The Basis for Electronic Mechanisms in Ovonic Phase Change Memories

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ABSTRACT

Ovonic phase change devices, both optical and electrical, have progressed impressivley since my inventions at ECD in the early 1960's. Researchers around the world are now detailing the major characteristics of devices outlined in my early work. The full potential of these devices is nearing realization with the increasing acceptance and exploitation of electronic mechanisms. Since people are increasingly using its electronic nature I will discuss the electronic mechanism that underlies the electronic nature.

Key Words: Ovonic, phase change, electronic, lone pairs

1. INTRODUCTION

It is not only an honor but such a pleasure to give the keynote at this historic 10th anniversary E*PCOS meeting. Phase change memory and switching devices have been an important part of my research for over 50 years. I would like to start with a little history of the conferences, briefly describing some important points. It is impossible for me to review and summarize today all of the important advances of this very active and successful field. I would instead like to highlight some recent work that I find particularly interesting. I will discuss the high amount of interest that is being generated by the various teams, for example, in Japan, Germany, the US, Korea, Italy, the UK and many other countries and many large companies, such as IBM, Samsung, Micron, etc. that are working in the field and for whom I have high regard. Then I would like to discuss my favorite subject, the electronic nature of our Ovonic devices.

2. HISTORY OF E*PCOS

First, the history. The several groups in Japan that were doing commercial development formed an industry-specific series of PCOS (Phase Change Optical Storage) conferences starting in 1990 with the first meeting at Iwate University. E*PCOS originated as an expansion of the Japanese PCOS Conferences. We owe very much to our Japanese colleagues and collaborators who contributed so much to the commercialization of phase change optical storage and who started PCOS. In 1996, featured speaker Professor Okuda presented a paper, "Optical Memory of Chalcogenide films: From S. R. Ovshinsky to Present Studies."

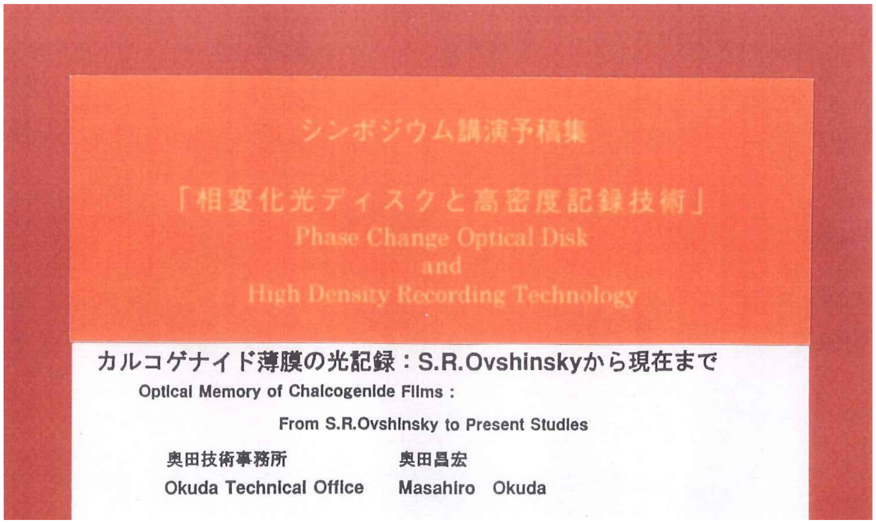
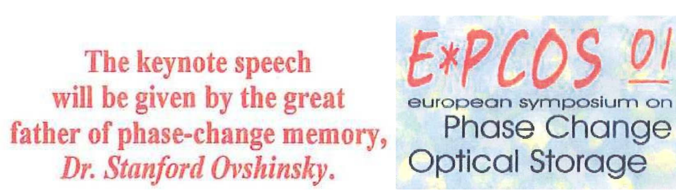


Figure 1. *Brochure for PCOS 1996*

I had my first opportunity to attend a PCOS conference in 1997. Figure 2 shows the group attending - over 100 people representing over 40 companies. They didn't all fit in the photograph so two group photos were taken. It was a marvelous meeting culminating in a typical Japanese bath. We owe much to our Japanese colleagues and collaborators for all their contributions to the field.

In 2001, key individuals in the industry from Japan and Europe started a European version of the conference. The size of the group was intentionally limited so that the attendees could better get to know one another, which has facilitated excellent discussions.

Announcement of the first E-PCOS



By 2004 the application of phase change to electrical memories was expanding dramatically and so the name was changed from European Phase Change Optical Storage to European Phase Change and Ovonic Science. This suitably encompasses a complete range of science of these materials and devices. Presently the conference is primarily focused on papers on electrical devices including electronic mechanisms such as shown in superlattices.

> E*PCOS 04
> European Symposium
> Phase Change and Ovonic Science
>
> Date: March 1st, 2004
>
> To: Dr. Stanford R. Ovshinsky
>
> Dear Dr. Ovshinsky-san
>
> As you know, phase change technology has made a paradigm shift from a magnetic tape to DVD disc, and furthermore is now expanding to an electronic memory device known as Ovonic device. Consequently **E*PCOS** now stands for "**the European Symposium on Phase Change and Ovonic Science".**
>
> The **E*PCOS** program committee would like to call you to be a **Key Note speaker** at the coming **E*PCOS 04.**

I am very happy that meetings are now becoming less focused on the thermal nature of the mechanisms that were attributed to Ovonic Phase Change devices to a much more interesting discussion of the unique electronic nature of the chalcogenide-based semiconductor materials and devices including the all-electronic Ovonic Threshold Switch and the electronic nature of Ovonic Phase Change Memory which we proved long ago [1].

Now we have reached the 10th E*PCOS conference. With the successes of the meetings, the contributions increasingly come from many different countries.

3. RECENT DEVELOPMENTS

One fascinating contribution is the work of Alexander Kolobov, Paul Fons, Junji Tominaga and their team. They deduce from their experiments that we are dealing with a phase change of a very novel kind and that is truly a paradigm shift. The phase change they propose is not necessarily classically speaking, a result of melting, crystallization, or fast quenching into an amorphous structure from the melt but a much more subtle change in structure of a solid - a small shift in the bonding configuration of germanium atoms in a basically rigid Ge-Sb-Te structure without rearrangement. The two states show amorphous and crystalline characteristics and the mechanism allows for fast and very reproducible switching with low energy pulses. This appears to be a novel kind of phase change! Kolobov and his collaborators deduced this from EXAFS fine studies measuring nearest neighbor distances between atoms in the crystalline and amorphous phases [2-4].

As a consequence of the spectrum of bonds in these materials and their natural distortion it has been found possible to initiate non-thermally the phase transition from crystalline to amorphous by rather weak light that excluded the conventional thermal path through melting [5].

Kolobov and Fons utilized these concepts by constructing superlattices with the c-axis of a hexagonal Sb2Te3 layer aligned with the 111 direction of a cubic GeTe layer. The superlattice allows Ge atoms to switch between octahedral sites and lower-coordination sites at the interfaces. Such interface phase-change memory allows data storage with faster switching speed and reduced switching energy [6-9].

The other work that struck my interest is that of Matthias Wuttig who found evidence for an Anderson transition from a non-metallic to a metallic conductivity state in the phase change material GeSb2Te4 [10]. The Anderson transition accompanies a change from a less ordered crystalline structure to a more ordered structure that is obtained at higher anneal temperatures. He recognized the possibility of making multistate memory devices from these crystalline materials, devices that can be programmed to different multiple resistance states. We also considered and patented such materials and devices for electrical [11] and optical applications [12].

So we first learned about a novel phase change, and superlattices and now the possibility of programming electrical memory devices without leaving the crystalline phase. This field is really exciting and it shows the great creativity of these scientists.

4. ORIGINS

Here I take a brief detour into the past, because for me the future is based on the past. The foundations of my work in multi-element atomic engineering of amorphous and disordered materials started with my investigations of brain function in the 1950's, moving on to inventing semiconducting devices that have similar and important kinds of functionality. My groundbreaking patent was filed in 1961 [13], and IBM was an important licensee in 1972. In 1964 I made my first of many publications in the technical journals [14] and in 1968 my Physical Review Letter was the first of many in the scientific journals [15]. My early work on optical memories was disclosed in a patent application in 1968 [16] and then announced in the Annual Report of ECD, at a meeting in Japan, and at the Gordon Conference, all in 1969.

Over 20 years ago, we made both optical and electrical multistate memory devices using GeSb2Te4 and related alloys which crystallize first in cubic and at higher temperatures in hexagonal form [17]. The resistivity drops continuously with increasing anneal and a semiconductor to metal transition is observed. We discussed shifts in the Fermi Level that accompany different amounts of order in the crystalline state, manifested as changes in resistivity. We also showed memories based on transitions between amorphous and cubic crystalline structures, achieved by differing volume fraction ratios. In this case each resistance state can be programmed with a specific voltage pulse regardless of the previous memory state. Since the reflectivity changes too, an optical multistate memory device can be made. Later we made devices that could be programmed electrically and read optically, and vice versa [18].

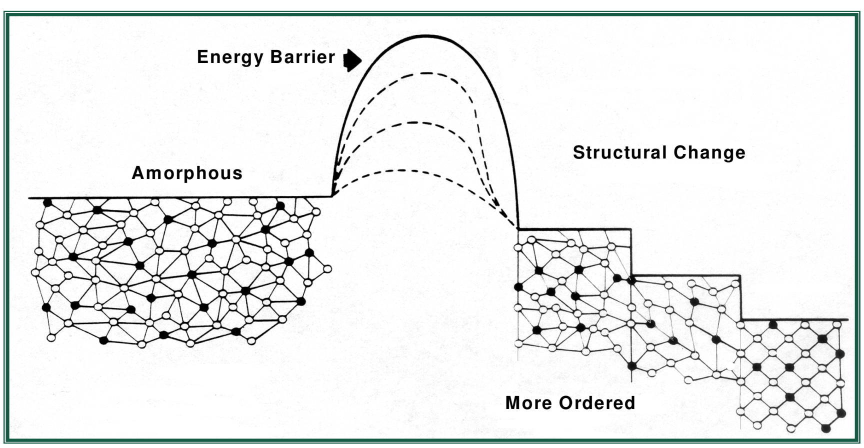


Figure 5.

In Figure 5 from 1973, I show the energy barrier that provided stability in amorphous structure [19]. The energy barrier can be reduced by any of the following-applied singly or in combination: light, heat, electric field, chemical catalyst and/or stress-tension pressure. Transformations in amorphous materials produce changes in: resistance, capacitance, dielectric constant, charge retention, index of refraction, surface reflection, light absorption, transmission and scattering, differential wetting and sorption and others, including magnetic susceptibility.

I also show in the figure the ability of the material to exist in different levels of order in the crystalline state. Each of these has detectably different electrical characteristics and so could be used in a multilevel electrical memory. However, we considered that two key properties of an electrical memory device were reversibility and direct overwrite. A device based only on crystalline states would be difficult to program in opposing directions; obtaining increasing order is straightforward but decreasing the order likely requires going back through an amorphous structure. Direct overwrite is the ability to attain any available state regardless of the starting state in a single application of energy. A crystalline-only device would require an erase step prior to reprogramming.

5. THE UNIQUENESS OF CHALCOGENIDES

Now I wish to address a very different but fundamental question: Why do all phase change materials contain a predominant amount of group VI elements such as Te? Why are they all chalcogenide alloys and what is so special about chalcogenides? The physics of Ovonic threshold and memory devices based on the amorphous materials provides degrees of freedom of atomic design and is related to stereochemistry and polymer science. It depends on the length of chains and size of rings, number and strength of cross-links, strength of bonding configurations and the spectrum of lone pairs.

Lone Pair elements (Te and Se) are based upon entirely different physics than conventional silicon. These properties make the group of chalcogenides a unique type of semiconductor. In the Ovonic Threshold Switch material, the number and strength of cross-links assures structural integrity, while non-bonded and weakly bonded lone pairs are excited by the electric field and form a high-current electronic plasma.

Lone pairs are important structurally, chemically and electronically. They influence the conformation/configuration of a molecule by exerting strong repulsive forces on the electron pairs in neighboring bonds and on other lone pairs. The strongest repulsions are lone pair - lone pair, then lone pair - bonding pair, and the weakest are bonding pair - bonding pair. Since lone pairs are not tied down into a bonding region by a second nucleus, they can contribute to moderately low energy electronic transitions. Therefore light and electric fields can couple to lone pairs.

The chalcogen elements have four outer p-electrons. Only two of them are used for their two-fold bonding. That leaves a non-bonding lone pair. These lone pair electrons overlap and form a valence band. This contrasts with most other covalently bonded semiconductors whose valence band is formed by overlapping bonding orbitals. In chalcogenides the lone pair orbitals form the valence band. These lone pairs are ready to form defect bonds allowed by the open structure of amorphous chalcogenides. These native defects, called valence alternation defects, have a negative correlation energy – another unique feature of amorphous chalcogenides. Their unique defect chemistry causes the Fermi level to be in the center of the gap between the valence and the conduction bands regardless of some additives or impurities. This guarantees the reproducible high resistance state of the amorphous phase. This is not a trivial feature. It is essential for our memory devices. It is a property unique to chalcogenides and not shared by other covalent semiconductors.

The lone pair electrons and valence alternation defects pairs play important roles in electronic switching of these devices, which I have no time to discuss here in detail. We are aware of the fact that a good fraction of the tellurium in many phase change materials is 3-fold coordinated, but there are enough others which can form negative correlation defects to pin the Fermi level in the high resistance state.

6. NEXT GENERATION DEVICES

A major reason the Ovonic chalcogenide devices are being commercialized is that they can be scaled to smaller sizes, hence larger array densities, than silicon devices. If silicon transistors are used as the access devices, however, the array density becomes limited by the size of the transistor or diode needed to provide isolation between devices when addressing each memory element. Now device developers are using the Ovonic threshold switch as the isolation element [20]. Not only does this provide the current density needed for programming in a small size (the allowable current density of the devices are 50 times higher than CMOS transistors) but it also simplifies fabrication. In essence, just a single layer of the chalcogenide-based threshold material is placed adjacent to the chalcogenide-based memory material layer. Both can be patterned together in a single step. Further, the combination of memory and access elements both formed using thin-film deposition processes opens the door to three-dimensional memory arrays that can have even far higher storage densities.

Ovonic multi-state phase change storage devices can be used singly and together in circuits to provide a huge range of capabilities. They can adapt some algorithms of quantum devices – ideal for factoring. They can perform simple mathematical functions such as addition, subtraction, division, multiplication. Plus, they have huge parallelism and can be used for weighted circuit interconnections. We have described a search engine based on this architecture that is not just matching, but intelligent; where the circuit learns as you search using associative capabilities.

Ovonic single state and multistate devices have the same properties as neurons and biological cells. The output of a switch fires when the threshold is reached by summing the inputs, and it does this instantly, continuously and reversibly. The Ovonic Cognitive Device does this through accumulation of input over time. This is the basis for a truly biomemetic device and circuit. These circuits are comprised of Ovonic memory devices used in two different programming modes. The first, shown in figure 6, is the accumulation mode. Here we use multiple identical low-level pulses. The first few pluses have insignificant effect of the device resistance, and then suddenly the resistance drops to a very low level. This mode is functionally equivalent to neuronal firing in a brain.

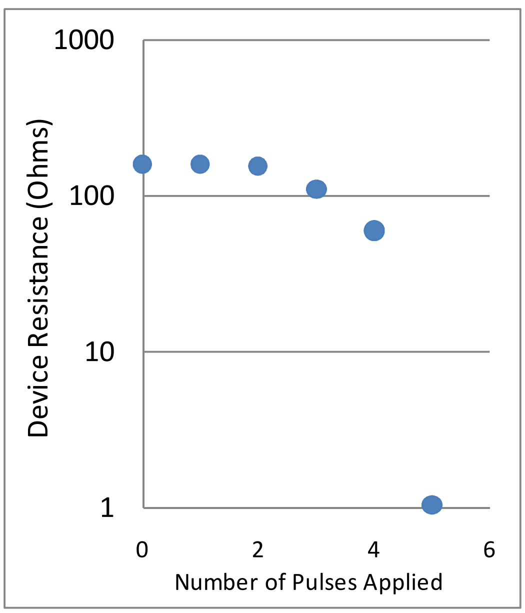


Figure 6. *Accumulation mode of Ovonic memory devices*

The second programming mode is conventional multi-level programming as shown in figure 7. Here, a single pulse of a selected amplitude will cause the device to be in a specific resistance state. Larger amplitude pulses will cause the device to be in a higher resistance state. These devices are used for interconnections between neurons, controlling the amplitude of the input pulses, and therefore the relative weight between inputs to the accumulation-mode devices.

The biological inspiration for a partial circuit of these devices is illustrated in figure 8, where the multistate level devices have the role of the weighted synoptic inputs and the accumulation-mode devices used as the nerve cells.

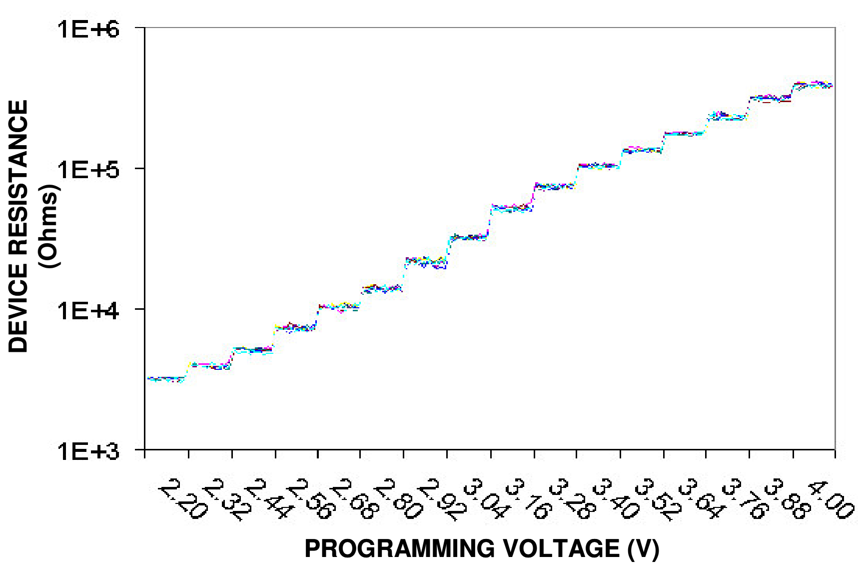
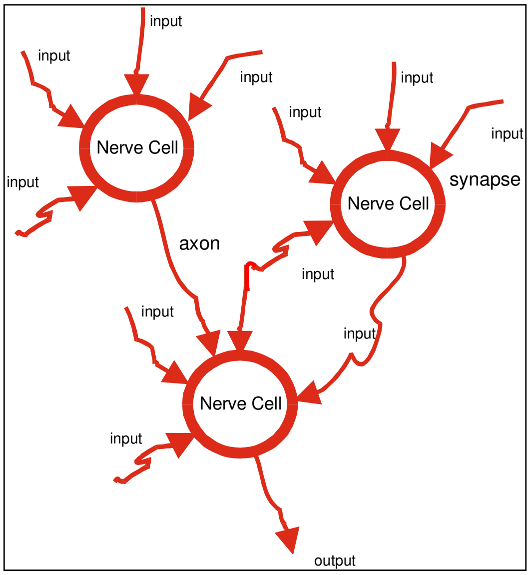


Figure 7. *Multi-level programming of Ovonic memory devices*

Figure 8. *Biological neural network*



We have expanded the Ovonic Threshold Switch to make three terminal control and processing devices. Addition of a third electrode between the conventional two electrodes gives control of the threshold switching voltage. Quantum effects in the space charge region can be exploited for further functionality

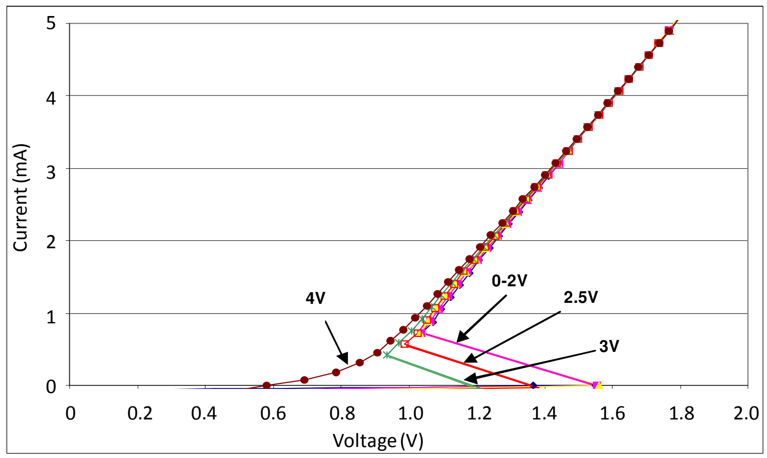


Figure 9. *I-V curve of the Ovonic Quantum Control Device*

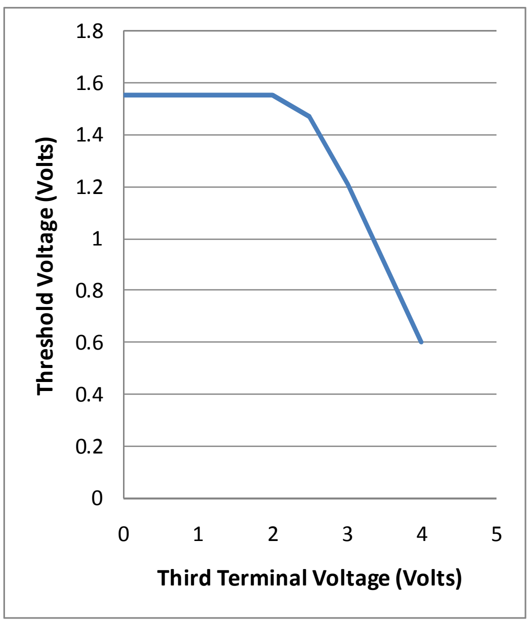


Figure 10. *Threshold voltage of the Ovonic Quantum Control Device as a function of voltage applied to the third terminal*

7. CONCLUSION

My work on chalcogenide devices for electrical and optical applications is a highlight of my life. Starting with my studies of brain function in the 1940's and 1950's [21, 22] and inventing semiconductor materials that can be used to emulate biologic function has evolved into phase change optical disks, semiconductor memories, and increasingly toward cognitive memories. The advances toward utilization of the electronic mechanism will result in faster devices with lower programming energies. I thank all who have contributed to the advancement of this field, and to the people who make conferences such E*PCOS a possibility and reality.

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9. BIOGRAPHY

Stanford R. Ovshinsky has dedicated his life to creating an entirely new area of physics and materials science, providing innovation in atomic engineering of amorphous and disordered semiconductors. In 1960, he and his late wife, Iris, founded the company Energy Conversion Devices, Inc. (ECD), to further develop and apply his inventions to the fields of information and energy creating a new field known as "Ovonics," attracting many scientists and technologists, resulting in unique switching devices, phase change memories, optoelectronic copying, and flat-panel liquid crystal displays. He has focused on using the Ovonic phase change memories and Ovonic threshold switches for 3-terminal devices and cognitive computing. He holds over 400 U.S. patents, resulting in basic new approaches to the uses of solar power and hydrogen fueled vehicles. His battery technology enabled electric and hybrid vehicles. His patents for a system that allows photovoltaic solar panels to be manufactured in long continuous rolls provided a revolutionary leap for solar energy. He has formed a new company named Ovshinsky Solar LLC in order to accelerate his work in energy, leading to basic solutions for pollution, climate change gases, and the need for oil. He is now making possible photovoltaics at a lower cost than burning fossil fuel and advanced chalcogenide devices. He has authored well over 300 scientific papers, and has received global recognition for his discoveries, including the Diesel Gold Medal for Invention, presented by the Deutscher Erfinderverband (German Inventors Association), for Ovonic Switching and his work in neurophysiology, the 2005 Innovation Award for Energy and the Environment by *The Economist*. He was named "Hero for the Planet" by *Time* magazine and with Iris named Heroes of Chemistry by the American Chemical Society. He has numerous honorary degrees, most recently receiving an Honorary Doctor of Science from the University of Michigan (2010), and is a fellow of the American Physical Society and the American Association for the Advancement of Science.