

*Many semiconductors retain their semiconducting properties when prepared in noncrystalline form. Although much of the band structure of the substance is retained during the transition from the crystalline to the amorphous state, certain changes in the physical properties accompany such a transition. The present article discusses the optical and electrical properties of amorphous semiconductors and their possible applications in electronic devices.*

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# AMORPHOUS SEMICONDUCTORS

**D**uring a recent conference on the Characterization of Materials,<sup>1</sup> the following words were used to describe a state of disorder in a solid: amorphous, noncrystalline, glassy, vitreous, liquid-like, disordered, and lacking long-range order. At the close of the conference, it was generally agreed that the terms could not now be distinguished. This was, moreover, the fourth conference within the year dealing specifically with noncrystalline materials. It is thus evident that considerable interest as well as vagueness surrounds the present-day studies of amorphous materials.

In this paper, the words "amorphous" and "noncrystalline" will be used to describe the lack of ordered structure in a material. Lack of structure or lack of long-range order implies the absence of a regular arrangement of atoms beyond one or two nearest neighbor positions. Short-range order may, and frequently does, exist. Fused silica, for example, consists of ordered  $\text{SiO}_4^{4-}$  tetrahedra which are randomly arranged throughout the material.

Any class of material (metal, insulator, semiconductor) may exist in the amorphous state; however, only semiconductors will be described here. There is considerable theoretical and practical interest in amorphous semiconductors because of their potential use in the electronics industry. The

interest at APL stems from possible applications under extreme environmental conditions of temperature and radiation.

## Formation of Amorphous Materials

Amorphous materials are generally produced by artificial means. Of the thousand or more minerals found in nature, less than 1% occur in noncrystalline form. Of these, fused silica ( $\text{SiO}_2$ ), opal ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ), and obsidian (volcanic rock) are perhaps the best known.

There are two principal techniques for obtaining amorphous samples: (a) cooling from the melt and (b) deposition on a substrate. In the first technique, the cooling rate is critical and depends on the particular sample. Oxide glasses (the window pane variety) are cooled very slowly while alloys and metals must be quenched rapidly. A popular rapid-quenching technique termed "splat" consists of allowing a molten drop to hit a cold surface. Many metastable amorphous phases may be formed by the splat technique.

The second method, deposition on a substrate or vapor quenching, is the one germane to this report. The technique is applicable to a large variety of material and produces samples in film form that are immediately useful for microelectronics. The material may be either evaporated in a vacuum or sputtered in a gas atmosphere. The temperature of the condensing surface is the critical factor, although deposition rates, purity, and gas contam-

<sup>1</sup>Second Conference on the Characterization of Materials, Rochester, N. Y., Nov. 8-10, 1967.

inates are also important. The following table shows the approximate substrate deposition temperature below which the amorphous phase is formed for the elemental semiconductors. Deposition is, in fact, the simplest method for producing amorphous semiconductors of these materials.

The stability of the amorphous phase after being formed obviously depends on the material. Tellurium films, for example, will immediately crystallize when warmed to room temperature; boron, on the other hand, will remain amorphous even at very high temperatures. The crystallization temperatures are roughly the same as the temperatures listed in the table.

Material	Approx. Substrate Temp. for Crystallization (°C)
Tellurium	10
Selenium	80
Germanium	350
Silicon	700
Boron	900

Of the materials listed in the table, boron, silicon, and germanium are the ones experimentally studied by the authors.<sup>2</sup> The materials were deposited in a vacuum of approximately  $10^{-5}$  Torr onto fused silica or glass substrates. A mass spectrometer was used to monitor the residual vapor in the vacuum. Substrate temperatures were kept around 100°C. Silicon was vaporized from a tungsten boat by joule heating. The deposition rate was approximately 800 Å/min. Boron, because of its very high melting point (2200°C), was heated by electron bombardment. Deposition rate for boron was approximately 100 Å/min.

## Structure

The atomic structure of the amorphous phase is determined, as in the case of the crystalline phase, by electron or X-ray diffraction. Electron diffraction is preferred because of the shorter wavelength. A diffraction pattern is obtained on a photographic plate in the form of rings corresponding to the scattering angle. Broad diffuse rings indicate the amorphous phase while sharp narrow rings indicate the polycrystalline phase. Figure 1 shows typical diffraction patterns for a boron film. Unfortunately, if the sample is composed of extremely small grains ( $<50\text{Å}$ ), the scattering is so

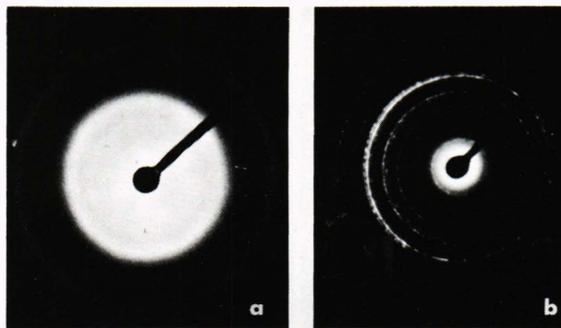


Fig. 1 — Electron diffraction patterns of  $\approx 300\text{Å}$ -thick boron films. (a) Pattern taken before heating; (b) pattern taken after heating to 920°C on tungsten screen.

great that diffuse rings are formed that are similar in appearance to the amorphous phase. It is consequently often difficult to distinguish between samples containing small crystallites and ones with amorphous structure. The entire diffraction pattern must be carefully analyzed.\* This is done by obtaining a radial distribution curve which is derived from the scattered intensity curve on the photographic plate.

The radial distribution curve gives the density of atoms as a function of distance from the average atom. A typical curve for boron is shown in Fig. 2. This curve is actually the deviation of the radial distribution curve from the average uniform atomic distribution and hence oscillates about zero. The coordination number, or the average number of nearest neighbor atoms around the given atom, is obtained from the area under the first peak (shaded portion) and the density of the sample. The value of the coordination number (which is

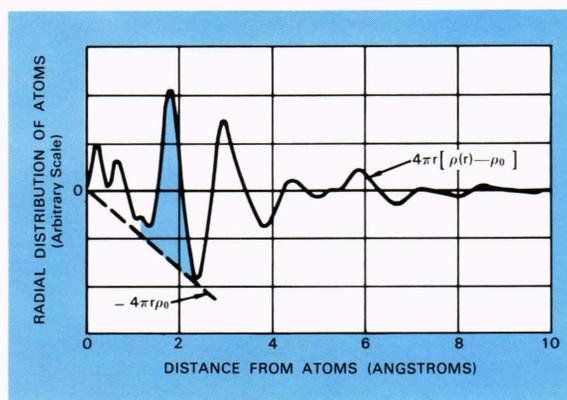


Fig. 2 — Radial distribution curve of amorphous boron.

<sup>2</sup>Experimental phases of this work were conducted at Melpar, Inc. under Contracts NOw 65-0390A and NASw-934. See, for example, "Final Report, Amorphous Semiconductors, 10 June 1964-2 August 1967," NASA Contract NASw-934.

\*Another aid in distinguishing the amorphous from the polycrystalline phase is a rapid transition at a definite temperature from the amorphous to the polycrystalline state. The infrared lattice spectra also furnish clues in some cases.

related to short-range order) gives a clue to the physical behavior of the amorphous sample. This will be discussed in the next section. The calculated coordination number for amorphous boron is 6.18, while that for amorphous germanium films is 4.26. The corresponding crystalline coordination numbers are 6 and 4 respectively.

## Theory

The properties of electrons in a crystalline solid are usually explained on the basis of the band theory of solids. In quantum mechanical calculations, the existence of energy bands of electrons in a solid is understood on the basis of periodic structure. That is, a structure with long-range order is generally deemed necessary for the presence of energy bands. Another consequence of the periodic structure is that the motion of an electron in a crystalline solid is described by Bloch wave functions.<sup>†</sup>

However, recently, considerable attention has been paid to the question whether the band model picture is also applicable to noncrystalline solids. The question arose mainly from the experimental observations<sup>3</sup> that many semiconductors retain their semiconducting properties when prepared in amorphous form (e.g., films) or even on melting. The problem is closely tied with the retention of the crystalline coordination number ( $N_c$ ) in the amorphous and liquid state. For example, the amorphous germanium film is a semiconductor ( $N_c = 4$ , i.e., same as in the crystalline state) while liquid germanium is a metal ( $N_c = 5$  or higher).

Various theoretical attempts have been made to study the band structure of disordered systems.<sup>4</sup> The three-dimensional problem has proved to be intractable and only one-dimensional disordered systems have been handled successfully both analytically and numerically.

The questions that one would like to answer are:

1. Do disordered systems possess band structure?
2. What are the changes (e.g., in band gap) that accompany the destruction of long-range order?
3. What is the nature of the electronic wave functions in disordered systems?

<sup>†</sup>A Bloch wave function is a free electron wave function multiplied by a function which has the same periodicity as that of the lattice.

<sup>3</sup>A. F. Ioffe and R. Regel, "Non-Crystalline, Amorphous and Liquid Electronic Semiconductors," *Progress in Semiconductors* **4**, 237-291, Heywood and Co., Ltd., London, 1960.

<sup>4</sup>K. Moorjani and C. Feldman, "Electrical Properties of Amorphous Semiconductors," *Rev. Modern Phys.* **36**, 1964, 1042-1049; A. I. Gubanov, *Quantum Theory of Amorphous Conductors*, Consultants Bureau, New York, 1965; N. F. Mott, "Electrons in Disordered Structures," *Adv. Phys.* **16**, 1967, 49-144.

Mathematically, the above questions would be answered if one could find the eigenvalues ( $E$ ) and the eigenfunctions ( $\psi$ ) of the Schrödinger wave equation,

$$\left[ -\frac{\hbar^2}{2m}\nabla^2 + \sum_i V(r - R_i) \right] \psi = E\psi, \quad (1)$$

where the potentials  $V(r - R_i)$  are arranged randomly and  $R_i$  denotes the position of the  $i^{\text{th}}$  atom.

ONE-DIMENSIONAL CASE—A number of studies exist on the solution of Eq. (1) in one dimension<sup>5</sup> and the important conclusions resulting from some of these studies are summarized below.

Gubanov<sup>4</sup> considered a one-dimensional disordered chain in which the distance between a pair of neighboring atoms is given by  $a(1 + \epsilon\gamma)$ , where  $a$  is the nearest neighbor distance in the ordered chain;  $\epsilon \ll 1$  measures the degree of departure from the short-range order and  $\gamma$  is a random variable which is different for different pairs of atoms. Assuming no change in the length of the chain as one goes from ordered to disordered state,  $\gamma_{av.} = 0$ . Further, the distribution of  $\gamma$ 's is assumed to follow normalized Gaussian distribution with normalization equal to unity;  $\gamma^2_{av.} = 1$ .

Gubanov finds that the effect of disorder is to broaden the allowed electronic energy bands by approximately

$$\Delta E_i \cong \epsilon E_i.$$

Thus, if  $E_1$  and  $E_2$  are the widths of the neighboring allowed bands then the band gap  $E_g$  will persist in a disordered chain provided that

$$E_g > \epsilon(E_1 + E_2).$$

That is, the forbidden band will disappear if the disorder parameter is greater than  $E_g/(E_1 + E_2)$ . In typical semiconductors, the width of the valence and conduction bands are of the order of 10 eV, and  $E_g \cong 1$  eV. Thus for the band gap to persist in a disordered system,  $\epsilon$  should be less than roughly 0.1.

This conclusion is strengthened by a numerical calculation on a disordered Krönig-Penny model ( $\delta$ -function type potentials) performed by Makinson and Roberts.<sup>5</sup> For a given potential strength, they find that for small values of the disordered parameter ( $\epsilon$ ), the forbidden energy band is altered by a finite density of states region near the edges of the allowed energy regions. Again the gap disappears for a value of disordered parameter approximately equal to 0.1. These results for a disordered Krönig-Penny model are also confirmed

<sup>5</sup>R. Makinson and A. Roberts, "Zone Theory of Liquids," *Australian J. Phys.* **13**, 1960, 437-445; R. E. Borland, "Existence of Energy Gaps in One-Dimensional Liquids," *Proc. Phys. Soc.* **78**, 1961, 926-931.

by the analytical treatment of Borland<sup>5</sup> who also investigated the nature of wave functions in a disordered system. Borland as well as Mott and Twose<sup>6</sup> conclude that all wave functions in a disordered one-dimensional chain are localized. That is to say, all wave functions have a maximum value for some value  $x_i$  and decay exponentially to zero as

$$\exp(-\beta|x-x_i|) \text{ as } |x-x_i| \rightarrow \infty.$$

These functions are illustrated in Fig. 3.

Even when localized wave functions have definite overlap in space, an electron cannot pass from one state to the other (since the wave functions correspond to different energies  $E_1$  and  $E_2$ ) without exchanging energy, normally with phonons (i.e., lattice). Thus conductivity at low energy is by hopping, and activation energy is needed for each jump.

**THREE-DIMENSIONAL CASE**—As mentioned earlier, the problem of three-dimensional disordered lattices has proved to be very difficult, and no solutions to Eq. (1) are presently available. Thus the questions raised in the previous section cannot be answered clearly and unambiguously.

However, from experimental observations it is clear that band gaps do persist in disordered lattices. It would thus seem that band structure is not determined by periodic structure but by interatomic distances, overlap of wave functions, etc. Or in other words, long-range order is not essential to the existence of electronic bands that are formed more by the short-range order.

Regarding the nature of wave functions, Mott<sup>4</sup> has proposed a conjecture partially supported by experimental data, that

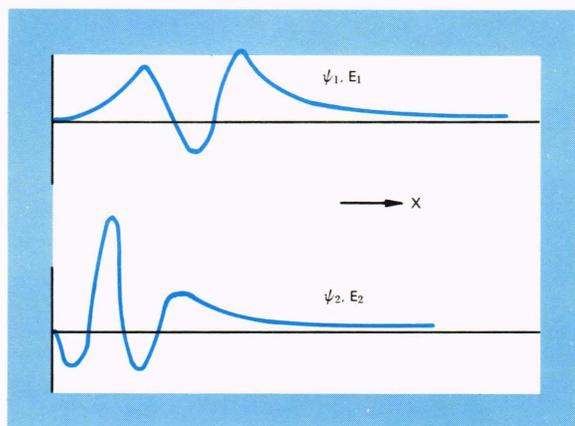


Fig. 3 — Localized wave functions (after Mott).

<sup>6</sup>N. F. Mott and W. D. Twose, "Theory of Impurity Conduction," *Adv. Phys.* **10**, 1961, 107-163.

1. In each allowed energy band, there exist critical energies  $E_c$  which separate the regions of localized states from the nonlocalized ones.
2. For localized states the wave function falls off as  $\sin kr e^{-\beta r}$  where  $\hbar k$  is the momentum of the wave and  $\beta \rightarrow 0$  as  $E \rightarrow E_c$ .

Various authors have suggested that localized states may exist in "tails" to the density of states near the top of the valence band and bottom of the conduction band. In other words, due to disorder, regions of low density of states appear near the band edges within the gap (as in the one-dimensional case). The situation is schematically illustrated in Fig. 4. If  $E$  is the energy required to create a free electron-hole pair in a crystalline substance,  $E + \Delta E$  is the corresponding energy in an amorphous substance (i.e., if one only considers nonlocalized states).

On the other hand, conduction of hopping type will be possible from one localized state to another and will be predominant at low temperatures.

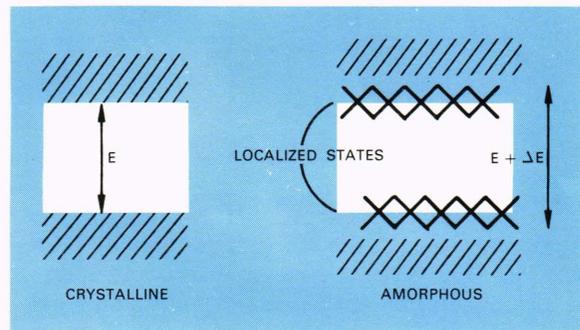


Fig. 4 — Localized states (after Banyai).

## Optical Properties

In examining the optical properties of a solid, one of the quantities of interest is the absorption coefficient  $\alpha(\omega)$ , or more appropriately, the imaginary part of the dielectric constant  $\epsilon_2(\omega) = n(\omega)c\alpha(\omega)/\omega$  ( $n$  = refractive index and  $c$  = velocity of light) as a function of the angular frequency  $\omega$  of the incident light.

A typical crystalline semiconductor at 0°K does not absorb incident light below a certain energy  $E_g$  ( $\cong 1$  eV). The absorption starts at energies above  $E_g$  and the absorption curve typically has the shape shown in Fig. 5. In the vicinity of  $E_g$ , the exact shape of the curve is determined by the nature of the electronic transition between the filled valence band and the empty conduction band. The transitions for which the momentum  $\mathbf{k}$  of the electron is conserved (direct transition), have the energy dependence

$\alpha(\omega) = C(\hbar\omega - E_g)^{1/2}$ , where  $\mathbf{k}(\text{initial}) = \mathbf{k}(\text{final})$ , while those which do not conserve momentum, (indirect or phonon assisted transitions) exhibit the energy dependence

$$\alpha(\omega) = C_1 (\hbar\omega - E_g - E_{ph})^2 + C_2 (\hbar\omega - E_g + E_{ph})^2$$

$$(\mathbf{k}(\text{final}) = \mathbf{k}(\text{initial}) \pm \mathbf{k}_{ph}),$$

where  $E_{ph}$  and  $\mathbf{k}_{ph}$  denote the energy and the momentum of the participating phonon and  $C_1$  and  $C_2$  are approximately constant.

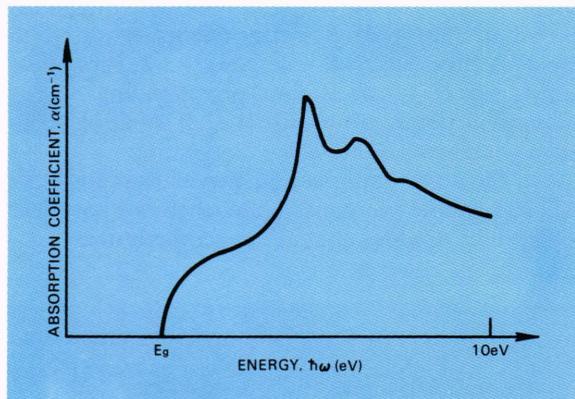


Fig. 5 — Absorption coefficient of a typical semiconductor.

The structure in the absorption curve at higher energies (Fig. 5) is caused by direct transition.

The absorption coefficients of amorphous films of germanium, silicon, and boron<sup>2</sup> were measured by the authors to study the effect of lack of long-range order on the fundamental band gap and the structure at high energies. The optical properties of amorphous germanium have also been studied by Tauc et al.<sup>7</sup> For amorphous germanium as well as silicon one finds that the structure of the absorption coefficient is completely smeared out; one obtains a broad absorption band instead. One concludes that all transitions between the uppermost valence band and the lowermost conduction band in amorphous germanium and silicon are indirect. Further quantitative support for this conclusion is obtained from the data of Tauc et al<sup>7</sup> on amorphous germanium in the region of the fundamental absorption edge (0.7 to 1.6 eV). They find that the gap is indirect and  $E_g = 0.88$  eV, showing no appreciable change from the value of the band gap in crystalline germanium.

From the absorption data in the energy range 0.1 to 0.6 eV, Tauc et al<sup>7</sup> conclude that the valence

band wave functions are well described by Bloch functions and even the degree of localization of conduction band wave functions is small.

It should be added that the authors' data in the vicinity of the band gap differ from that of Tauc et al<sup>7</sup>. The difference is probably due to the way one obtains the absorption coefficient from the measured values of transmission of thin films. One must take into account the interference effects in the film and multiple reflections in the substrate. The formula incorporating these effects is rather complicated, but through the use of the computer at APL consistent results for the optical constants of amorphous boron have been obtained.<sup>†</sup> The curve for the absorption coefficient of amorphous boron is shown in Fig. 6. For comparison, the curve for crystalline boron<sup>8,9</sup> is also included. For crystalline boron, one observes peaks in absorption at approximately 1.90 eV, 4.95 eV, and 5.45 eV.

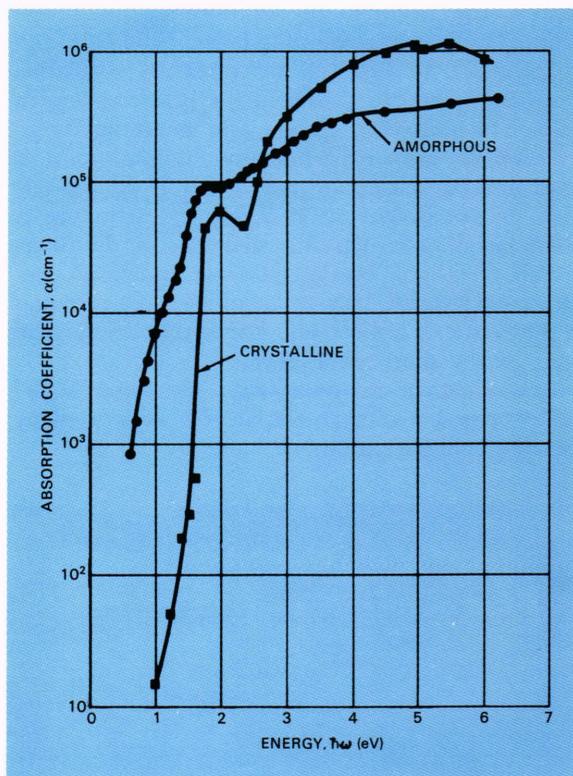


Fig. 6 — Absorption coefficients of crystalline and amorphous boron.

<sup>†</sup>The programming was kindly performed by Mr. J. Engle.

<sup>8</sup>Sh. Z. Dzhamagidze, R. R. Shvangiradze, Yu. A. Mal'tev, and M. F. Gvilava, "Investigation of the Self-Absorption Edge of Boron," *Soviet Phys.-Solid State* 7, 1965, 1259-1260.

<sup>9</sup>E. Kierzek-Pecold, J. Kozodziejczak, and I. Pracka, "Optical Constants of  $\beta$ -Rhombohedral Boron in the Region 1.2 to 6.2 eV," *Physica Stat. Sol.* 22, 1967, K147-K150.

<sup>7</sup>J. Tauc, R. Grigorovici, and A. Vancu, "Optical Properties and Electronic Structure of Germanium," *Physica Stat. Sol.* 15, 1966, 627-637.

There is also a sharp rise in absorption at 2.2 eV. Analogous to observations on amorphous germanium and silicon, the high energy peaks (at 4.95 eV and 5.45 eV) are smoothed out in amorphous boron. However, the peak at 1.9 eV and the second absorption edge are still retained in the amorphous state though they are shifted to slightly lower energies. The peak now appears at 1.75 eV and the absorption edge at 2.1 eV. Above 2.1 eV the rise in absorption is much slower in amorphous boron, and its magnitude is roughly half that of crystalline boron.

The fact that part of the structure is retained in amorphous boron shows that either the direct transitions retain their identity in the amorphous state (contrary to amorphous germanium) or that the peak at 1.9 eV is caused by an excitonic transition which is shifted to lower energy in amorphous boron due to modified exciton-phonon interaction.<sup>10</sup> (An exciton is a coupled hole-electron pair.) Further experimentation, particularly at low temperatures, is needed to decide between the two choices.

For crystalline boron, in the region of the fundamental absorption edge, Dzhamagidze et al<sup>8</sup> have reported the existence of indirect transitions in the energy region 0.8 eV to 1.45 eV, while direct transitions are dominant in the region 1.45 eV to 1.7 eV. The energy gap values for crystalline boron are  $E_g(\text{indirect}) = 0.93$  eV, and  $E_g(\text{direct}) = 1.47$  eV. We find that in amorphous boron, these transitions maintain their identity with somewhat modified values of energy gaps:  $E_g(\text{indirect}) = 0.74$  eV and  $E_g(\text{direct}) = 1.38$  eV. However the absorption coefficient in this region is about two orders of magnitude higher in amorphous boron. Clearly, there is a shift in the density of states in the bands as one goes from the crystalline to the amorphous state.

## Electrical Properties

All elemental amorphous semiconductor studies (B, Si, Ge, Se, and Te) exhibit the following characteristics:

1. Retention of crystalline coordination number.
2. *p*-type conduction.
3. Much higher resistivity in the amorphous state than in the crystalline state.
4. Low mobilities ( $\sim 10^{-2}$  cm<sup>2</sup>/Vsec).
5. Resistivity is a function of field strength, except in Te.

The *p*-type conduction in amorphous semiconductors is probably due to broken bonds leading to atomic vacancies.

In amorphous boron, the thermal band gap is found to be 0.92 eV (see next section) which is the same as the indirect optical band gap in crystalline boron,<sup>8</sup> but is about 0.2 eV higher than the lowest optical band gap in amorphous boron. The situation is similar in amorphous germanium where the thermal band gap is 0.2 eV higher than the optical band gap. It was to explain this result that Banyai<sup>11</sup> suggested the existence of localized levels near the valence and conduction band edges. The thermal band gap would necessarily measure the transitions between nonlocalized parts of the bands while the optical band gap measures the gap between localized levels. The difference, 0.2 eV, is understood if the extent of localized regions is taken to be 0.1 eV. However, the localization near the valence band edge is in contradiction with the results of optical measurements, which indicate that valence band wave functions are well described by Bloch waves.

The thermoelectric power measurements on amorphous tellurium indicate that the valence band is parabolic, and therefore there is no appreciable localization of wave functions. It may be that the localized regions are restricted to the vicinity of conduction band edges only.

To account for the high resistivity and low mobilities of amorphous semiconductors, Stuke<sup>12</sup> has suggested that there are potential barriers in these systems which the current carriers must overcome. However, no quantitative calculations are available at the moment.

Another contradictory aspect of the problem is that a region of temperature exists in which the sign of the thermoelectric power of amorphous germanium is positive, showing *p*-type conduction,<sup>13</sup> while the Hall coefficient is negative,<sup>14</sup> indicating *n*-type conduction. There is also a change of sign of thermoelectric power from *p* to *n* at high temperature.

There has been no systematic study of the role of impurities in amorphous semiconductors. At least for one case (amorphous tellurium), it is known that impurities are as active in the amorphous state as in the crystalline.<sup>12</sup> One would expect this for

<sup>11</sup>L. Banyai, "On the Theory of Electric Conduction in Amorphous Semiconductors," *Proc. International Conf. on Physics of Semiconductors, Paris, 1964*, 417-421, Dunod, Paris, 1964.

<sup>12</sup>J. Stuke, "Über den Elektrischen Leitungsmechanismus von Hexagonalen Selen-Einkristallen," *Physica Stat. Sol.* **6**, 1964, 441-460.

<sup>13</sup>R. Grigorovici, N. Croitoru, A. Devenyi, and E. Teleman, "Band Structure and Electrical Conductivity in Amorphous Germanium," *Proc. International Conf. on Physics of Semiconductors, Paris 1964*, 423-428, Dunod, Paris, 1964.

<sup>14</sup>A. H. Clark, "Electrical and Optical Properties of Amorphous Germanium," *Phys. Rev.* **154**, 1967, 750-757.

<sup>10</sup>K. Moorjani, "Excitonic Transition in Amorphous Boron," *Bull. Am. Phys. Soc.* **13**, 1968, 28.

deep impurities or for shallow acceptors when the degree of localization near the valence band edge is insignificant. As discussed in the next section, the existence of a deep impurity level in amorphous boron is necessary to understand the behavior of switching phenomena.

### Applications—A Thin-Film Amorphous Switch

As mentioned in the previous section, the striking electrical property of amorphous semiconductors is their extremely high resistance. All practical noncrystalline devices make use of this fact. The process of xerography is based on an amorphous selenium layer which exhibits strong photoconductivity along with this high resistivity. The photoconductivity allows a charge placed on the surface to leak off when light strikes a particular area on the surface.

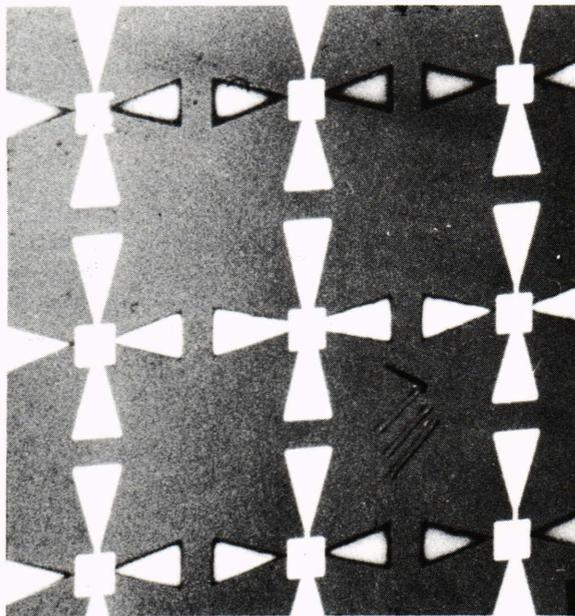


Fig. 7 — Photograph of boron thin-film switching device.

The device to be discussed here is a switching diode. This simple device has many potential applications and has been considered at APL by Perschy<sup>15</sup> for computer applications. A version of the device using mixtures of amorphous semiconductors is currently being explored commercially.<sup>16</sup> Experimental studies are now underway by the authors at APL. In this diode, the resistance is

large and little current flows until a threshold voltage is reached. At this point, the resistance suddenly decreases permitting a higher current to flow.

The thin-film switch consists of amorphous material sandwiched between two metal electrodes. Most of the work carried out by the authors concerns silicon and boron with titanium electrodes.<sup>17</sup> The samples are deposited on a substrate through masks which allow many devices to be fabricated at the same time. A typical configuration is shown in Fig. 7. The electrodes are broad at the ends in order to allow easy contact. When a varying voltage is placed across the sample, current-voltage traces such as those shown in Fig. 8 result. The figure also illustrates that similar behavior is obtained for both boron and silicon. The cause of the switching is currently under investigation and will only be briefly described here.

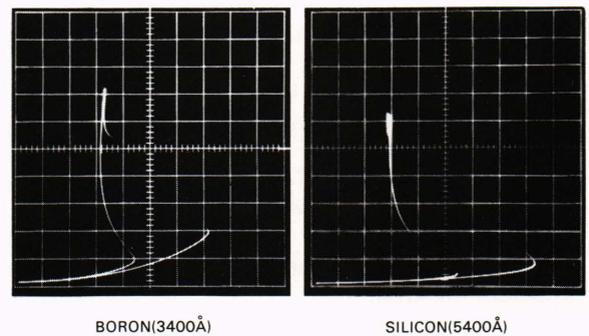


Fig. 8 — Oscilloscope traces of switching in amorphous films. Electrodes: titanium; load: 1K; area:  $10^{-4}$  cm<sup>2</sup>. The vertical scale is 1 ma/div. and the horizontal scale is 1 v/div.

From the discussion of the properties of amorphous semiconductors, it is clear that a band gap exists in the material. This is easily demonstrated in the diode configuration by making a plot of log-current vs.  $1/T$  where  $T$  is the temperature ( $^{\circ}$ K). (See Fig. 9.) According to the following usual relation for activation energy ( $E$ ), a straight line should result:

$$i = i_0 \exp(-E/KT),$$

where  $K$  = Boltzmann constant. One, in fact, observes two straight lines, one corresponding to a band gap ( $E_g$ ) and the other to an impurity or defect level ( $E_i$ ). The impurity level always exists in samples which show switching characteristics. The role of impurities or defects in noncrystalline material, as mentioned previously, is somewhat vague at present.

<sup>15</sup>J. A. Perschy, "Memory Addressing Glass Systems Using Semiconductors," *Electronics* 40, 1967, 74-84.

<sup>16</sup>S. R. Ovshinsky, U. S. Patent No. 3, 721,591, Sept. 6, 1966.

<sup>17</sup>C. Feldman, "Amorphous Boron Films," *Materials Research Bulletin* 3, 1968, 95-106

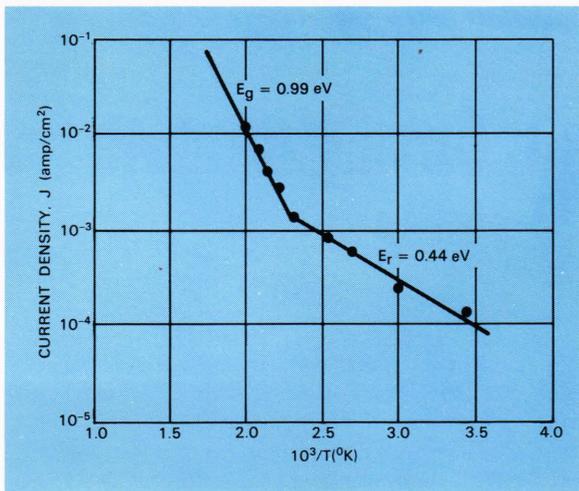


Fig. 9 — Log current density vs.  $1/T$  in boron films.

An analysis of the switching may be carried out by taking a log-log plot of Fig. 8 as shown in Fig. 10. Following the curve from left to right, the current at low voltage is ohmic. Following this, there is a region with a  $V^2$  dependency (characteristic of space-charge-limited currents), and finally, there is a steeper rise characterized by a high power of the voltage ( $V^7$ ) until a threshold voltage ( $V_{th}$ ) is reached. The slope of the negative sweep is determined by the load. Increasing the voltage beyond the sustaining voltage ( $V_s$ ) leads, in most cases, to destructive breakdown. The sample resistance at this point is determined primarily by the lead or electrode resistance. On reducing the voltage, the sample shows hysteresis and finally returns to the original current.

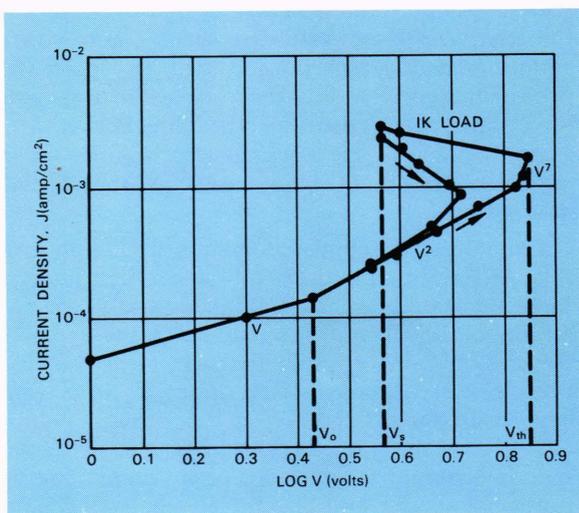


Fig. 10 — Log current vs. log voltage of switching characteristics.

An important feature of the switch is the consistency of the switching and sustaining voltages, which do not appear to depend on the particular sample or sample thickness. Table I shows some representative switching voltages as a function of sample thickness. Note from the table that the ratio of the threshold voltage to the sustaining voltage is about equal to the ratio of the band gap ( $E_g$ ) to the impurity activation energy ( $E_r$ ). The average thermal band gap from this table, plus others not listed is about 0.92 eV.

TABLE I  
SWITCHING PARAMETERS

Thickness (Å)	Threshold Voltage $V_{th}$ (Volts)	Sustaining Voltage $V_s$ (Volts)	$E_g$ (eV)	$E_r$ (eV)	$\frac{V_{th}}{V_s}$	$\frac{E_g}{E_r}$
535	4.06	2.40	0.92	0.53	1.69	1.73
1900	4.03	2.09	0.84	0.44	1.93	1.91
2200	4.80	2.20	0.96	0.45	2.18	2.13
2675	4.37	2.46	0.73	0.42	1.78	1.74
3300	5.60	2.50	0.99	0.43	2.24	2.30
6955	5.72	2.70	0.99	0.47	2.12	2.11
9000	3.82	1.72	0.80	0.37	2.22	2.16

A possible explanation of the switching behavior is based on a change in electron capture cross-section caused by the emptying of positively charged impurity (recombination) centers. This has been suggested by Lampert<sup>18</sup> and co-workers for double injection phenomena. The impurity level in the case of boron is emptied of holes by avalanche ionization (the  $V^7$  region). The avalanche is a consequence of the high resistance which enables a high field to be set up across the thin sample.

## Summary

It is apparent, from this brief discussion of amorphous semiconductors, that a great many questions remain unresolved. Many experimental facts seem to be in conflict and no clear model for conduction exists. A similar state of uncertainty exists for amorphous metals and insulators. As understanding increases, more sophisticated devices will result and the application of non-crystalline material to electronics will increase. As noncrystalline devices become available, material restrictions imposed by strict periodicity should relax and device operating conditions may extend to higher temperature and radiation environments. APL, through its program in thin-film research, hopes to contribute to this development.

<sup>18</sup>M. A. Lampert, "Double Injection in Insulators," *Phys. Rev.* **125**, 1962, 126-141.