Chalcogenide Glasses: A Decade of Dissension and Progress

Crystalline semiconductors first emerged as viable candidates for electronic devices when researchers changed the focus of their attention from the intrinsic properties to the role of various structural imperfections in controlling the electrical and optical behavior of these materials. Now there seems to be a similar shift under way among those studying a class of amorphous semiconductors known as chalcogenide glasses.

Chalcogenide glasses live up to their classification as amorphous or disordered materials in more ways than one. For starters, the disorder extends to their contentious history, due in no small part to one man and his efforts to inhabit simultaneously the worlds of the scientist and the entrepreneur struggling to keep a small company afloat.

The unusual glasses take their name from the group VI elements of the periodic table (chalcogens), which they contain in abundance. Nearly a decade ago, these controversial materials were the subject of spectacular assertions by Stanford Ovshinsky of Energy Conversion Devices (ECD), Troy, Michigan, that they could transform the electronics industry. But investigators are only now obtaining the understanding needed to transform the chalcogenide glasses into commercially viable entities in the form of a computer memory. And this will probably have an impact much more modest than once claimed.

This is the second of two Research News articles on amorphous semiconductors.

The atomic structure of the chalcogenide glasses is significantly different from that of other amorphous semiconductors. Amorphous elemental semiconductors, such as silicon, are disordered in that the atoms do not sit precisely on the sites of a crystalline lattice, although, when viewed at short range, the environment around a given atom is only slightly distorted as compared to the crystalline form. Chalcogenide glasses, however, tend to be polymer-like and do not have a rigid three-dimensional structure. As amorphous materials, they can be quite "floppy"—that is, a given species of atom can find itself in a wide variety of atomic environments and needs relatively little energy to move from one environment to another. One effect of the nonchalcogen atoms in the glass is to modulate the ease of these local structural changes or floppiness, according to the ideas developed by Ovshinsky.

Although research on amorphous chalcogenide glasses had been reported as early as the mid-1950's, the field livened up considerably in late 1968. At that time, Ovshinsky, who had no formal college education, had himself been studying amorphous materials for 10 years. He then published a low-key report of a phenomenon called switching in chalcogenide glasses and held a press conference, in which he claimed that chalcogenide glass switches promised practical benefits beyond what transistor technology could offer. Impressed by the article in the prestigious journal (*Physical Review Letters*) and the highly enthusiastic pronouncements of some high-caliber physicists, reporters wrote lengthy articles about the new materials.

Ovshinsky's Role

An uproar ensued in the scientific community, characterized in part by acrimonious exhanges at meetings where chalcogenide glasses were discussed (*Science*, 15 August 1969, p. 673). Among the principal objections was that the switching phenomenon was not new at all but was, at that time, already several years old. Moreover, it was said to have been observed in numerous types of materials, of which the chalcogenide glasses were only one. As one scientist said, "Almost anything will switch under the right conditions." Thus, many felt that Ovshinsky was palming off as revolutionary something already well known. The widespread publicity given to what became known as the Ovshinsky effect only added fuel to the fire.

The contention of Ovshinsky and several academic scientists who consulted at his company has always been that the switching phenomenon reported on was in fact a qualitatively new one. But, in retrospect, it appears that no one understood amorphous materials well enough at the time to know for sure.

One outgrowth of the "Ovshinsky effect" uproar was a polarization into two camps over the issue of the mechanism by which switching, which involves a rapid change of several orders of magnitude in the electrical conductivity of a chalcogenide glass when a high enough voltage is applied, takes place. Many initially thought that a thermal mechanism involving heating of the material and a possible structural modification with atomic motion was the explanation. Others, including Ovshinsky, asserted that only electrons were involved in bringing about the change. Often participants seemed more interested in proving themselves correct than in getting at the truth. The answer has commercial implications as well, because a thermal mechanism, as compared to an electronic mechanism, would imply an inherently less stable and reliable device.

During the first years after the press conference, there was a moderate amount of federal support aimed at increasing both the basic understanding of chalcogenide glasses and the performance of devices made from them. But, when progress proved to be equally moderate, funding dwindled to a few basic research contracts. In the meantime, ECD has limped along on a combination of stock sales, technology licensing agreements, and research contracts. It has an accumulated debt of about $20 million and is only now close to having marketable products.

The application of chalcogenide glasses that is closest to commercialization is much more limited than the initial claims for them. Although the application—a kind of computer memory known as an electrically alterable read-only memory—is of considerable interest, it also indicates that the chalcogenide glasses are not yet a threat to crystalline silicon as the foundation of the digital electronics industry. As for Ovshinsky, few any longer doubt his sincerity or that he has made substantial contributions to the field of amorphous semiconductors. He has, however, been unable to shake his image as a promoter.

The current interest in the chalcogenide glasses is that research seems to be entering a new phase in which investigators will better be able to relate materials behavior to specific structural features. What nearly everyone agrees was the turning point that marked the onset of this new phase was a 1975 proposal by Philip Anderson, now at Princeton University. Anderson showed how the disorder characteristic of an amorphous semiconductor could permit two electrons, which would normally be pushed apart by their like electric charges, to coexist as pairs bound to one another. What might seem to be rather esoteric behavior is now considered by many to be one of the keys to understanding chalcogenide glasses.

The first effect of Anderson's proposal was to answer the long-standing question: Why didn't the chalcogenide glasses exhibit any paramagnetic properties? The model of these materials, which was called the CFO model (after Morrel Cohen and Hellmut Fritzsche* of the University of Chicago, and Ovshinsky), seemed to require the presence of large numbers of unpaired electrons that were thought to dominate the electrical and optical properties of the chalcogenide glasses. At low temperatures, the spin angular momenta of the unpaired electrons should have become aligned with an external magnetic field and paramagnetic behavior observed, but none was. By devising a mechanism whereby two electrons with oppositely directed spin angular momenta could coexist as pairs, Anderson explained the absence of paramagnetism—the spins canceled each other.

Robert Street, now at the Xerox Palo Alto Research Center, and Sir Neville Mott of the Cavendish Laboratory, Cambridge, took Anderson's idea a step further by proposing that the paired electrons were not due simply to the disorder of the chalcogenide glasses but were actually specific structural defects. Previous work by Mott had developed the idea that the structure of an amorphous semiconductor, being less rigid than that of its crystalline analog, could locally be distorted in such a way that all atoms of a given chemical species would use all their valence electrons in bonding. Occasionally, however, because of missing atoms or insufficient distortion, some atoms would not be able to use all their valence electrons. The leftovers were called dangling bonds. Each dangling bond contains one electron and is regarded as electrically neutral.

Street and Mott's suggestion was that pairs of positively and negatively charged dangling bonds were responsible for the paired electrons. The positively charged dangling bond has given up its electron, which has been accepted by the negatively charged dangling bond. The negative bond now contains two electrons with opposite spins. A change in the bonding of the atoms near the dangling bonds was postulated to release enough energy to overcome the repulsive force between the two electrons on the negative dangling bond.

An important experimental verification of the general features of these ideas came from Stephen Bishop, Ulrich Strom, and Craig Taylor of the Naval Research Laboratory. These researchers observed a phenomenon called optically induced electron spin resonance. In their experiments on the amorphous compounds As_2Se_3 and As_2S_3, which are often used as models for chalcogenide glasses in place of the more complicated multicomponent materials found in Ovshinsky's switches, the investigators first shined a red (As_2Se_3) or green (As_2S_3) light on the materials, which were maintained at cryogenic temperatures. After this light was absorbed, they then observed the spin resonance.

Since spin resonance only takes place with unpaired electrons, the interpretation was that the absorption of the light was causing unpairing of the normally paired electrons. Absence of an optically induced spin resonance would have meant that there were no paired electrons and researchers would have been thrust back to the frustrating condition existing before the paired electron theories emerged.

Lone Pairs a Big Difference

A second key concept, in addition to that of paired electrons, was introduced even earlier in 1972 by Marc Kastner, now at the Massachusetts Institute of Technology (MIT). Kastner pointed out that not all of the outer shell electrons in the chalcogen elements were used up in bonding. Chalcogens usually form chains and thus bond with two nearest neighbors, but they have four electrons that could be used to form chemical bonds. The two nonbonding electrons were called lone pairs, and their existence marked a major difference between the chalcogenide glasses and other materials.

Subsequent research by Kastner, David Adler of MIT, and Fritzsche of Chicago showed that, because of the lone pairs, the neutral structural imperfections with the lowest energies are not dangling bonds. Instead, the lowest energy defects, which are the most stable and hence most likely to exist, are related to changes in the coordination of the chalcogen atoms—that is, a change in the number of neighboring atoms with which bonds are formed. The most likely defects of all, however, are charged and consist of a positively charged chalcogen with three nearest neighbors and a negatively charged chalcogen with one nearest neighbor, as with the dangling bond model.

The lone pair concept was also a boon to Ovshinsky, who found in it the first concrete demonstration that chalcogenide glasses were in fact fundamentally different from other materials that exhibited switching. Because of his lack of formal training, Ovskinsky has had to rely on his academic consultants to translate his insights into acceptable scientific language. Recently, for example, Melvin Shaw and his colleagues at Wayne State University, together with Adler, have used the Kastner-Adler-Fritzsche model of defects in chalcogenide glasses, together with Ovshinsky's ideas, as a basis for a specific electronic mechanism for the switching.

Numerous experiments by, among others, Heinz Henisch and his co-workers at Pennsylvania State University, Shaw and his associates, Gary Vezzoli of the Picatinny Arsenal, and Kurt Peterson of MIT and Adler have claimed to settle the electronic versus thermal switching controversy in favor of an electronic mechanism. A typical cautious judgment is that of Jan Tauc of Brown University, who says that he is confident that switching can be completely electronic because four different experiments of different types all point in that direction. There are, however, those who disagree. For example, Malcomb Thompson of the University of Sheffield writes that, "All is not solved," and that switching will probably be shown to involve thermal effects. Curiously enough, two other holdouts are ex-ECD researchers. Ron Neale, who is now investigating chalcogenide glasses for Harris Semiconductor, Melbourne, Florida, is basing his research on the premise that the mechanism is initially electronic but ends up thermal. And Derek Buckley, now at Perkin-Elmer, thinks that the definitive experiment is yet to be done.

Absence of a universally agreed upon explanation of how the chalcogenide glasses work has not prevented their exploitation in devices. For example, two companies, the Burroughs Corporation and Harris Semiconductor, are working on an electrically alterable read-only computer memory based on one form of chalcogenide glass switch—the memory switch. The memory switch remains in its high conductivity state after removal of the applied voltage, and it returns to the high resistivity state after application of a second voltage pulse. The two states provide a way to store information. Burroughs is working on memory devices by way of a 2-year-old joint venture agreement with Ovshinsky's company, whereby the computer manufacturer took over ECD's memory division. Harris is working independently.

The reason for the memory effect is that, after the switching (whether it is thermal or electronic) takes place, heat

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*Fritzsche is on the board of directors of ECD.

generated by the passage of a large electrical current causes the amorphous chalcogenide to crystallize. It takes a second voltage pulse to melt the crystalline chalcogenide, which then cools so fast that it returns to the amorphous state. A typical composition for a memory switch chalcogenide glass is $Te_{81}Ge_{15}Sb_2S_2$, as compared to $Te_{40}As_{35}Si_{18}Ge_7$ for a nonmemory switch material. It is the absence of substantial amounts of arsenic in the memory material which permits crystallization. The arsenic tends to cross-link the tellurium chains, making the material less floppy.

The same sort of transition can be brought about optically by shining an intense light on the material. A basis therefore exists for potential application of chalcogenide glasses to photographic films because the amorphous and crystalline materials have different optical properties. For example, one form can be transparent and the other opaque. (ECD does have a number of photographic films under development, but the film materials do not necessarily involve either chalcogenide glasses or amorphous to crystalline transformations, according to Ovshinsky.)

There is in fact a wide variety of optically induced structural transitions in chalcogenide glasses that can be reversed by either heat or light in some instances but are irreversible in others. Understanding these so-called photostructural transformations may be the next frontier in chalcogenide glasses, says John deNeufville of the Exxon Research and Engineering Company. One reason for this enthusiasm is that photostructural transformations seem to be naturally related to effects such as the optically induced electron spin resonance first observed at the Naval Research Laboratory and therefore to the structural defects mechanisms devised to account for pairing of electrons.

Recently, for example, Street at Xerox has used the defect models to explain how the absorption of light could lead to a local rearrangement of the bonds between chalcogen atoms in a chalcogenide glass. Street further proposes that this bond rearrangement could account for one particular type of photostructural effect known as photodarkening. In photodarkening, a material like As_2Se_3 will absorb light of a wavelength to which it was previously transparent after first being exposed to light of shorter wavelength.

Energy is where the action is these days, so it is not surprising that one of the more interesting applications of chalcogenide glasses may turn out to be their use as solar cells. However, a recent announcement from ECD is giving some observers a sense of deja vu.

Early this summer, Ovshinsky announced at a press conference in Britain's House of Commons that his company has shown that it can make noncrystalline materials suitable for energy conversion at low cost, and that energy conversion can be a near-term solution to energy production problems. By energy conversion was meant the use of heat or sunlight to produce electricity by way of extremely inexpensive thermoelectric and solar cells.

The basis for this optimism is the demonstration that it is possible to chemically modify the chalcogenide glasses in such a way that their electrical and optical properties could be independently varied by adjusting the concentration of the modifying elements. This ability, which was previously thought to be impossible in the chalcogenides, is akin to the "doping" process whereby researchers can vary the electrical conductivity of crystalline semiconductors over several orders of magnitude by the addition of impurities in concentrations of a few parts per million.

In the present instance, Ovshinsky and his colleagues use considerably larger concentrations of modifying elements, up to 11 percent in the case of $Ge_{32}Te_{32}Se_{32}As_4$, where the electrical conductivity at room temperature could be controlled over a range eight orders of magnitude wide, according to Richard Flasck and his co-workers at ECD.

Reserving Judgment on Solar Cells

In actuality, however, researchers at ECD have not yet reported any working energy conversion devices. What they have shown, in two papers delivered at a recent meeting on amorphous semiconductors, is that by the addition of moderate amounts of transition metals or group IV elements they could vary the electrical conductivity of a wide variety of amorphous materials including, but not limited to, chalcogenide glasses. The ability to modify nonchalcogenides, such as silicon, means that, as with the photographic films, chalcogenide glasses may not turn out to be the best choices for all devices.

Most researchers in amorphous semiconductors are reserving judgment. David Adler, who is a consultant with ECD, acknowledges that solar cells are only a possibility, not a probability. And Gerald Lucovsky of the Xerox Palo Alto Research Center points out that more optical absorption data have to be obtained to verify the general claim that electrical and optical properties can be independently varied, which must be demonstrated if devices are to follow.

Not all of the caution expressed was of strictly the scientific kind, for Ovshinsky, in trying to walk a narrow line between the worlds of the basic researcher and the entrepreneur, seems to have been uncommonly successful in incurring the distrust of the former with his unconventional behavior, despite the endorsements of some respected scientists and a gradually developing acceptance of many of his concepts. Observers, admirers and skeptics alike, shower him with accolades such as "amazing intuitive grasp of science" and admit that "some excellent technology has emerged from ECD." But, at the same time, many of the same observers fault him for often implying or claiming advances for which the publicly available evidence is insufficient. One electronics executive offered the judgment that Ovshinsky, by his tendency to play to the popular press, has actually done himself a disservice because "his effects are real."

Specific models for how chemical modification takes place are just becoming available. Fritzsche in Chicago, who is working on one with Kastner, points out that the method of preparation is one key. In the past, researchers have occasionally demonstrated limited effects of additives on the electrical conductivity of chalcogenide glasses. But Ovshinsky's new materials are made by a process called co-sputtering, whereas previous chalcogenide glasses were made by rapidly cooling a liquid (quenching). Fritzsche explains that sputtering, although it involves vapor species rather than liquid, is effectively equivalent to an exceptionally rapid quench, and the resulting material is even more disordered than usual. This condition changes the electrical effects of the impurities.

Whether a specific structural defect model can be devised to explain chemical modification remains to be seen. In spite of the seemingly great success of defect models so far in explaining a wide variety of chalcogenide glass behavior, there are researchers who are following other lines of thought. David Emin of Sandia Laboratories, Albuquerque, believes he can account for many previous experimental observations without invoking imperfections of any kind, for example. And, while most observers are inclined to believe that the Street-Mott and Kastner-Adler-Fritzsche approaches to defects are in the right direction, they agree that experiments capable of separating models are still in the future.

—Arthur L. Robinson