The devices can be programmed to intermediate states between the fully amorphous and the fully crystalline, and so multiple bits can be stored in each cell. Sixteen clearly distinguished levels have been demonstrated [23]. The device resistance can theoretically be programmed to all levels between the highest and lowest, and as the technology matures more levels will be used to store larger numbers of bits per cell. OUM can be applied not only as leading memories as Flash, DRAM and SRAM, but also in a variety of other products including FPLD, FPLA, embedded macros, SOC macros and more. Its ease of fabrication and compatibility with conventional silicon devices using minimal added steps and excellent scaling position it as an ideal memory technology for generations of products to come.

4. Ovonic cognitive computer

The Ovonic phase change memory material has the plasticity that enables it to perform neurosynaptic functions, and that makes it capable of being used to make a cognitive computer. A single device realistically simulates the neurosynaptic behavior of biological neurons. Like biological neurons, the device is capable of synaptic function such as receiving and weighting multiple inputs that result in threshold activation, an operational mode in which it accumulates input energy signals without responding until the total accumulated energy reaches a threshold level. Once the threshold is reached, the device undergoes an abrupt transformation from a high resistance state to a low resistance state in a process that mimics the firing of a biological neuron. This is shown schematically in Fig. 8.

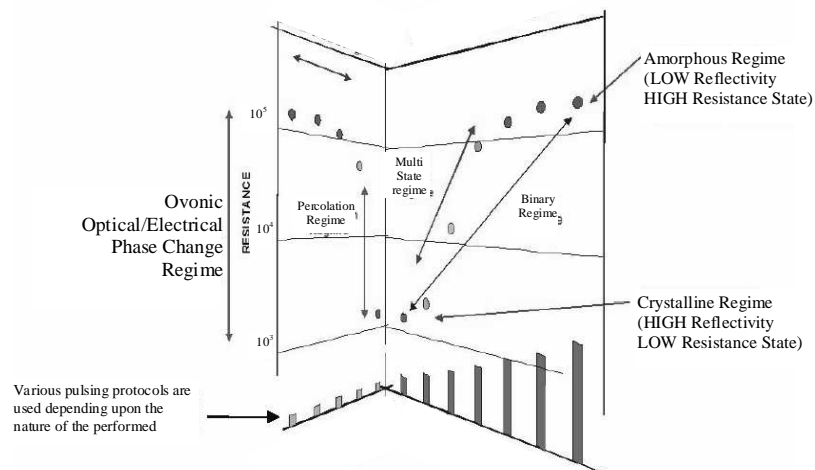


Fig. 8. Detailed programming characteristics of an Ovonic phase change device, showing OUM binary operation, multi-state operation and cognitive operation regions.

The low resistance crystalline state can be achieved by a single pulse of appropriate amplitude and duration. If the total time of the crystallization pulse is parsed into multiple shorter pulses, the device will crystallize to a state having essentially that same resistance when the cumulative time of the shorter pulses reaches the time of the single longer pulse. However, with less total time, the device remains in the high resistance state. This is a novel way to encode and store information. Fig. 9 shows how the resistance of a device is changed from that of the initial amorphous state to that of the crystalline state by applying five pulses of the same amplitude. We can achieve this result using other numbers of pulses, as long as the total time for crystallization accumulates to the value used in a single pulse. We have shown analogous behavior is also possible in optical storage [24].

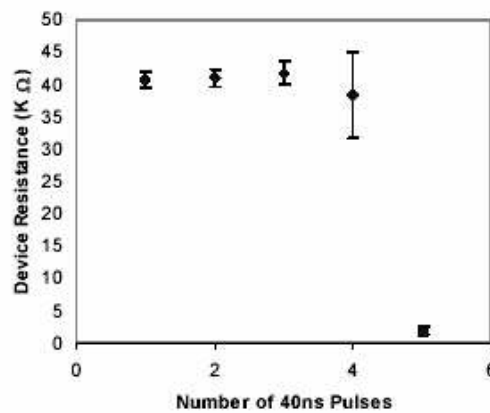


Fig. 9. Threshold firing operation of an Ovonic Cognitive Device.

The simplest model for the behavior is based on incremental crystal growth. After application of each of the information containing pulses there is additional crystal growth. Since after the first few pulses the individual crystallites do not form a conductive path between the two electrical contacts, the resistance is essentially unchanged. Since the inherent conductivity of the material in the amorphous structure is so low, even when the current must pass through only a small distance of amorphous material the device resistance is high. The resistance decreases dramatically when the accumulated pulses reach the time used in the single pulse, because the crystallites reach a percolation limit. In this state, there are paths through the phase change material between the two electrical contacts where current can travel completely through crystalline material. This transition from before to beyond the percolation limit leads to a large decrease in device resistance. By this mechanism information can be passed to the next stage in a cognitive circuit.

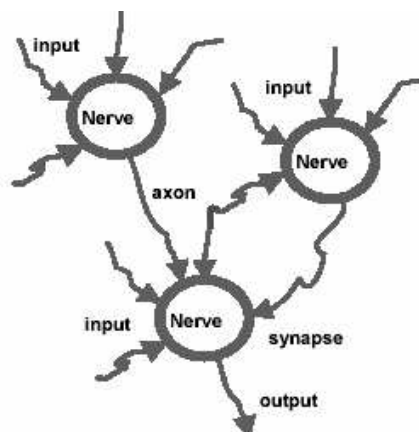


Fig. 10. Biologic neurons. The plasticity of the Ovonic Cognitive device can effectively emulate this operation.

By measuring the device resistance using a comparator and applying successive pulses, the point when the resistance goes below a threshold value can be determined, and then the initial state of the device has been determined. This read mechanism is destructive, but its importance lies in the fact that the read process is also a computation process. The device operation is a semiconductor analog to the biologic processes involved in cognitive process in the human brain, where neurons accumulate input pulses from synaptic connections and then fire when a threshold is surpassed (Fig. 10). The Ovonic Cognitive Devices both store information and process it, leading to application in advanced cognitive computation.

The characteristics of the Ovonic Cognitive device make it possible to fulfill the long-awaited goal of achieving intelligent computing, a new paradigm. While a single Ovonic Cognitive device (or in some cases, two devices) of subnanometer size is able to have many multiple functions such as the demonstration of addition, subtraction, multiplication and division, along with the standard binary activity of any computer, it also can do nonbinary processing, modular arithmetic and encryption as well as factoring. It has the plasticity of a biological neurosynaptic cell and is based on a densely interconnected network of proprietary Ovonic Cognitive Devices where even a single device has such computing qualities [25-27]. Individual Ovonic devices can be readily interconnected to many other such devices in highly dense two-dimensional arrays or in three-dimensional, vertically integrated networks. The threshold level of individual Ovonic devices can be controlled by various means. A remarkable multi-terminal thin-film device -- the Ovonic Quantum Control Device (Fig. 11) -- which can replace transistors as well as adding new functionalities, offers new degrees of freedom to the design of computer architecture. The plasticity of the Ovonic neurosynaptic arrays opens up possibilities of unifying software and hardware. They can also be integrated and imbedded, that is hybridized with conventional silicon circuitry. Very importantly, they are scalable. A single device can operate at extremely small dimensions, for example under 100 angstroms. In fact, its characteristics improve the smaller the dimension. Therefore, as photolithography goes to smaller sizes it is advantageous to our device operation.

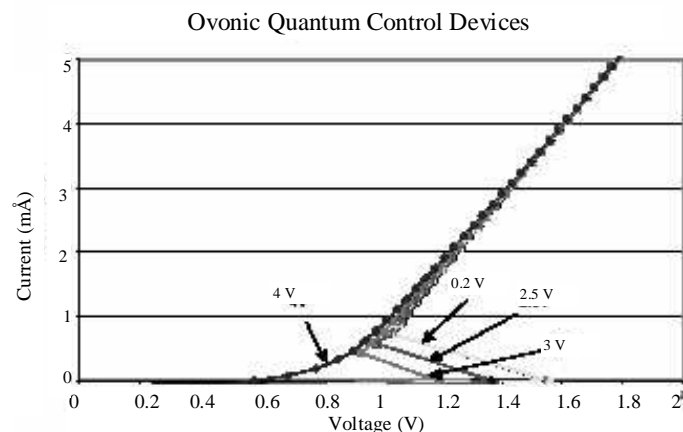


Fig. 11. IV Curves of Multi-Terminal OQCD.

The combination of small device size, speed, intrinsic neurosynaptic device functionality and dense device parallelism and interconnectivity in three dimensions offered by the Ovonic devices provides the Ovonic Cognitive Computer with a functionality and highly parallel mode of operation that follows the neurophysiological activity of the biological brain. Inherently, individual Ovonic devices within a network are adaptive and can also be configured to function as weighting devices that can be used to control the interconnection strength between Ovonic devices configured to function neurosynaptically. Since the interconnection strength is adjustable, networks formed from Ovonic devices display learning and adaptive properties analogous to those of biological neurosynaptic networks.

The Ovonic device, singly (or in networks), is able to both process and store information in a reconfigurational nonvolatile manner and, as a result, such unique multifunctionality obviates the customary need to separate memory and logic functions in computers. Of great interest is that these

devices also can operate in a manner analogous to the much-talked about quantum computer. They have several important advantages in that they, of course, operate at room temperature and higher, are robust, and they are demonstrable now. In other words, they are real world devices that can be used for various functions, for example, encryption.

5. Summary

Ovonic phase change materials have been designed and engineered into optical storage, semiconductor storage and semiconductor processing devices. Work is also ongoing building optical routers using phase change materials, and with the practical realization of so many types of devices the future portends rapid expansion of Ovonic devices and products.

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