SEMICONDUCTOR AND SUPERCONDUCTOR MATERIALS

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MATERIALS FOR MOLECULAR ELECTRONICS

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The words "molecular electronics" have become household words in recent years, but the definition of these words can become extremely tricky. The definition that strikes at the basis of the matter says molecular electronics is "the synthesis of matter with predetermined electronic properties so that under particular stimuli the matter exhibits complex and complete electronic functions previously performed by distinctive combinations of active and passive components." (1)

To realize the full potential of the concept of molecular electronics, three areas of endeavor must be mentioned. These areas are materials, the discovery and use of physical and electrical phenomena to perform electronic functions, and the techniques for fabrication of reliable, complex functional blocks.

It is not the intention of this paper to enumerate or debate the potential advantages of the molecular electronics concept. Nor is it intended to discuss the more familiar aspects of solid state materials and phenomena, but rather to review some of the newer approaches to solving the problems encountered in solid state electronics.

The material of interest in molecular electronics is a single crystal. For airborne applications, the greatest efforts have been in silicon, with some in germanium, followed by gallium arsenide and others of the III-V compounds.

It was only natural and most expedient that the beginnings of molecular electronics should be based on the well-known semiconductors and their technologies. However, the concept of molecular electronics must necessarily embrace all materials that have even a remote chance of being useful for performing electronic functions. The expansion into the areas of light utilization and thermoelectricity as well as other fields of application has led to new interest in expanding the list of useful electronic materials. Obviously many arrays of inorganic compounds with predictable properties can be drawn from the elements and the large number of common stoichemetric ratios.

Such an array of compounds, related to the periodic chart, serves a very useful purpose in the selection, preparation and estimation of properties of semiconducting compounds. Many compounds included in the arrays may not exist. If the compound does exist, the value of its melting point, energy gap and electron mobility, generally fits into a uniform pattern related to adjacent compounds. The crystal structure of semiconducting compounds has been shown to be of second order importance in preparing arrays. Grouping semiconductors by crystal types loses overall relationships that exist between many compounds. The reasons for the lack of data on these compounds is not that workers in the field are unaware of the large number that exist, but rather the lack of experimental work confirming the existence of a large number of suspected semiconducting compounds. (2)

For the tailoring of materials, the arrays of compounds offer an excellent starting point. The energy gap, physical, and electrical properties can be changed in a controlled manner by the addition or subtraction of one or more atoms. In the ideal situation, the device engineer would list the desired properties for a material for a particular application, then the chemist and physicist would prepare and optimize such a material.

In recent years interest has been building in the electronic behavior of organic materials. This is a logical extension of scientific endeavor, since the number of possible atomic combinations, molecular structures and physical properties attainable in organic chemistry is very large. A great amount of experimental work has been carried out on organic materials of dubious purity from a semiconductor viewpoint. As a result much data of questionable value has been accumulated on the electrical properties of organic materials.

It is not expected that any exotic devices fabricated from organic semiconductors will be available for some time. However, some of the pyropolymers appear to be medium quality semiconductors, that is, by one researcher's definition (3), material having an electron mobility in the range of 5 to 500 cm/volt-sec, which places them in the same class with tellurium, selenium, diamond and silver chloride. There are a number of unsolved puzzles in trying to reconcile theory and experimental data in the organics. For example, the calculated activation energies for some of the compounds are an order of magnitude higher than any observed values. The usual band theory predicts that the conductance of the liquid compared to the conductance of the solid should be less than one. However, the organics differ by 1000, 10,000, or 15,000 times with the liquids conducting better than the solids.

The ultimate relevance in this field comes in the understanding of the function of structure in determining the particular chain of reactions that take place. It is hoped that an understanding of electron transfer processes in the simplest of organic single crystals cannot fail to reveal the basic mechanisms of electron transfer through an ordered array. This information will be invaluable to the field of bionics and can contribute significantly to the uncovering of additional electronic phenomena. There is a crying need for the correlation of the data of the chemists, the biochemists and the measurements of the physicists in the organic semiconductor fields.

The paramagnetic, ferroelectric and ferromagnetic materials can all make significant contributions to the total concept of molecular electronics. Devices fabricated of paramagnetic materials are being used as amplifiers and oscillators, in addition, to the use of the materials in LASER and MASER applications. The most advanced use of ferroelectric devices are as active elements in parametric and harmonic generators. The thin film form of the ferroelectrics used as an active element is arousing great interest. Devices of ferromagnetic materials are used actively as frequency multipliers and as Suhl amplifiers. In addition, both the ferroelectrics and ferromagnetics are used passively as phase shifters and crystal protectors.

These materials are all useful to molecular electronics only when the physical and electrical phenomena of the materials are used to perform electronic functions. This is the key on which significant advances in the state of the art must depend.

There are approximately one hundred fifty known solid state phenomena (4). Of this number about 80 percent are unique phenomena and about 80-90 percent of the unique phenomena are useful. This means there are approximately one hundred phenomena which can be used to perform electronic functions.

The first step in the phenomena phase is to learn the types of functions which are needed. This can be determined by a study of circuits, subsystems and systems aimed at delineating possible functional blocks. Then the processes of creative thought based on the knowledge of the materials and phenomena are applied to develop a functional block which will do the job.

Some devices operating on unusual phenomena of solid state materials have been described. Experimental work is under way on a tunnel emission amplifier; a magnetic domain interaction amplifier; and a device called a neuristor. The tunnel emission amplifier utilizes conduction by majority carriers and theoretically should have extremely high frequency capabilities. The magnetic domain interaction amplifier has the potential for handling low level input signals; the ability to function at elevated temperatures and at a low noise level. The neuristor is a proposed device which propagates a discharge wave of constant amplitude, at a constant velocity and with a finite refractory period during which it is incapable of being triggered. The discovery and exploitation of these phenomena leading to the feasibility of solid state detection, amplification and generating devices operating in the microwave frequency spectrum will provide a unique capability in the fields of communications, navigation, guidance and fire control.

In the past much emphasis has been placed on the high temperature properties of solid state materials. Recently, investigations of physical and electrical phenomena at cryogenic temperatures have been started, and attempts made to establish techniques for applying cryogenic principles for device and circuit improvement. Phenomena exhibited only at very low temperatures may be useful in the design of low noise detectors, for harmonic generation, frequency mixing, low noise amplifiers, or computer elements. The cryogenic property of superconductivity has been used to demonstrate a tunneling type device which is potentially capable of operating as a very high frequency low power oscillator, a computer element or as a high frequency low noise amplifier.

Some of the more familiar phenomena such as piezoelectricity are forming the basis for new and useful devices. At the New York meeting of the IRE in March, Dr. D. L. White of the Bell Telephone Laboratories described a new ultrasonic transducer for use at microwave frequencies. Its frequency range extends from near 300 mc to perhaps higher than 10,000 mc. The electromechanical coupling is due to piezoelectricity in a material which is simultaneously an extrinsic semiconductor. All the III-V compounds are piezoelectrics as is cadmium sulfide. (5)

There are the photo-phenomena, thermoelectric properties, magnetic properties as well as the more familiar phenomena of rectification, and amplification that need to be exploited and used to the fullest. The combination of two or more phenomena to perform a single function or series of functions becomes a fascinating exercise. Such a complex begins to fulfill the true concept of molecular electronics.

The important point is that the uses of solid state phenomena can be and should be extended to create the functions required to construct electronic systems. The inevitable result will be new functions, which in turn will augment the repertory of the system designer.

The materials will be made available, the phenomena will be described and it now remains to develop the techniques and processes whereby the properties of the materials can be made available in the best possible form.

Control is the key word which links processing techniques with molecular electronics. In the past semiconductor device structures took form in accordance with the existing technologies. The development of each new fabrication method and combinations of methods permitted the exploration of broader device applications. As a rule, all of the useful semiconductor process tended to require large amounts of time to yield a complete structure capable of satisfactory electrical performance.

Recently attention has been focused on the field of semiconductor technology in an attempt to solve the problems of the expanding field of molecular electronics. Efforts expended on solid state circuits, functional electronic blocks, thin film circuit functions and integrated circuits have stressed the need for more sophisticated process tools.

The dendritic technique for forming single crystal ribbons has received a great deal of attention in the last few years. This technique has its greatest value in the elimination of processing steps, thereby, decreasing costs, increasing yields and giving greater uniformity of devices. There is an outgrowth of the dendrite technology that is even more exciting than the original process. It has been demonstrated that webs or sheets of material may be grown by a simple modification of the dendrites process. With very little attempt at controlling the growth parameters, sheets of silicon have been grown that are single crystal, have no twin planes, and have the good surfaces associated with dendrites. At this writing, 1 cm-wide sheets, 5- to 35-mils thick, without twin planes have been grown. Sheets up to 3 cm in width with one or more twins also have been grown. Evaluation of this material along with studies of parameter control are in progress. Semiconductor material of good quality in sheet form stirs the imagination. Immediately its application to large area devices and solar cells is apparent, and it has real possibilities when applied to integrated circuitry and functional blocks.

The use of thin metallic and dielectric films as passive devices is quite common, but a combination and refinement of these are the basic techniques for the newer tunneling functions. The thin film technique is being extended to include other solid state materials and particularly the semiconductors. Single crystal thin film junction devices will be especially valuable to integrated circuitry when combined with other active and passive elements. In addition to the small size and weight of thin films, this technique could facilitate the use of phenomena which may be unique with films or are masked by the bulk material.

The technique of epitaxial crystal growth has proved to be most useful and is being extended to the newer materials. This technique will be useful not only for fabricating new devices but for highly desirable improvements in old devices. Epitaxial growth makes possible graded energy gap devices, potentially better solar cells, and has been used successfully with mixed intermetallic compounds.

Techniques for preparing solid state materials such as vapor and vacuum deposition, vapor and solution growth, vapor phase reaction and transport, flame fusion and hydrothermal methods are being extended, modified, and improved. The areas of electrochemical and electron beam techniques promise significant improvement in the formation and control of junctions.

Many funds and great efforts have been expended on investigating and attempting to understand the surfaces of solid state materials. Many methods of protecting surfaces have been proposed but always these methods have been a passive treatment. That is, devices are given the final etch and washing and then a "gunk", inert gas or a vacuum are used along with a hermetically sealed can. These procedures have served for a while although the techniques for encapsulation left much to be desired in operating performance and reliability.

With the advent of molecular electronics and functional blocks, the problems of surfaces become even more challenging. Several approaches are being pursued but the most promising have in common an active ambient principle. That is, the protection of the surface is achieved by deactivation or trapping, of mobile ionic species by reaction with a suitable chemical sink. These techniques offer surface stabilization, improvement of device yield, reliability, reduction of costs and size, and the thin film, hermetic sealing of large surface area devices. The protection of integrated circuits, functional blocks, electroluminescent devices and solar cells are areas of potentially useful applications.

The primary purpose of this paper has been to emphasize the interdependence of the areas of materials, phenomena and techniques in achieving the potential offered by the molecular electronics concept. The efforts to develop a new electronics materials technology based on the synthesis of materials with tailored electronic properties; to exploit and develop new or enhanced physical and electrical properties of solid state materials; and to develop the techniques to combine the materials and phenomena into functional electronic units that will amplify, detect, oscillate, or otherwise perform as an active device together with associated passive devices must all be pursued concurrently. To divorce one area of effort from the other will do real damage to the whole. With the increased dependence of weapons systems on electronics and the increased emphasis on reliability of molecular electronics promises to meet many requirements for advanced systems. However, considerable additional effort needs to be expended to obtain data on modes of failure rates, and a correlation of this data with materials, phenomena, applications, techniques and processes information.

To achieve the advantages offered by the molecular electronics concept, all the disciplines of the scientific world must be utilized to solve the difficulties and attain the necessary revolutionary breakthroughs. All aspects of the problem must be considered and particularly the relationship of each phase one to the other. The coordinated efforts and results of basic and applied research, electrical and electronic engineering, device and system design are required to provide a capability in molecular electronics.

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