

Over the next few years, his group achieved efficient carrier injection, the predicted electrical and optical confinement, and low-threshold pulsed room-temperature lasing in such devices. And in 1970, continuous-wave (CW) room-temperature semiconductor lasers were at last reported, in GaAs–GaAlAs DHS devices, by Alferov in the Soviet Union and, one month later, by Izuo Hayashi and Morton Panish at Bell Labs in the US.⁵

‘Heterostructures for everything’

GaAs–GaAlAs heterostructures were by no means the only devices being pursued. Ternary compounds, such as GaAsP and InGaAs, and quaternary compounds like InGaAsP also received much attention. Armed with new deposition techniques—molecular beam epitaxy, developed by Alfred Cho, John Arthur, and their Bell Labs coworkers, and metalorganic chemical vapor deposition of semiconductors, pioneered by Harold Manasevit, Russell Dupuis, and Paul Dapkus at Rockwell International Co—researchers could fabricate almost any structure that could be drawn, ultimately with single-atom thicknesses.

The controlled layer deposition facilitated the fabrication and study of heterostructure superlattices by Leo Esaki, Raphael Tsu, and Leroy Chang at IBM, which have in turn led to resonant tunnel diodes and, recently, to quantum cascade lasers developed by Federico Capasso at Bell Labs Lucent Technologies. The improved control has also allowed the reduction of the middle layer of the DHS sandwich. In 1974, Raymond Dingle and company at Bell Labs reported observing quantized size effects. Exploiting this reduced dimensionality, Dupuis, Dapkus, Holonyak, and coworkers reported a CW room-temperature quantum well laser in 1978. From heterostructures with two-dimensional quantum wells, researchers have gone to even fewer dimensions—one-dimensional quantum wires and zero-dimensional

quantum dots. And vertical device geometries, with high-quality optical cavities fabricated into the structure, have emerged with vertical-cavity surface-emitting lasers.

Near-infrared semiconductor lasers and LEDs are now commonplace. The telecommunications industry has blossomed with the development of long-wavelength InGaAsP heterostructure lasers, lattice-matched to InP substrates, for use with optical fibers (see *PHYSICS TODAY*, September 2000, page 30). And the recent development of AlGaInN devices (see *PHYSICS TODAY*, October 2000, page 31) has produced blue and violet heterostructure lasers and LEDs.

Heterostructures are also prevalent in transistors. In addition to HBTs, field-effect devices with very high mobilities have been developed. Called HEMTs, for high electron-mobility transistors, these heterostructures, which use dopants in high-bandgap materials to generate a high-density two-dimensional electron gas (2DEG) with low defects in a quantum well, can operate at very high frequencies and with low noise. Such devices, primarily of GaAs–GaAlAs and GaAs–InGaP but increasingly of Si–Ge alloys, can be found in cell phones and satellite receivers.

In addition to being key components in the billion-dollar optoelectronics and consumer electronics industries, heterostructures have also become fundamental structures for basic physics research. The fractional quantum Hall effect was observed by Horst Stormer and Daniel Tsui in 2DEG heterostructures (see *PHYSICS TODAY*, December 1998, page 17). Ballistic transport and quantum-dot “artificial atoms” are among the many other research topics made possible with heterostructures.

Heterostructures have emerged as the basic building block of semiconductor devices. “Over 99% of the semiconductor research today involves het-

erostructures,” says Alferov. The title of a talk Kroemer gave in 1980 has come true: “Heterostructures for Everything.”

Biographies

Born in Vitebsk, Byelorussia, USSR, in 1930, Alferov has been at Ioffe in Saint Petersburg since he graduated in 1952 from the Ulyanov Electrotechnical Institute in the same city. He has been director of the institute since 1987, and is also a member of the Russian Duma.

Kilby was born in Jefferson City, Missouri, in 1923 and received his MS in 1950 from the University of Wisconsin in electrical engineering. He worked for Centralab in Milwaukee until 1958, when he joined TI. A co-inventor of the pocket calculator and the thermal printer and holder of more than 60 patents, Kilby took a leave of absence from TI in 1970, was a professor at Texas A&M University from 1978 to 1984, and now is an independent consultant.

A native of Weimar, Germany, Kroemer got his start in semiconductor physics at age 24 with a PhD dissertation on the then-new transistor from the University of Göttingen in Germany in 1952. He held positions at various laboratories in Germany and the US until 1968, when he joined the faculty of the University of Colorado. In 1976 he moved to the University of California, Santa Barbara, where he is a professor in the department of electrical and computer engineering and the materials department.

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Nobel Prize in Chemistry Salutes the Discovery of Conducting Polymers

In 1976, a serendipitous chain of events brought together three individuals from different academic and geographical cultures to study a curious polymer: polyacetylene. The trio soon discovered that doping this polymer can change its behavior from insulating to metallic. For that work, the three—Alan Heeger, a physicist now at the University of California,

Conducting polymers have found applications ranging from anti-static coatings to all-polymer integrated circuits.

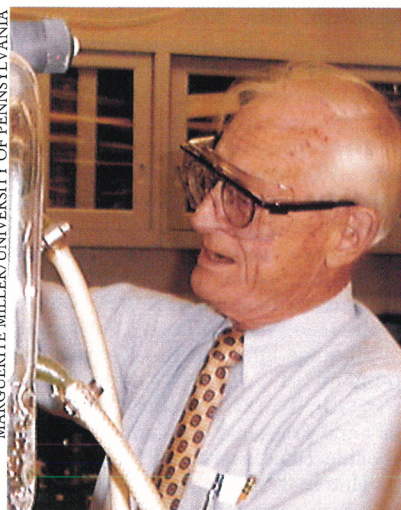
Santa Barbara; Alan MacDiarmid, a chemist from the University of Pennsylvania then specializing in inorganic chemistry; and Hideki Shirakawa, a

polymer chemist who has recently retired from Japan's Tsukuba University—have now earned the 2000 Nobel Prize in Chemistry “for the discovery and development of conductive polymers.”

Heralded at the time, the discovery of conducting polymers has become even more significant in hindsight as this class of materials has proven to be



ALAN HEEGER



ALAN MACDIARMID



HIDEKI SHIRAKAWA

not only of intrinsic scientific interest but also of great technological promise. Conducting polymers have been put to use in such niche applications as electromagnetic shielding, antistatic coatings on photographic films, and windows with changeable optical properties. And the undoped polymers, which are semiconducting and sometimes electroluminescent, have led to even more exciting possibilities, such as transistors, light-emitting diodes (LEDs), and photodetectors.

The Nobel Committee stressed the applications that have sprung from this year's prizes in both chemistry and physics. With the physics prize, the committee is honoring research that has led us into the world of microelectronics and the information age (see the previous story). With the chemistry prize, it is envisioning this revolution being carried forward by molecular electronics.

Separate threads come together

The story of conducting polymers began in the 1960s with attempts by Shirakawa, then working on his PhD under Sakuji Ikeda at the Tokyo Institute of Technology, to form polymers from acetylene using a so-called Ziegler-Natta catalyst to bind the molecules into long chains. Shirakawa wanted to elucidate the polymerization process for these triple-bonded molecules. One day, through a miscommunication, a visiting scholar from Korea added 1000 times more catalyst than specified by Shirakawa, and a shiny, filmlike substance formed on the surface of the catalyst solution. This product was far more intriguing than the rather uninteresting brown-black polyacetylene powder that was normally produced.

The effect of the higher concentration of catalyst apparently was to produce more polymer chains. Shirakawa subsequently devised a procedure to synthesize large quantities of polyacetylene film and also to control the proportions of two isomeric forms known as cis- and trans-polyacetylene.

The reflectance of the silvery polyacetylene film was suggestive of metallic behavior. Shirakawa measured its conductivity but found it no higher than the conductivity measured in the 1960s on the black polyacetylene powder; nor did its electrical behavior change (although its optical properties did) when the shiny film was exposed to chlorine.

Meanwhile, Heeger, who was at Penn in the 1970s, had been interested in the metal-insulator transition, a rather hot topic at the time. He started experimenting with organic conductors as models of quasi-one-dimensional systems. In the mid-1970s he grew excited about a report that the inorganic polymer poly(sulfur nitride), or $(\text{SN})_x$, was metallic and even superconducting, albeit only at extremely low temperatures. He told MacDiarmid about this result, hoping to interest him in synthesizing some samples. MacDiarmid had done his master's thesis in New Zealand on sulfur nitride crystals (because, he confesses, he loves colors and was attracted by the crystals' bright orange hue). Heeger talked with MacDiarmid for an hour or so about the intriguing metallic properties of what he was calling "S-N-x," but MacDiarmid failed to get interested in what he was hearing as " Sn_x ," that is, metallic tin! Once the two surmounted this language barrier, they began to collaborate.

In 1975, MacDiarmid lectured in Japan about their work, displaying golden crystals and films of $(\text{SN})_x$. At a tea break, MacDiarmid was introduced to Shirakawa. Once the Japanese chemist saw MacDiarmid's samples, he showed off his own silver films of polyacetylene. Immediately intrigued, MacDiarmid sought funding to bring Shirakawa to Penn for a year to collaborate with him and Heeger. MacDiarmid credits Kenneth Wynne, his contract officer at the Office of Naval Research, with the foresight to fund Shirakawa's visit.

Working together, Heeger, MacDiarmid, Shirakawa, and their colleagues learned to make very pure samples of polyacetylene and decided to try doping them by exposure to bromine vapor. To their great astonishment, the conductivity rose by seven orders of magnitude.¹ Heeger quips that his instrument was burned out by the unexpected current. Today, the best polyacetylene has a conductivity close to that of copper.

Although interesting as a model system, the unstable polyacetylene was never a candidate for applications. In the two decades following the discovery of conducting polymers, chemists have made great strides in perfecting inexpensive and easy ways to synthesize more stable conducting polymers, such as polyaniline and polypyrrole. Even though these polymers typically have conductivities that are at most several orders of magnitude less than the best conventional metals, such conductivities are good enough for many purposes and the materials can be easily processed into useful shapes by the low-cost methods characteristic of polymer technology.

How does charge transport occur?

Ever since the discovery of conducting polymers, theorists have tried to explain the fundamental mechanism. To get a very simple understanding of the kinds of electron states present in a doped polymer, picture trans-polyacetylene as a chain of carbon atoms with hydrogens attached, as in the adjacent figure. Like all conducting polymers, this structure is a pi-conjugated polymer; that is, the bonds between adjacent carbon atoms alternate between single (sigma) bonds and double (sigma plus pi) bonds. The pi electrons are not very tightly bound, and they become delocalized along the polymer chain. Studies of one-dimensional metals became of interest in the 1950s after Rudolf Peierls found that it was energetically favorable for such a chain to distort spontaneously, creating a gap between the filled valence band and the unfilled conduction band and converting the chain from a conductor to a semiconductor. In polyacetylene, this distortion causes alternating pairs of carbon atoms to move closer to one another.

When a pi-conjugated polymer is doped with, say, an acceptor atom such as iodine, each iodine atom grabs an electron from a pi band, creating a hole on the pi-conjugated chain. The negatively charged iodine ion remains associated with the polymer, but is not as mobile as the hole. The hole, together with the local distortion it produces in the carbon chain, is called a polaron, as illustrated in panel b of the figure. Bound pairs of polarons are called bipolarons.

Another type of excitation can exist in degenerate polymers—that is, ones that are the same after a reversal of the bond alternation pattern, as illustrated in panel c. The “kink,” or domain boundary, thus produced is known as a soliton. Solitons can carry spin but no charge, or charge but no spin. Although ideas of an excitation associated with a bond-alternation defect had previously been floated in the chemistry literature, in 1979, Heeger, with Robert Schrieffer and Wu Pei Su, then his colleagues at Penn, made specific predictions of solitons in polyacetylene.² Similar models were independently put forward by Michael Rice at Xerox Corp³ and by Sergey A. Brazovskii and Natasha Kirova in Moscow.⁴ Experiments in the 1980s showed that solitons can be excited by photons and current injection as well as by doping.

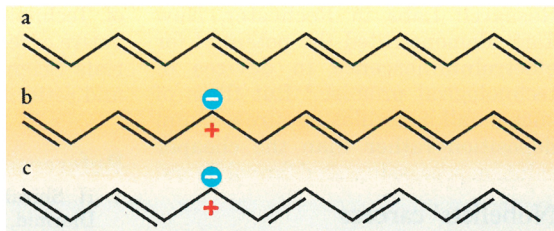
The details of how polymers carry

current are still not fully understood. As Arthur Epstein of Ohio State University explained it, most models were initially based on long, isolated chains. Then theorists successively added in the role of electron-phonon interactions, interchain effects, and so forth. “As you add this hierarchy of effects,” says Epstein, “it becomes increasingly difficult to do accurate first-principles calculations.” Despite the uncertainty about the details of some models, researchers have nevertheless been able to make many materials nearly by design. “That’s part of the richness that exists in a chemical embodiment of physics,” he says.

Many challenges remain. A major one is to raise the carrier mobility and the conductivity, which are currently limited by the defects in the polymers. When cast from solution as thin films, the polymers remain largely a tangle of spaghetti-like strands. Transport along the ideal linear chain can proceed no farther than the length of the fully extended chain; then the charge must hop to another chain. As good as they are, Heeger points out, even the best conducting polymers today are still just on the metallic side of the metal-insulator transition. With improved ordering of the polymer chains, however, the conductivity could exceed those of even the best metals.

Applications as semiconductors

The excitement over conducting polymers had just about died down when these compounds were discovered to have another fascinating property: electroluminescence. Conducting polymers, which all have beautiful intense colors in solution, were known to luminesce when exposed to light, but the effect was always fleeting. In 1990, however, Richard Friend and his group at the University of Cambridge’s Cavendish Laboratory made a very simple LED⁵ by sandwiching undoped, hence semiconducting, films of poly(p-phenylene vinylene), or PPV, between two metallic electrodes. Friend confesses his surprise when visible radiation came from the admittedly simple device: “We had thought you’d have to work very hard to ensure that electrons and holes would be simultaneously injected from opposite electrodes.”



SIMPLE MODEL OF A PI-CONJUGATED POLYMER.

(a) Long chain of carbon atoms with attached hydrogens is linked by alternating single and double bonds. (b) When the chain is doped with iodine, a hole is added (plus sign), and the negative iodine ion (blue) remains associated with the polymer. The distorted chain surrounding the hole is a positive polaron. (c) A topological kink, or soliton (red), develops if the alternating pattern of double–single bonds is reversed. The soliton shown here is positively charged.

The quantum efficiency (the ratio of photons out to electrons in) of the Cambridge polymer LED was a mere 0.01%, but subsequent work⁶ quickly raised it to about 1%. Polymer LEDs now have efficiencies of above 10%, and they can shine in a variety of colors. The upper limit of efficiency was once put at 25% because, it was thought, excitons would be equally likely to form in a singlet state or one of three triplet states and only the singlet state can decay radiatively. Experiments now indicate that the singlet formation may be preferred, so that higher efficiencies are possible. Friend tells us that more than once, those—including himself—who predicted limits on the behavior of electronic polymers have been proved wrong. “You almost have to suspend disbelief,” he says.

The semiconducting properties of electronic polymers have also been exploited to make field-effect transistors. Until recently, however, only the semiconducting thin film was made from a polymer; the rest of the device had to be made from conventional inorganic materials using standard lithographic and etching techniques. But in recent years, researchers have developed all-polymer transistors made with simple printing techniques, and have even developed all-polymer integrated circuits.^{7,8} (See PHYSICS TODAY, November 2000, page 9.) Possible uses include supermarket bar codes and flexible displays. MacDiarmid sees this work as the start of a new era of cheap, plastic, throwaway electronics.

Polymers were not the first organics to be used as semiconductors. In 1963, Martin Pope and his group at New York University found single crystals of anthracene to be electroluminescent. In 1987, Ching-Wai Tang and Steven van Slyke of Kodak

Research Labs in Rochester, New York, demonstrated the potential for electroluminescence in devices of technological promise.⁹ But films of such small molecules require vacuum deposition rather than the cheaper solution processing used for polymers.

Nobelists' careers

Born in 1936, Heeger earned his PhD at the University of California, Berkeley in 1961. He went to Penn in 1962, where he directed the Laboratory for Research on the Structure of Matter from 1974 to 1980. He has been a professor of physics at UCSB since 1982, and is director of its Institute for Polymers and Organic Solids. With Paul Smith, he co-founded UNIAX Corp in 1990 to develop commercial products based on electronic polymers. (DuPont acquired UNIAX in March.)

MacDiarmid was born in New Zealand in 1927 and received PhD degrees from the University of Wisconsin in 1953 and the University of Cambridge in 1955. He has been at Penn since 1956 and was named the Blanchard Professor of Chemistry in 1988.

Shirakawa, who was born in 1936, holds a PhD from the Tokyo Institute

of Technology (1966). He spent his entire career at the Institute of Materials Science at Tsukuba University and retired at the end of March.

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Simple Mechanisms Help Explain Insect Hovering

The flapping motion of insect wings is qualitatively different from fixed airplane wings or even the rotation of helicopter blades. It's perhaps not surprising, then, that the quasi-steady-state analysis that works so well for aircraft predict for insects an amount of lift that's insufficient to keep them in the air.

Over the past two decades, the importance of the unsteady flows created by the flapping motion of insect wings has become better understood. Recently, Jane Wang of Cornell University has performed detailed two-dimensional (2D) computational fluid dynamics studies of insect hovering, which show that the vortices shed from the leading and trailing edges of the wings during the flapping motion can generate sufficient lift to support a typical insect's weight.¹ Wang's calculations join earlier experimental work on insect flight^{2,3} in identifying the responsible mechanisms.

Stroke dynamics

When an insect is hovering, its wings execute what's called a "figure 8" stroke, which resembles the arm motions of a person treading water or

Experimental models and two-dimensional computer simulations of insect hovering provide insight that is missing in steady-state analysis.

the movement of the oar blade in a rowing stroke. This motion combines pitching and heaving, that is, rotational and translational movement, as illustrated in the figure on page 23. The plane of the stroke during hovering varies from insect to insect. It's nearly horizontal for bumblebees and fruit flies (and for people treading water), but is nearly 60° from horizontal for dragonflies.

Just as a spoon stirred in a cup of coffee produces swirls on either side of it, an insect's flapping wings produce vortices in the air (see the figure). The detailed behavior of the air surrounding the wings is governed by the Navier-Stokes equation, and the Reynolds number parameterizes the relative contributions from viscous and inertial effects. Insects are in an intermediate regime in which neither effect can be neglected. Consequently, the analysis of dynamics in this regime can be quite messy, and

researchers have turned to empirical studies, models, and computers for insight.

In 1996, Charles Ellington and coworkers at the University of Cambridge used smoke to image the airflows around a tethered hawk moth, and built a large-scale flapping model with the same Reynolds number as the moth to better study the dynamics.² They found that the vortex that forms on the leading edge of the wing spirals out away from the insect's body and toward the tip of the wing. This outward motion stabilizes the vortex and keeps it from separating from the wing during translational motion; such separation would produce stall and cause all the lift to be lost. These observations confirmed earlier work by Tony Maxworthy.⁴

Last year, Michael Dickinson and colleagues at the University of California, Berkeley, reported studies on their own dynamically scaled model insect, a robotic fruit fly, complete with sensors for monitoring the time-dependent aerodynamic forces.³ In addition to spiral vortices during the wings' translation motion, the researchers found that the circulation induced by the wing rotation could produce significant lift, if the rotation was properly phased with the translational motion. They also proposed a third lift mechanism: wake capture, in which vortices created during one half-stroke interact with the wing to create lift at the beginning of the next half-stroke.

A minimal model

Computational studies of insect hovering face several challenges: nonlinear partial differential equations, dynamic boundary conditions, and a very narrow wing edge on which much of the key behavior depends. "It's no small feat to resolve vortex structures," notes Wang, who painstakingly compared detailed features in her simulations with existing experiments to ensure things were working before turning to insect hovering.

For her hovering computations, Wang chose a minimal model, to see if she could reproduce, in two dimensions, the essential elements of hovering flight. She considered a transverse cross section of the wing, modeled as an ellipse, perpendicular to the length of the wing. The center of the wing section moved up and down sinusoidally along the inclined stroke path. In addition to this translational movement, the angle of the wing section oscillated sinusoidally with the same period (see the figure). The