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Characteristics of Semiconducting Glass Switching/Memory Diodes

Abstract: Semiconducting glass diodes can exhibit at least three conducting states: a high-resistance, or "off" state; a low-resistance, or "on" state; and a negative resistance state. When appropriately pulsed they can also display a memory function. The laboratory operation of simple diodes and the methods of inducing transitions among the various states are described. In addition, the possible role of phase changes in the mechanism of device operation is discussed, and new evidence in support of a filamentary conduction hypothesis is presented.

Introduction

The switching and memory effects to be described in this paper are quite general to a large number of semiconducting glasses. Indeed, they may be general to all semiconducting glasses. In particular, all glasses examined at our laboratory, with resistivities in the range 10^2 to 10^8 ohm cm, show the switching and memory effects. It is important also to note that all given devices we have examined show both the switching and memory effects when subjected to appropriate electrical pulsing. In addition, if a constant current power supply is used, negative resistance is also displayed by the devices. Table 1 shows some of the glass systems which have been studied and which have been observed to show the memory and switching phenomena. The glasses listed here fall into three groups. The chalcogenides are relatively low melting glasses, the vanadium phosphate systems melt at intermediate temperatures, and the sodium titanium borate glasses are even more refractory. As a general rule, the switching voltage of a glass diode will increase as the resistivity of the glass increases and also as the softening temperature of the glass increases. Although all of the glasses listed here show the effects to be discussed, most of the work was carried out on the chalcogenide systems, and these will therefore be given the most emphasis.

Table 1 Semiconducting glass systems

As-Te-I As-Te-Br As-Te-Se As-Tl-Se	Low melting glasses
V-P-O V-P-O-Ba V-P-O-Pb	Intermediate melting glasses
Na-B-Ti-O	High melting glasses

Experimental

The circuit employed to do the experiments that originally demonstrated switching in the chalcogenide glasses[1] consisted of a 90-volt battery connected through two potentiometers. Pick-offs from these potentiometers were used to apply voltage from 0 to 90 volts across the device, which had a milliammeter in series with it to record current flow. A vacuum tube voltmeter recorded the voltage drop across the device. The experimental diode structure itself consisted of a brass base plate on which was mounted an insulated phosphor bronze spring carrying a tungsten point contact. The sample under investigation was a small fragment of glass obtained by fracturing a large piece of glass. It was placed in a pool of liquid indium-gallium alloy on the brass base plate under the point contact. The phosphor bronze spring held the point with gentle pressure against the glass fragment. The atomic percentage composition of the glass was, respectively, As 53, Te 43 and I 4. The experiment was carried out in a room temperature ambient.

The voltage-current characteristic of the device was obtained by increasing the voltage stepwise and recording the current that flowed at each step. The characteristic

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that was obtained is shown in Fig. 1. The behavior on initially increasing the voltage is ohmic up to somewhat above 20 volts, but above this level the current begins to increase at a faster rate than would be expected for ohmic behavior. At about 23 volts an abrupt change in the conduction characteristics of the device takes place, the voltage abruptly dropping to something less than two volts with an attendant increase in current to 35 milliamps. Subsequent readings provided the high conductivity part of the characteristic. On reducing the voltage to zero, the device switched abruptly back to the high-resistance condition. This whole cycle could be traversed apparently indefinitely. In addition, when the polarity of the device, base to point, reversed, the same behavior was observed, indicating that the device characteristic was symmetrical in the first and third quadrants.

Subsequent investigation showed that there were additional states in which the device could operate. The first was a so-called memory state of high conductivity, apparently coincidental with the "on" state of the switching device, but stable at zero bias. This memory state is realized by passing current through the device in the "on" state so that a critical current is exceeded. This critical current varies depending upon the composition of the glass being used, the device thickness, the temperature, and perhaps other parameters. The device can be made to switch back from the memory state to the high-resistance "off" state by passing through it a pulse of current, again greater than some particular critical value that is related to composition and geometry, and having a sharp trailing edge. The second additional state which can be realized in these devices consists of a negative resistance condition. This can be obtained by operating the device using a constant current power supply. Alternatively a series resistor having a very large value compared to the off resistance of the device may also be used to approximate constant current conditions.

Figure 2 shows an *x-y* recorder trace of a device of the previously mentioned composition displaying some of its modes of operation. A constant-current power supply was used to obtain the trace. Under first application of voltage, a high-resistance condition is observed which at somewhat less than 20 volts begins to pass current at a rate in excess of that due to ohmic behavior. This current increases in a somewhat erratic fashion until a value of about three milliamperes is reached, whereupon the device "breaks down" along the formation line. In this case, the device was then found to be in the memory state. The device could then be driven up and down line 3 and had a resistance of about 400 ohms in this condition. Subsequent abrupt current interruption from about 3.3 mA showed the device returning to zero bias along line 4. Reapplication of voltage then showed the device to be in the high-resistance condition. This changed over at

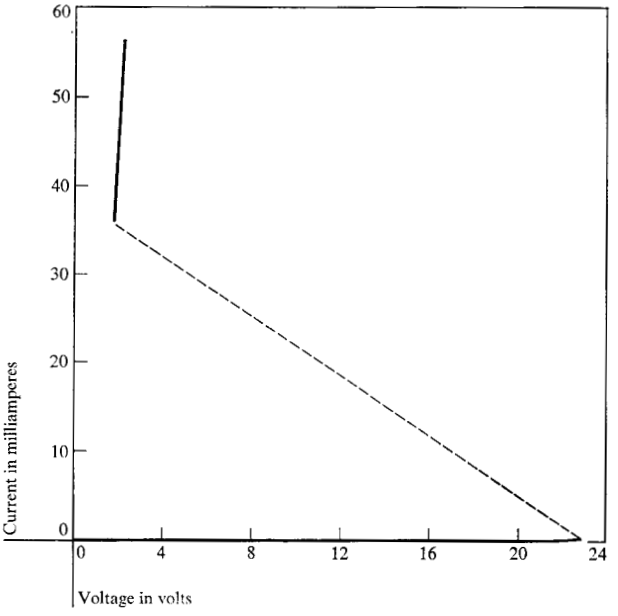
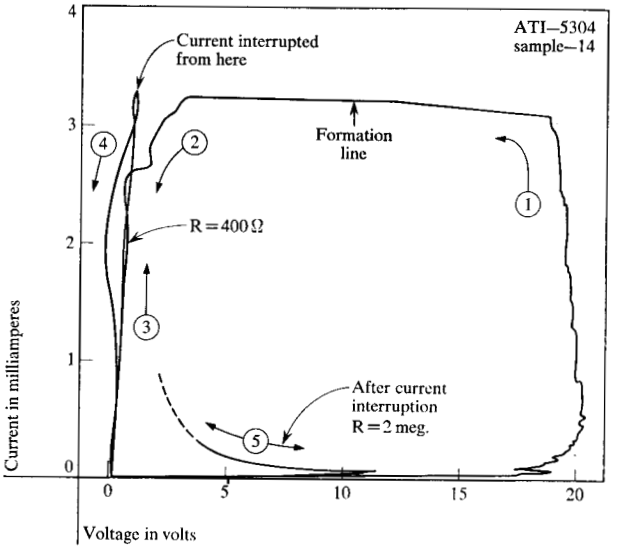


Figure 1 Original experiment showing switching in the first quadrant.

Figure 2 X-Y recorder trace of device behavior under constant current conditions.



about 12 volts into the negative resistance state, 5, which was stable and reproducible.

Operation of a device under square wave pulsing is illustrated in Fig. 3. The device in this case was operated with a 10,000 ohm series resistor. The top part of the oscilloscope trace shows the voltage drop across the device and the series resistor. At the bottom of the figure is shown the voltage drop across the device itself. As can be seen, the application of each square wave pulse produced

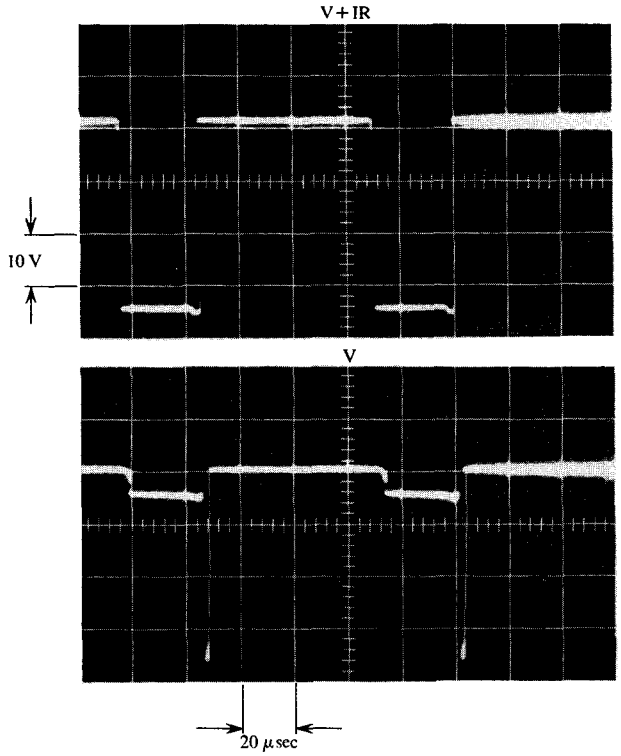
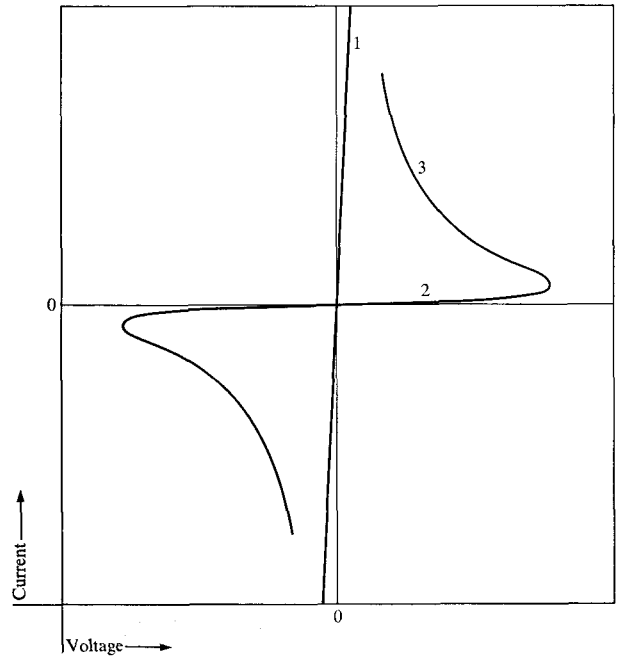


Figure 3 Oscilloscope trace of device behavior under square wave pulsing.

Figure 4 General *I-V* characteristic of semiconducting glass diode.



an almost instantaneous switching to a low-resistance condition. The time scale on both the photographs is 20 microseconds per division. It appeared then that the switching time was at least faster than one microsecond. The whole device characteristic is summarized[2] in Fig. 4, where region 1 represents the "on" or high-conductivity state, region 2 the "off" or low-conductivity state, and 3 represents the negative resistance state. Fast switching from 2 to 1 and 1 to 2 is achieved under nonconstant current conditions. If the critical current for the particular device is exceeded the memory state 1 will be observed. Under constant current conditions, the negative resistance state 3 is seen.

Mechanism

In the original reports[1,2] on these effects, it was noted that in the materials that had been studied up to that time phase changes took place on heating. It was also suggested that these might form the basis of a mechanism for the switching and memory effect if one further assumed that high conductivity paths or filaments were thereby created. It seemed apparent that some kind of semipermanent phase change was required, at least to explain the memory state, which was stable under zero bias. An electron micrographic examination of glass samples from which switches and memories had been made showed clearly that phase separation was present in all the compositions that had been melted in bulk form.[3] Figure 5 shows one of these micrographs, in which a large number of submicron size particles can be seen clearly. The electron micrographs were prepared from replicas of fresh fracture surfaces.

Since that time in our studies we have yet to see a homogeneous semiconducting chalcogenide glass prepared by bulk fusion. All such samples show the presence of second phases. A possible exception would be in the case of evaporated films of chalcogenide glass, some of which show phase separation and some of which do not.* However, the latter usually exhibit phase separation in the electron beam of the microscope, which is indicative of the relative instability of such glasses. The idea of phase changes producing filaments responsible for the mechanism of the switching and memory operation was also suggested by Eaton[4] in 1964. He showed that joule heating during the operation of the device was sufficient to allow phase changes to take place, producing regions of high conductivity material between the electrodes.

The question then naturally arises, "Can such a mass transport mechanism reasonably explain a phenomenon with such a short time constant?" In the early work,[1,2] switching speeds of faster than one microsecond were

* Note added in proof. Very recently B. G. Bagley has reported that $2As_2Se_3 \cdot As_2Te_3$ glass is homogeneous and does not crystallize, at least in "laboratory times". This work is to be published in *J. Noncryst. Solids*.

suggested, and a recent report by Ovshinsky[5] indicates that switching speeds as fast as 150 picoseconds are realizable. We may answer this question by considering that the fastest speed at which a phase change might be expected to travel would be the speed of sound in the material. Unfortunately, the values of the speed of sound are not available. However, a figure of 4,000 m/sec would not be unreasonable. Then, for a sample thickness of one micron, one would calculate a time of 250 picoseconds for the phase change front to travel through the sample from one electrode to the other. If the new phase grew simultaneously from many nuclei, already present in the glass, then this 250 picosecond figure could be expected to be considerably reduced.

Further recent experiments[6] have indicated more support for the filamentary conduction hypothesis. In this work, the diode structure consisted of evaporated As_2SeTe_2 glass and metal films (10 μm thick) on a glass substrate, as illustrated in Fig. 6. The diodes were operated with a 1,000 ohm series resistor, and 60 cycle ac was applied via a variable transformer. The *I-V* characteristic of the device was displayed on an oscilloscope. The device on its glass substrate was mounted on a microscope stage and observed through the microscope while switching was occurring. Enough power was dissipated as the device switched at 60 cycles so that a burned spot in the upper electrode surface appeared, due to the poor heat dissipation properties of the whole structure. Photomicrographic color motion pictures were made as the diode switched at 60 cycles and careful studies of these revealed that the burned spot had a complex structure. It consisted of a dark, apparently solid central region, usually about 10 μm in diameter. The perimeter of the spot, representing the unaffected lead electrode, was about 40 μm in diameter. During the time the switching operation continued, an elongated region of liquid phase connected the unburned lead electrode to the central dark spot. This liquid phase was in constant erratic circular motion and projected radially from the central dark spot. Thus, one end of the liquid phase always remained anchored to the central spot as it pivoted around it.

The spot is thought to be the end of a conducting filament, between the two electrodes, and the liquid phase provides a mobile high-conductivity bridge between the filament upper end and the upper lead electrode. The sort of structure envisaged is shown in the cutaway picture in Fig. 7. Figure 8 shows three consecutive frames from the motion picture film illustrating the filament end and the highly reflecting liquid conducting phase. It should be noted, however, that the fact that a liquid phase was observed on the surface of the device may well be an artifact of the particular geometry employed, together with its poor heat dissipation properties. There is no need to assume that the whole conducting path between the

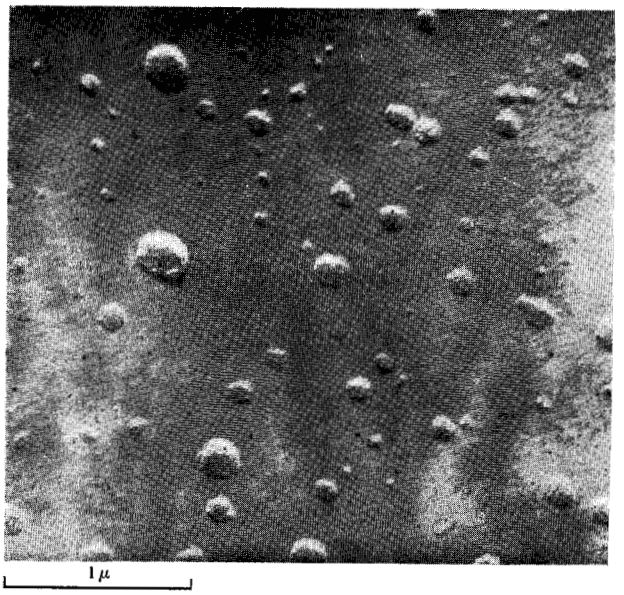


Figure 5 Phase separation in $Tl_2SeAs_2Te_3$ glass. Fresh fracture surface, direct replica technique.

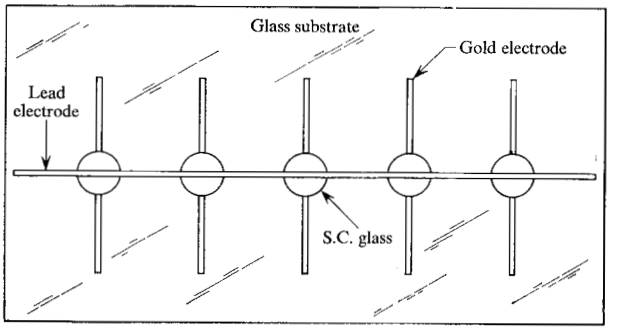


Figure 6 Thin film diode geometry. Gold, lead and semiconducting As_2SeTe_2 glass films are each approximately 10 μm thick.

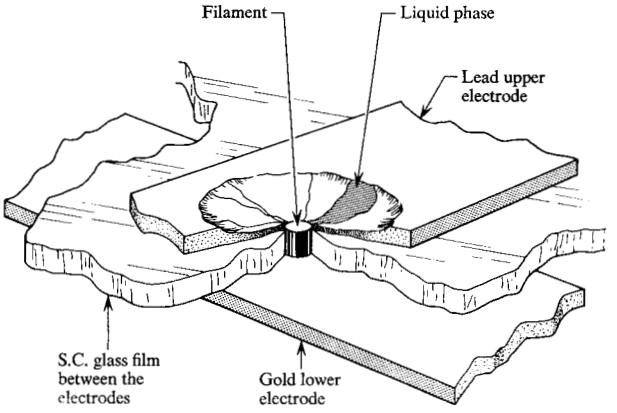


Figure 7 Cutaway representation of thin film diode.

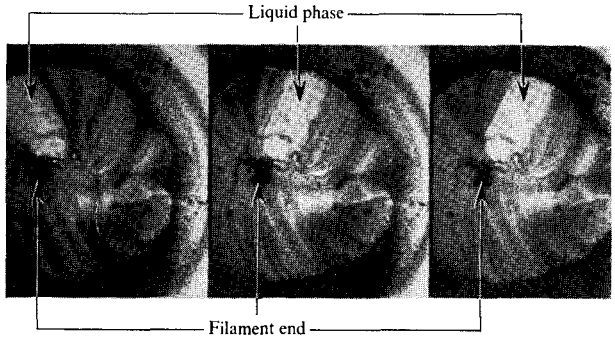


Figure 8 Consecutive frames from photomicrographic motion picture (16 frames/sec). Note the movement of the liquid phase between frames (a) and (b).

electrodes is molten, and, in fact, the black central spot gave no indication of melting during the observations.

Discussion

The existence of the memory state is presently best explained by means of a phase change mechanism. It seems reasonable to propose that the passage of large currents in the "on" state of the switch results in enough joule heating to allow phase separation to occur. If the new phases, which are probably crystalline, are of high conductivity and extend continuously between the electrodes, then they would form a conducting path which would be stable at zero bias. The passage of a critically large current pulse in the memory state would result in the fusion of "hot spots" along this path. If the current ceased abruptly, these fused regions would be quenched to the glassy state. Since this has a high resistivity the device would then be "off." Slow cessation of current flow would result in slow cooling of the fused "hot spots" and recrystallization or phase separation to reform the continuous conducting path. Thus, under these conditions the device would remain in the memory state.

The answer to central question of whether the switching mechanism of these devices depends upon phase changes or upon electronic effects must at present be much more speculative. Certainly the speed at which phase changes can travel is adequate to explain the switching speeds which have been observed. However, this does not mean that the phase change mechanism of switching is definitively proved. The same also applies to speculations on electronic mechanisms for the switching operation. No data published or presented to date prove the validity of either proposed mechanism. Any electronic explanation of the switching phenomenon must recognize the fact that phase separation has been observed during operation. It must also make clear the reasons for the close association between the electrical behavior of the devices and the attendant phase changes.

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