Glassy Semiconductors Show Switching and Memory Effects

Switching and memory behavior in glassy semiconductors has been reported by Stanford R. Ovshinsky (of Energy Conversion Devices, Inc., Troy, Michigan) in the 11 Nov. issue of *Phys. Rev. Letters.*[1] The report made headlines in newspapers like *The New York Times* and *The Wall Street Journal,* which played up the potential commercial and military applications of Ovshinsky's report.

Other work. Some solid staters, electronics engineers and materials scientists have been talking about the effects for years, but the systems developed have tended to be unstable. Little has actually been published in physics journals. A not necessarily complete list of those finding a switching or memory effect in glassy semiconductors includes A. David Pearson, J. F. Dewald and their collaborators at Bell Telephone Laboratories, B. T. Kolomiets and his colleagues at the Ioffe Physicotechnical Institute, Ovshinsky, David L. Eaton at Corning Glass Works, and William R. Eubank at Minnesota Mining and Manufacturing Co.

Kolomiets has been reporting on electronic conduction in chalcogenide glasses since 1955. (Chalcogenides are compounds containing elements from group VI of the periodic table—sulfur, selenium, tellurium.) In 1963 he and E. A. Lebedev[2] reported switching behavior in glasses of the class $TlAs(Se, Te)_2$. They measured the effect with a thin-film structure consisting of a metallic point contact, glass and a layer of colloidal silver.

In 1962 Pearson, Dewald, W. R. Northover and W. F. Peck Jr[3] reported at two conferences the observation of switching and memory behavior in chalcogenide glasses. They measured current–voltage characteristics when a point contact was applied to a slice (about 0.02-cm thick) of As-Te-I glass with a broad-area low-resistance contact on the back face of the slice. As they increased the applied voltage to a critical value, the material would abruptly switch to a highly conductive state in less than a microsecond.

The current-voltage characteristic was symmetrical in the first and third quadrants; two regions had widely different positive resistance, and at least one region had negative resistance. Fast reversible switching between the two positive states was obtained. Additional studies showed that the low-resistance lines, as well as the high, could be made to pass through the origin of the current-voltage plot, the diode "remembering" in which state it was put for times at least as long as days. Pearson and his collaborators have two patents associated with the work.

Two years later Eaton reported[4] that he, too, found switching behavior in As-Te-I glass and proposed a mechanism to explain the effect.

Eubank holds a patent on switching characteristics of Sb-S-I glass to which silver, copper or indium is added.

Ovshinsky reported that he has found reversible electrical threshold-switching behavior in a broad range of amorphous materials. In particular, he discussed the properties of a glass made of tellurium (48 atomic per cent), arsenic (30%), silicon (12%) and germanium (10%); the device was an evaporated film, 5×10^{-5} cm thick, between two carbon electrodes with a contact area about 10^{-4} cm^2.

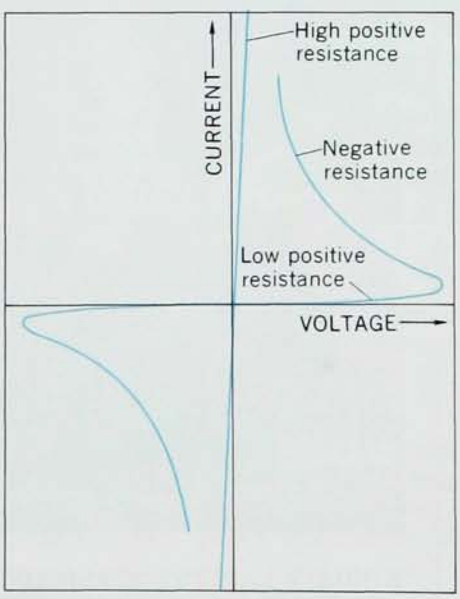
- The threshold-switching effect is demonstrated by the following: As current is reduced below a characteristic "holding current" the system switches back to the original high-resistance state along the load line.
- The current–voltage characteristic is symmetrical in the first and third quadrants, even when the semiconducting materials are varied considerably.
- In the high-resistance state, the sample is ohmic at fields below 1000 V/cm. At higher values dynamic resistance decreases monotonically as voltage is increased.
- When applied voltage exceeds a threshold value, the system switches along the load line to the conducting state. However, the system cannot be held at an operating point between the highly resistive and the conducting state.
- In the conducting state, current can be raised or lowered without significantly affecting the voltage drop.
- Alternating or full-wave unfiltered rectified voltages have been applied to samples for many months without noticeable changes in their characteristics.

By varying the components in the glass, Ovshinsky found a memory effect. He says that after switching from a high-resistance state, structural changes preserve the conducting state even when the current is totally removed. He notes that the material can be reversibly switched back to the high-resistance state by applying a threshold-current pulse of either polarity.

According to Ovshinsky, memory devices have been stored for over five years in either the high- or low-resistance states. Similar devices have been cycled 10^{12} times, he told us.

Ovshinsky has patented the switching behavior and his firm, Energy Conversion Devices, has been marketing the devices.

Why? Despite the great interest in glassy semiconductors, they are not well understood. Theorists are enthusiastically trying to explain how an amorphous material can undergo rapid



CURRENT-VOLTAGE characteristic of As-Te-I glass reported by Pearson, Dewald, Northover and Peck.[3] The group obtained fast reversible switching between the two positive-resistance states.

transition from an insulating state to a conductive state. A variety of models has been proposed, but little experimental verification exists for any of them. —GBL

References

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Is There A New Mechanism For Superconductivity?

The model proposed for the large positive isotope effect that Robert D. Fowler and his collaborators found last year in superconducting alpha uranium (under 10–11 kilobars of pressure) (PHYSICS TODAY, December 1967, page 60) has been criticized by Herbert Capellmann and J. Robert Schrieffer of the University of Pennsylvania (*Phys. Rev. Letters* **21**, 1060, 1968).

The Fowler group at Los Alamos Scientific Laboratory had found that the superconducting transition temperature T_c varied as $m^{2.0}$ for U^{235} and U^{238}; for other known substances T_c goes as m^{α} with α negative or zero. They suggested that the pairing interaction causing superconductivity in alpha uranium is due to an electronic-core polarization involving low lying f states; lighter atoms are more susceptible to lattice vibrations, which would reduce electronic-core polarization.

Capellmann and Schrieffer argue that the Fowler proposal would only account for an α of about 10^{-2}. Assuming that the attractive interaction V in alpha uranium is due to electronic-core polarization, they show that another source of mass dependence of T_c is the dependence of V on interatomic spacing. As $V = |M|^2/E$ where M is the matrix element describing the scattering process and E is the energy of the low lying f states with respect to the Fermi energy, the dependence can occur either through a shift of E or a change in M or both. Since the amplitude of zero-point atomic motions depends upon mass, T_c would depend on mass. A rough calculation using the observed pressure dependence of T_c yields $\alpha = 0.44$.

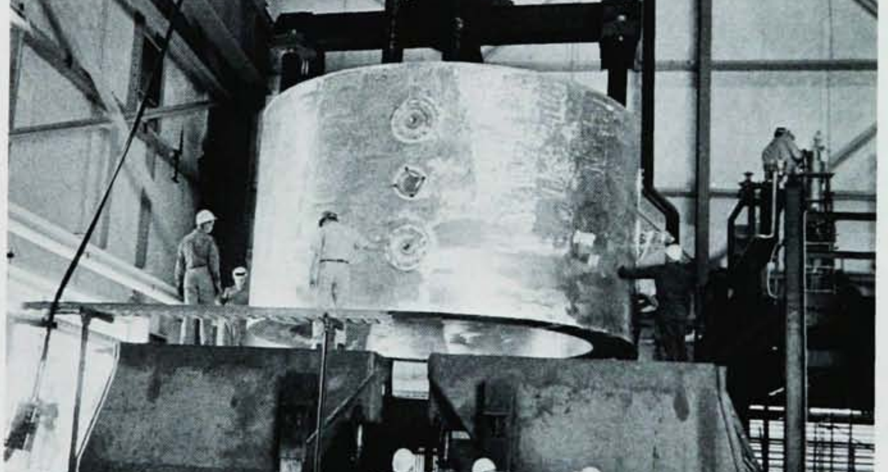
We asked Hunter Hill, one of Fowler's collaborators, to comment on Capellmann and Schrieffer's Letter. Hill was pleased that the Penn physicists had demonstrated that low lying f levels could produce a sizable positive isotope effect through electronic core polarization. He pointed out that $\alpha \approx 2$ is not excluded by their order-of-magnitude calculation.

The Penn physicists note work by James Garland and F.M. Mueller, who pointed out at the Washington APS meeting last spring that the uranium positive isotope effect could still be explained by the phonon mechanism provided it acted in a region of rapidly varying density of states, such as the f bands.

Hill finds it difficult to comment in detail on Schrieffer and Capellmann's belief that the electron-phonon mechanism can explain the positive isotope effect in alpha uranium, since the work of Garland and Mueller has not been published. He says, "It does seem unfortunate, however, that the authors are inclined to revert to this position after having come so close to providing valuable insight into the peculiar properties of alpha uranium."

Since the value of α depends sensitively upon the band structure of alpha uranium and thus cannot be calculated from first principles, Garland and Mueller are using the experimental value of $\alpha \approx 2$ in order to fix the energy of the bottom of the f band in alpha uranium. Garland says they are using the model to attempt to explain the peculiar normal state properties of alpha uranium.

Capellmann and Schrieffer emphasize that there is still no positive proof that a new superconductivity mechanism is required to explain the effect.



WORLD'S LARGEST SUPERCONDUCTING MAGNET is lowered into its steel frame at Argonne National Laboratory. The 110-ton magnet will produce an 18-kG field for the laboratory's 3.7-meter bubble chamber, whose usable volume is 20 m³. The Mirabelle chamber nearing completion at Serpukhov is longer (4.5 m), but its usable volume is only 6 m³.

Batavia Accelerator Staff Plans for Bubble Chambers

Plans involving two bubble chambers for the National Accelerator Laboratory at Batavia, Ill. (née Weston) are going forward. NAL officials are exploring with Argonne National Laboratory and the Atomic Energy Commission the possibility of moving the 3.7-meter hydrogen bubble chamber (photo, left) now under construction at ANL. A decision will be made a year or two before the 200-GeV machine is turned on. At the same time NAL and Brookhaven groups will