Amorphous Silicon: A New Direction for Semiconductors

The ability to manipulate the electrical behavior of ultrapure crystalline silicon is the cornerstone of the solid state electronics revolution. By contrast, scientists' inability to control the properties of noncrystalline or amorphous silicon has limited interest in the latter material mainly to basic researchers. But in the last 2 years, the discovery that hydrogen can play a key role in determining the electrical and optical properties of amorphous silicon has led to the distinct possibility of its technological exploitation in the form of extremely inexpensive solar cells. Other devices requiring large areas of material, such as an economical flat screen display, are also conceivable. These developments have led to a renaissance in research on amorphous semiconductors.

One of the biggest advantages conferred by the use of any amorphous semiconductor is its potential for being manufactured inexpensively. The low cost stems in part from the materials' lack of crystallinity, so that amorphous semiconductors do not need to undergo costly crystal growing operations, although for most electronics applications the "clean room" conditions characterizing the fabrication of today's microelectronic devices may be required. Therefore, when made in the form of thin films with a thickness of about 1 micrometer, amorphous materials can make large area devices economically viable.

This is the first of two Research News stories on amorphous semiconductors.

The disadvantages have been that the disordered structure and an insensitivity to contaminating species seemed to imply that there was little hope of controllably modifying the electrical and optical properties of amorphous semiconductors in a way analogous to that used for crystalline semiconductors—namely, by the addition of minute amounts of impurities (doping). Numerous attempts by experimenters over the years to dope amorphous semiconductors confirmed this gloomy prognosis.

Thus, researchers reacted with a great deal of excitement to the 1975 reports by Walter Spear and Peter Le Comber of the University of Dundee in Scotland that they had varied the electrical conductivity of a certain type of amorphous silicon (now known to have contained several percent hydrogen) by ten orders of magnitude by the addition of small amounts of the two most common dopants of crystalline silicon, phosphorus and boron. Subsequently, Spear, Le Comber, and Stewart Kinmond of Dundee, together with Marc Brodsky of IBM's Yorktown Heights laboratory, fabricated a particular type of semiconductor structure known as a p-n junction, which is used in most crystalline solar cells, and thus set the stage for the demonstration of an operating cell made from amorphous silicon by David Carlson and Christopher Wronski of RCA Laboratories, Princeton.

The RCA workers, who had been engaged in a parallel but proprietary research effort, were therefore forced to disclose, in June of last year, the construction of a modified p-n junction solar cell that converted sunlight to electricity with an efficiency of 2.4 percent. Further research by the RCA researchers and their colleagues has resulted in a quite different structure called a Schottky barrier solar cell that has an efficiency of up to 6 percent. The best crystalline silicon solar cells have efficiencies above 15 percent, but are far too expensive for large-scale use (*Science*, 29 July, p. 445).

Researchers' folklore (although solar systems designers might disagree) has it that even a cost-free cell would have to have a 10 percent efficiency for solar photovoltaic production of electricity to be economically viable. This requirement follows from the costs associated with land, d-c to a-c converters, energy storage devices, and other structures. The rapid transition from frustration to the prospect of having the nearest thing imaginable so far to a free solar cell has tremendously thrilled investigators of amorphous semiconductors. "If anybody gets a 10 percent cell," says John Knights of the Xerox Palo Alto Research Center, "things will really fly." Moreover, a mini-explosion of amorphous silicon research has begun, and such big American laboratories as Bell, IBM, Xerox, and Exxon are showing varying degrees of interest in addition to RCA. Plessy in England and Thomson-CSF in France are also getting involved.

The amorphous silicon success story begins in the late 1960's when Robert C. Chittick, J. H. Alexander, and Henley Sterling of Standard Telecommunications Laboratories in Harlow, England, made thin films of amorphous silicon by a process not previously used for that purpose and which proved to be the basis of later advances. In this process, silane (SiH_4) gas molecules are torn apart under the action of either a d-c or high-frequency a-c electric field in a vacuum chamber filled with silane at a pressure of a few torr or less. Silicon atoms from the decomposed silane deposit on a heated substrate and slowly build up a thin layer of amorphous silicon. The technique is called glow discharge decomposition. The remarkable thing about the British group's experiments was that even at that time they demonstrated a limited doping effect. By adding 200 parts per million of phosphine (PH_3) to the silane, the investigators were able to increase the conductivity of amorphous silicon by a factor of 600. The phosphine acted as a source of phosphorus atoms which presumably doped the amorphous silicon in much the same way it affects crystalline silicon.

Inexplicably, research on glow discharge silicon was judged unpromising at the telecommunications laboratories and discontinued. Spear's group at Dundee did, however, pick up on the technique and began a period of basic investigations on the electrical and optical properties of amorphous silicon produced in this way. The essence of these studies was that this kind of silicon contained far fewer electrically active structural defects than amorphous films made by evaporation or sputtering techniques, the two most commonly applied methods. For one thing, its electrical conductivity, which is due to electrons associated with these intrinsic defects, was several orders of magnitude lower than that of evaporated or sputtered amorphous silicon.

The effect of the greatly reduced concentration of electrically active defects was that the influence of moderate amounts of doping impurities, such as phosphorus and boron, could be observed. In the past, dopants had been obscured by the intrinsic structural defects. Thus it was that Spear and Le Comber began their doping experiments with two gases: diborane (B_2H_6) and phosphine, which acted as sources of boron and phosphorus, respectively. By adjusting the pressure of these gases admitted to a mixing chamber with silane, the investigators could control the concentration of dopants in the deposited silicon.

What they found was that, as the phosphine pressure was increased, a maximum of 0.1 percent electrically active phosphorus could be incorporated into the silicon, raising its conductivity by seven orders of magnitude. As the diborane pressure was increased, the conductivity first decreased by a factor of 10^3, then increased to about the same value as that achieved with phosphine.

The Dundee researchers interpreted these results in terms of a model similar to that of crystalline silicon, in which the conductivity can be ascribed to two types of charge carriers: free electrons and holes. Free electrons are the most loosely bound electrons in a semiconductor. They are not localized around any particular silicon atom, and thus can freely move in an applied electric field. The valence electrons that actually form the bonds between silicon atoms are more tightly bound, and normally do not contribute to the conductivity. But missing bonding electrons, which are called free holes, can act in every way like free electrons, except that they are positively charged. Like an electron, the missing bond flows from silicon atom to silicon atom when a field is applied.

In the doping experiments, phosphorus acted as a source of free electrons, whereas boron was a source of free holes. The initial drop in the conductivity of amorphous silicon as boron was added came about because the small number of free electrons normally existing in undoped material "filled" the holes, so that there were neither free electrons nor holes present. When the number of boron atoms added exceeded the number of free electrons initially in the silicon, then the free hole population could build up and the conductivity along with it.

X-ray experiments with arsenic doped silicon by Timothy Hayes, Knights, and James Mikkelson of Xerox have also provided the first microscopic view of how doping atoms are bonded in amorphous silicon. In crystalline material, arsenic and phosphorus, which have five outer shell electrons rather than the four of silicon, are sources of free electrons, as only a small amount of energy is needed to release the fifth electron, which is not needed for bonding. In amorphous silicon, doping could occur in the same way, although it was long argued that the material would instead become locally distorted so that each arsenic or phosphorus would have only enough silicon neighbors to satisfy its bonding requirements and thus not dope at all. The existence of a doping effect is strong circumstantial evidence that what is happening is similar to what takes place in crystalline silicon. But the x-ray experiments show directly that about 20 percent of the arsenic, when present in low concentrations, is in fact surrounded by four silicon neighbors, the configuration needed for a true doping effect.

Hydrogen Is the Key

An important question for researchers has been what it is about glow-discharge silicon that provides it with its superior electrical properties. The answer, initially suggested by experiments of William Paul's group at Harvard University on germanium, now seems clearly to be the presence of hydrogen that is incorporated in the material along with silicon when the silane is decomposed. The Dundee group has resisted this interpretation, preferring instead to believe that the glow discharge decomposition process was inherently somehow gentler than the others and did not cause defects in the deposited material. But a steadily growing body of experimental results has pretty much resolved what was once a vigorous controversy. The evidence is that large concentrations of hydrogen (up to 50 percent, depending on the silane pressure and the temperature of the substrate on which the silicon is deposited) form chemical bonds with silicon atoms in the amorphous layer. The "best" amorphous silicon is really a silicon-hydrogen alloy!

The role of the hydrogen is to tie up what are called dangling bonds in silicon. A dangling bond occurs on each of the atoms surrounding the site of one or more missing silicon atoms. With one electron (against the two electrons in the normal bond), the dangling bonds are the intrinsic structural defects that give rise to the conductivity in evaporated or sputtered layers. Each hydrogen, with one electron itself, forms a bond with one of the silicon atoms surrounding the vacancy, thus removing a dangling bond. It remains a matter of some controversy how many missing silicon atoms are associated with each defect in actual amorphous material.

Paul's group at Harvard later repeated their germanium experiments with silicon and thereby produced one strong piece of evidence for the role of hydrogen. The Harvard investigators used a different method of preparation—sputtering—which allowed them to control the concentration of hydrogen incorporated into their amorphous silicon, whereas hydrogen is necessarily always present when silane is decomposed during the glow discharge.

In one set of experiments, Paul, Adam Lewis, Neville Connell, and Theodore Moustakas of Harvard showed that, when 6 percent hydrogen was added, they could reduce the electrical conductivity of amorphous silicon by a factor of 10^7 as compared to material containing no hydrogen. Moreover, the same researchers also observed substantial doping effects when phosphorus or boron was incorporated into the hydrogenated amorphous silicon. And, finally, they were able to construct a p-n junction. Thus, essentially all the results achievable in glow discharge silicon could be reproduced by adding hydrogen to sputtered silicon, suggesting that the presence of hydrogen is essential.

More direct evidence comes from measurements of hydrogen actually found in the glow discharge silicon. For example, Helmut Fritzsche and his colleagues at the University of Chicago determined the amount of hydrogen evolved when amorphous silicon films were heated to above the temperature at which the material turns crystalline. The investigators found that the hydrogen content varied strongly with the temperature at which the films were deposited, ranging from 35 percent for material deposited at 300°K to 13 percent for that deposited at 540°K.

More recently, studies by Brodsky and his colleagues at IBM, in collaboration with William Lanford of Yale University, provided somewhat more quantitative results than the Chicago group's volumetric measurements. Using a nuclear reaction involving hydrogen as a probe, the investigators found the concentration of hydrogen in amorphous silicon to depend both on the deposition temperature and on the silane pressure. The concentrations ranged from 14 to 35 percent. Mass spectroscopy studies of thermally evolved hydrogen confirmed the results of the nuclear experiment.

Infrared absorption and Raman spectroscopy studies of the vibrations of silicon-hydrogen bonds in hydrogenated amorphous silicon by Brodsky and Jerry Cuomo of IBM, together with Manuel Cardona of the Max Planck Institute for Solid State Research, Stüttgart, have shown that it is possible to put in too much hydrogen. The highest concentrations (35 percent) are obtained when the silane pressure is high and the deposition temperature low. In this circumstance, the investigators concluded, more than one hydrogen atom forms bonds with a particular silicon atom, so that species such as SiH_2 and SiH_3 coexist along with SiH. According to Brodsky, this form of amorphous silicon has poorer electrical and optical properties than one containing less hydrogen (14 percent) that is formed at lower silane pressures and higher deposition temperatures. Only

SiH species exist in the material produced under the latter circumstances.

Carlson, Wronski, and their colleagues at RCA are the only group that has reported on solar cells at present. The Dundee group reportedly has been unable to get support for this kind of research, and American laboratories may be going slow until the strength of RCA's patent position is clarified.

The RCA group has found that the best solar cell configuration is that of the Schottky barrier, which has an estimated theoretical efficiency of about 15 to 20 percent. As made by RCA, the solar cell consists of undoped, hydrogenated amorphous silicon onto which a thin transparent layer of metal, such as platinum, is evaporated. At the junction between the silicon and the platinum, an internal electric field exists—the Schottky barrier. Absorption of sunlight passing through the metal layer by the silicon results in the creation of equal numbers of free electrons and holes. The electric field drives the electrons across the silicon away from the junction, whereas it pulls the holes toward the junction. A second thin layer of amorphous silicon doped with phosphorus sits across the cell from the junction. The purpose of this layer is to collect the photogenerated free electrons and transmit them to a stainless steel substrate on which the entire assembly resides. No barrier must exist at the junction between the stainless steel and doped silicon because it would give rise to an electric field that would drive the free electrons back into the silicon. The accumulation of free electrons and holes on opposite sides of the cell gives rise to a voltage, hence the name photovoltaic solar energy.

Wronski of RCA points out that there are a number of differences between amorphous and crystalline silicon solar cells. As has long been known, amorphous silicon absorbs sunlight much more strongly than crystalline material. Thus, thin films of amorphous silicon of the order of 1 micrometer or less can make efficient solar cells, whereas much thicker cells of crystalline silicon are needed. The addition of hydrogen has relatively little effect on the absorption of sunlight.

What is not yet so well appreciated is that doped amorphous silicon seems to contain new defects introduced by the doping process itself. These defects hamper the transit of free electrons and holes through the silicon, reducing the efficiency of the cell greatly. For this reason, unlike the case in crystalline cells, the most efficient cells must be made largely from undoped amorphous silicon, and the doped layer needed for facilitating a good electrical contact between the silicon and the stainless steel substrate is made as thin as possible.

The development of useful solar cells awaits better understanding of the properties of amorphous silicon. For example, a major factor limiting solar cell efficiency is the tendency of the photogenerated holes to become trapped in the silicon before reaching the Schottky junction. Understanding why the holes are trapped and how to prevent them from being so is high on the agenda of the RCA researchers. Moreover, Peter Zanzucchi, Wronsky, and Carlson have shown that the type of glow discharge (whether it is d-c or high-frequency a-c) is one more parameter that affects material quality. And David Staebler of RCA and Wronski have found that long-term exposure to light can also change the behavior of amorphous silicon. A systematic sorting out of the effects of different preparation and operating conditions is sorely needed before the results of researchers in different laboratories can be meaningfully compared.

In the meantime, investigators of amorphous silicon are elated and point gleefully to an analogy between the present state of knowledge of amorphous semiconductors and that characterizing crystalline silicon 25 years ago—just before the solid state revolution began.

—ARTHUR L. ROBINSON

Viral Messenger Structure: Some Surprising New Developments

A recent discovery about the synthesis of some of the messenger RNA's of two unrelated animal viruses has excited molecular biologists. The findings* appear to confirm what many investigators have long suspected but have had difficulty proving; that is, that the control of gene expression in higher organisms is different from that in more primitive bacterial cells. Several groups of investigators have independently found that there is a major structural difference between the animal viral messengers and those of well-characterized bacterial systems.

In all cells, gene expression occurs when the DNA of the genes directs the synthesis of messenger RNA's (mRNA's), a process called transcription, and the mRNA's in turn direct the synthesis of proteins (translation). In bacteria, as far as is known, transcription is straightforward in that it begins at a start signal on DNA, continues along the DNA molecule, often for a length of several genes, and terminates at a stop signal. The resulting messengers undergo few, if any, structural modifications before being translated into protein structures—in fact, they are exact copies of the transcribed DNA without any missing regions.

A similar mechanism probably also operates in the nucleated cells of higher organisms, but investigators have now found that certain mRNA's synthesized by adenovirus 2 and SV40 consist of contiguous segments that are coded for by widely separate portions of the viral DNA. They think that what they are learning about the viral messengers probably applies to at least some of those of the animal cells where the viruses multiply, because the same cellular enzymes synthesize both kinds of messengers.

Although there are at least four possible mechanisms that might account for the synthesis of mRNA's with these unusual structures, the researchers think that the evidence currently favors the hypothesis that the entire stretch of DNA, encompassing both the segments found in the viral messengers and those that are missing, is copied to form large mRNA precursors. The appropriate intervening sequences are then excised to produce the actual messengers.

Some of the investigators postulate that, during the excision, the regions of the RNA that will become adjacent are brought together by a looping-out of the intervening sequences, and the regions are subsequently joined by an intramolecular ligation reaction (Fig. 1b). The mechanism that accomplishes the specific joining of the sequences is unknown, and further work will be needed to confirm whether the hypothesis is correct. But even if the viral mRNA's prove to be synthesized by another process, the structural findings indicate that the messengers of these animal viruses—and possibly those of the cells they infect—are produced in a manner unlike any described previously. Provided that a similar phenomenon does not turn up in bacteria, the current findings support the hypothesis that there may be fundamental

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*Most of the articles on which this news account is based are in press at *Cell*, the *Journal of Biological Chemistry*, and the *Proceedings of the National Academy of Sciences*.