Materials research

Noncrystalline semiconductors

New materials free of the constraints of long-range periodic order have applications ranging from optical memory disks and photovoltaic cells to diffraction gratings and x-ray lenses.

Hellmut Fritzsche

After rapid growth over the past 15 years, research on noncrystalline semiconductors is now one of the most active and exciting areas in condensed-matter physics. Technological interest has always been an important stimulant for fundamental materials research, and work on noncrystalline semiconductors is no exception. The field is active because the unique properties of these new semiconductors, together with techniques for spreading thin films over large areas, open many new possibilities for applications. Among the noncrystalline semiconductor devices at one or another stage of research or development are optical memory disks with extremely high information density, large-area electronic circuits on thin flexible substrates, faster and more durable photoreceptor drums for xerographic copying machines, x-ray lenses, holograms and inexpensive photovoltaic cells, just to mention a few.

Research in noncrystalline semiconductors is exciting because we are often baffled by the outcome of our experiments and have to revise our concepts and models more frequently than is necessary in other fields of science. Part of the intellectual fascination with these new materials stems from the challenge of finding new concepts to describe their properties—without the help of Brillouin zones, selection rules, symmetry arguments or the other theoretical tools that depend on translational symmetry and hence do not apply to disordered systems.

The challenges for experimentalists—this field more than others is an experimental science—stem also from the lack of long-range order. Many classical semiconductor experiments either cannot be carried out or lose their simple interpretation when the mean free path of charge carriers is of the order of atomic distances. Moreover, most spectroscopic techniques yield broadened and featureless spectra and lack the distinctive signatures that have helped us understand the electronic structure of crystals.

On the other hand, the lack of crystalline constraints permits one to synthesize an immense variety of new materials as well as exotic layered structures, or "superlattices" (figure 1). For the first time, synthesis of a material is not restricted by what nature permits us to grow in single-crystal form.

Even though this field is in its early adolescence, it is already becoming clear that different classes of noncrystalline semiconductors and insulators share many common features, which we are beginning to understand. For this article I have selected a few of these to illustrate some unique features of noncrystalline semiconductors and their technological attractiveness.

Structure

In a crystal, the arrangement of atoms is periodic; in a gas, it is completely random. Yet both these systems lend themselves to very precise mathematical treatments. Noncrystalline semiconductors, in contrast, pose tremendous difficulties. Between perfect order and disorder there are innumerable configurational and topological arrangements of atoms for which we do not have even a descriptive terminology. Nonetheless, one finds close structural similarities between crystalline and noncrystalline semiconductors, particularly in the nearest-neighbor sphere around each atom, because the same chemical forces and the same covalent bonds hold both kinds of solids together. On the other hand, the freedom associated with lifting the restrictions of crystalline symmetry allows large deviations from stoichiometric compositions and many new atomic configurations. These give noncrystalline semiconductors unique properties such as new low-energy elementary excitations, two-level tunneling states in which atoms move by tunneling between potential-energy minima, and photoinduced reversible structural changes, all of which I will discuss below.

It is clear that many details of the structure of a noncrystalline solid depend on how one prepares the material, for the same substance can attain a large variety of noncrystalline configurations, each of which is stabilized by steric and kinetic barriers. Among the preparation techniques are sputtering, plasma deposition, chemical vapor deposition, cooling from the melt and

Hellmut Fritzsche is professor of physics at the University of Chicago.

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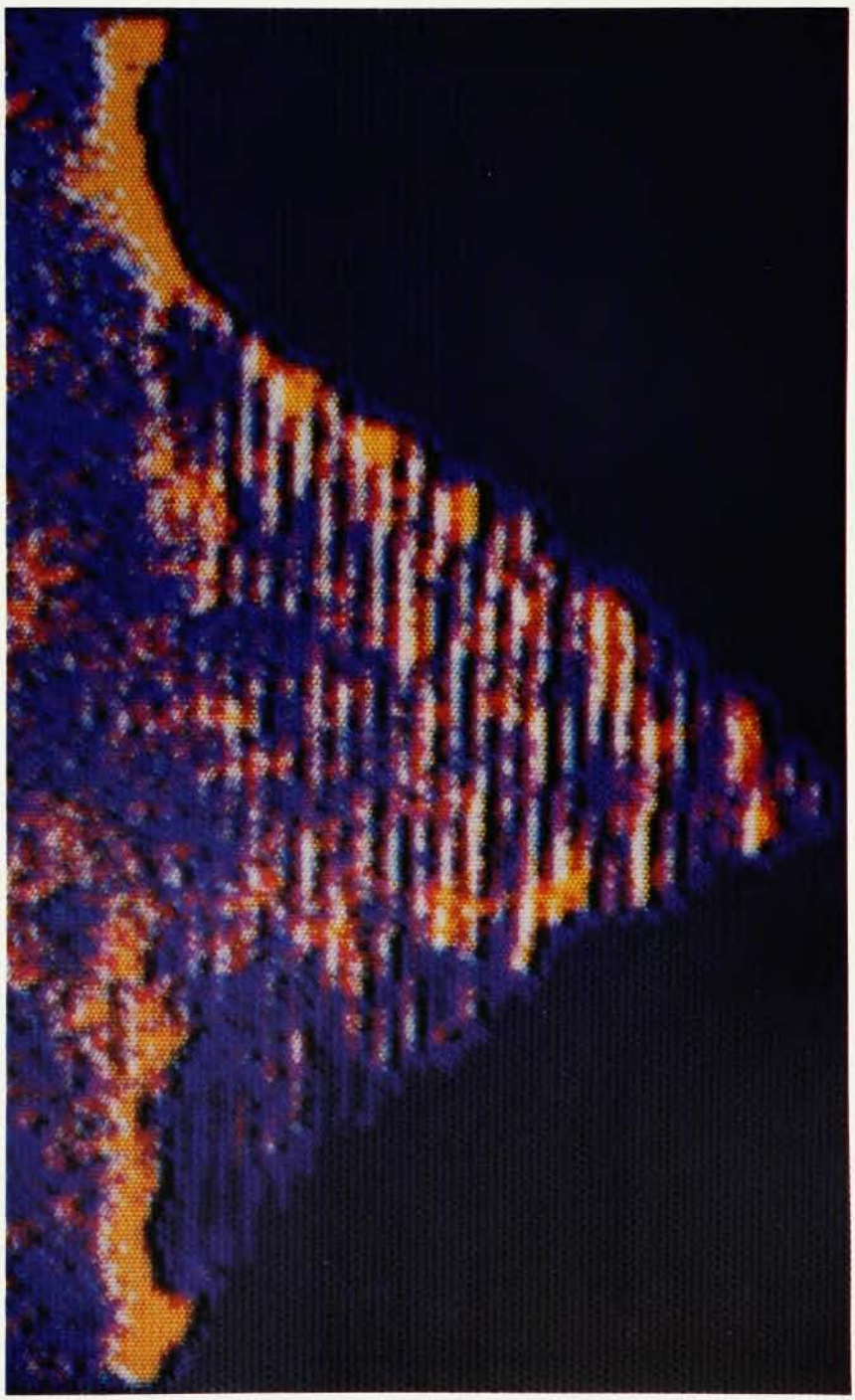
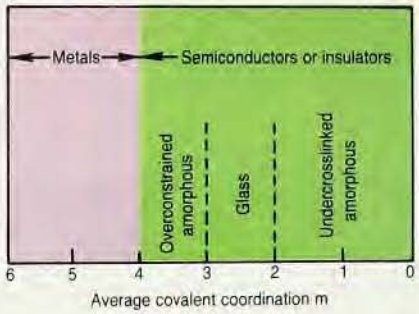


Multilayer cone made up of amorphous semiconductor materials. This transmission electron micrograph shows alternating layers of silicon–hydrogen alloy and germanium–hydrogen alloy, with a repeat distance of 28 Å. Such multilayer films of different composition have applications as x-ray optical elements. The layers are remarkably smooth—random fluctuations do not exceed about 4 Å—probably because the plasma deposition process etches away rough spots that form. (From reference 23. Color by Bill Lampeter, Laboratory for Laser Energetics, University of Rochester.) Figure 1

amorphization of a crystal by ion bombardment. The mechanisms by which the material relieves strain can lead to the formation of domains, the separation of phases, or other structural heterogeneities, which require additional medium-range topological characterizations.

Stanford R. Ovshinsky pointed out[1] that the important parameter that determines a noncrystalline material's stability and overall strain is the covalent connectivity of the network of atoms that make up the material. The number of neighbors to which the average atom in a network has covalent bonds—its covalent coordination—determines the connectivity of the network. The average covalent coordination number m, shown in the broad classification scheme in figure 2, is approximately equal to $8 - \langle N \rangle$, where N is the constituent atoms' column number in the periodic table. The major constituents of noncrystalline semiconductors from groups IV, V, VI and VII satisfy their valence bond requirements by being 4-, 3-, 2- or 1-fold coordinated, respectively.

I find it useful to distinguish between glasses and amorphous materials. Glasses have very similar structures in the liquid and solid states. One can think of a glass as a liquid whose atoms have been frozen in place at the glass transition temperature. I use the term amorphous for noncrystalline materials that are far from equilibrium; these materials can normally be prepared only in the form of thin films by



Classification of noncrystalline solids. An atom's covalent coordination is the number of neighbors to which it has covalent bonds. Figure 2

deposition on substrates that are kept below the crystallization temperature.

Compositions that are easily formed into glasses have a connectivity m between 2 and 3. James C. Phillips has suggested[2] that the optimal value is 2.45. With this connectivity the short-range order imposed by bond stretching and bond bending forces is just sufficient to exhaust the local degrees of freedom, and the glass-forming tendency is greatest. Materials with higher connectivities of 3 to 4 are overconstrained amorphous, and those with connectivity less than 2 are insufficiently crosslinked and also amorphous. The average coordination m of 4 separates noncrystalline metals that have close-packed structures from covalently bonded semiconductors or insulators.

The composition As_2S_3 is nearly as close as one can get to an ideal glass. It is therefore tempting to imagine its structure to be a covalent random network as described[3] by William H. Zachariasen in 1932, with each arsenic atom surrounded by three sulfur atoms, and each sulfur atom by two arsenic atoms. Such a simple structure would require only small variations in bond angle, and would keep the bond length essentially fixed at its lowest energy value. Nevertheless x-ray diffraction of As_2S_3 suggests that nature prefers a different arrangement. The first diffraction peak is unexpectedly narrow, and what is even more surprising, it grows as the temperature is raised above that of the solid-to-liquid transition. Radial distribution functions do not give us sufficient information to deduce a definite structure. However, because the position of the first diffraction peak corresponds to the layer separation of crystalline As_2S_3, the diffraction data may be interpreted as indicating the presence of remnants of groups of layers that retain a certain coherence but are oriented at random to yield the overall isotropy of the glass. Furthermore, the temperature dependence suggests, contrary to one's intuition, that at least one component of local ordering decreases with decreasing temperature and continues to change far below the glass transition temperature.

Because of the orbital structure of silicon, amorphous silicon tends toward tetrahedral coordination. However, a covalent random network with a coordination of 4 has to find ways to lower its huge strain energy. Indeed, one finds that evaporated or sputtered films of amorphous silicon contain a network of voids, and about one percent of the silicon atoms are only threefold coordinated, which means that one of their tetrahedral sp^3 orbitals remains nonbonding. These nonbonding orbitals have a single unpaired electron, and are therefore easy to observe by spin resonance. The energy of the nonbonding states lies right between those of the bonding and antibonding states, that is, in the gap between the valence and the conduction bands. Because of its void structure and large defect density, this material is of no scientific or technical interest.

However, Walter A. Spear and Peter LeComber[4] of Dundee University in Scotland, and Ovshinsky,[5] found that by attaching hydrogen or fluorine to the dangling bonds, one can reduce the number of defect states in the gap from 1 percent to 10^{-5} percent of silicon atoms. This allows doping of the material and the preparation of p–n junctions, field-effect transistors, solar cells and many other semiconductor devices.

We then ask: What is the structure of the hydrogenated or fluorinated amorphous silicon that is commonly prepared by radio-frequency plasma deposition? One finds that about half of the hydrogen, which makes up 7 to 12 atomic percent of the material, is incorporated randomly, and the remainder is clustered forming internal surfaces or pockets of hydrogen-rich material. This submicrosopic phase separation appears to be the result of a strain relief process. The topology depends upon the conditions of preparation, but is not known in detail.

Defects

Despite our lack of knowledge of the structure, we have made great progress in understanding the origin and the nature of the dominant defects in hydrogenated and fluorinated amorphous silicon. This statement appears less paradoxical in the light of what we mean by a defect-free material: one in which all atoms have satisfied their valence bond requirements. This yields a filled valence band and an unoccupied conduction band. Nonetheless, the density of states in these bands does not drop to zero at band edges as in crystalline semiconductors, where the spatial periodicity of the potential produces strictly forbidden gaps. In noncrystalline semiconductors the density of states in the bands instead decreases without reaching zero. We can approximate this by an exponentially decreasing tail of states. Without defects, then, the energy gap is essentially free of states because the exponential decay of the tails is quite steep, giving them a width that is small compared to the band separation. This allows us to make an analogy with crystalline semiconductors and to define defects in amorphous semiconductors as those atoms whose covalent coordination exceeds or is less than the normal value.

Even though the number of undercoordinated silicon atoms is greatly reduced by the presence of hydrogen, they are still the main defect centers in hydrogenated amorphous silicon. The dangling-bond state of a three-fold coordinated silicon atom can pair its spin by accepting another electron. This negatively charged state D^- has an ionization energy E_1:

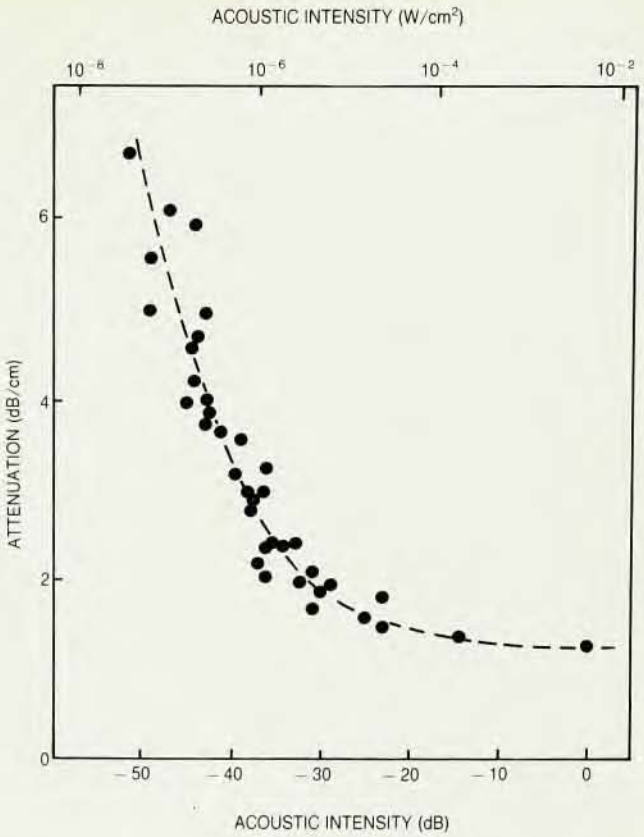
$$D^- + E_1 \rightarrow D^0 + e^-$$

The second electron can be released to the conduction band with energy E_2:

$$D^0 + E_2 \rightarrow D^+ + e^-$$

The neutral center D^0 can therefore act as an acceptor or donor. Because of Coulomb repulsion between the two electrons, the first ionization energy E_1 is normally smaller than the second ionization energy E_2. The effective correlation energy U, defined as $E_2 - E_1$, is estimated to be about 0.3 eV in amorphous hydrogenated silicon. The dangling bonds appear to be the predominant defects governing the lifetime of photocarriers, the luminescence efficiency and many other semiconductor properties. The concentration of dangling bonds is about 5×10^{15}/cm^3 in high-quality material.

The nature and characteristics of



Ultrasonic attenuation versus acoustic intensity in silica. Data were taken at 0.5 K with 950 MHz ultrasound. (From reference 15.) Figure 3

defects are much more interesting in semiconducting glasses whose major constituents are chalcogens. These group-VI elements have four p-electrons but are only two-fold coordinated; two of the four p-electrons form a lone pair that does not participate in bonding. The band of states occupied by these two electrons lies therefore between the bonding and the antibonding bands. Hence, in contrast to tetrahedrally bonded semiconductors, the valence band in chalcogenide glasses is the lone-pair band and not the bonding band. The existence of these lone-pair electrons has a profound influence on the defect chemistry of chalcogenide semiconductors, as we shall see shortly.

Because normal covalent bonds have two electrons with opposite spins, and therefore zero net spin, one expects to detect defects easily by electron spin resonance if defects represent either overcoordinated or undercoordinated atoms. That is how researchers first detected and measured the concentration of the dangling-bond defects in amorphous silicon. In chalcogenide glasses, on the other hand, no spins could be found.[6] It became clear that one could not take the diamagnetism of these materials as proof that they are free of defects. On the contrary, the relatively small photoconductivity, our inability to change the conductivity significantly by doping or by inducing a space charge with a transverse electric field, our inability to form a rectifying Schottky barrier, and many other characteristics suggested the presence of a sizeable concentration of defects.

After several years this puzzle found an elegant solution, which opened up a new and interesting defect chemistry that has no counterpart in the thoroughly studied crystalline semiconductors because it follows from the presence of lone-pair electrons.

Several ideas led to the understanding of the peculiarities of these new defects. First, Philip W. Anderson suggested[7] that strong electron–phonon coupling in noncrystalline semiconductors causes electrons in localized states to attract each other, thus favoring a paired-electron ground state. This would be similar to a superconducing Cooper pair except for the fact that the pair would be localized and unable to contribute to an electric current. Robert A. Street and Nevill Mott applied[8] this concept to chalcogenide semiconductors and suggested that point defects such as dangling bonds are the site of the paired electrons. Anderson's negative effective correlation energy is then realized when the second ionization energy E_2 is less than the first ionization energy E_1. Under these circumstances the reaction

$$2D^0 \rightarrow D^+ + D^-$$

becomes exothermic, and the paramagnetic D^0 defects spontaneously convert into diamagnetic charged D^+ and D^- defects by the transfer of an electron. This is plausible because of the strong local relaxation and new bonding configurations involving lone-pair electrons of neighboring chalcogens.

In 1976, Marc Kastner, David Adler and I proposed[9] the "valence alternation" model, which identifies the positive defects D^+ with overcoordinated (and the negative defects D^- with undercoordinated) group-VI or group-V atoms. Because the total number of bonds in a glass does not change when these defects are created two at a time, the energy needed to create two defects, one undercoordinated and one overcoordinated, is relatively small: 0.5 to 1.0 eV. The concentration of these valence alternation defects is equal to their equilibrium density near the glass transition temperature, below which the concentration of defects cannot decrease because atomic diffusion essentially ceases.

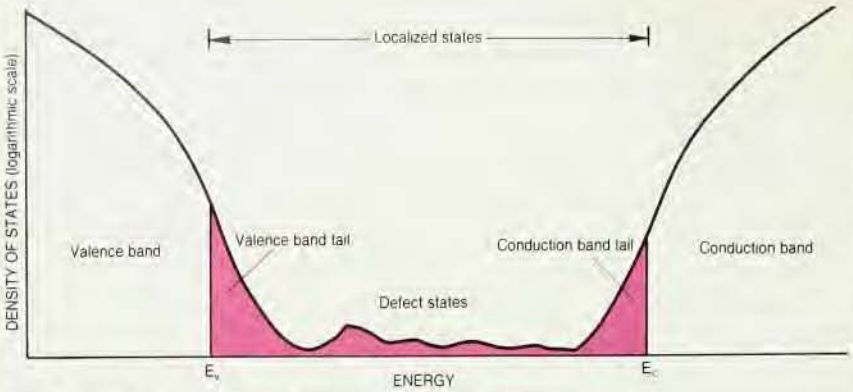
This defect model and the negative effective correlation energy successfully explained a large variety of properties of chalcogenide semiconductors.

Low-temperature anomalies

As the temperature decreases and the wavelength of prevailing phonons increases, the structural disorder of glasses should become less and less important, and the thermal properties of glasses should become identical to those of crystalline insulators. These properties are well understood in terms of a continuum elastic Debye theory that makes no distinction between solids having long-range periodicity and those that do not.

It was therefore very surprising when in 1971 Robert C. Zeller and Robert O. Pohl of Cornell University published[10] convincing evidence that the thermal properties of noncrystalline solids at low temperatures are entirely different from their crystalline counterparts.

Even before 1971, work such as that of Ansel C. Anderson of the University of Illinois at Urbana–Champaign had shown[11] that the thermal conductivities of essentially all noncrystalline insulators have the same temperature



Band model of a noncrystalline semiconductor. The continuous distribution of states in the energy gap is not seen in crystalline semiconductors. The energies E_v and E_c, called mobility edges, mark the boundaries of the mobility gap. Figure 4

dependence and nearly the same magnitude regardless of the chemical composition, local structure and impurity content of the insulators. Zeller and Pohl pointed out that this strange behavior of glasses is very likely associated with another remarkable anomaly: At low temperatures the heat capacity of glasses does not follow the prediction of the Debye theory but instead is considerably larger.

The discovery of the anomalous heat capacities suggested the presence of new elementary excitations that are characteristic of the noncrystalline state. In 1972, two groups suggested[12,13] independently that in disordered materials some atoms or groups of atoms can move by quantum-mechanical tunneling between two (or more) nearly equivalent potential minima. These two-level tunneling centers couple to the outside world through the strain field or through an electric field because a change in dipole moment is normally associated with the movement of atoms.[14] Hence these centers scatter phonons and also give rise to dielectric loss.

A number of elegant experiments have verified that these new centers essentially consist of only two low-lying energy levels, although there may exist higher energy levels that do not come into play at low temperatures. One experiment involves ultrasonic waves, which cause transitions between the two levels. The wave is attenuated as long as the lower states are more populated than the upper states. As the ultrasound power increases, the two-level centers saturate and cease to contribute to the attenuation. In the curve in figure 3, this is seen[15] as a leveling off. The critical acoustic power needed for this to happen yields the lifetime of the upper energy state.

The greatest triumph of the tunneling theory for the two-level centers was the prediction[13] and later experimental verification[16] that the specific heat is time-dependent, that is, the specific heat increases with the time spent measuring it. This is because the distribution in the heights of the tunnel barriers yields a wide spectrum of transition times or tunneling probabilities. As the time scale of the experiment is lengthened, say from one microsecond to several hundred seconds, an increasing number of tunnel states have transition times within this scale and hence can contribute to the specific heat.

With so many pieces of the jigsaw puzzle in our hands, do we now have a fairly good picture of the microscopic processes responsible for the low-temperature anomalies in glasses? The answer is no. An increasing number of discrepancies are being discovered between different experiments that depend on the same parameter of the tunneling model. For instance, the magnitude of the excess heat capacity of SiO_2, and hence the number of tunneling centers, can be changed tenfold by adding K_2O, without, however, noticeably affecting the heat conductivity. Postulating different classes of tunneling centers is unsatisfactory for explaining such different sensitivities, because it merely rephrases the problem. Instead, one tries to formulate more precisely the relaxation time regime to which a specific experiment is responsive. Perhaps the thermal conductivity, ultrasonic behavior and dielectric properties are governed by centers with short relaxation times whereas thermal expansion and heat capacity are affected by centers covering a much wider relaxation time regime.

Photoinduced structure changes

A noncrystalline material can exist in many different structural configurations. On a scale of a few angstroms these configurations differ in their average local steric and bonding arrangement. On a scale of 50 Å, they show different clustering of molecular units. And over even larger dimensions, they have different topological features. Each noncrystalline configuration is hindered from changing into another of lower total energy by the strong and directional covalent bonds that act as kinetic barriers.

It is therefore very surprising that one can change the bonding configuration and structure of chalcogenide glasses (and to a very different extent that of hydrogenated amorphous silicon) by exposing these materials to photons of considerably smaller energy than that of the covalent bonds that hold these noncrystalline materials together. The minimum energy needed is about equal to that of the energy gap, or the energy required to produce an electron–hole pair.

The largest photostructural changes have been observed in chalcogenide films such as GeS_2 and $GeSe_2$ that had been deposited onto a substrate at an oblique angle. Such films have a columnar void structure caused by the shadows cast by the growing deposits. After a day of strong illumination corresponding to about 10^{23} photons absorbed per cm^3, the very loose structure of these films becomes up to 20 percent denser. This major rearrangement of atoms happens at a temperature that can be several hundred degrees below the solidification temperature and is set in motion by photons that have only half the energy needed to break a covalent bond.

Another example is the photoinduced polymerization or cross-linking of molecular units in evaporated films of As_2S_3. After exposing the film for a few hours to light at the band-gap energy, one finds that its Raman spectrum is similar to that of an annealed film. These structural changes, and the concomitant changes in density, hardness, optical properties and chemical properties, are irreversible, because the photoexcitation gives the material enough energy to overcome a barrier and reach a structural configuration of lower free energy.

In addition to these irreversible effects, there are photoinduced changes of physical and chemical properties that one can reverse by annealing near the glass transition temperature. The 2.4 eV energy of the optical absorption edge of As_2S_3, for instance, decreases by 2 percent; the density by 0.5 percent, and the first x-ray diffraction peak by 1.5 percent after exposure to light at room temperature. In addition, one finds changes in the refractive index, microhardness, electrical properties and ultrasonic absorption, as well as in the chemical solubility in alkaline solutions. These photostructural changes saturate after the absorption of about 10^{22} photons/cm^3.

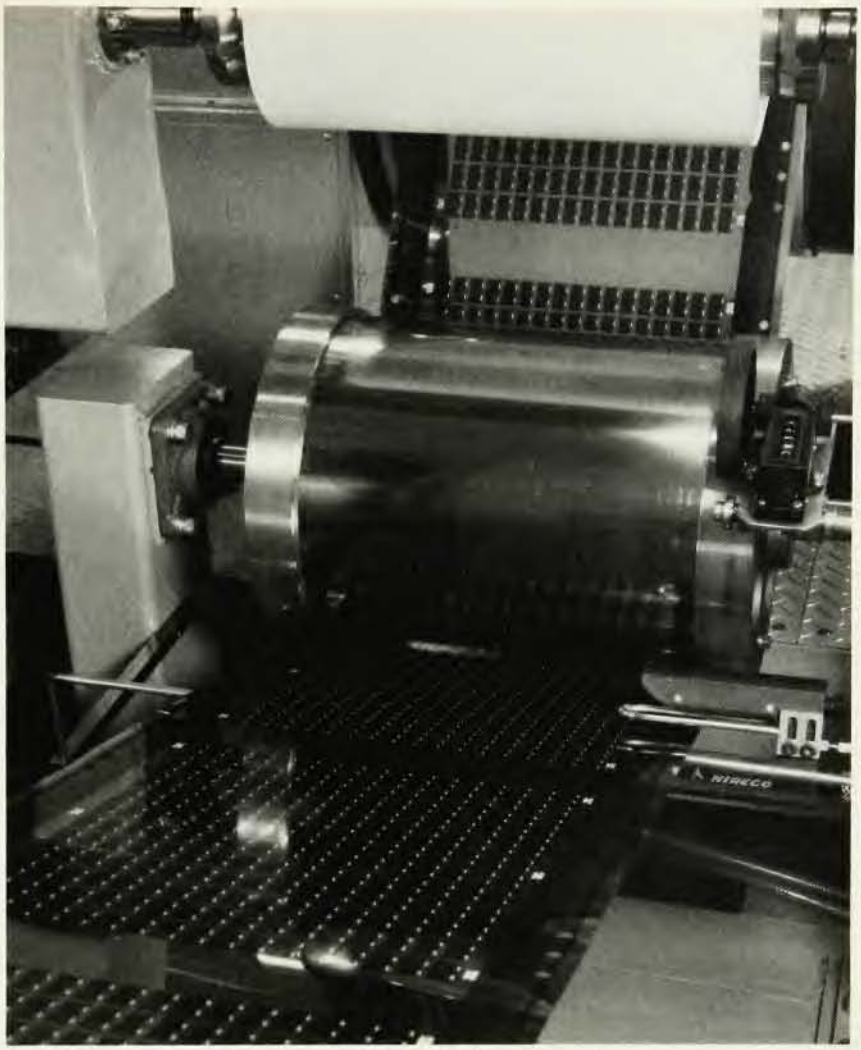
Unlike the irreversible photodensification and photopolymerization, the reversible changes correspond to increases in disorder and volume. We have no clear microscopic model of these photoinduced processes. One wonders how these quite drastic changes affect the density of the two-level tunneling centers, which give rise to the low-temperature anomalies. Surprisingly, no one has studied this question yet.

I emphasized earlier that the photons producing these structural changes have insufficient energy to break a covalent bond. However, it takes only about one electron volt to create a pair of valence alternation defects. Moreover, these defects and the photostructural changes are both linked to the presence of chalcogen atoms and lone-pair orbitals. Indeed, Street and David K. Biegelsen of Xerox, Palo Alto, found[17] that strong light exposure increases the concentration of valence alternation defects and that the annealing kinetics of this excess concentration is similar to that of the reversible photostructural changes. On the other hand, the concentration of new defects is $10^{19}/cm^3$, which appears to be much too small to account for the magnitudes of the observed changes in x-ray diffraction, density and all other properties.

There is a way out of this dilemma. The photocreation of a pair of valence alternation defects can lead to any of several different bonding configurations. The defects can either become metastable and be detected by their photoinduced paramagnetism at low temperatures, or the defect atoms may restore their normal bonding coordination. This latter process can, however, easily produce new bonding configurations that are different from the original one. In As_2S_3, for instance, the number of As–As and S–S bonds can increase in such a photoexcited two-step process, at the expense of the more stable As–S bonds. Having normal coordination, atoms in these new configurations would not show up in tests for defects, but they could produce the observed reversible physical and chemical changes. Raman studies have indeed shown an increase in As–As vibrations at a wavenumber of 231 cm^{-1} and of S–S vibrations at 491 cm^{-1}.

Another striking effect[18] is the photo-enhanced diffusion of silver from a layer of silver deposited onto the surface of chalcogenide glasses. This photodoping effect is probably related to the photochemical activities that are set in motion when an electron is photoexcited from a lone-pair orbital, which then turns into a highly reactive free radical.

Both the reversible and the irreversible photostructural changes, as well as photoinduced diffusion, lead to new materials that offer many new device applications. These materials are useful in the construction of diffraction gratings and holograms, and have applications in imaging and offset printing. Optical memory disks using these materials to achieve extremely high information density are under development. As photoresists, very thin chalcogenide glass films have many advantages over the conventional polymers. These inorganic photoresists require fewer processing steps while offering better contrast, resolution and resistance to etching by acid solutions.



Production machine for tandem photovoltaic cells. This continuous-roll production machine was developed by Energy Conversion Devices, Inc., of Troy, Michigan. Figure 5

Electronic properties

To use amorphous materials in semiconductor devices, we must be able to control their electrical conductivity. There are now two methods for doing this. One is conventional doping,[19] which has been done in hydrogenated or fluorinated amorphous silicon. Group-III and group-V elements act as acceptors and donors, respectively, as they do in crystalline silicon. The other is chemical modification, which is useful in a wide variety of amorphous materials.[20] A band model for a non-crystalline semiconductor gives a distribution of electronic states as sketched in figure 4. Note that unlike crystalline semiconductors, amorphous semiconductors have a continuous distribution of states in the energy gap between the valence and conduction bands.

Many challenging problems remain unsolved. Our understanding of the motion of carriers and the recombination of photoexcited or injected excess carriers is rudimentary. We have not been able to determine the density of states at the mobility edges E_c and E_v defined in figure 4. We do not understand the frequency dependence of the conductivity, and there is still a question as to whether electronic conduction takes place in the conduction band

Millionth photocopy from a drum covered with an amorphous silicon photoreceptor material. Silicon has some advantages over the traditional selenium coatings. (Courtesy of Canon Corp, Japan.) Figure 6

or by phonon-assisted hopping in the localized band tails. There is no satisfactory explanation for the observation that the sign of the Hall effect is positive for electron conduction and negative for hole conduction, opposite from the normal. We do not know whether polarons form, and we do not know how the conduction is influenced by spatial fluctuations of the potential, which are caused by random strain fields and the distribution of charged states.

This long list of open questions does not impede the inventive drive that utilizes the unique properties of amorphous semiconductors and that gave this field its original momentum.[20]

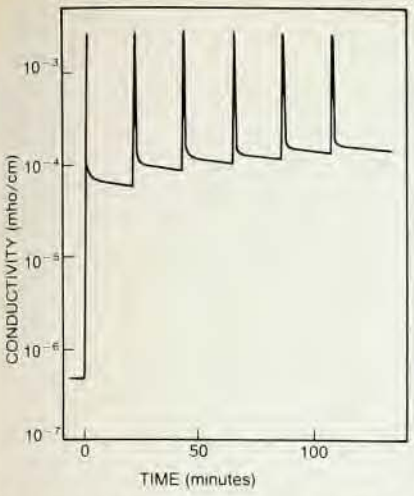
The outlook for amorphous silicon in future large-scale solar photovoltaic technology is very good (see figure 5). By using tandem arrangements of optically complementary alloys that respond to different portions of the solar spectrum, one should be able to fabricate amorphous silicon photocells with efficiencies that exceed the 15% desired for large-scale applications. Layers of amorphous silicon less than one micron thick are sufficient because the structural disorder improves the efficiency of light absorption. In amorphous semiconductors a photon can excite any electron from the valence band to any state in the conduction band. This is because wave number need not be conserved in materials that do not possess the translational symmetry associated with long-range order. Because amorphous solar cells can be thin and still strongly absorb sunlight, the drift range of the photoexcited carriers need not be very long, so that amorphous cells achieve quantum efficiencies close to 100% despite the very low mobilities of the charge carriers. Another use of amorphous silicon is to cover large areas with thin-film field-effect transistors or pin diodes to make isolation and address circuits; these circuits make it possible to build large-area flat-panel liquid-crystal displays for computer graphics terminals.

One of the earliest important applications of semiconducting glasses was the use of vitreous selenium as the photoreceptor coating on the drums of xerographic copying machines. Much current research is aimed at improving the mechanical durability of the photocopier material and at expediting the charge relaxation that limits the copying speed. It turns out that amorphous silicon, in the form of multijunction layers that reduce lateral charge flow and optimise other performance parameters, may prove to be a superior photoreceptor. The smaller bandgap of amorphous silicon compared to that of amorphous selenium assures not only the faster discharge times that allow higher copying speeds, but also the possibility to write information directly from a computer to a copying drum with light from a relatively inexpensive semiconductor-junction laser. Such a device would replace the printer at the computer output. Figure 6 illustrates the impressive quality and durability of the amorphous silicon photocopier material: It shows the millionth copy produced by an amorphous silicon drum.

Amorphous multilayers

Amorphous materials are already entering the exciting new field of "superlattices"—alternating layers of different crystals—that Leo Esaki and Raphael Tsu started[21] at IBM in 1970 with crystalline GaAs–GaAlAs multilayers. However, in growing such alternating layers, one must carefully choose the materials so that their natural crystal periodicities match at the interfaces. With amorphous materials, in constrast, one is free of this constraint and hence able to choose from a large combination of materials. The field has developed so rapidly that commercial amorphous superlattice devices were on the market before the publication of scientific papers on the electronic and optical properties of these materials. These devices are focusing and dispersive elements for vacuum ultraviolet light and x rays down to wavelengths of a few angstroms. Large differences in the x-ray scattering factors of the materials available, and the possibility of depositing amorphous superlattices on preshaped or flexible substrates, offer great advantages for a new generation of x-ray optical devices.

Several groups recently started studies[22] of amorphous semiconductor multilayers. It seems appropriate to end this article by giving a first glimpse of the properties of these new materials. Because plasma-deposited silicon–hydrogen alloy has the best semiconducting properties, researchers have deposited layers of this material alternating either with amorphous germanium–hydrogen alloy or with insulating layers of amorphous silicon nitride or silicon oxide. Other studies have focused on doping-modulated multilayers made of an amorphous silicon–hydrogen alloy arranged in layers that are alternately doped n, p, n, p and so on. I



Conductivity of a doping-modulated film of silicon–hydrogen alloy as a function of time and exposure to light. The multilayer amorphous film has an n–p repeat distance of 280 Å. The film was exposed to heat-filtered white light several times (spikes). After 20 hours the excess conductivity had decayed by not more than a factor of three. Figure 7

use the word "multilayers" instead of "superlattices" to describe the electronic and optical properties of these amorphous systems to avoid giving the impression that coherent effects arising from periodicity are expected or seen in these materials with such short mean free paths.

Figure 1 shows a transmission electron micrograph taken[23] by a group at Exxon of a multilayer film made up of alternating layers of silicon–hydrogen alloy and germanium–hydrogen alloy, with a repeat distance of 28 Å; more precisely, the object of the micrograph is a small cone that was shaped by a novel plasma etching technique from such a film. What one sees in this picture are the 25 layer pairs at the very top of a film containing several hundred layers.

By sandwiching layers of amorphous semiconductor material (amorphous silicon–hydrogen alloy) between wide-band-gap insulators (amorphous SiN_x or amorphous SiO_x), one finds that the optical absorption gap increases as the thicknesses of the semiconductor layers decrease below 50 Å. This phenomenon appeared in samples with several hundred layers of 10-Å-thick amorphous silicon–hydrogen alloy and 25–35-Å-thick silicon nitride, produced by plasma deposition. The simplest explanation is that the layers cause a one-dimensional quantum-well confinement of the wavefunctions, which pushes to higher energies the first extended states and hence the mobility edges of the semiconductor's valence and conduction bands.

When the sublayers are thicker, there is a transfer of charge between them because of their different work functions. This changes by many orders of magnitude the conductivities and photoconductivities of the layers of amorphous silicon–hydrogen alloy. This "charge-transfer doping" raises or lowers the Fermi level in the semiconductor without introducing chemical dopants, which are always accompanied by defects. The nitride layers donate electrons to the amorphous silicon–hydrogen alloy and make it strongly n-type, whereas layers of amorphous SiO_x remove electrons and make it p type.

When one interleaves layers of amorphous silicon with insulating layers, the band gap varies in space between the smaller value of the semiconductor and larger value of the insulator. On the other hand, in doping superlattices in which n-type and p-type doped layers alternate in a periodic fashion, a constant band gap oscillates up and down in energy as one moves through the layers; that is, the top and bottom of the gap move up and down together. Quite different phenomena are expected in such materials. Gottfried Döhler of the Max Planck Institute in Stuttgart predicted, for instance, that the internal fields of each of the many p–n junctions would separate photoexcited electron–hole pairs and trap them in different regions. Recombination of such spatially separated carriers would be possible only by the very slow process of phonon-assisted tunneling. These effects appear in crystalline superlattices at temperatures near 4 K. James Kakalios and I observed this effect in a much more dramatic fashion, even at room temperature, in a doping-modulated multilayer film of silicon–hydrogen alloy, as figure 7 shows.[24] This phenomenon has all the attributes of the photoinduced stored charge effect predicted by Döhler for doping superlattices, but more detailed studies are required to rule out alternative explanations.

No area of science remains isolated. Our understanding of crystals is already benefitting from our experience with amorphous materials. Glass-like two-level tunneling centers in the form of random interacting dipoles were predicted and then found to exist in some crystals; experiments have identified defects with negative effective correlation energies at vancancies and surfaces of crystals; theorists now use the concept of mobility edges to describe the metal–nonmetal transition in doped semiconductors and in two-dimensional inversion layers; and the chemistry of valence alternation defects should prove useful in any material containing pairs of nonbonding electrons. Future attempts to understand materials of higher complexity, such as organic and living matter, will probably benefit most from an understanding of amorphous semiconductors.

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