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Past & Present

The science of atomic engineering of chalcogenide glasses

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We briefly describe how science, invention, and technology affected and stimulated an unexplored field of material science, disordered and amorphous semiconductors, which resulted in unexpected and useful new physical, electronic, and stereochemical mechanisms. Our special focus is on chalcogenide glasses and the unique electronic devices that are made from these materials.

1 Introduction We all want to honor the memory of Boris Kolomiets. His work in the field of chalcogenide materials deserves the recognition and the praise we all owe him. My best way of honoring him is to continue as if he is still among us, remembering the frank discussions we engaged in when we were together, always in friendship and always stimulating.

We first met at a small glass meeting (Fourth Symposium on Vitreous Chalcogenide Semiconductors) in Leningrad in 1967. After my talk on switching and memory effects in amorphous chalcogenides he said to the audience, “this work will transform the amorphous field” whose progress to date he noted is slowly rising in a horizontal line but will rapidly rise to an almost vertical future (he drew this on the blackboard). His prediction fortunately came true. The recognition that he gave to our work then showed a generosity that was very much appreciated. The rest of that meeting was devoted to the point that chalcogenide glasses were considered useful for infrared windows and other optical applications.

Of course, one did not expect these low mobility semiconductors to become useful for high current fast switching and for electronic and optical computer memory elements.

Boris Kolomiets was not familiar nor could he understand how an inventor could operate in the United States, and he certainly was not familiar with my viewpoint that I did not recognize human imposed borders on scientific disciplines. He was accustomed to thinking in terms of state laboratories and academia. I remember telling him that nature did not make disciplines, humans did and that clearly the development of the amorphous field was a unification of all of the various disciplines. It is physics, chemistry, and materials science all together expressed in unique devices. My driving force was to atomically engineer, i.e., invent, new physical electronic and chemical mechanisms that required personal intuition and would result in new science. Obviously this meant there would be unique functionalities that would be best expressed in a device form. Of course quantum mechanics and modern day semiconductors go hand in hand. What I was working on was not quantum mechanics based upon crystallinity from which the transistor originated but quantum mechanics in a field that was considered Schmutz. Most scientists expressed doubt that quantum mechanics could deal with disordered materials at all. Despite that, and very early in the 1960s, I first named what is now the Ovonic device the Quantrol device.

One can understand why the topic of this paper reflects the fruitful symbiosis of science, invention, and technology in opening a new field of materials, disordered and amorphous semiconductors, in particular the field of chalcogenide glasses and the remarkable mechanisms that can be atomically designed into them. I will start with a brief review of the unexpected features of these synthetic materials and then will discuss the present large and important activity in the field of phase change memories.

2 Special features that can be designed into chalcogenide glasses and devices Unlike the common semiconductors, crystalline silicon, and germanium, taught in all textbooks in the 1960s, the chalcogenide glasses were not just new semiconductors, they demanded new concepts for understanding their properties and new preparation techniques for their reproducible manufacture. Device development fertilized the research of the materials and *vice versa*. New mechanisms gave unusual functionality to devices that opened up technologies which are different from and complementary to the crystalline semiconductor technologies.

Among the new concepts were the mobility gap, mobility edges, the realization that the non-bonding p-orbital electrons, the lone-pair electrons, form the valence band of the chalcogenides, and the concept of covalent connectivity and various forms of controlled/design cross-linking for either stability or for reversible phase change of the vitreous or amorphous structure. I realized and utilized the structural and compositional degrees of freedom available in non-periodic materials for atomic and orbital engineering of the compositions of chalcogenide glasses to produce desired device performances, but more of that in the later sections.

My late dear wife, Iris, and I co-founded our company in Detroit, MI and for a brief time at the very beginning we called it Energy Conversion Laboratory. Our company, which we later named Energy Conversion Devices, became the center for material science of disordered materials with scientists visiting us from many universities and notably Sir Neville Mott from Cambridge whose support continued until the end of his life. What was heart warming as well were the many great scientists who became my close friends, confidants, and supporters, such as I. I. Rabi, Bob Wilson, Linus Pauling, and John Bardeen. And the very gifted individuals that became my colleagues and collaborators, particularly Hellmut Fritzsche who was very highly recommended to me by John Bardeen, and of course, David Adler, Morrel Cohen, Artie Bienenstock, Heinz Henisch, and so many others including those whom we taught and raised in our laboratory.

It was a glorious time and the contributions that were being made by our team supported our growth into other important fields. It was very helpful to have such a culture in the various stages of our growth.

The importance of the non-bonding lone-pair electrons for creating useful chalcogenide devices cannot be overstated [1]. They form the basis of the unique defect chemistry of chalcogenide glasses; the natural defects are charged valence alternation pair defects with negative correlation energy. They pin the Fermi energy close to the center of the mobility gap of these materials guaranteeing the high resistance of the OFF state of the threshold and memory devices, something we take for granted but a feature not easily obtained in crystalline semiconductors. The lone-pair electrons play a crucial role in the switching of threshold and memory devices and for the unusual solid state plasma state which provides the unusually high current densities of the conducting state of these devices after switching from their high resistance state as explained in the following.

3 Threshold switch A look at the periodic table brought the groups IV, V, and VI elements to mind, but what I needed were thin films and not crystals. Pure elements were useless but amorphous films could be made in many different compositions. My driving motivation since the early 1950s and particularly 1955 was my work in neurophysiology where I worked to develop an inorganic analogue of a neuron and its synapses. In order to do that I really wanted to concentrate my activities to very small dimensions and very thin devices now called nanotechnology.

Neurons certainly are not crystalline. I understood from my results in the 1950s that this could lead to important new areas of information through new concepts and that these concepts could have far reaching consequences beyond neurophysiology. That is why Iris and I named our company Energy Conversion Devices in 1959–1960. We viewed energy and information as the twin pillars of our economy. They are opposite sides of the same coin as I felt information is encoded energy. It is very important to understand that amorphous and disordered materials are making very important contributions to solving the energy problems of our times.

In those early days my tools were simple, an oscilloscope, various meters, and power supplies. But most importantly I relied on my feel and understanding of elements and the possibility of their preferred bonding in response to new degrees of compositional, translational, and positional degrees of freedom. This meant in terms of the threshold switch assuring the structural integrity of the amorphous material under severe conditions of high field switching and high current densities, which also meant materials without electrodiffusion and non-reacting ohmic contacts able to inject the carriers needed to sustain the unusually high current densities of the ON state after switching. Fortunately, one has the freedom to choose and change the composition of glasses and amorphous materials. It was very helpful that the Fermi level was pinned in the gap which I attributed at the time to the compensating quality of the materials which would make for an inherently intrinsic OFF state. I wanted to be able to control the threshold and to achieve the orders of magnitude increase in current densities equally important in both the threshold switch and the phase change memory.

What was absolutely important was being able to invent new mechanisms to achieve new physical and electronic mechanisms that would achieve my purposes, i.e., atomic and orbital design of multielements.

What has bothered me despite the many talks I have given and papers I have written, is that those early scientists would use contact materials that interacted with the materials permitting the materials to be affected by moisture and oxygen, a deadly combination. One would not treat crystalline material to such unwanted contamination.

Briefly, the threshold switch consists of a thin film of a well cross-linked chalcogenide amorphous semiconductor between two non-reacting contacts. The elements cross-linking to tellurium were primarily silicon, germanium, and arsenic and the contacts were carbon. When an applied voltage of either polarity reaches a critical threshold field of a few 10^5 V/cm, the high resistance OFF state switches in less than picoseconds to an unusual and conducting ON state. This ON state has a dynamic resistance close to zero at a voltage drop which is close to the band gap of the material divided by the electronic charge. The relatively small value of this voltage and the fact that it drops adjacent to the injecting contacts allows rather large ON state currents without thermal damage of the device. The voltage drop along the ON state current path is very small in comparison. The charge plasma of the ON state current is confined in a channel between the electrodes whose diameter adjusts to the current. Below a certain holding current value recombination dominates injection and the device returns to its original high resistance state. A demonstration of the reliability and life of the threshold switch is still running in my basement where a device built and attached to a 60 Hz AC circuit and an oscilloscope in the mid-1960s is still switching 120 times per second after more than 45 years. I have another one in my office that has been operating for the same length of time.

4 Memory devices It is one challenge to design a chalcogenide glass that retains its structure and composition under the stresses of high electric fields, high current densities, and heating cycles. It is easy to find glasses that crystallize. The material engineering task for phase change memories however, is more difficult. One needs a material whose amorphous and crystalline structures have nearly the same energy, which undergo phase changes very fast and with minimal energy input and which do not phase separate in the process [2, 3]. And like the threshold switch one must absolutely use non-reacting electrodes.

Problems of electrodiffusion and contact reactivity were solved for the threshold switch by using carbon. An additional factor to be considered is the contraction and expansion accompanying the phase change. My phase change alloys proved to be the first which fulfilled these conditions. The electric memory devices withstood more than 10^{12} phase changes (which is not its limit by the way) between the amorphous and crystallized states without fail. Similarly long cycles were obtained by Panasonic with our optical disc memories. These successes resulted from my first choices of phase change materials, alloys close to the GeTe eutectic composition with appropriate additions of cross-linking elements such as antimony to promote amorphization of the easily crystallizing eutectic. In other words, many fewer and weaker cross-links than used for the uni-phase switching alloys.

The field of optical and electrical phase change memories has taken a strong new momentum during the past years which is thought to be coming to international maturity. Yet I notice that the principal ideas of material design and science have remained the same for almost 50 years and I can say that there are so many new generations of threshold and phase change devices yet to be commercialized that the science and technology is still truly young.

5 Final remarks Since the early days I sought to use science and technology to be helpful to the entire globe establishing fraternal scientific relationships with other countries even though the cold war was still in place. I not only gave talks in the Soviet Union, but showed my latest devices and sought to help my colleagues to have their rightful place. Unfortunately Kolomiets, who was raising and has raised so many wonderful scientists that are now still contributing to our field was not able to attend our international meetings.

This early isolation resulted in many missed opportunities. I knew he felt badly about this. I also knew that national pride in the case of our Russian colleague was an issue of not only science but of idealogical politics. We are again in the norm of international fraternalism, collegiality, and collaboration that is essential for science. Science is the basis of our civilization. Let us all learn lessons from the past at a time when civilization is again threatened. Our planetary problems know no barriers.

Let us all use this occasion of honoring Boris Kolomiets to remember that the desire to change the world for the better can only become actuality through the wonderful area of science and technology. None of us should think of technology as something different than science. Technology is the most important expression of science. Innovation is still the most powerful tool in the advancement of science. There is no national science only science with its unifying beauty.

References

[1] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).
[2] H. Fritzsche and B. Schwartz (eds.), Stanford R. Ovshinsky: The Science and Technology of an American Genius (World Scientific Publishing Co. Pvt. Ltd., Singapore, 2008).
[3] T. Ohta and S. R. Ovshinsky, Phase-Change Optical Storage Media, in: Photo-Induced Metastability in Amorphous Semiconductors, edited by A. V. Kolobov (Wiley-VCH, Weinheim, 2003), p. 310.