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PRINCIPLES AND APPLICATIONS OF AMORPHICITY, STRUCTURAL CHANGE, AND OPTICAL INFORMATION ENCODING

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Abstract. - Information and energy are areas of greatest importance to our highly technological society. Restrictions of crystalline symmetry and depletion of natural material resources have made both these subjects materials limited. Amorphous materials are the common media for the expression of the transformational processes of energy and information. The ability to synthesize materials in which many elements of the periodic table are combined in ways previously forbidden to them by crystalline constraints opens up new fields of invention and application as well as the new area of science that is rapidly growing.

INTRODUCTION. - Materials have always been the basis for new advances in civilization. The use of materials such as stone, iron, bronze, and the tools made from them are the result of the inventive process, and have been used to define the ages of humankind.

We are now faced with momentous problems stemming from the depletability of our natural resources. The challenges can and will be met by the invention of new synthetic materials that can interface with nature and generate the energy so necessary for future progress. The invention of these materials, which can convert various forms of energy directly into electricity, is already taking place.

The key issues of our present industrial society are energy and information. They are actually opposite sides of the same coin. Our energy problems are, in reality, difficulties involving the conversion of one form of energy (light, chemical, etc.) to another (mechanical, electrical, etc.). Storage and processing of information also necessarily involve energy conversion and dissipation (1,2). The transformations that take place in an amorphous solid have to do with both its informational and energy content. Figure 1 illustrates our concept of energy conversion which we approach in two ways-one, as a process by which light, heat, or chemical energy can be transformed into electrical energy through a suitable material; the other, where energy is used as a means of encoding and expressing information through the transformation that takes place in materials so that an input of one form of energy, such as light, electricity, or heat, can be recorded, stored, retrieved, transmitted, that is, communicated or switched into another intelligible form of information, such as computer memories, imaging films, or switching matrices. The common denominator is that the interactions and conversions take place in amorphous materials where the indivisibility of energy and information is uniquely expressed.

When I started work in this area in the 1950's, amorphous materials were not considered scientifically understandable nor to have any particular use. The selenium drum which gained popularity in the 1960's in xerography had evolved empirically and its amorphicity was considered incidental (3).

We founded ECD in 1960 to develop a broad and basic approach to amorphous materials with applications such as various types of switching and control de-

vices, memories, imaging films, diversified coatings, and energy conversion devices based upon principles described herein:

PRINCIPLES. - 1. Amorphicity is a generic term referring to lack of X-ray diffraction evidence of long-range periodicity and is not a sufficient description of a material. To understand amorphous materials, there are several important factors to be considered: the type of chemical bonding, the number of bonds generated by the local order, that is its coordination, and the influence of the entire local environment, both chemical and geometrical, upon the resulting varied configurations. Amorphicity is not determined by random packing of atoms viewed as hard spheres nor is the amorphous solid merely a host with atoms imbedded at random. Amorphous materials should be viewed as being composed of an interactive matrix whose electronic configurations are generated by free energy forces and can be specifically defined by the chemical nature and coordination of the constituent atoms. Utilizing multiorbital elements and various preparation techniques, one can outwit the normal relaxations that reflect equilibrium conditions and, due to the three-dimensional freedom of the amorphous state, make entirely new types of amorphous materials--chemically modified materials (4-3).

There are at least two systems operating in amorphous materials: the normal structural bonding which makes up the great majority of the bonding configurations of the solid and controls its structural integrity and its optical energy gap, and the deviant electronic configurations (4,7) which are generated by the three-dimensional spatial freedom of individual atoms counter-balanced by the chemical forces surrounding them, their environment (4,5,7, 9-15).

The creation of deviant electronic configurations can be understood simply by viewing even an elemental amorphous material as having several different bonding configurations as available energetic options. It is vital to understand that the same atoms can be found in the same material in different configurations. For example, elemental amorphous silicon, while normally tetrahedrally bonded, has some atoms in which the coordination is not tetrahedral. The same is true of nontetrahedral amorphous materials exemplified by the chalcogenides (14) where deviations from primary divalency are inexorably present. Local order is always specific and coexists in several configurations in every amorphous semiconductor. Steric and isomeric considerations are involved both with the factors which encourage amorphicity and those that create defects in the materials. The constraints in amorphous materials are not those of crystalline symmetry but are involved with asymmetrical spatial and energetic relationships of atoms permitted by the varying three-dimensional chemical and geometrical possibilities afforded by the amorphous In such a solid, the bonding options are not only of the conventionally solid. considered covalent type, but involve coordinate, or dative bonds with their charge-transfer characteristics (4,9, 11-14). There is not only a spectrum of bonding which spans from metallic to ionic in one and the same solid (10) but a spectrum of bonding strengths. A major factor involved in the spectrum of bond strengths in amorphous materials is the counteracting or competitive force of the chemical environment which acts to influence and alter the bond energy. We therefore can have a greater number of weaker bonds in an amorphous semiconductor than one would find in a crystalline solid.

Physicists have taken for granted that there is a thermodynamic drive toward crystallinity. We emphasize that there is an equally important energetic process that leads to amorphicity, that is, the preferred chemical bonding of atoms and the charge field produced by nonbonding electrons can alter a molecular structure so that it has an anticrystalline state. Crystals by definition have geometries that allow for repetition of the basic cell structure. The shapes that I am discussing are not rigid spherical balls but complex distorted shapes formed by localized pressures, repulsions, and attractions of surrounding forces, compressed here, elongated there, twisted along another axis, the very antithesis of a crystal cell model. These tangled networks are further inhibited from crystallinity by crosslinks and bridging atoms. They are constrained by virtue of the electron orbital relationships, including those of the lone-pair electrons, the chemical

influence, the mechanical presence, and the spatial relationships of their nearest neighbors. Such complex three-dimensional forms favor chain and ring formation and are chemically characterized by fluctuations of valency and coordination and can have varied charge conditions. The electron-electron and electron-phonon interactions, therefore, cannot be characterized in a simple manner and the energetic considerations required to complete coordination depend upon the ability to spatially and energetically mate bonding positions (11-14,16). This becomes increasingly difficult as one goes to the tetrahedral condition which is the reason why elemental amorphous silicon does not have completed structures but has weakened bonds, dangling bonds, and voids. In such cases, other elements with the proper size and charge are necessary, such as fluorine and hydrogen to make up the structural units that complete its bonding and provide stabilizing forces. While the bonding is more complete in materials made of silicon and hydrogen than in elemental silicon, the addition and substitution of fluorine for hydrogen is necessary to have an amorphous silicon-based alloy of optimum stability (9, 17-19) However, once this is accomplished, one no longer has elemental amorphous silicon, but an allov.

2. Amorphous materials can be separated into two types: unistable, in which the material's local order does not alter within a given range of temperature or excitation, and bistable, in which structural rearrangements and relaxations occur (10, 20). These can be of a reversible nature and result in a spectrum of changes from subtle nearest neighbor changes to those where many bonds are broken, resulting in various new types of short-range, intermediate and long-range order. Excitation causes conformational changes which result in structural changes so important for the information side of our work. Depending upon the design of the materials, there is again a range of these structural changes that can occur in amorphous materials. These can be detected chemically, for example by etching, electronically by changes of resistance, as well as optically. All these effects can be made reversible, especially in the nontetrahedrally bonded materials such as the chalcogenides (see Figure 2) (21-24).

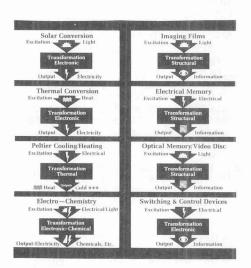


Fig. 1: ECD's energy conversion processes for energy and information.

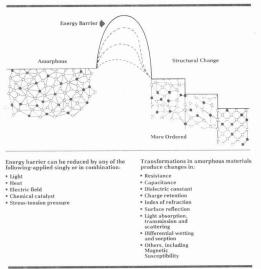


Fig. 2: Information storage/retrieval and display by structural transformation.

- 3. The structural configurations in both unistable and bistable materials play a role in establishing the physical, chemical, and electrical properties of the materials. Crosslinks and bridging atoms are not only structural factors stabilizing amorphicity, but also contribute to the distribution of band states (16,25). The density of states in the gap of an amorphous material controls its transport properties. The nature and number of the states not only affect the electrical conductivity but are also related to the chemical reactivity of the material (16,20).
- 4. In amorphous solids, internal topology can result in another physical parameter, porosity, which results from all of the energetic and three-dimensional spatial factors discussed above, and which can be an important design factor not found in crystalline materials (26).
- 5. Even elemental amorphous materials such as selenium, silicon, boron, etc. do not have uniform internal topology as do their crystalline counterparts but have various structural configurations such as rings, chains, voids, etc. I consider elemental materials to be in a sense structural alloys. Compositional alloys have diversity of structure based upon composition; elemental amorphous materials have diversity of structure based upon positional and translational relationships of similar atoms. The local environment in amorphous single elemental materials differs in important ways from that of their crystalline counterparts, and even though both types of materials may have common deviant bond structures, the number and type of such defect states are different in amorphous materials than in their crystalline counterparts. The total environment must be taken into account in the amorphous case in order to properly define the defect states (9.12).
- The major thrust of ECD's activities is centered on our conviction that amorphous materials are most interesting in their non-elemental form such as alloys or modified materials. The latter refers to materials in which the normal equilibrium bonding is disturbed by creating new configurations through the insertion of a perturbing element or elements with multi-orbital possibilities (4,7). For example, alloying allows the optical band gap to be designed at will and yet chemical modification or doping by affecting gap states can independently affect and control the electrical conduction process. Alloys or modified materials can be made using many of the elements in the periodic table and the possibilities can be expanded by introducing as modifiers multi-orbital elements such as the d-band elements. These "pin cushion" orbitals (4,6) interact with the matrix and each other in ways that are unique. They can enter the bonding matrix but, most importantly, these multidirectional orbitals by their interaction can eliminate or create states in the gap. When they generate states, they can be of a much larger number than is allowable by alloying or even doping. Bonding possibilities in the amorphous state include coordinate bonds, three-center bonds, and the multi-orbital options of carbon (4,7).
- 7. The elimination of the crystalline constraints and the consequent additional three-dimensional freedom afforded by the amorphous state permit the widest variety of bonding and antibonding orbital relationships that can be found in a solid and are our key to the ability to synthesize new inorganic materials not found in nature.
- 8. The understanding of spin pairing is involved with the structural flexibility of the amorphous material and the nature of the surrounding environment. Electron-phonon interactions in amorphous materials can be varied by changing either the composition or the preparation conditions. Spin pairing is not an inherent feature of all amorphous materials as has been suggested by Anderson (27). As I previously pointed out (11,28), it takes too much energy to pair spins in materials with a rigid matrix, for example, there is not enough bonding flexibility in sputtered amorphous tetrahedral materials to overcome the energy barrier between different configurations. However, the flexibility afforded by for example primarily divalent chalcogenide (lone pair) materials encourages the necessary

electron-phonon interactions to drive the bonding deformation necessary to pair all the spins (9,11-13). The energy barriers between such rearrangements are minimized by the effective electron-phonon coupling permitted through the relaxation modes available in amorphous materials designed with a flexible matrix. This is analogous to the competition between crystal-field effects and magnetic interactions in transition-metal compounds, leading to a high-spin state in some materials and a low-spin state in others.

In summary, the transport properties of amorphous materials can be understood from their deviant bonding character just as those of crystalline materials are understood and controlled by the deviations from long-range order. In amorphous materials, these deviations are directly involved with fluctuations of coordination and directionality of the bonding and nonbonding orbitals. The intersection of these spatially and energetically varied orbitals in three-dimensional space provides the opportunity for unusual electronic excitation and recombination mechanisms as well as the possibility for structural change if bistability is desired. In either case, bistable or unistable, deviant short-range order viewed against a background of the more commonly occurring normal short-range order is the Rosetta Stone for the understanding of electronic activity in amorphous materials (4,7,14).

INFORMATION. - As we have indicated above, the amount of stiffness in an amorphous matrix is a designable parameter. The most flexible structures are the reversible chalcogenide bistable materials which have an inherent plasticity in which information can be encoded by virtue of a structural change--from subtle bonding changes in the amorphous phase to an amorphous-to-crystalline transition. The alteration in the material reflects the informational content of the energy put in in either digital or analog form, that is, either in series or in parallel, and can be detected and read in any number of ways (see Figure 2). As one adds stronger bonds and more crosslinks in building a more rigid material, reversibility of the amorphous to crystalline phase is diminished, for example, in amorphous silicon-based materials. These nonreversible materials can have device usages as well.

1. Ovonic memory switches. The reversible amorphous to crystalline transformation has become increasingly important as microprocessors have gained utilization in the office, factory, and business environment. There is a great need for a high-density, short-access-time, nonvolatile random access memory. The new improvements in the Ovonic EEPROM technology are most timely in this context.

The basic Ovonic memory switch can be used in a memory matrix to achieve a fast, completely nonvolatile EEPROM (electrically erasable programmable read-only-

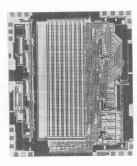


Fig. 3: 1024 bit current mode logic Ovonic EEPROM measuring 136 mil by 160 mil.

	1975	Now
VThreshold	22V	8V
IWrite	150ma	5ma
IRead	1ma	1ma
Write Time	10ms	1ms
Read Time	45ns	15ns
Processing Temperature (Max)	80°C	200℃
Storage Temperature (Max)	80°C	175℃
Operating Temperature (Max)	80°C	110℃
Cell Size	4mil ²	0.75mil ²

Fig. 4: Recent improvements in operating and manufacturing parameters of the Ovonic EEPROM device technology.

memory) device. In conjunction with Burroughs, and now with Sharp Corporation, a 1024 bit BCML (Burroughs Current Mode Logic) Ovonic EEPROM has been produced with access times of less than 15 nanoseconds (Figure 3). Further materials development has subsequently improved the basic cell characteristics. The performance improvements are summarized in Figure 4. These performance advantages are achieved by grading from tellurium-rich alloys on the top to a germanium-rich alloy on the bottom (29-31).

2. Optical memories. Since the 1960's (22-24, 32-38), ECD has pioneered in and developed various types of optical memories based upon the principles of bistability. Ovonic materials have characteristics which make them ideally suited for optical information storage requiring high-density recording and high signal-to-noise ratios. The materials utilized exhibit a bistability in which both the amorphous and crystalline state can co-exist at ambient conditions. There are many properties which exhibit a dramatic difference between the two states. For an optical memory the characteristics that are important are the index of refraction and the absorptivity. The change in these two provides a film that can be read in either the reflective or transmissive mode. The materials are reversible (erasable) and have superior image quality.

The change in state of Ovonic material coated on an optical memory disc can be accomplished by a variety of methods. For example, a laser beam focussed to a sub-micron spot can be used to both crystallize and revitrify a single track or portion thereof on a spinning disc. A laser pulse that will vitrify the crystalline portion of the material can be used to recrystallize the same material by simply lowering the intensity by two thirds. Therefore, depending upon the laser intensity, the same spot can be repeatedly switched. Bulk erasure can also be accomplished by several means.

The application of light is all that is required to complete the change of state. No further processing is necessary. Lasers whose outputs range from the ultraviolet to the infrared can be used. The energy required to switch one square micron of material is between 0.1 and 0.2 nanojoules. On a disc spinning at 1800 rpm, this corresponds to less than 10 milliwatts of light at the disc.

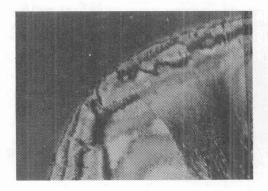
The image quality is excellent. Figure 5 shows the ability to achieve a dot with an edge sharpness of 100Å. The resolution of the medium exceeds one thousand line pairs per millimeter. The spot size is not diffraction limited. The threshold recording aspects of the material can be used to record a smaller than diffraction limited spot by utilizing the Gaussian distribution of the intensity. Applications include archival and updatable computer storage, large volume data storage, consumer and industrial video disc and video disc mastering.

3. <u>Instant Dry Process Imaging Film</u>. We have developed a silverless dry process imaging film based upon an organotellurium compound. This film also utilizes an amorphous to crystalline phase transition and offers continuous tone with exceptionally high resolution and radiometric speed.

The mechanism can be described as an initial event resulting in the electronic excitation of a photosensitive reactant to a highly reactive species which then, through chemical action, initiates a reducing step forming a latent image. Through either simultaneous or sequential heat treatment, the organotellurium compound undergoes autocatalytic decomposition to tellurium which in the latter stages of thermal development generates crystallites in the form of needles which constitute the visible image (34,39). Figure 6 is the reproduction of such an image.

4. Photostructural Films (40). We early developed materials which can be affected by light so as to make them selectively etched (10,33). One such film is in production in Europe by Agfa-Gevaert for application as a graphic arts film. This nonsilver film has very high contrast coupled with high resolution. It is a

contact speed film, available in both reversal and nonreversal forms. It can be used either for photographic or mask-making purposes.



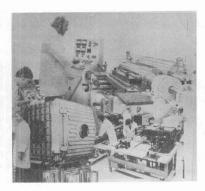
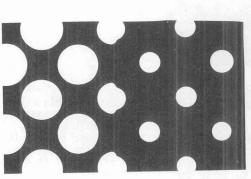


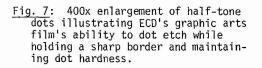
Fig. 5: Transmission electron photograph of a section of a crystalline dot on an amorphous background. The featureless area is the amorphous region.

Fig. 6: Ovonic nonsilver photoduplication film.

The dot edge sharpness (see Figure 7) is unexcelled. Dot edge sharpness refers to the linear distance over which the film is able to go from its lowest to its highest density. Since the film has only two available densities, the transition distance becomes virtually zero. The resolution of this film exceeds 600 line pairs per millimeter.

5. Microvonic File System. (See Figure 8). The essence of this system is a low melting alloy coated on polyester to form a fiche card which displays photostructural changes upon exposure to a given threshold level from pulsed energy sources. Typically, xenon flash or laser sources are used with pulse durations of 1μ - 1ms and energy values on the order of 0.1 joule/cm² to 1 joule/cm².





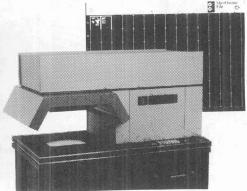


Fig. 8: MicrOvonic File: this system permits not only the recording of documents on fiche but also provides for deletion and addition of all information.

6. Unistable Materials. - Amorphous materials can be designed from the chalcogenide to the tetrahedral type so as to be structurally stable under the influence of excitation processes. The threshold type is exemplified by the Ovonic threshold switch which I invented in 1960 and which has been fully described elsewhere (21, 41-42). Its switching speed at room temperature is comparable to that of Josephson diodes which require cryogenic temperatures. As digital applications increase, it is anticipated that this switch will find increasing utility. Transistor-type action in our Si:F:H alloy indicates that large-area thin-film transistors will soon see application.

ENERGY. - Amorphous materials for energy usage are almost entirely of the unistable type. While there are many uses of amorphous materials utilizing the principles that we have outlined ranging from thermoelectricity and electrochemistry to superconductivity, the area of greatest immediate interest is photovoltaics.

We announced a silicon-fluorine-hydrogen alloy and described its material and photovoltaic device properties (17-19, 43-50). The efficiencies are very promising and Madan is reporting on them at this meeting. Figure 9 shows a one square foot array developed by Izu and his group at ECD. This device represents a great deal of attention to the production technology so necessary to utilize the inherent value of a large-area film. For the first time, alternative energy has the possibility of being competitive in cost to coal, gas, oil, and uranium. Our targeted efficiencies for near-term production are 7-10% for these one square foot cells. We will report on newer alloys and configurations with even more optimal characteristics in the near future.

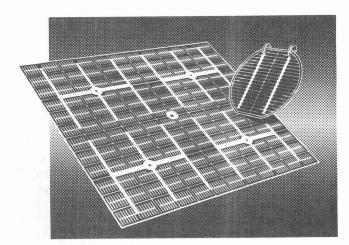


Fig. 9: Ovonic photovoltaic cell 1 ft. x 1 ft. compared to typical 4 in. diameter crystalline cell.

SUMMARY.- There is a chemical and structural basis for amorphous materials which has guided our work from its very beginning. It has allowed us to alter band gaps at will through alloying, understand and define defect states and spin pairing, introduce doping in chalcogenides and modification across the periodic table. It has permitted us to utilize the super halogenicity of fluorine for its organizing (inductive) influence to manipulate size and charge of various atoms, and to design atomic and molecular configurations best suitable for specific tasks. The electronic excitatory processes in these materials have unique attributes that are reflected both in speed of switching and the highly conductive state seen in threshold switches. We have been able, through modification, to break the lockstep which has connected the optical band gap, electrical activation energy and even the thermal conductivity of materials. By independently controlling and manipulating

these important parameters, new areas of applications are possible. The ability to selectively retain or alter structure, the latter even in a reversible manner, has valuable device implications as well.

We believe the old debate whether or not one has to work with elemental amorphous semiconductors in order to understand the amorphous state has been resolved. Our view is that alloys and modified materials based upon structural and chemical considerations outlined herein are best suited not only to clarify the scientific understanding of amorphous materials but as a vehicle for new technology which will be beneficial to society.

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