Amorphous semiconductors

Research on their electronic states, vibrations and structural changes helps us understand these glasslike materials, which show promise in switching and amplification, as memories, and for silverless photography.

Jan Tauc

In recent years the physics of amorphous semiconductors has developed into a field so extensive and ramified that it is difficult to review in one paper. Various researchers emphasize different achievements; my choice of these is based on an attempt to give the reader an idea of the breadth of the research—from fundamental questions on electron states and atomic motions to the principles underlying some of the applications. The main difficulty with such a presentation of a more or less consistent picture is that there will necessarily be an inadequate discussion of alternative interpretations, so that the reader may get the mistaken impression that the suggested models were uniquely deduced from the experimental data. Unfortunately, crucial experiments that distinguish between different interpretations are still scarce. Nevertheless, experimental and theoretical work in the last five years have shown that some previously suggested plausible assumptions were incorrect, and the field has achieved, besides its extensive growth, significant progress in the understanding of the fundamental physics.

Electronic states

In a 1971 PHYSICS TODAY article,[1] Morrel Cohen summarized the understanding of the electronic properties of amorphous semiconductors that is obtainable from a model based on the work of Philip Anderson, Sir Nevill Mott, Cohen and others. In this model the energy gaps typical of crystalline materials are replaced by pseudogaps, in which the density of states is low but not zero as in a real gap. The wavefunctions of the states in the pseudogap extend only over limited distances, and so the states are referred to as "localized." But even in amorphous solids we expect the existence of extended states (typical of crystals) because an electron is only slightly scattered by fluctuations of a potential that is sufficiently small compared with the electron energy. One may then argue that in a homogeneous system the separation between the localized and extended states, the so-called "mobility edge," illustrated in figure 1, must be sharp, because a localized and an extended state can not exist at the same energy. This model has been widely accepted as a framework for discussing the electronic states in amorphous nonmetallic solids. In the last few years, many experiments were devised to learn about the character of various electronic states, their densities and their dependences on the solid's structure, chemical bonding and composition.

Extended states of amorphous solids were studied by the same methods as those in crystal physics: optical and photoemission spectroscopy. As expected, the spectra of amorphous solids do not show the sharp structures, due to singularities, that are associated with the long-range order of crystals. But the spectra definitely can not be interpreted as merely broadened versions of the spectra of the corresponding crystal. Figure 2 shows, for example, that the density of states in the valence band, as determined by photoemission, has three main bands in crystalline silicon but only two bands in amorphous silicon.

The results of calculations by Marvin Cohen, John Joannopoulos and their collaborators indicate that this difference is due to changes in the short-range order rather than to the loss of the long-range order: The basic structural elements of both amorphous and crystalline silicon is the tetrahedron, but the second-neighbor coordination is different. In the crystal structure there are only sixfold rings while in the amorphous structure there are also odd-numbered rings (fivefold, sevenfold); the model in figure 3 illustrates this. Rings such as these are present in some high-pressure crystalline modifications of silicon for which it was possible to calculate the optical spectra and to compare the results with the data on amorphous silicon. These studies showed that, if we disregard the sharp structures in the spectra, the topological similarity or dissimilarity between networks is more important that the long-range order.

Ideal glass

States in the mobility gap (figure 1) are of two kinds: intrinsic and extrinsic (produced by defects and impurities). How this distinction is to be made may not always be clear, especially in complicated glasses. In this article we consider only simple glasses, and for them it appears possible to postulate the concept of an "ideal glass," defined as an amorphous solid with no impurities and no defects. I shall elaborate later on the concept of a "defect" in a glass; for the moment we may identify the defects as broken chemical bonds, and define an ideal glass as a pure glass in which all chemical bonds are satisfied. Such a solid may never rigorously exist, because the amorphous structure may necessarily imply the existence of some broken bonds.

An example of the ideal structure is the Polk model[1] of amorphous germanium, depicted in figure 3. This is constructed as a random, completely interconnected, network built from the same tetrahedra as in the crystal, but slightly deformed. Dennis Weaire[2] and others gave a mathematical proof that an energy gap exists in this random structure is the matrix el-

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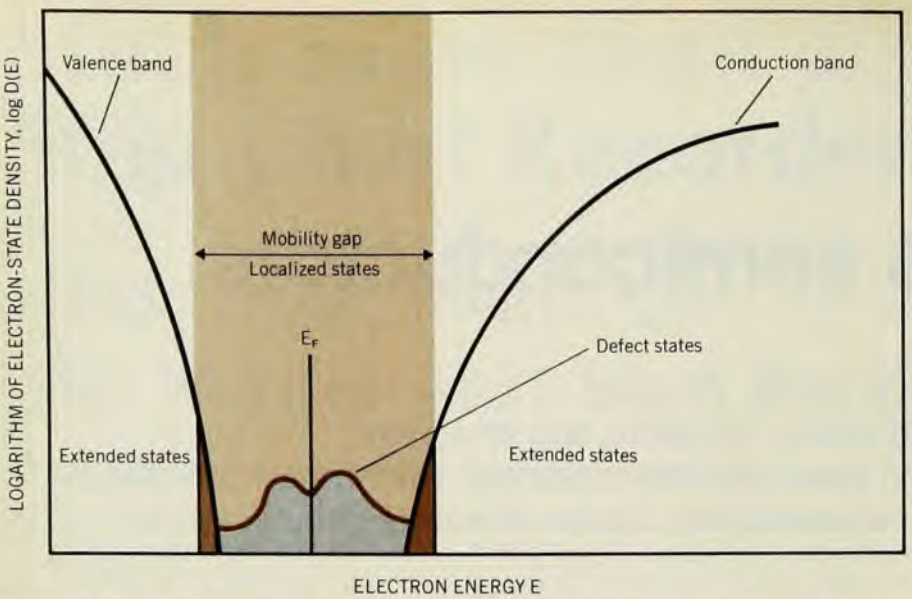

Density of electron states $D(E)$ in amorphous semiconductors. The "intrinsic" localized states were found to be restricted to energy intervals less than 0.1 eV. The other localized states in the mobility gap (shown here as a light colored band) are associated with defects and impurities (solid colored line). E_F is the Fermi level. Figure 1

ements of the hamiltonian between the electron orbitals of the neighboring atoms and neighboring bonds in the same atoms are constant throughout the solid. However, a distribution of the matrix elements—due to the distribution of the bond angles and interatomic distances as found in actual structures—produces states in the gap.

An important result of the experimental evidence was the realization that these so-called "intrinsic" states in the gap do not form broad distributions deep into the gap, as originally expected, but that they are restricted to energy intervals very close to the band edges (see figure 1). Therefore the absorption edges of pure glasses (such as amorphous SiO_2) can be as sharp as those in crystals, and the absorption below the gap can be extremely low. A striking example of this is in the glass fibers developed for optical communications, the absorption coefficient of which has been reduced to 10^{-6} cm^{-1} (at the light wavelength of one micron) by careful purification as discussed by Alan Chynoweth in the May 1976 issue of PHYSICS TODAY.

This result on the distribution of intrinsic states is far from trivial. In amorphous germanium, the distributions of matrix elements estimated from the fluctuations of angles and distances gives much broader edges than those observed experimentally. The reason why this is so leads to a deep problem typical of glasses. We can calculate the electronic properties of crystals starting from known structure; in glasses, all we know is the average structure. James Phillips suggested that the atomic structure may adjust itself during glass formation so that the energy of the system (electrons plus ions) locally reaches a minimum. This would happen if the electron–lattice interaction is strong, as one expects it to be for localized states in glasses. The binding energy of electrons is increased by the deformation of the lattice (Franck–Condon effect). Anderson presented plausible arguments that these energy shifts pull the energy states from the gap and sharpen the edges.

More recently, Anderson[3] developed the idea of the electron–lattice interaction further and suggested that it produces a strong attractive interaction between electrons in nonmetallic glasses that outweighs the coulombic repulsion of two electrons in a localized state. As a consequence, most localized states in the gap would be doubly occupied, just as the extended states are; therefore would not produce electron-spin resonance signals or paramagnetic contributions to the magnetic susceptibility. We shall examine this idea further when we consider the defects in chalcogenide glasses.

Defects and impurities

Except for the states very close to the edges, the states in the gap are due to impurities or defects. These can be of many kinds, as in crystals, and it appears that their electronic structures are also similar to those in crystals. Nevertheless, they may behave differently in various kinetic processes, because the carriers are much less mobile in glasses than in crystals.

The simplest defect is a broken bond. Two electrons ($\uparrow\downarrow$) are shared in a chemical bond between two atoms. In some structural configurations the atoms are not able to share the electrons and the bond is broken. This is a "dangling" bond, sketched in figure 4. Dangling bonds occur in glasses as well as in crystals; for example, on internal surfaces of microvoids, and in vacancies and multivacancies. A dangling bond is neutral (D^0) when occupied by a single electron; this defect produces esr. The dangling bond can attract an electron, and become negatively charged (D^-); or a hole, and become positively charged (D^+); in these states it does not produce electron-spin resonance.

Freshly evaporated sputtered films of Ge and Si contain large concentrations of dangling bonds that are associated with microvoids and divacancies. They make a paramagnetic contribution to the magnetic susceptibility and produce esr signals that can be reduced by annealing or, very effectively, by incorporating hydrogen, which apparently binds chemically to the dangling bonds. Amorphous Si films made from the gas phase by the decomposition of pure silane (SiH_4) in an rf glow discharge have a small concentration of states in the gap and approximate the ideal glass. Walter Spear and Peter LeComber[4] have shown that by admixing impurities such as phosphine or di-borate into silane one can change the value and the type of the conductivity—in the same way that one can dope crystalline semiconductors. It was even possible to make a p–n junction with these doped amorphous silicon films. These p–n junctions are now studied in several laboratories as photovoltaic cells, possibly suitable for solar-energy conversion. The simplicity of their construction makes them attractive for large-scale applications if their efficiency can be made high enough. Previous attempts to dope evaporated or sputtered amorphous Ge or Si films by group IIIA or VA elements and influence their conductivity failed; this was apparently due to the concentration of the defect states in the gap in these materials, which was high compared with that of the states introduced by doping.

The understanding of the states in the gaps of simple chalcogenide glasses (such as Se, As_2S_3, As_2Se_3 and As_2Te_3) is a more difficult problem. The spectroscopic data (absorption edge) and the magnetic data (magnetic susceptibility and esr) revealed very low concentrations[5] both of states in the gap and of single spins (below 10^{16} cm^{-3}). From these experiments, chalcogenide glasses appear as ideal, and we may argue that the chemical bonds can be completely satisfied because, during the relatively slow formation of these glasses by the quenching of the melt, the bonds have time enough to form.

David Emin[6] proposed a theoretical explanation of various transport effects in chalcogenide glasses that appears to be in good agreement with experiment. In his theory it is not necessary to assume any defect-related electron states in the gap; the strong electron–lattice interaction ("small polaron formation") makes the electron states and dynamics substantially different from those found in ex-

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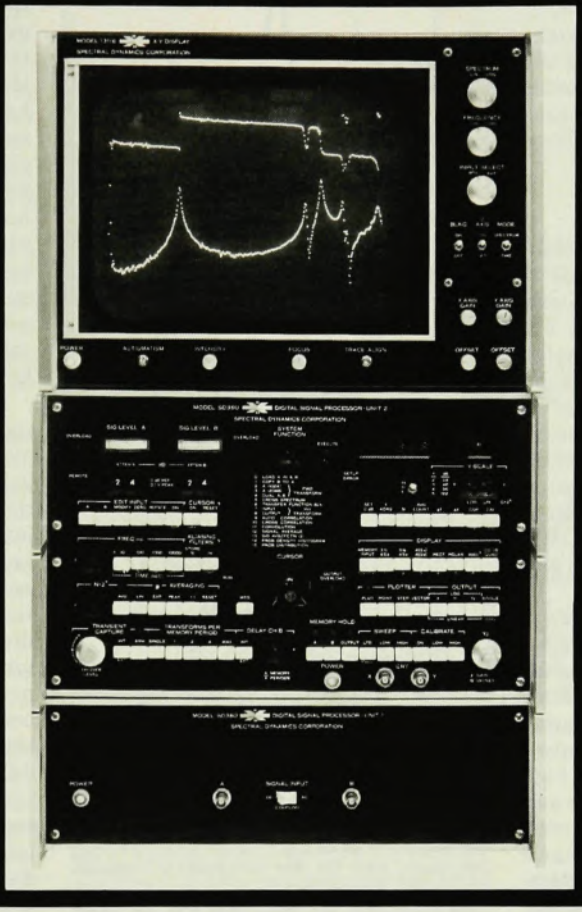

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tended states in crystalline semiconductors.

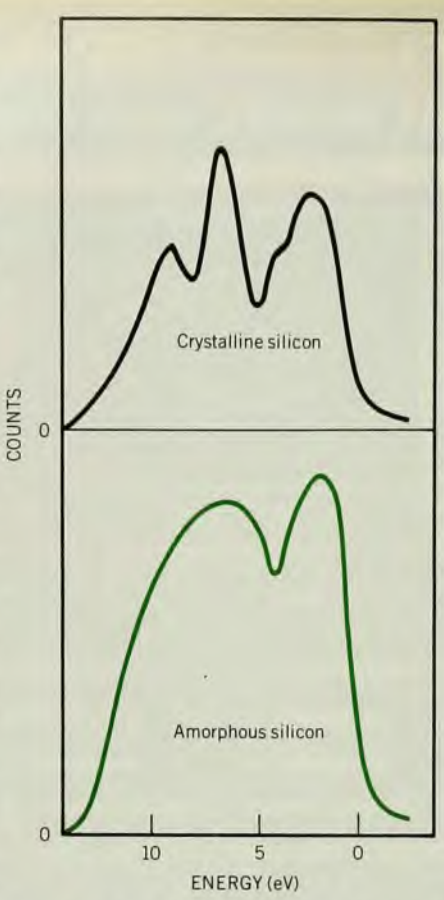
An alternative approach (to be discussed below) starts from an interpretation of some experimental data as evidence for the existence of some kind of electronic states in the gap of chalcogenide glasses. The relevant effects are the ac conductivity, glow curves, field effects, the impossibility of changing the conduction type by doping with impurities, and the pinning of the Fermi level.

Paired states

Mott and his collaborators[7] have elaborated a model of these states that is based on Anderson's idea, mentioned above, that paired electron states are preferred in these materials. The energy of two neutral dangling bonds D^0 is assumed to be higher than the sum of energies of D^- and D^+ states. The reason is that the charged states have their energies lowered by a strong interaction with the distortion of the environment—the polaron effect. In this case only paired defect states are found in the material: $D^-(\uparrow\downarrow)$ and D^+ (no spins).

The position of the Fermi level is determined by these two-electron states. By definition, the Fermi level is the energy per electron needed to introduce electrons into the system; in our case, this energy is smaller if we introduce two electrons at a time instead of one. A high density of two-electron states in the gap will pin the Fermi level, in our case near the center of the gap. The states at and below the Fermi level are occupied two-electron states ("bipolaron" states). Therefore they are not detected by the magnetic or esr measurements, do not produce optical absorption and do not contribute to the dc conductivity; they can, however, be seen in the ac conductivity (which one can intuitively visualize as due to oscillatory motion of the electron pair). The defect states D^- and D^+ are charged, and we expect strong electric fields in the samples. According to Robert Street, the presence of charged centers is essential for the understanding of luminescence and recombination.

Stephen Bishop and his co-workers illuminated amorphous As_2S_3 with photons with energies in the absorption edge.[8] These photons generated singly occupied electron states, which produced both optical absorption below the absorption edge and esr signals. The singly occupied states are presumably the D^0 states mentioned above, and this powerful technique has allowed them to study the characteristics of these excited states. They were able to show, for example, that the excited state in amorphous As_2S_3 is a hole in the upper part of the valence band, formed by the lone-pair electrons in sulfur, as diagrammed in figure 5. Although photoluminescence is observed both in crystalline and amorphous As_2S_3 and As_2Se_3, its similarity indicating the presence of similar defects in both phases, the generation of esr-active states was observed only in the glasses.



X-ray electron photoemission spectra of crystalline and amorphous silicon show the density of electron states in the valence bands. Note that there are three main bands for the crystalline form, two for the amorphous material. (These are schematic versions of spectra presented in L. Ley, *et al*, Phys. Rev. Lett. **29**, 1088; 1972.) Figure 2

This work on states in the gap of chalcogenide glasses has initiated studies on the chemical nature of defects in these materials; basic kinds of these defects were recently discussed by Marc Kastner, David Adler and Hellmut Fritzsche.

Transport effects

So far this discussion has been dominated by arguments based on spectroscopic and resonance data. However, there exists a wealth of data obtained from transport experiments.[9] Two essentially different types of conduction can be envisioned:

- high-mobility conduction in extended states (analogous to the usual semiconductor band conduction), and
- low-mobility hopping conduction, involving either band-tail states, defect states in the gap or intrinsic small-polaron conduction.

In chalcogenide glasses, the temperature dependence of the electrical dc conductivity σ at high temperatures is a simple exponential function, as in intrinsic crystalline semiconductors for which it holds,

$$\sigma = \sigma_0 \exp(-E_g/2kT)$$

E_g being the gap width. This suggests that the conduction may take place in extended states. Analysis of the data on the dc conductivity, thermoelectric power, Hall mobility and photoconduction, however, requires a more complicated model. Mott and his collaborators[7] explain the data in terms of a model that involves the extended-state motion of holes, combined with the variable-range-hopping conduction described below. Emin[10] pointed out that the data on chalcogenide glasses are consistent with the idea that the dominant charge carriers are holes that form small polarons hopping between chalcogen atoms.

If the one-electron density of states at the Fermi level $D(E_F)$ is sufficiently large, electronic hopping between states with energies close to the Fermi level will dominate the transport of electrons. This appears to occur in evaporated or sputtered films of amorphous Ge, Ge alloys, Si and III–V compounds deposited at low temperatures.[9] Mott[11] has noted that in disordered systems the electrons may hop much longer distances than between nearest neighbors, to achieve the best compromise between a large overlap of the wavefunctions and a small energy difference between initial and final states ("variable-range hopping"). If the energetic disorder is sufficiently great, long-range hops will dominate the conduction at sufficiently low temperatures. Using an *ad-hoc* expression for the site-to-site jump rate and neglecting correlations between hops, Mott found that the conductivity in this case will vary as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}]$$

where T_0 is a constant that depends on the density of states at the Fermi level and on the spatial extent of the electronic wavefunctions.

Excess carriers injected into amorphous semiconductors behave differently from those injected into crystalline semiconductors. The unusual features of the propagation of carrier pulses through films of amorphous materials were shown by Harvey Scher and Elliott Montroll[13] to be due to non-Markoffian transport processes. W. van Roosbroeck and others studied the effects that occur when the recombination time is short relative to the dielectric relaxation time.[9,14] This "relaxation regime" may occur in amorphous semiconductors as well as in some poorly conducting crystalline semiconductors.

Vibrations

In a crystal, the periodic arrangement of atoms makes it possible to decouple the vibrations of a large interconnected network by performing the Fourier transform from real space (local atomic displacements) into **k** space (plane waves). In

this case, the calculation of vibrational frequencies is reduced to solving the eigenvalue problem in the unit cell for each **k** vector in the first Brillouin zone. In an amorphous structure, however, the Fourier transform does not produce this decoupling, and the transformation into **k** space does not have any obvious advantages. Of course, if the amorphous structure could be obtained by a small perturbation of a crystalline structure, a description of vibrations as damped plane waves might be useful. However, this is usually not the case, as the topologies of the amorphous and crystalline structures are different. No general method for dealing with vibrations in amorphous solids is known. We will discuss two different approaches to this problem, again using amorphous As_2S_3 and Ge as typical examples.

The fundamental structural units from which crystalline, amorphous and liquid As_2S_3 are built are AsS_3 pyramids, which are coupled together through the S atoms. Gerald Lucovsky and Richard Martin showed that the Raman and ir spectra of amorphous As_2S_3 can be interpreted as produced by vibrations of an AsS_3 pyramid with all apex angles equal. This is remarkable inasmuch as the AsS_3 units are strongly coupled together through the As–S bonds.

Alfred DeFonzo and I analyzed under what conditions the vibrations of a small molecular unit can be decoupled from the rest of the network and treated in first approximation as vibrations of a molecule.[15] The condition in the case of As_2S_3 is that the neighboring units must have particular orientations. If this "decoupled network" method is applicable, one can obtain useful information about the atomic arrangement, beyond the first neighbors, in amorphous solids. The molecular signature of the spectra of chalcogenide and other glasses is rather common and has been used extensively to obtain information about the nearest neighbors.[16]

The vibrations of tetrahedrally bonded amorphous structures can not be decoupled by this method, and different approaches have been tried. If the matrix elements are constant, the intensity of both the Raman and ir spectra is proportional to the density of the vibrational states (no **k**-vector selection rule). Experiments suggest that this density has a structure similar to that of the phonon density in the corresponding crystals.

To obtain a better understanding of the actually observed spectra, Richard Alben and his colleagues made calculations on clusters of atoms and successfully interpreted the fundamental features of the spectra.[17] However, it was difficult to draw definite conclusions about the structure beyond the first neighbors.

A basic problem with the cluster is the necessity of considering a small cluster (less than 100 atoms); for these the number of surface atoms exceeds the number of interior atoms, and one must use some more or less arbitrary methods for discarding the surface modes. This strong-coupling case is obviously a much more difficult problem than the weak-coupling case of decoupled networks.

A model of the structure of amorphous germanium or silicon. In addition to the sixfold rings typical of the diamond structure, fivefold and sevenfold rings are evident as well. (Photo courtesy of G. A. N. Connell, Harvard University.)
Figure 3

Tunnelling states

In crystals the only allowed atomic motion is a vibration about the equilibrium position; in liquids, the atoms have translational motions as well. For a glass-forming substance the translational degrees of freedom are frozen in if the temperature is lowered below the glass-transition temperature T_g. The atoms in a glass can still have more than one position with approximately the same energy. However, these positions are not accessible since the alternative configurations are separated by barriers that are too thick or too high to allow a change of configuration by either tunnelling or thermal excitation.

It was suggested[18] that some of these barriers between configurations with slightly differing energies are thin enough that the atoms can tunnel from one local minimum to the other, as illustrated in figure 6. A typical property of this system is that it has two energy levels, with their populations determined by quantum statistics.

The existence of these processes was proposed to explain an extra contribution to the specific heat found in glasses at very low temperature.[19] The observed linear dependence of this specific heat on temperature follows from the tunnelling model if one makes some simple assumptions about the distribution of the tunnelling states. A remarkable fact is that the magnitude of the measured linear specific heat was found to be quite similar in different glasses (Se, As_2S_3, SiO_2, Na_2O–$3SiO_2$ and others) although the underlying atomic motions must be different. This may be explained by assuming that the feasibility of the tunnelling process determines those states that contribute to the specific heat. The concentrations of these states (a small part of the whole distribution of states with two possible equilibrium positions) are approximately the same in different glasses. Although tunnelling states may exist in some crystals, their broad distribution, essential for the occurrence of the linear specific heat in the tunnelling model, is a property typical of amorphous systems.

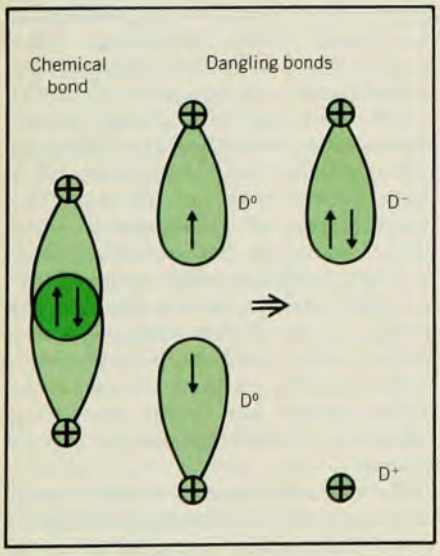
We may ask, of course, why is it necessary to assume the tunnelling mechanism rather than some vibrational processes peculiar to glasses. The reason is that a system such as a harmonic oscillator, with many energy levels, can not explain the dependence of the attenuation of ultrasound (long-wavelength phonons) on the

intensity of the waves, such as that observed in glasses at temperatures below 1 K. The attenuation of these waves is large if their power is small and it decreases with increasing power. This is explained in a natural way by assuming that the photons are resonantly scattered by two-level systems. The phonons change the relative population of the levels; eventually, sufficiently intense waves equalize the population of both levels and this kind of scattering disappears. The tunnelling model was recently tested in detail by several other experiments, and it appears to be well established.

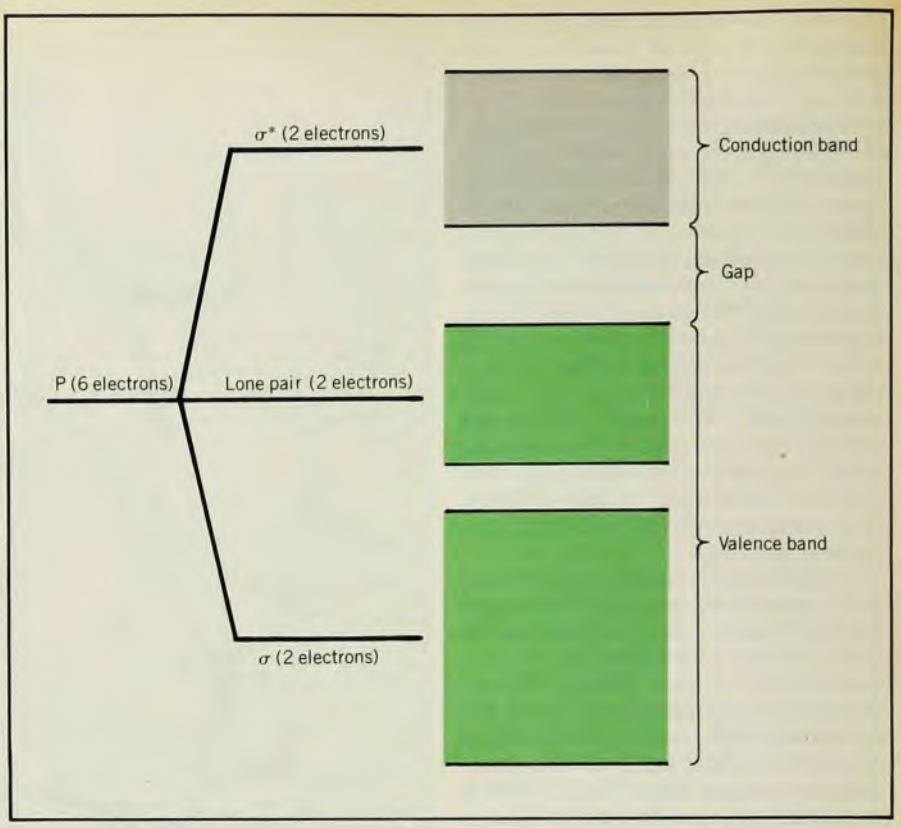
Structural changes

An amorphous solid is in a metastable state; its structure can be changed by heat, light, electron irradiation or electric field. Because many of the physical and chemical properties (such as electrical conductivity, optical constants, chemical reactivity, wettability and secondary electron emission) are affected by these structural changes, this ability of amorphous solids to change their structure opens a wide range of applications.[20]

Structural changes in tetrahedrally bonded semiconductors are irreversible: A film of amorphous germanium can be made to crystallize, but there is no way to make it amorphous again (except by, say, ion bombardment). However, if some of the atoms are twofold coordinated it is possible to change the structure reversibly. Chalcogens (S, Se and Te) produce twofold coordinated chainlike configurations, and therefore glasses containing chalcogens are of particular interest. The stability of the structure can be enhanced by chemical cross-linking between the chains of chalcogens through the elements of groups III, IV or V and can therefore be widely influenced by composition.[20] For example, a few percent of As in Se significantly increases the resistance against crystallization of Se films used in photocopying machines.



Dangling bonds. This sketch shows the generation of two (neutral) dangling bonds, D^0, from a chemical bond. If the reaction $2D^0 \rightarrow D^+ + D^-$ is exothermal, two charged states, D^+ and D^-, are formed, as shown at right. Figure 4



Electronic states in chalcogens. The atomic P levels (six states occupied by four electrons) form one bonding state σ with two electrons and one unoccupied antibonding state σ^*. The remaining two electrons do not participate in chemical bonding and form a "lone pair" localized at the atom. In this schematic representation we neglect the possible hybridization with the lower-lying s states of the chalcogen. The states are broadened into bands in the solids. The importance of the lone-pair band for understanding chalcogenide glasses was first pointed out by Marc Kastner in Phys. Rev. Lett. **28,** 355 (1972); the nature of the excited states was discussed by Ovshinsky and Sapru in reference 25. Figure 5

Glasses containing tellurium are most suitable for reversible changes. Figure 7 shows resistivity and differential-thermal-analysis curves of $Te_{81}Ge_{15}Sb_4$, a material that exhibits such reversible structural changes.[20] On heating the material the resistivity, proportional to $\exp(E/kT)$, is continuous at the glass-transition temperature T_g (defined as the temperature at which the viscosity decreases sharply; it is seen in DTA curves). At T_1, a structural change occurs: Finely divided crystalline tellurium precipitates in the glassy matrix, increases the conductivity and decreases its temperature dependence. At T_m the tellurium crystallites melt and the liquid material again has a semiconductor-like resistivity. During slow cooling (less than 25 deg C/min), tellurium crystallizes at a temperature somewhat lower than T_m (due to the supercooling shown in the figure) and the solid is in a high-conductivity state at all temperatures. When the material is cooled rapidly (more than 250 deg C/min), the amorphous state of the liquid is quenched, and it is in the semiconducting state over the entire range of temperature.

Photoinduced crystallization was observed in selenium[21] and As_2Se_3,[22] and photo-induced phase separation in As–S glasses.[23] When freshly evaporated amorphous films of As_2S_3 and As_2Se_3 are exposed to light ($h\omega \geq E_g$) structural changes occur that are similar to those induced by annealing (polymerization of the molecular units and changes in local configurations)[24] The detailed mechanisms of these effects are not clear but they appear to be related to the nonrigidity of the network structures and the particular electronic structure of the chalcogenides, shown in figure 5. When light creates a hole in the lone-pair localized state, it produces a singly occupied orbital on the chalcogen. This state has a high reactivity, which may be satisfied by an atomic rearrangement.[25] Since the structural changes are accompanied by shifts in the absorption edge and in the index of refraction, these effects are of interest for photographic applications, holography, optical digital memories and so on. Materials that are actually used for photographic applications are organic compounds containing tellurium (organochalcogenides). For example, these

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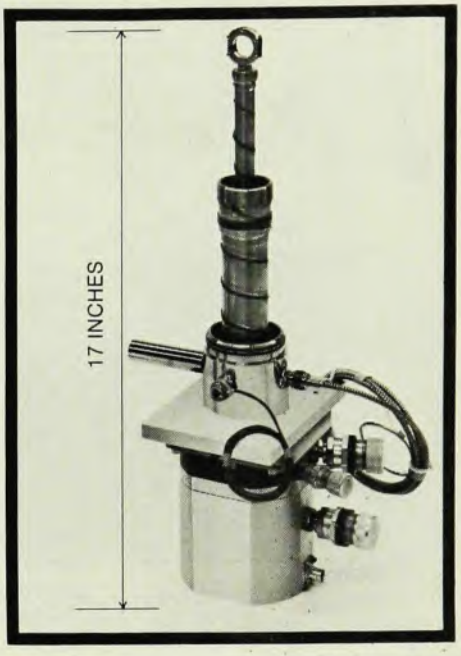

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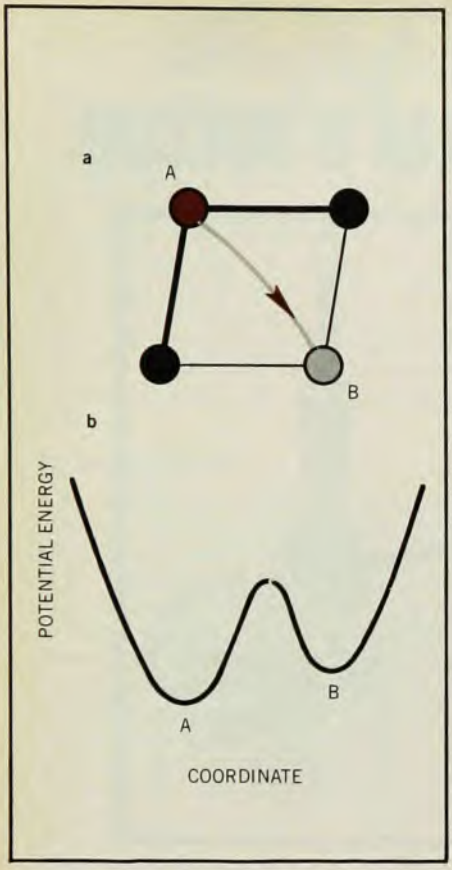
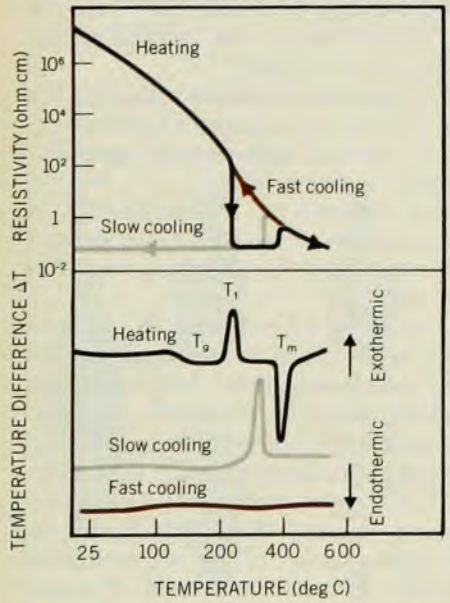


Tunnelling in glasses. An atom may occupy either of the two positions A or B shown in figure 6a. The potential-energy curve of figure 6b shows the potential barrier that separates the two positions. Note that the potential energies of the two sites A and B are not the same, because of their different environments in the glass. Figure 6



Resistivity and differential-thermal-analysis curves of a material that exhibits reversible structural changes ($Te_{81}Ge_{15}Sb_4$). Three conditions are shown: heating, slow cooling (less than 25 deg C per min) and fast cooling (more than 250 deg C per min). See text for a discussion. (After reference 20.) Figure 7

may have the form R_2TeCl_2, in which the organic reactant R is a ketone such as acetophenone or a derivative of acetophenone.[26]

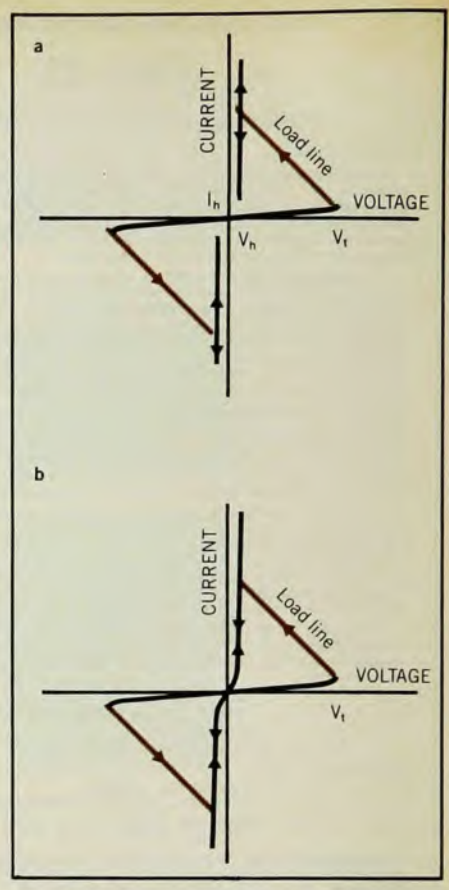
The changes in the optical properties induced by exposure to light can be substantially enhanced by subsequent heat treatment; apparently the light produces a metastable state (perhaps characterized by holes in the lone-pair states) that relaxes by atomic rearrangement during the thermal annealing. The image consists of crystalline Te needles, about 1000 Å long, dispersed in the organic matrix.[27]

Switching

The current–voltage characteristics of a thin film of a chalcogenide glass sandwiched between two metallic electrodes is shown in figure 8a. If a certain threshold voltage V_t is exceeded, the device switches from the high-resistivity "off state" into a low-resistivity "on state." The switching process is very fast (about 4 sec) and the device can be used as a switch. However, the breakdown appears to be a rather drastic process, and there have been questions about the lifetime of these devices and the reproducibility of the switching process.

The on state is characterized by a high-conductivity channel between the two metallic electrodes. Some physicists have advocated the idea that the switching process is always thermal and the result of the high temperature of the material in the channel that makes the material highly conducting. If this were so, we would necessarily have to expect cumulative changes of the material in the channel and a deterioration of the device. However, an alternative explanation, namely that the switching is an electronic process, has been steadily gaining ground and appears to be now firmly established. Heinz Henisch laid the foundation to the proof of electronic switching by pioneering fast switching techniques. Kurt Peterson and David Adler[28] measured, by several methods, the diameter of the conducting channel in the on state and found it relatively large; therefore the temperature in the channel must be low (below 100 deg C); the conductivity is far too small to account for the observed current. Peterson, Adler and Melvin Shaw constructed an n–p–n transistor in which the emitter is made of a chalcogenide glass and in the on state emits electrons into the base, made of crystalline p-type silicon. The device works as a threshold amplifier.

If the switching material is a chalcogenide glass that easily undergoes a structural change (as discussed above), atomic rearrangement in the conducting channel may take place in the on state and the conductivity of the material can remain high permanently, as figure 8b shows. This is the so-called "memory switch." The device can be brought back again into the off state by increasing the



Threshold (a) and memory (b) switches. V_t is the threshold voltage; V_h and I_h are the holding voltage and holding current in the threshold switch. (After reference 20.) Figure 8

temperature to melt the material in the channel—compare with figure 7. This can be done by applying a sufficiently strong current pulse in the on state. This effect can be used for making memory devices operated by electrical pulses. The read-out process can be extremely fast (it is just a resistance) but the write-in process now takes a few milliseconds. Therefore it is used for "read-mostly" memories for applications requiring a permanent yet electrically alterable memory.

The actual industrial applications of some of the effects that we have been discussing are presented in the Box on page 31. They do not exhaust, by far, the potentialities of this field, which holds many promises for the future.

* * *

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Applications of amorphous semiconductors

There is no doubt that the effects observed in amorphous semiconductors offer a vast number of potential applications. A well established one is in the photocopying machines, such as Xerox, that use the photoconductive process in amorphous selenium (doped with arsenic) as shown in the figure in this Box.

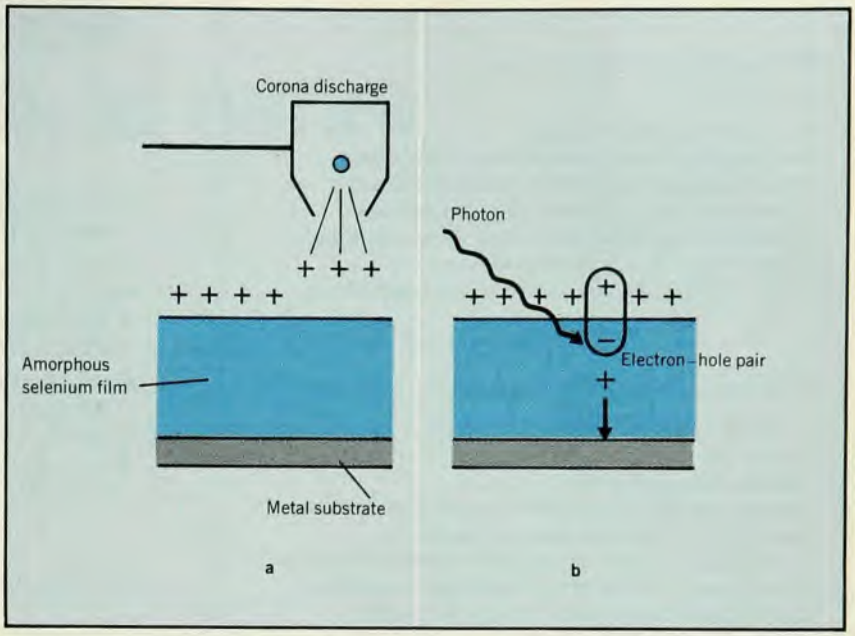
The most imaginative suggestions for new devices have originated from Stanford Ovshinsky. The industrial applications of amorphous semiconductors has proven to be more difficult than anticipated, for various reasons:

- The switching devices have to compete with the extremely advanced, reliable and inexpensive silicon technology.
- For data processing it is difficult to beat MOSFET (metal-oxide semiconductor field-effect transistors) or charged-coupled devices unless some unique valuable feature of the new devices becomes important (such as the high speed of the switching process in threshold switches or the retention of the memory state without applied power in the memory arrays). The new technology is, however, compatible with the silicon technology, and the devices developed by the Energy Conversion Company make use of this feature. So far the most successful have been the read-mostly memories, because they can perform functions not accessible by silicon technology alone. These devices have been perfected as to the packing density, operating temperature, energy requirements and lifetimes; about 10^8 failure-free programming cycles of 1024-bit memory arrays have been achieved. They are now produced by Burroughs and used for small computer applications, for example, by DuPont in blood chemical analyzers.

The photographic applications have several points that favor these materials against the silver-based materials:

- The development process is dry (just passing the light-exposed film through a heater),
- the contrast and resolution of some materials can be extremely high, and
- the films are very resistant to mechanical handling, temperature extremes and humidity.

These properties are of much interest for the applications in the graphic arts (in which well defined dots are needed) and for microfilm files. The materials potentially offer a far wider applications range, because by changing their composition one can make the films sensitive in various spectral ranges or have different contrast (the gray scale required in picture photography). Their present disadvantage is their low sensitivity; however, the development of these materials is only beginning. It is interesting to note that some leading imaging companies such as Agfa Gevaert, Fuji Film and Minnesota Mining and Manufacturing have joined Energy Conversion in developing this area. This alternative to the present photographic materials may become vitally important if the shortage of silver foreseen by some experts develops.



Initial steps in the xerographic copying process. A high-resistivity film of amorphous material is charged by a corona (part a). At the illuminated parts of the surface, an absorbed photon creates an electron–hole pair (part b). The electron neutralizes the positive ion on the surface; the hole moves through the film to neutralize the counter charge on the electrode. The remaining positive charge at the non-illuminated spots attracts a powder of negatively charged particles (toner) that become attached to the surface (the latent image) and then are fixed on a paper that passes over the surface.

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