R. W. Keyes
M. I. Nathan

Semiconductors at IBM: Physics, Novel Devices, and Materials Science

Work on semiconductor physics, devices, and materials science carried on at IBM in the last twenty-five years is reviewed. Topics covered include hot electrons, inversion layers, the injection laser, electroluminescence, the Gunn effect, MESFETs, solar cells, superlattices, and amorphous materials and effects.

Introduction

The discovery of the rectifying germanium diode and the bipolar transistor in the 1940s created great interest in crystalline semiconductors of the fourth group of the periodic table. The relevance of the new phenomena to the needs of the information processing industry was apparent and investigation of the properties of semiconductors was inaugurated at the IBM Poughkeepsie Laboratories. L. Hunter, a well-known solid state scientist, joined the company in 1951 to establish this new effort and began the study of transistors with R. F. Rutz, R. A. Henle, and H. Fleisher. The effort grew rapidly to encompass both devices and semiconductor science and spread to the IBM Watson Laboratory at Columbia University.

The directions that semiconductor research should take were not clear in the 1950s. The basic physics of semiconductors was only poorly understood. Almost any measurement of a semiconductor property had an element of novelty and the solid state science community devoted a large share of its experimental effort to developing a body of knowledge on the physical properties of a wide variety of semiconductors. Ideas about devices also rested on a poorly developed foundation. Early transistors were made with germanium and many years passed before it became obvious that silicon would dominate digital electronics. The role of transistors was not firmly established; the invention of the tunnel diode in 1957 initiated a long series of attempts to build digital systems around it. Semiconductor physics and electronics were in very exploratory phases.

We cannot hope to cover all pertinent fields in this review, and instead restrict our treatment to IBM's work on traditional semiconductors such as Ge, Si, GaAs, and similar materials, since this is where our expertise lies. It should be noted that a large body of important IBM work on silicon, including processing work on n-FETs, C-4 bonding, and capsule diffusion, is partially covered in other articles in this issue [1], and therefore will not be repeated here. We do not intend to try to cover every single IBM contribution in these areas, but rather to give a sampling of key research work. The omission of other subjects such as magnetic semiconductors, organic semiconductors, and wide-gap insulators is not meant to reflect on their significance to the field of semiconductor science; rather it is a result of limitations in our particular background and interests as well as space in this journal.

1. Early work

Much of the early work cannot be organized into a coherent theme since it was the work of a new laboratory getting into a rapidly growing field. Some of this work is mentioned mainly because of its early date in our history; however, some of this work has proved to be important from a fundamental point of view.

The earliest IBM work was devoted to the theory of transport properties, primarily the Hall effect, and to the study of electron states. One significant early result was obtained by J. A. Swanson [2], who showed that the well-known result for the saturation Hall constant R_s (the value at high magnetic field) is given by

$$R_s = \frac{1}{p - n} ec ,$$

where the density of electrons (holes) n (p) is independent of band structures and scattering mechanisms. Swanson and R. Landauer [3] discussed the importance of diffusion and nonequilibrium carrier densities to the Hall effect in near-intrinsic semiconductors. H. J. Juretschke of Brooklyn Polytechnic Institute, Landauer, and Swanson calculated the Hall effect in porous materials, *i.e.*, materials with macroscopic inhomogeneities [4]. Pioneering work was done by Landauer and J. C. Helland [5] and Landauer [6] in the field of electronic states in disordered systems. With the present interest in amorphous semiconductors, this has become a very active field, and the importance of their work has been recently recognized [7]. Landauer and Helland calculated the distribution of states in a one-dimensional disordered chain. They discussed band-edge smearing and found that the states for particular energy ranges are localized in certain regions of space. Landauer related the resistance to the transmission coefficients. This viewpoint has recently become very popular and is used in numerous papers.

In addition to work on germanium and gallium arsenide, there were some studies on more "exotic" semiconductors in the 1950s. S. P. Keller, G. Cheroff, R. C. Enk, and G. D. Pettit measured optical properties of zinc sulfide [8–10]. The most interesting result was the observation by Cheroff and Keller [8] of photovoltages greater than the energy gap. Swanson [11] partially explained this result by a model involving a series of asymmetric p-n junctions in the material, but could not account for the reversal of sign of the photovoltage with photon energy observed by Cheroff and Keller.

Studies of II-V compounds were pursued by W. J. Turner, A. S. Fischler, and W. E. Reese [12–13]. These materials, which are not cubic, are compounds of zinc and cadmium with arsenic and antimony. They are notable for their very high carrier mobilities. The observation of cyclotron resonance by M. J. Stevenson in ZnSb, CdSb, and CdAs [14] marked the only such measurements at the time in materials other than the group IV and III-V semiconductors. Turner and Reese also studied the optical properties of AlSb [15] and InP [16]. In AlSb, they were first to observe multi- (greater than two) phonon absorption.

2. Hot electrons

Investigations of hot electrons (electrons subjected to high electric fields) began in the mid-1950s and continue to be of interest to IBM today. The early work was on germanium and began with a study of impact ionization of shallow donors at 4 K by P. J. Price, S. H. Koenig, and G. R. Gunther-Mohr [17]. Koenig and R. D. Brown observed the far-infrared electron-ionized donor radiation induced by an electric field [18]. Koenig, in collaboration with Brown and W. Schillinger, continued this work and made an extensive study of both ohmic and nonohmic behavior of the conductivity [19]. Koenig and M. I. Nathan, in collaboration with W. Paul and A. C. Smith at Harvard, studied the pressure dependence of the drift velocity *versus* electric field at room temperature, demonstrating the effect of changes in band structure [20, 21]. Anisotropy in the drift velocity at 77 K and 300 K was shown to be consistent with the symmetry of the band structure [22], as suggested by Price.

E. Erlbach and J. B. Gunn undertook the study of hot-electron noise [23]. This work permitted the determination of the temperature of hot electrons, which exceeds the lattice temperature. It was in the course of studying this phenomenon in GaAs that the Gunn effect was discovered [24]; see Section 5D.

Koenig's work continued with more detailed studies of transport in semiconductors. Some of the highlights of his work were the determination with J. J. Hall of the deformation potential constants [25] and the observation with M. J. Katz and A. A. Lopez of anisotropy of the scattering and deviations from effective mass theory [26]. Price pursued theoretical interests in ohmic and hot-electron transport in semiconductors. An important contribution was the formulation of a generalized Boltzmann equation that takes account of quantum effects and allows calculation with fields varying rapidly in space and time [27]. Price and P. A. Lebwohl also carried out extensive Monte Carlo calculations of hot-electron transport [28]. A calculation of the time development of domains in the Gunn effect was stimulated by the widespread interest in transferred electron phenomena around 1970 [29].

W. P. Dumke [30] formulated a theory for avalanche breakdown in InSb, which was experimentally verified by J. C. McGroddy and Nathan [31]. McGroddy, Nathan, and J. E. Smith observed and studied the Gunn effect in a variety of materials other than GaAs: n-germanium [32], strained germanium and silicon [33], and InSb under hydrostatic pressure [34]. (This last material shifts from avalanche breakdown to Gunn effect as the band structure is changed by pressure.) McGroddy, M. R. Lorenz, and T. S. Plaskett observed the phenomenon in GaInSb alloys [35].

3. Elastic properties

After the discovery of large piezoresistance effects in the multivalley semiconductors germanium and silicon, R. W. Keyes appreciated the importance of a class of effects that were in a certain sense inverse to these. The piezoresistance effects (effects of elastic strain on resistivity) arise because shear strains change the energies of the valleys and remove the energy degeneracy that exists in the unstrained crystal. Electrons then preferentially occupy the lower energy valleys and, since the contribution of each valley to the conductivity is very anisotropic, the redistribution produces large changes in the resistivity. The concept of an "inverse effect" arises when one considers that if strain changes the energy of an electronic state, then occupancy of that state by an electron changes the energy needed to strain the semiconductor crystal [36].

A related effect occurs when the electrons are bound to donor atoms; in this case the wave function of the ground state of the electrons contains equal contributions from each valley. Price developed a model that shows how, in the presence of strain which removes the degeneracy of the valleys, the wave function of the lowest state changes to one constructed primarily from the lowest energy valley [37]. Although Price's model was oriented towards an interpretation of the effect of strain on transport properties, it has found application to many other phenomena observed in doped n-type silicon and germanium.

The first application of this inverse-effect concept was to the thermal resistance of lightly doped semiconductors. It was known that donor concentrations of only 10^{-6} atom percent produced a significant increase in the thermal resistance of germanium at low temperatures. Keyes developed a model of scattering by donors which showed that donors act as point-defect phonon-scattering centers with a strength six orders of magnitude greater than that of the usual point-defect scatterers such as mass defects [38]. The model also explained another unusual feature: There was a range of temperatures in which the strength of the phonon scattering decreased as the temperature increased, in contrast to other known scattering processes.

At about the same time, Keyes was able to predict from the energetics of the electrons that doping with donors should cause a significant reduction in certain shear elastic constants of multivalley semiconductors [35]. The effect occurs because shear strain changes the energies of the valleys, destroying the energy degeneracy that exists in the unstrained crystal. To first order in the strain, there is no change in the energy of the crystal, as is required by symmetry. However, electrons scatter from the higher to the lower energy valleys, reducing the energy in terms of second order in the strain. The decrease of the elastic constant amounts to several percent in heavily doped germanium and silicon. The elastic constants affected, C_{44} in germanium and C_{11}-C_{12} in silicon, depend on the symmetry of the valleys.

L. J. Bruner and Keyes experimentally found the electronic effect on elastic constants in germanium [39]. The effect was first observed in silicon by N. G. Einspruch and P. Csavinsky at Texas Instruments [40]. It was extensively studied by Hall in a sample of silicon doped to 2×10^{19} cm^{-3} [41]. Other predictions of the theory included a very large change (on the order of 100%) in a third-order elastic constant, which was found by Hall and by J. R. Drabble and J. Fendley [42–43] and an electronic effect on elastic constants in p-type semiconductors, which was experimentally observed by the Texas Instruments workers and more extensively investigated by workers in the USSR [36–45]. The subject of electronic effects in elastic properties was reviewed at length by Keyes [46], who has also recently considered their role in the thermal properties of semiconductors [47].

The interaction of electrons with elastic waves is manifested in additional ways. Several of these were studied by M. Pomerantz. Pomerantz was able to observe amplification of phonons in germanium through the deformation potential interaction, rather than through piezoelectric coupling, which is operative in the III-V and II-VI compounds [48(a)]. He also studied the absorption of microwave and, with R. von Gutfeld, thermal phonons in silicon and germanium, thereby quantifying various aspects of the scattering of elastic waves by electrons in multivalley semiconductors [48(b)].

In a continuing study of the elastic constants of the tetrahedrally bonded semiconductors, Keyes discovered that much of the variability among materials can be removed by expressing the elastic constants in dimensionless form by division by e^2/a^4, where e is the electronic charge and a is the lattice constant of the semiconductor [49]. This has since become the accepted normalization in comparisons of various materials [50]. Much of the remaining variability could be related to the degree of ionic character of the materials, as shown by a respective decrease in the normalized shear elastic constants in going from the group IV materials to the III-V compounds to the II-VI compounds [49]. The relation to ionic character has been thoroughly studied and put on a quantitative-microscopic basis by R. M. Martin [51] of Xerox.

4. Inversion layers

The study of quantization effects in silicon inversion layers is one of IBM's most important contributions to the field of semiconductor physics. It is unusual in the sense that pioneering work in technology [the n-channel Si field effect transistor (FET)] at IBM led to pioneering work in physics at IBM. In fact, the physics work actually led to a new field of semiconductor physics with its own biannual international conference.

An inversion layer is formed when a sufficiently strong electric field is applied to a semiconductor surface, attracting carriers opposite in sign to those in the bulk to the surface. The carriers attracted to the surface are confined in a very narrow potential well in which their motion in the direction normal to the surface is quantized. Thus, a unique two-dimensional system is formed at low temperatures when carriers are contained in the lowest quantum level. This system is of scientific importance since the concentration of electrons can be varied easily and continuously (by variation of the applied voltage) in a single sample, making the system ideally suitable for the study of a wide variety of phenomena. Inversion layers are also well suited to the study of localization effects and impurity scattering because the densities of electrons and scattering centers can be independently varied over a wide range in a single sample. This is important technologically because the phenomenon occurs in a normal FET structure.

In 1956, J. R. Schrieffer [52] had noted the possible presence of quantum effects due to the confinement to two dimensions of the space-charge layers but thought these effects would be obscured by level broadening due to surface scattering. Beginning in 1964, F. F. Fang and then W. E. Howard and A. B. Fowler [53, 54] undertook an extensive study of transport properties in silicon inversion layers. The key experiment carried out the following year by Fowler, Fang, Howard, and P. J. Stiles [55] was a modified Shubnikov-de Haas experiment in which the Fermi level is swept through Landau levels in a fixed magnetic field by varying the carrier concentration by means of the gate voltage. This experiment indicated the presence of equally spaced oscillations characteristic of a two-dimensional system. This was the first clear demonstration of an electron gas with reduced dimensionality and represented a quantum jump in the understanding of this field, thus marking the beginning of modern work on inversion layers.

The work on inversion layers at Yorktown has continued from 1965 to the present. We mention some of the major contributions. Fang and Fowler continued the systematic study of transport properties of inversion layers and published a classic paper on ohmic conductivity and the Hall effect [56]. Their work established the scattering mechanisms and gave the first evidence of thermally activated conductivity at low temperatures. The latter has subsequently been interpreted in terms of localization effects and has become a very actively studied aspect of the subject. Fang and Fowler also studied the nonohmic behavior of inversion layers [57], properties which are important in the design of MOS devices.

The early theoretical work was done by Fang and Howard [54] and by F. Stern and Howard [58]. They calculated the electronic energy level structure of inversion layers including the effects of conduction-band anisotropy and the effects of Coulomb centers near the interface. It is necessary to solve Poisson's equation for the potential and the Schrödinger equation in a self-consistent manner, in the spirit of the Hartree method used for atoms. The Stern-Howard paper was of fundamental importance to subsequent theoretical and experimental work. In addition, Stern was the first to calculate the wave vector and frequency dependences of the dielectric response of a two-dimensional electron gas [59] and gave the earliest description of self-consistent energy levels for a range of temperature and other parameters [60]. Stern also performed the first calculation of exchange energy with realistic wave functions [61] and was the first to discuss the effects of graded interfaces [62]. By measurement of Shubnikov-de Haas oscillations in a tilted magnetic field, Fang and Stiles [63] determined the g-factor to be as high as 3.2 at low carrier concentration, as compared to the free-electron value of two. J. Janak [64] showed that this high g value can be attributed to electron-electron interaction. This paper really began the many-body theory of inversion layers, which has been actively pursued because the effects are particularly important in two-dimensional systems. More recently, A. Hartstein and Fowler [65] have studied the effects of interface charges at the Si-SiO_2 interface [61] and have clearly shown the existence of an impurity band. They have also measured the activation energies for motion in the impurity band and for excitation to the conduction band.

5. Gallium arsenide and other III-V compounds

In 1952 H. Welker recognized the similarity between the properties of compounds made by combining atoms of groups III and V of the periodic table with those of germanium and silicon, and appreciated the importance of this new class of semiconductors, the III-V compounds [66]. The new materials attracted great interest as alternatives to silicon and germanium in devices and provided many more opportunities for testing an emerging theoretical foundation for semiconductor science. Gallium arsenide appeared to be the most promising of the III-V compounds for devices because its electron mobility and energy gap were both larger than those for silicon and germanium. A survey in 1961 was able to report that practically all of the p-n junction devices known in the fourth-group semiconductors had been realized in GaAs [67].

A. Materials studies

The study of various aspects of GaAs devices and of the associated materials science was inaugurated in the IBM Research Laboratory in the late 1950s. Although the technology of growing germanium from the vapor phase by halide reactions was well known, early work by J. C. Marinace and R. L. Anderson involving the deposition of germanium on GaAs substrates to form heterojunctions opened an area of research that continued for many years (see later discussion) [68–70]. Other interests centered on tunnel diodes and heavily doped GaAs. It became apparent that realization of the full potential of GaAs as an electronic material and achievement of the electron mobilities known to be possible were being obstructed by difficulties in preparing pure materials. Since silicon was a prevalent impurity in GaAs that reduced mobilities through ionized impurity scattering, N. G. Ainslie and S. E. Blum focused their attention on reducing the concentration of silicon in GaAs in 1961 [71, 72]. The silicon impurity apparently originated from the SiO_2 crucibles that were ordinarily used to contain molten GaAs during the crystal growth process. One technique for reducing the silicon in the GaAs involved introducing an oxygen-containing atmosphere over the molten GaAs. The oxygen drives the reaction

$$SiO_2 + 4Ga \leftrightarrow 2Ga_2O + Si$$

toward the SiO_2 and reduces its decomposition. Another technique eliminated the silicon by growing crystals from an aluminum nitride crucible. Both of these methods permitted the growth of pulled crystals of high mobility [71, 72].

B. The injection laser

Radiation produced by the recombination of carriers injected into GaAs was observed in 1955 [73]. The efficient production of radiative emission by injection with p-n junctions was reported in 1962 [74–77]. Such light sources cannot be made in silicon and their discovery in GaAs led to increasing attention to luminescent properties of GaAs after 1960. Lasers had been demonstrated in early 1960 and great excitement was attached to the search for new kinds of lasers. There existed the understanding that injection of electrons and holes in semiconductors might lead to population inversion and stimulated emission of recombination radiation. The discovery of the high electroluminescent efficiency in 1962 focused attention on GaAs as a candidate material for the search for a semiconductor laser pumped by injection [74–78]. In addition, calculations by W. D. Dumke and G. J. Lasher showed that free-carrier absorption in indirect-energy-gap semiconductors was large and would make lasing action difficult to achieve [79–80]. Dumke pointed out that band-to-band optical transitions are much stronger in a direct-gap semiconductor, where no change of crystal momentum is involved in the interband transition, and that such transitions can overcome the absorption by free carriers. This turned attention from germanium and silicon, which have indirect bandgaps, to the direct-gap semiconductors, in particular GaAs.

Early thinking at IBM about the feasibility of semiconductor injection lasers was spelled out in a proposal written by Keyes with a contribution by Lasher to the U.S. Army Signal Research and Development Laboratory at Fort Monmouth in January 1962. This proposal was accepted and work on the injection laser at IBM over the next few years was partially supported by the U.S. Army. Lasing in GaAs diodes was achieved at IBM Research by Nathan, Dumke, G. Burns, F. H. Dill, Jr., and Lasher, and at other laboratories in late 1962 [81–83]. Diode lasers were realized in several other III-V compounds within the next year [84–89].

The injection laser differed in several qualitative aspects from other lasers known at that time. It was quite small, only about 0.25 mm long, so that a very high optical gain per unit length was required. The fabrication of high-reflectivity end mirrors, which was necessary in gas and other solid lasers, could be avoided because the discontinuity between the high refractive indices of GaAs and air provided sufficient reflectivity. The discovery that end faces with satisfactory planarity and excellent parallelism could be formed by cleaving GaAs on [110] planes greatly simplified the fabrication of injection lasers [90]. Interest shifted from the discovery of new laser materials to attempts at perfecting the material and physical characteristics of the laser to permit continuous operation at the highest possible temperature and at unraveling the physical mechanisms involved in laser operation. Both IBM's contributions to the laser field and the subject of injection lasers as a whole have been amply reviewed in this journal and elsewhere, and as such will not be covered in detail here [91–101]. IBM contributions are also described in reports submitted under Army contracts DA36-039-AMC-02349(E) and DA36-039-SC-90711.

Development of injection laser technology that was oriented towards specific applications continued from the late 1960s to the present. A proposal for an optically addressable disk memory used GaAs lasers as the light source for writing and reading [102, 103]. The memory system operated at a temperature of 77 K, which made the use of GaAs lasers feasible since the requirement for continuous operation could not be satisfied at 300 K at that time. Large numbers of lasers were required and a planar diffusion method for fabricating laser arrays was developed [104-106]. The fabrication of ten lasers on a single chip created a high concentration of power dissipation and a novel heat sink was designed [104]. Although the technical objectives of this beam-addressable memory were met, rapid development of conventional magnetic disk technology excluded it from a place in the information storage device market. An optically written liquid crystal display was another product-oriented concept that used semiconductor lasers [107]. Double-heterostructure lasers that could be operated continuously at 300 K were chosen for this application. A review of the technology developed in an effort to achieve reproducible lasers with long operating life has recently appeared [108].

C. Near-infrared and visible luminescence

The discovery of efficient junction electroluminescence also stimulated efforts to perfect the GaAs light-emitting diode (LED) as a useful source of infrared light. The ease and rapidity with which the light output of an LED can be modulated suggested its use in high-speed optical communication [109-110]. This application required maximizing the speed of response of the light output to electrical signals while maintaining high luminescent efficiency; therefore, considerable attention was devoted to studying the time dependence of the optical response of GaAs LEDs [111-112]. B. R. Shah at the IBM Federal Systems Division and K. L. Konnerth at IBM Research were among the leaders in the exploration of the optical communications application. IBM's Federal Systems Division established and operated an optical data link at Montreal in connection with Expo 67 to demonstrate the feasibility of the new technology [110]. Since the Montreal link transmitted light through the atmosphere, it was subject to interruption by unfavorable atmospheric conditions and was not pursued further.

Another effect that was discovered soon after interest in electroluminescent devices developed was a gradual decrease of the light output with time when the devices were operated. An extensive diode life testing program was established that enabled the effect of different processing methods on the degradation of light output to be compared [113]. Experience had indicated that growth of diodes by liquid-phase epitaxy (LPE) yielded lifetimes much longer than those obtained when junctions were prepared by diffusing Zn into n-type GaAs [114]. However, the ability to test and compare large numbers of diodes made the development of a diffusion procedure that produced long-lived diodes possible. The research on response times and degradation was largely empirically based, although attempts to identify underlying microscopic mechanisms were not neglected [115-116]. Even today, however, complete understanding of the atomic phenomena underlying degradation has not been achieved [117-118].

Another line of development was aimed at extending the high efficiency of GaAs diodes from the infrared into the visible part of the spectrum. Rapid success was attained by replacing part of the arsenic in GaAs with phosphorus to form alloys with compositions $GaAs_{1-x}P_x$. Indeed, the second material from which an injection laser was made was such an alloy [84]. These alloys have larger energy gaps than GaAs and exhibit direct optical transitions up to values of x of about 0.44, at which the peak wavelength of the emitted light is 620 nm, well into the red region of the visible spectrum. Although this area of research was explored at IBM [119-120], another approach was also investigated. The LPE growth of III-V compounds had been demonstrated at RCA [121]. H. S. Rupprecht and J. M. Woodall discovered that high-quality $Ga_{1-x}Al_xAs$ could be grown by this LPE process [122]. The lattice constant of these alloys closely matches that of GaAs. Over a range of x the $Ga_{1-x}Al_xAs$ alloys have a direct bandgap, allowing the fabrication of efficient visible LEDs and injection lasers [123-124]. The preparation of layers of $Ga_{1-x}Al_xAs$ alloys by LPE subsequently became the basis for the fabrication of the confinement layers of heterojunction injection lasers [98-100].

Much work was done to further the understanding of semiconductor lasers and laser materials. Nathan and Burns [125] and Turner, Pettit, and Ainslie [126] measured photoluminescence of GaAs, elucidating some of the recombination mechanisms. K. Weiser and R. S. Levitt [85] demonstrated the third semiconductor laser material, n-InP. Photoluminescence [127] and optical absorption [128] were obtained in InP by Turner, Pettit, and W. E. Reese. F. Morehead, G. Mandel, and P. Wagner furthered the understanding of self-compensation, which limits the conductivity of the II-VI compounds [129]. Mandel and Morehead observed efficient luminescence from CdTe p-n junctions [130]. The self-compensation theory was modified by F. A. Kroger [131] and B. L. Crowder [132]. Efficient low-temperature luminescence in ZnTe was observed by Crowder, Morehead, Pettit, and R. S. Title [133-135].

Work on GaP, which is used today in light-emitting diodes, was started at IBM by L. M. Foster and T. S. Plaskett. Lorenz and M. H. Pilkuhn [136] applied epitaxial solution growth techniques to GaP and obtained reproducible red-light-emitting diodes. A. Onton and Lorenz [137] substantially improved the efficiency of the red-light-emitting diodes by studying annealing effects. Much effort has been expended to obtain p-n junction light emission at wavelengths shorter than the red from a direct bandgap semiconductor so that high-efficiency light-emitting diodes could be fabricated. The problem was to find a direct-gap material in which a p-n junction could be made. Lorenz, W. Reuter, Dumke, R. J. Chicotka, Pettit, and Woodall extended the wavelength range to the green with $In_xGa_{1-x}P$ alloys [138].

D. Gunn effect

Another consequential series of events was also set in motion in early 1962, at about the same time that the possibility of injection lasers was being recognized. Gunn, who had been investigating hot-electron effects in germanium, turned his attention to GaAs and in a difficult experiment with Erlbach had measured the noise temperature of hot electrons in germanium [139]. Germanium was the most popular vehicle for scientific studies of semiconductors at that time because the technology of its purification and crystal growth was furthest advanced. However, when GaAs of reasonable quality became available, an opportunity arose for comparing its effects with those of germanium.

Gunn soon discovered that hot-electron phenomena in GaAs are quite different from those in germanium [24, 140–141]. It eventually turned out that a quite complex set of phenomena were occurring in the GaAs. Hot electrons were being transferred from the lowest part of the conduction band to another conduction band extremum at somewhat higher energy where they had a much lower mobility. (The transfer of hot electrons had been theoretically predicted [142–143].) The transfer of electrons from high mobility states to low mobility states produced a negative resistance; *i.e.*, the current decreased when the electric field was increased. In such a circumstance, there is an instability: the electric field splits into a high field domain and a low field domain. The domains travel through the GaAs and, upon reaching an electrode, cause a perturbation of the current and voltage. When one domain disappears at an electrode another forms and travels through the device, creating oscillations of the voltage and current in the microwave frequency range. The device excited great interest as a potential simple source of high-frequency microwaves and became known as the "Gunn oscillator" [144–153].

In fact, over two years were required to sort out the picture just presented. Gunn has given a detailed and personal account of the events which took place during that time [154]. Many difficult experimental problems had to be solved. The high fields needed to produce hot electrons led to high current densities that required the development of a new process for making ohmic contacts [155]. The time scale of the phenomena involved was very short and innovations in techniques for electrical measurement of short pulses were needed [154, 156–159]. Extremely difficult problems of material quality were encountered; high purity was desired to reduce the conductivity and thereby the current, thus minimizing the heating of the device during the time that the high field was applied. Material inhomogeneities were very important, as they could affect the nucleation and motion of domains and obscure the interpretation of observations made at the terminals of a device; therefore, a novel method of characterizing homogeneity was developed [160–161]. Workers in many organizations contributed to the final understanding of the mechanisms involved. Perhaps the most crucial experiment, appearing at a critical time, was the demonstration that the Gunn effect disappears at high pressure, which raises the energy of the high-mobility states, so that the electrons are in the low-mobility states even at zero electric field [162]. Later IBM work in this area has already been discussed in Section 2.

E. The high-frequency MESFET

Work directed toward utilizing the high mobility of GaAs in transistors was carried on in the European laboratories of IBM during the 1960s. The existence of semi-insulating GaAs, material with a resistivity of about 10^8 ohm-cm, permitting simple isolation of devices, was another attractive feature not found in silicon [163]. Double-diffused planar bipolar transistors of both npn and pnp types were successfully fabricated in Boeblingen [164–165]. These bipolar transistors did not have superior characteristics that would allow them to displace silicon devices and were not intensively developed. However, many detailed questions of material science and planar technology, such as diffusion constants and procedures, and masking, etching, contacting, and passivating methods, were solved and formed useful additions to GaAs technology for a variety of devices.

Meanwhile, interest in high-frequency transistors had developed at the IBM Zürich Research Laboratory in the middle 1960s. G. Kohn selected the MESFET as a vehicle for exploration and initiated work on this device. The MESFET is a field effect transistor consisting of a Schottky barrier gate between ohmic source and drain electrodes on a thin conductive layer. Potentials applied to the Schottky gate can deplete the conductive layer of electrons, thus controlling the source-drain current.

Obtaining high-frequency response in a MESFET depends on making very narrow gate electrodes. Techniques for fabricating one-micron gates were developed and a 12-GHz MESFET transistor, comparable to the best bipolar transistors, was constructed in an n-type silicon layer on a p-type substrate [166–167]. It was recognized, however, that a similar structure in GaAs would have enhanced high-frequency capability because of the higher electron mobility of GaAs [168]. H. Statz and W. von Muench transferred to Zürich from Boeblingen to introduce the GaAs technology there. They soon were able to fabricate MESFETs with 4-μm gate length on GaAs [169]. Efforts to reduce the gate length to one micron in GaAs met with success and a transistor with power gain up to 30 GHz was reported by K. E. Drangeid, R. Sommerhalder, and W. Walter in 1970 [170]. The conductive layer in this high-frequency transistor was epitaxially grown on a chromium-doped, semi-insulating substrate. The feasibility of the MESFET was also demonstrated in several other laboratories in the late 1960s [171–173]. The narrow-gate GaAs MESFET in an epitaxial layer on a semi-insulating substrate has since become the standard very-high-frequency microwave transistor [174]. The frequency capability has been improved by reducing the gate width to 0.5 micron [174–175].

The workers at IBM Zürich were aware of the potential use of MESFETs for digital circuits and the group led by Drangeid fabricated MESFET memory cells in silicon [176]. Very notable advances in the implementation of high-speed digital logic with GaAs MESFETs have been made in recent years [174, 177]. However, it was not apparent at that time that MESFETs could play a role in digital electronics in the face of the rapidly advancing silicon technologies. Since microwave devices had no place in IBM's technological needs, interest in the further development and optimization of both high-frequency MESFETs and Gunn effect devices declined.

F. Solar cells

A further application of the LPE growth of $Ga_{1-x}Al_xAs$ alloys emerged in the early 1970s. H. Hovel's long-standing interest in heterojunctions led him to an interest in the GaAs-$Ga_{1-x}Al_xAs$ heterojunction, which Woodall had been exploring for several years and which was already being used in the fabrication of low-threshold injection lasers to confine electrons to the active region. Hovel and Woodall soon recognized that the same confining action, stemming from a discontinuity in the energy bands at the interface that kept electrons from entering the aluminum alloy, could be used to prevent electrons from reaching the surface of GaAs solar cells. It was known that GaAs might be a vehicle for solar cells comparable to silicon cells in efficiency and possessing advantages in being less affected by high temperature and ionizing radiation [178]. However, the potential of GaAs cells had never been realized because a large fraction of the electron-hole pairs generated by sunlight recombined rapidly at the surface of the GaAs, rather than contributing to the electrical output by being collected by a p-n junction. This problem was much more severe in GaAs than in silicon because the strong direct bandgap optical transition of GaAs, which was so favorable to electroluminescence and injection lasers, implied very strong optical absorption. Thus, the electron-hole pairs were produced close to the surface in GaAs.

Hovel and Woodall were soon able to apply this idea to the fabrication of an efficient GaAs solar cell [179]. A p-n junction was formed in the GaAs and a layer of $Ga_{1-x}Al_xAs$ covered the surface. The new cell had an efficiency of 15% in normal sunlight, higher than that of other junction solar cells [179]. The alloy layer had another favorable characteristic: It had a large bandgap and a high-energy absorption edge that permitted much of the solar spectrum to pass through it, yet it could be doped to provide reasonable conductivity. Thus, a thick layer of alloy could be used to provide a low-sheet-resistance contact to the thin p-GaAs layer [180].

The discovery of the efficient heterojunction solar cell attracted wide interest. The GaAs cell was clearly more expensive than the silicon cell and seemed unlikely to displace it in many applications. Its properties were particularly favorable in two cases, however. For use in space, the GaAs cell's good ultraviolet response and insensitivity to temperature and radiation damage were attractive. The cell's high efficiency and its thinness, a result of the high absorption coefficient for radiation, implied savings in weight. Work at IBM aimed at optimizing the heterojunction cell for space applications continued with support from the National Aeronautics and Space Administration. Efficiencies of 22% at the earth's surface (AM2) and 18.5% in the solar spectrum of outer space (AM0) were eventually achieved [181]. The other application in which the heterojunction solar cell appeared advantageous was the generation of electricity from concentrated sunlight. Here high light intensity raises the temperature of the cell and the higher energy gap of GaAs is favorable. The high efficiencies (up to 25%) of GaAs in concentrated sunlight help to compensate for their high cost.

As mentioned in Section 5A, Anderson initiated the study of Ge-GaAs heterojunctions at an early date. He introduced a model in which there were sharp discontinuities in the band edges at the Ge-GaAs interface. As techniques of crystal growth improved, the heterojunction studies were continued and refined by Howard and various collaborators [182–185]. They showed that the discontinuities of the band edges depend on the crystallographic orientation of the interface, an effect attributed to dipole layers associated with the bonds between germanium and gallium and arsenic atoms. They further measured the pressure dependence of the energy discontinuities and found that the heterojunction model was consistent with the known effects of pressure on the individual semiconductors [186].

G. Superlattices

The search for fast negative resistance effects has been a persistent theme of semiconductor research both past and present. It was fueled in the early years by the discovery of the tunnel diode and the Gunn device, and in 1970 L. Esaki and R. Tsu proposed that a one-dimensional periodic potential formed by periodically varying the composition in a semiconductor would exhibit a negative resistance [187]. The action of the proposed device depended on the quantization of the energy levels of a particle in a very narrow well. According to the Anderson model of heterojunctions, such wells could be formed by interspersing layers of a semiconductor of higher energy gap. Current flows by tunneling through the high-gap material into the wells, and the current then depends strongly on the thickness of the layer between wells, or the energy width of the quantum levels.

Since the layer thicknesses required to cause the necessary degree of quantization and to permit tunneling were only on the order of 0.1 nm, their fabrication posed a very difficult problem to materials technologists. Early attempts to fabricate a structure of the desired type, called a "superlattice" in analogy with a well-known crystallographic concept, by vapor and liquid phase epitaxial methods did not show effects due to quantization in wells, apparently because of their failure to produce the needed fineness, uniformity, planarity, and freedom from interdiffusion and strain [188–192]. It was soon recognized that the technique of molecular beam epitaxy (MBE) of GaAs and $Ga_{1-x}Al_xAs$ alloys, pioneered by A. Y. Cho, offered a promising route towards realization of the superlattice [193–196]. Esaki, L. L. Chang, Howard, and V. L. Rideout constructed a computer-controlled MBE apparatus in which the computer monitored deposition rates and conditions to achieve precise control of composition. In addition, the shutters that alternated the composition of the superlattice layers were automatically controlled when predetermined layer thicknesses were reached to ensure good periodicity [197]. The x-ray analyses made in collaboration with A. Segmüller showed that nearly ideal structures could be made [198–199].

The predicted negative resistance was soon observed [196]. In fact, the crossings of the numerous energy levels as the voltage was varied led to quite complex patterns in current-voltage characteristics [197]. The additional quantization of energy levels in the superlattice also produced easily measurable changes in optical properties [200]. The fundamental absorption was split into lines corresponding to absorption into the various discrete levels of a well. Magneto-oscillatory studies of conductivity clearly demonstrated the two-dimensional nature of the electron system [201]. The possibility of varying layer thicknesses, barrier heights (through control of the aluminum content of the wide-gap layers), and doping levels allowed a very wide spectrum of properties to be produced and an exceptionally rich variety of phenomena to be observed. Current solid state theory has proved adequate to the task of interpreting the many phenomena found in superlattices, and their properties are well understood.

Superlattices can, of course, be built from other chemical systems for which MBE techniques have been mastered. One of the more interesting alternatives is the InAs-GaSb system and its alloys with GaAs [202–203]. Here it turns out that a heterojunction is formed in which the bottom of the conduction band of the InAs lies at a lower energy than the top of the valence band of the GaSb. There is no gap in the distribution of electronic states; electrons can pass freely through the structure and metallic conductivity is observed. However, when the energy levels are forced away from the band extrema by quantization in narrow layers, the overlap of the energy levels can be removed and an energy gap produced, leading to semiconducting behavior. Thus a metal-to-semiconductor transition can be produced by varying some parameter of the structure, such as layer thickness [204]. The Landau quantization in high magnetic fields can also modify the levels in such a way as to produce a metal-to-semiconductor transition [205].

6. Amorphous semiconductors

Studies of amorphous semiconductors started at IBM in 1968 with work both on the chalcogenides and the group IV semiconductors (mostly silicon). Weiser, M. H. Brodsky, and R. Fisher [206–207] studied the optical and electrical properties of arsenic telluride and selenide films. They showed that the photoluminescence efficiency depends on the photon energy. This observation has been important for subsequent models which hypothesized that the luminescence is from self-trapped centers. P. Chaudhari and R. Laibowitz [208] observed the structural changes that occur when a chalcogenide undergoes electrical switching. Chaudhari, in collaboration with J. Graczyk and S. Herd, characterized the structure of the chalcogenides [209]. Brodsky and Title [210] were the first to observe electron spin resonance in amorphous Si, Ge, and SiC. They showed that the spin resonance was associated with dangling bonds and, by annealing studies, that spin resonance correlated with optical absorption and electrical conductivity. An IBM laboratory was the first to prepare amorphous silicon by all four methods presently available—evaporation, sputtering, ion implantation, and glow-discharge decomposition of silane—and to show that the dangling bonds are passivated in the last method [211]. J. Smith, Jr., Brodsky, B. Crowder, Nathan, and A. Pinczuk [212] measured Raman spectra of amorphous silicon, germanium, and several III-V compounds and found that the spectra gave the density of states of the phonons directly. Similar results were obtained through infrared absorption by Brodsky and A. Lurio [213]. Chaudhari, Herd, and Brodsky, along with D. Ast and R. von Gutfeld [214], showed that there were no microcrystallites in amorphous Si.

D. Henderson and F. Herman [215] constructed a model containing 61 atoms of amorphous Si with periodic boundary conditions. This model has been useful in a variety of structural, vibrational, and electronic calculations. Brodsky, in collaboration with the Dundee group, made the first p-n junction in amorphous Si [216]. Subsequently, in collaboration with M. Frisch and J. Ziegler, and with W. Lanford at Yale University, he made the first quantitative measurement of hydrogen in amorphous Si with electronically interesting properties [217].

7. Defects and defect control

Ion implantation studies were started at IBM by Rupprecht in 1965. Fang, Crowder, and Rupprecht developed a self-aligned process for making a very-high-frequency FET [218]. Crowder and Morehead determined the critical dose of ions for conversion of silicon to the amorphous state [219]. K.-N. Tu, Chaudhari, K. Lai, Crowder, and S. Tan [220(a)] found that the density of this amorphous ion-implanted silicon was about 5% smaller than the crystalline form, and L. Glowinski, Tu, and P. Ho [220(b)] characterized the defects in the material.

S. Hu studied the thermal stress and dislocations generated due to processing of Si [221]. In this work, he discovered the emitter edge defect. He developed a method termed "indentation dislocation rosette" to study structural properties, including dislocation motion [222]. He was the first to propose an implied model to explain oxidation-enhanced defects and oxidation-enhanced diffusion [223]. Hu and S. Schmidt did the first modeling of diffusion and they predicted impurity profiles in silicon [224]. S. Mader and A. Michel used TEM to study damage induced by ion implantation and found several dislocation sources [225].

Studies of defects have also been carried out in other materials. Some of this work was discussed in Section 5C. In addition, T. Morgan did extensive work on defects in GaP. In collaboration with B. Welber and R. Bhargava, he showed that red luminescence is due to cadmium-oxygen or zinc-oxygen complexes rather than pairs, as had been previously supposed [226]. With H. Maier, Morgan demonstrated the importance of strain in determining ionization energies of defects [227] and applied the analyses to the oxygen center [228]. P. Yu and various collaborators have used resonant Raman and Brillouin scattering to obtain extensive information about excitons and point defects mostly in II-VI compounds. He recently reviewed this and related work [229].

IBM was responsible for some of the earliest work in laser annealing. In 1968 G. H. Schwuttke, J. Howard, and R. Ross showed that impurities could be diffused locally using laser heating [230]. They filed a patent which covered, among other things, laser annealing of amorphous layers on crystalline substrates, which is widely investigated today [231]. In 1974 R. Laff and G. Hutchins demonstrated recrystallization of fine-grain polycrystalline silicon into similar large-grained material, from which devices were then fabricated [232]. The theory for this effect was worked out by R. Ghez and Laff [233]. More recently, E. Yoffa has studied the mechanism for energy transfer from the laser to the semiconductor lattice and has shown that electron and hole diffusions substantially enlarge the excited volume [234]. J. A. Van Vechten, Tsu, F. Saris, and D. Hoonhout have studied the annealing process and suggested a nonthermal mechanism for annealing [235]. G. Sai-Halasz and Fang [236], and Nathan, R. Hodgson, and Yoffa [237] have presented experimental evidence for the thermal annealing process. Tsu, Hodgson, T. Tan, and J. Baglin [238], in contrast to the usual experiment, have used ultraviolet pulsed laser heating to transform crystalline to amorphous silicon. Fowler and Hodgson have spatially selectively annealed ion-bombarded silicon, taking advantage of the difference in optical absorption of doped and undoped silicon [239].

8. Photoemission

No account of IBM's contribution to semiconductors would be complete without some mention of the extensive work of D. Eastman and his colleagues on photoemission. Eastman is responsible for several important experimental technique advances in photoemission. Although his results cover several kinds of materials, some of the most significant results involve semiconductors. Together with W. Grobman and F. Himpsel, he directly observed intrinsic surface states on Si [240–241]. He and his coworkers also determined the energy band structures of many solids, including GaAs [242–243], using the new technique of angle-resolved photoemission excited by synchrotron radiation. K. Pandey has calculated the photoemission spectra of hydrogenated Si surfaces and obtained good agreement with experiment [244].

9. Concluding statement and acknowledgments

We have attempted to cover a by no means exhaustive selection of IBM work in key areas of semiconductor physics and novel semiconductor devices. In preparing this article, we have had discussions with a great number of our colleagues throughout IBM. We apologize in advance to anyone whose work may have been omitted or mentioned only briefly. We acknowledge S. P. Keller, R. W. Landauer, J. Riseman, F. Stern, and E. J. Yoffa for their critical readings of this manuscript.

References and notes

1. E. W. Pugh, D. L. Critchlow, R. A. Henle, and L. A. Russell, *IBM J. Res. Develop.* **25**, 585 (1981, this issue); E. J. Rymaszewski, J. L. Walsh, and G. W. Leehan, *IBM J. Res. Develop.* **25**, 603 (1981, this issue).
2. J. A. Swanson, *Phys. Rev.* **99**, 1799 (1955).
3. Rolf W. Landauer and J. A. Swanson, *Phys. Rev.* **91**, 555 (1953).
4. H. J. Juretschke, R. W. Landauer, and J. A. Swanson, *J. Appl. Phys.* **27**, 838 (1956).
5. Rolf W. Landauer and Joseph C. Helland, *J. Chem. Phys.* **22**, 1655 (1954).
6. Oral paper presented at the Conference on Statistical Mechanics and Irreversibility, Queen Mary's College, London, England, 1960; published much later: Rolf Landauer, *Phil. Mag.* **21**, 863 (1970).
7. E. Abrahams and M. J. Stephen, *J. Phys. C: Solid State Phys.* **13**, L337 (1980); B. J. Andereik and E. Abrahams, *ibid.*, L383.
8. George Cheroff and Seymour P. Keller, *Phys. Rev.* **111**, 98 (1958).
9. Seymour P. Keller and G. D. Pettit, *Phys. Rev.* **115**, 526 (1959).
10. G. Cheroff, R. C. Enck, and S. P. Keller, *Phys. Rev.* **116**, 1091 (1959).
11. John A. Swanson, *IBM J. Res. Develop.* **5**, 210 (1961).
12. W. J. Turner, A. S. Fischler, and W. E. Reese, *J. Appl. Phys.* **32**, 2241 (1961).
13. G. A. Silvey, V. J. Lyons, and V. J. Silvestri, *J. Electrochem. Soc.* **108**, 653 (1961).
14. M. J. Stevenson, *Proceedings of the International Conference on Semiconductor Physics*, Prague, 1960, Publishing House of the Czechoslovak Academy of Science, Prague, 1961, pp. 1083–1088.
15. W. J. Turner and W. E. Reese, *Phys. Rev.* **127**, 126 (1962).
16. W. J. Turner, W. E. Reese, and G. D. Pettit, *Phys. Rev.* **136**, A1467 (1964).
17. S. H. Koenig, G. R. Gunther-Mohr, and P. J. Price, *J. Phys. Chem. Solids* **2**, 208 (1957).
18. S. H. Koenig and R. D. Brown III, *Phys. Rev. Lett.* **4**, 170 (1960).
19. S. H. Koenig, R. D. Brown III, and W. Schillinger, *Phys. Rev.* **128**, 1668 (1962).
20. S. H. Koenig, Marshall I. Nathan, William Paul, and Arthur C. Smith, *Phys. Rev.* **118**, 1217 (1960).
21. S. H. Koenig, *Proc. Phys. Soc.* **73**, 959 (1959).
22. M. I. Nathan, *Phys. Rev.* **130**, 2201 (1963).
23. E. Erlbach and J. B. Gunn, *Phys. Rev. Lett.* **8**, 280 (1962).
24. J. B. Gunn, *Solid State Commun.* **1**, 88 (1963).
25. Seymour H. Koenig and John J. Hall, *Phys. Rev. Lett.* **5**, 550 (1960).
26. M. J. Katz, S. H. Koenig, and A. A. Lopez. *Phys. Rev. Lett.* **15**, 828 (1965).
27. P. J. Price, *IBM J. Res. Develop.* **10**, 395 (1966).
28. P. A. Lebwohl and P. J. Price, *Solid State Commun.* **9**, 1221 (1971).
29. P. A. Lebwohl and P. J. Price, *Appl. Phys. Lett.* **19**, 530 (1971).
30. W. P. Dumke, *Phys. Rev.* **167**, 783 (1968).
31. J. C. McGroddy and M. I. Nathan, *J. Phys. Soc. Jpn.* **21**, 437 (1966).
32. J. C. McGroddy and M. I. Nathan, *IBM J. Res. Develop.* **11**, 337 (1967).
33. J. E. Smith, J. C. McGroddy, and M. I. Nathan, *Proceedings*, International Conference on Physics of Semiconductors, Leningrad, USSR, 1968, p. 950.
34. Sylwester Porowski, William Paul, J. C. McGroddy, Marshall I. Nathan, and J. E. Smith, Jr., *Solid State Commun.* **7**, 905 (1969).
35. J. C. McGroddy, M. R. Lorenz, and T. S. Plaskett, *Solid State Commun.* **7**, 901 (1969).
36. R. W. Keyes, *IBM J. Res. Develop.* **5**, 266 (1961).
37. P. J. Price, *Phys. Rev.* **104**, 1223 (1956).
38. Robert W. Keyes, *Phys. Rev.* **122**, 1171 (1961).
39. L. J. Bruner and Robert W. Keyes, *Phys. Rev. Lett.* **7**, 55 (1961).
40. Norman G. Einspruch and P. Csavinszky, *Appl. Phys. Lett.* **2**, 1 (1963).
41. John J. Hall, *Phys. Rev.* **161**, 756 (1967).
42. John J. Hall, *Phys. Rev.* **137**, A960 (1965).
43. J. R. Drabble and J. Fendley, *Solid State Commun.* **3**, 269 (1965); *J. Phys. Chem. Solids* **28**, 669 (1967).
44. G. L. Bir and A. Tursunov, *Sov. Phys. Solid State* **4**, 1925 (1963).
45. P. Csavinszky and Norman G. Einspruch, *Phys. Rev.* **132**, 2434 (1963).
46. R. W. Keyes, *Solid State Physics*, Vol. 20, Academic Press, Inc., New York, 1967, pp. 37–90.
47. (a) Robert W. Keyes and Nobuyoshi Kobayashi, *Solid State Commun.* **27**, 63 (1978); (b) R. W. Keyes, *Solid State Commun.* **32**, 179 (1979).
48. (a) M. Pomerantz, *Phys. Rev. Lett.* **13**, 308 (1964); (b) M. Pomerantz, *IEEE Trans. Sonics Ultrasonics* **11**, 68 (1964); M. Pomerantz and R. von Gutfeld, *Proceedings*, Ninth International Conference on Physics of Semiconductors, Nauka, Leningrad, 1968, p. 690; M. Pomerantz, *Phys. Rev. B* **1**, 4029 (1970).
49. Robert W. Keyes, *J. Appl. Phys.* **33**, 3371 (1962).
50. See, for example, J. C. Phillips, in *Bonds and Bands in Semiconductors*, Academic Press, Inc., New York, 1973, Ch. 3.
51. Richard M. Martin, *Phys. Rev. B* **1**, 4005 (1970).
52. J. R. Schrieffer, *Semiconductor Surface Physics*, R. H. Kingston, Ed., University of Pennsylvania Press, Philadelphia, 1957, pp. 55–69.
53. A. B. Fowler, F. Fang, and F. Hochberg, *IBM J. Res. Develop.* **8**, 427 (1964).
54. F. F. Fang and W. E. Howard, *Phys. Rev. Lett.* **16**, 797 (1966).
55. A. B. Fowler, F. F. Fang, W. E. Howard, and P. J. Stiles, *Phys. Rev. Lett.* **16**, 901 (1966).
56. F. F. Fang and A. B. Fowler, *Phys. Rev.* **169**, 619 (1968).
57. F. F. Fang and A. B. Fowler, *J. Appl. Phys.* **41**, 1825 (1970).
58. F. Stern and W. E. Howard, *Phys. Rev.* **163**, 816 (1967).
59. Frank Stern, *Phys. Rev. Lett.* **18**, 546 (1967).
60. Frank Stern, *Phys. Rev. B* **5**, 4891 (1972).
61. F. Stern, *Proceedings*, Second International Conference on Solid Surfaces, Kyoto, *Jpn. J. Appl. Phys. Suppl.* **2**, Pt. 2, 323 (1974).
62. Frank Stern, *Solid State Commun.* **21**, 163 (1977).
63. F. F. Fang and P. J. Stiles, *Phys. Rev.* **174**, 823 (1968).
64. J. Janak, *Phys. Rev.* **178**, 1416 (1969).
65. A. Hartstein and A. B. Fowler, *Surface Sci.* **73**, 19 (1978).
66. H. Welker, *Z. Naturforschung* **11**, 744 (1952).
67. C. Hilsum and A. C. Rose-Innes, *Semiconducting III-V Compounds*, Pergamon Press, Inc., Elmsford, NY, 1961, pp. 196–227.

68. J. C. Marinace, *IBM J. Res. Develop.* **4,** 280 (1960).
69. R. L. Anderson, *IBM J. Res. Develop.* **4,** 283 (1960).
70. R. L. Anderson, *Solid State Electron.* **5,** 341 (1962).
71. N. G. Ainslie, S. E. Blum, and J. F. Woods, *J. Appl. Phys.* **33,** 2391 (1962); K. Weiser and S. E. Blum, paper presented at the Electrochemical Society Meeting, Houston, TX, 1960.
72. N. G. Ainslie, U.S. Patent 3,353,912, filed March 20, 1962; issued November 21, 1967.
73. R. Braunstein, *Phys. Rev.* **99,** 1892 (1955).
74. J. J. Pankove and M. J. Massouliè, *Bull. Amer. Phys. Soc.* **7,** 88 (1962), abstract of talk ZA5, Program of the 1962 Annual APS Meeting, New York City, Vol. 1, pp. 24-27.
75. J. I. Pankove and J. E. Berkeyheiser, *Proc. IRE* **50,** 1976 (1962).
76. R. J. Keyes and T. M. Quist, *Proc. IRE* **50,** 1822 (1962).
77. J. Black, H. Lockwood, and S. Mayburg, *J. Appl. Phys.* **34,** 178 (1963).
78. W. J. Turner and W. E. Reese, *Phys. Rev.* **117,** 1003 (1960).
79. W. P. Dumke, *Phys. Rev.* **127,** 1559 (1962).
80. G. J. Lasher, *IBM J. Res. Develop.* **7,** 58 (1963).
81. Marshall I. Nathan, William P. Dumke, Gerald Burns, Frederick H. Dill, Jr., and Gordon J. Lasher, *Appl. Phys. Lett.* **1,** 62 (1962).
82. R. N. Hall, G. E. Fenner, J. D. Kingsley, T. J. Soltys, and R. O. Carlson, *Phys. Rev. Lett.* **9,** 366 (1962).
83. T. M. Quist, R. H. Rediker, R. J. Keyes, W. E. Krag, B. Lax, A. L. McWhorter, and H. J. Zeigler, *Appl. Phys. Lett.* **1,** 91 (1962).
84. Nick Holonyak, Jr. and S. F. Bevacqua, *Appl. Phys. Lett.* **1,** 82 (1962).
85. K. Weiser and R. S. Levitt, *Appl. Phys. Lett.* **2,** 178 (1963).
86. I. Melngailis, *Appl. Phys. Lett.* **2,** 176 (1963).
87. I. Melngailis, A. J. Strauss, and R. H. Rediker, *Proc. IEEE (Correspondence)* **51,** 1154 (1963).
88. R. J. Phelan, A. R. Calawa, R. H. Rediker, R. J. Keyes, and B. Lax, *Appl. Phys. Lett.* **3,** 143 (1963).
89. C. Benoit á la Guillaume and P. Lavallard, *Solid State Commun.* **1,** 148 (1963).
90. F. H. Dill, Jr. and R. F. Rutz, U.S. Patent No. 3, 247, 576, 1966; F. H. Dill, Jr., *1963 International Solid State Circuits Conference Digest*, Lewis Winner, New York, 1963, pp. 110–111.
91. P. P. Sorokin, *IBM J. Res. Develop.* **23,** 476 (1979).
92. F. Stern, in *Semiconductors and Semimetals*, Vol. 2, R. K. Willardson and A. C. Beer, Eds., Academic Press, Inc., New York, 1966, pp. 371–411.
93. M. I. Nathan, *Appl. Opt.* **5,** 1514 (1966).
94. W. P. Dumke, in *Advances in Lasers*, Vol. 2, A. K. Levine, Ed., Marcel Dekker, New York, 1968, pp. 257–293.
95. Yu M. Popov, *Appl. Opt.* **6,** 1818 (1967).
96. W. V. Smith and P. P. Sorokin, *The Laser*, McGraw-Hill Book Co., Inc., New York, 1966, Ch. 7.
97. M. H. Pilkuhn, *Phys. Status Solidi* **25,** 9 (1968); also *J. Lumin.* 7, 269 (1973).
98. H. Kressel, in *Laser Handbook*, F. T. Arecchi and E. D. Schulz-Dubois, Eds., North-Holland Publishing Co., Amsterdam, 1972, pp. 441–95; F. Stern, *ibid.*, pp. 425–440; see also *Lasers*, A. K. Levine and A. J. Demaria, Eds., Marcel Dekker, New York, 1971.
99. H. C. Casey and M. B. Panish, *Heterostructure Lasers*, Academic Press, Inc., New York, 1978.
100. H. Kressel and J. K. Butler, *Semiconductor Lasers and Heterojunction LEDs*, Academic Press, Inc., New York, 1977.
101. G. Burns and M. I. Nathan, *Proc. IEEE* **52,** 770 (1964).
102. G. Fan and J. H. Greiner, *J. Appl. Phys.* **41,** 1401 (1970).
103. A. H. Eschenfelder, *J. Appl. Phys.* **41,** 1372 (1970).
104. J. C. Marinace, *IBM J. Res. Develop.* **15,** 258 (1971).
105. G. J. Sprokel, *IBM J. Res. Develop.* **15,** 265 (1971).
106. H. Wieder and H. Werlich, *IBM J. Res. Develop.* **15,** 272 (1971).
107. A. J. Dewey, *Proc. SID* **19,** 1 (1978).
108. R. T. Lynch, Jr., M. B. Small, and R. Y. Hung, *IBM J. Res. Develop.* **23,** 585 (1979).
109. R. J. Keyes, T. M. Quist, R. H. Rediker, M. J. Hudson, C. R. Grant, and J. W. Meyer, *Electronics* **36,** 38 (April 5, 1963).
110. K. L. Konnerth and B. R. Shah, *IEEE Spectrum* **7,** 37 (September 1970). This paper reviews early work in optical communication with LEDs and injection lasers.
111. K. Konnerth and C. Lanza, *Appl. Phys. Lett.* **4,** 120 (1964).
112. J. C. Marinace and K. L. Konnerth, *IBM J. Res. Develop.* **12,** 272 (1968).
113. C. Lanza, K. L. Konnerth, and C. E. Kelly, *Solid State Electronics* **10,** 21 (1967).
114. K. L. Konnerth, J. C. Marinace, and J. C. Topalian, *J. Appl. Phys.* **41,** 2060 (1970).
115. G. H. Schwuttke and H. Rupprecht, *J. Appl. Phys.* **37,** 167 (1966).
116. Edward S. Yang, *J. Appl. Phys.* **42,** 5635 (1971).
117. A. A. Bergh and P. J. Dean, *Light Emitting Diodes*, Clarendon Press, Oxford, 1976. This book contains a thorough review of all aspects of visible LEDs with exhaustive references.
118. K. Seeger, *Semiconductor Physics*, Springer-Verlag, New York, 1973, Ch. 13.
119. N. Ainslie, M. H. Pilkuhn, and H. Rupprecht, *J. Appl. Phys.* **35,** 105 (1964).
120. M. R. Lorenz, *Metallurgical Soc. AIME Trans.* **245,** 539 (1969).
121. H. Nelson, *RCA Rev.* **24,** 603 (1963).
122. H. S. Rupprecht and J. M. Woodall, U.S. Patent 3,773,571, filed 1967, issued 1973.
123. H. Rupprecht, J. M. Woodall, and G. D. Pettit, *Appl. Phys Lett.* **11,** 81 (1967).
124. H. Rupprecht, J. M. Woodall, G. D. Pettit, J. W. Crowe, and H. F. Quinn, *IEEE J. Quantum Electron.* **QE-4,** 35 (1968).
125. M. I. Nathan and G. Burns, *Appl. Phys. Lett.* **1,** 89 (1962); *Phys. Rev.* **129,** 125 (1963).
126. W. J. Turner, G. D. Pettit, and N. G. Ainslie, *J. Appl. Phys.* **34,** 3274 (1963).
127. W. J. Turner and G. D. Pettit, *Appl. Phys Lett.* **3,** 102 (1963).
128. W. J. Turner, W. E. Reese, and G. D. Pettit, *Phys. Rev.* **136,** A1467 (1964).
129. G. Mandel, F. Morehead, and P. Wagner, *Phys. Rev.* **136,** A826 (1964).
130. G. Mandel and F. Morehead, *Appl. Phys. Lett.* **4,** 143 (1964).
131. F. A. Kroger, *J. Phys. Chem. Solids* **26,** 1717 (1965).
132. B. L. Crowder, *Research Report RC-1567*, IBM Thomas J. Watson Research Center, Yorktown Heights, NY, 1966.
133. F. F. Morehead and B. L. Crowder, *Proceedings of the International Conference on Luminescence*, Hungarian Academy of Sciences, 1966, pp. 1785–1792.
134. B. L. Crowder and G. D. Pettit, *Phys. Rev.* **178,** 1235 (1969).
135. B. L. Crowder, R. S. Title, and G. D. Pettit, *Phys. Rev.* **181,** 567 (1969).
136. M. R. Lorenz and M. Pilkuhn, *J. Appl. Phys.* **37,** 4094 (1966).
137. A. Onton and M. R. Lorenz, *Appl. Phys. Lett.* **12,** 115 (1968).
138. M. R. Lorenz, W. Reuter, W. P. Dumke, R. J. Chicotka, G. D. Pettit, and J. M. Woodall, *Appl. Phys. Lett.* **13,** 421 (1968).
139. E. Erlbach and J. B. Gunn, *Phys. Rev. Lett.* **8,** 280 (1962).
140. J. B. Gunn, *IBM J. Res. Develop.* **8,** 141 (1964).

141. N. Braslau, J. B. Gunn, and J. L. Staples, *IBM J. Res. Develop.* **8,** 545 (1964).
142. B. K. Ridley and T. B. Watkins, *Proc. Phys. Soc. (Lond).* **78,** 293 (1961).
143. C. Hilsum, *Proc. IRE* **50,** 185 (1962).
144. G. Hobson, *The Gunn Effect*, Clarendon Press, Oxford, England, 1974.
145. B. Bosch and R. W. H. Engelmann, *Gunn-Effect Electronics*, John Wiley & Sons, Inc., New York, 1975.
146. P. J. Bulman, G. S. Hobson, and B. C. Taylor, *Transferred Electron Devices*, Academic Press, Inc., New York, 1972.
147. H. Hartnagel, *Gunn-Effect Logic Devices*, American Elsevier, New York, 1973.
148. J. B. Gunn, *IBM J. Res. Develop.* **10,** 300 (1966).
149. J. B Gunn, *IBM J. Res. Develop.* **10,** 310 (1966).
150. J. B. Gunn, *Electro-technology* **80,** 67 (1967).
151. J. B. Gunn, *IEEE Trans. Magnetics* **MAG-3,** 176 (1967).
152. J. B. Gunn, *IEEE Trans. Electron Devices* **ED-14,** 720 (1967).
153. J. B. Gunn, *IBM J. Res. Develop.* **13,** 591 (1969).
154. J. B. Gunn, *IEEE Trans. Electron Devices* **ED-23,** 705 (1976).
155. N. Braslau, J. B. Gunn, and J. L. Staples, *Solid-State Electron.* **10,** 381 (1967).
156. J. B. Gunn, *Electron. Lett.* **2,** 172 (1966).
157. J. B. Gunn and B. J. Elliott, *Phys. Lett.* **22,** 369 (1966).
158. N. Braslau, *Phys. Lett. A* **24,** 531 (1967).
159. N. Braslau and P. S. Hauge, *IEEE Trans. Electron Devices* **ED-17,** 616 (1970).
160. M. E. Drougard, *J. Appl. Phys.* **37,** 1858 (1966).
161. C. A. Bryant and J. B. Gunn, *Rev. Sci. Instrum.* **36,** 1614 (1965).
162. A. R. Hutson, A. Jayaraman, A. G. Chynoweth, A. S. Coriell, and W. L. Feldman, *Phys. Rev. Lett.* **14,** 639 (1965).
163. W. von Münch, H. Statz, and A. E. Blakeslee, *Solid-State Electron.* **9,** 826 (1966).
164. Von Waldemar von Münch, *Z. Angew. Physik* **18,** 129 (1964).
165. H. Statz, *Solid-State Electron.* **8,** 827 (1965).
166. Karsten E. Drangeid, Rudy Jaggi, S. Middelhoek, Theo. Mohr, Andres Moser, Giovanni Sasso, Rudy Sommerhalder, and Peter Wolf, *Electron. Lett.* **4,** 362 (1968).
167. The technologies used to fabricate the one-micron MESFETs were described in a series of five papers and two communications: *IBM J. Res. Develop.* **14,** 82–151 (1970).
168. K. E. Drangeid and R. Sommerhalder, *IBM J. Res. Develop.* **14,** 82 (1970).
169. H. Statz and W. v. Muench, *Solid-State Electron.* **12,** 111 (1969).
170. K. E. Drangeid, R. Sommerhalder, and W. Walter, *Electron. Lett.* **6,** 228 (1970).
171. C. A. Mead, *Proc. IEEE* **54,** 307 (1966).
172. W. W. Hooper and W. I. Lehrer, *Proc. IEEE* **55,** 1237 (1967).
173. P. L. Hower, W. W. Hooper, D. A. Tremere, W. Lehrer, and C. A. Bittmann, *Proceedings of the 1968 Symposium on GaAs*, C. I. Pedersen, Ed., Institute of Physics, Physical Soc., London, 1969, pp. 187–194.
174. Charles A. Liechti, *IEEE Trans. Microwave Theor. Tech.* **MTT-24,** 279 (1976).
175. W. Baechtold, K. Daetwyler, T. Forster, T. O. Mohr, W. Walter, and P. Wolf, *Electron. Lett.* **9,** 232 (1973).
176. K. E. Drangeid, Ronald F. Broom, Wilhelm Jutzi, Theodor O. Mohr, Andreas Moser, and Giovanni Sasso, *IEEE J. Solid State Circuits* **SC-7,** 277 (1972); paper presented at the International Solid State Circuits Conference in 1971 as paper WPM6.5.
177. R. C. Eden, B. M. Welch, R. Zucca and S. I. Long, *IEEE J. Solid State Circuits* **SC-14,** 231–239 (1979).
178. A. R. Gobat, M. F. Lamorte, and G. W. McIver, *IRE Trans. Mil. Electron.* **MIL-6,** 20 (1962).
179. J. M. Woodall and H. J. Hovel, *Appl. Phys. Lett.* **21,** 379 (1972).
180. Similar progress was made in the USSR. See Zh. I. Alferov *et al.*, *Sov. Phys.-Semicond.* **4,** 2047 (1971).
181. J. M. Woodall and H. J. Hovel, *Appl. Phys. Lett.* **30,** 492 (1977).
182. L. Esaki, W. E. Howard, and J. Heer, *Surface Sci.* **2,** 127 (1964).
183. L. Esaki, W. E. Howard, and J. Heer, *Appl. Phys. Lett.* **4,** 3 (1964).
184. F. F. Fang and W. E. Howard, *J. Appl. Phys.* **35,** 612 (1964).
185. W. E. Howard, A. B. Fowler, and D. McLeod, *J. Appl. Phys.* **39,** 1533 (1968).
186. H. J. Hovel, in *Semiconductors and Semimetals*, R. K. Willardson and A. C. Beer, Eds., Academic Press, Inc., New York, 1975, Vol. 11.
187. L. Esaki and R. Tsu, *IBM J. Res. Develop.* **14,** 61 (1970).
188. L. Esaki, L. L. Chang, and R. Tsu, *Proceedings of the 12th International Conference on Low Temperature Physics*, Kyoto, 1970, p. 551; L. Esaki, *Proceedings of the International Conference on the Physics and Chemistry of Semiconductor Heterojunctions*, Budapest, 1970, pp. 1–13.
189. A. E. Blakeslee and C. F. Aliotta, *IBM J. Res. Develop.* **14,** 686 (1970).
190. Zh. I. Alferov, Yu. V. Zhilyaev, and Yu. V. Shmartsev, *Fiz. Tekh. Poluprov.* **5,** 196 (1971) [*Soviet Phys.-Semicond.* **5,** 174 (1971)].
191. A. E. Blakeslee, *J. Electrochem. Soc.* **118,** 1459 (1971).
192. J. M. Woodall, *J. Cryst. Growth* **12,** 32 (1972).
193. A. Y. Cho, M. B. Panish, and L. Hayashi, *Proceedings, Symposium on GaAs and Related Compounds, Aachen, 1970*, Institute of Physics, London, 1971, p. 18.
194. A. Y. Cho, *J. Appl. Phys.* **42,** 2074 (1971).
195. A. Y. Cho, *Appl. Phys. Lett.* **19,** 467 (1971).
196. L. Esaki, L. L. Chang, W. E. Howard, and V. L. Rideout, *Proceedings, 11th International Conference on the Physics of Semiconductors*, Polish Academy of Science, PWN-Polish Scientific Publishers, Warsaw, 1972, p. 431.
197. For a review of work in the early 1970s, see L. Esaki and L. L. Chang, *Crit. Rev. Solid State Sci.* **6,** 195 (1976).
198. Armin Segmüller, P. Krishna, and L. Esaki, *J. Appl. Crystallogr.* **10,** 1 (1977).
199. L. L. Chang, Armin Segmüller, and L. Esaki, *Appl. Phys. Lett.* **28,** 39 (1975).
200. R. Dingle, W. Wiegmann, and C. H. Henry, *Phys. Rev. Lett.* **33,** 827 (1974).
201. L. L. Chang, H. Sakaki, C. A. Chang, and L. Esaki, *Phys. Rev. Lett.* **38,** 1489 (1977).
202. H. Sakaki, L. L. Chang, G. A. Sai-Halasz, C. A. Chang, and L. Esaki, *Solid State Commun.* **26,** 589 (1976).
203. G. A. Sai-Halasz, L. Esaki, and W. A. Harrison, *Phys. Rev. B* **18,** 2812 (1978).
204. L. L. Chang, N. Kawai, G. A. Sai-Halasz, R. Ludeke, and L. Esaki, *Appl. Phys. Lett.* **35,** 939 (1979).
205. N. J. Kawai, L. L. Chang, G. A. Sai-Halasz, C.-A. Chang, and L. Esaki, *Appl. Phys. Lett.* **36,** 369 (1980).
206. K. Weiser and M. H. Brodsky, *Phys. Rev. B* **1,** 791 (1970).
207. K. Weiser, R. Fisher, and M. H. Brodsky, *Proceedings of the Tenth International Conference on the Physics of Semiconductors* (U.S. Atomic Energy Commission, Washington, DC, 1970), p. 667.
208. P. Chaudhari and R. B. Laibowitz, *Thin Solid Films* **12,** 239 (1972).
209. P. Chaudhari, J. Graczyk, and S. Herd, *Physics of Structurally Disordered Solids*, S. S. Mitra, Ed., Plenum Press, New York, 1968, pp. 31–44.
210. M. H. Brodsky and R. S. Title, *Phys. Rev. Lett.* **23,** 581 (1969).

211. M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, *Phys. Rev. B* **1**, 2632 (1970).
212. J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, M. I. Nathan, and A. Pinczuk, *Phys. Rev. Lett.* **26**, 642 (1971).
213. M. H. Brodsky and A. Lurio, *Phys. Rev. B* **9**, 1646 (1974).
214. P. Chaudhari, S. Herd, D. Ast, M. Brodsky, and R. von Gutfeld, *J. Noncrystalline Solids* **8–11**, 900 (1972).
215. D. Henderson and F. Herman, *J. Noncrystalline Solids* **8–10**, 359 (1972); D. Henderson, *J. Noncrystalline Solids* **16**, 317 (1974).
216. W. E. Spear, P. G. Le Comber, S. Kinmond, and M. H. Brodsky, *Appl. Phys. Lett.* **28**, 105 (1976).
217. M. H. Brodsky, M. A. Frisch, J. F. Ziegler, and W. A. Lanford, *Appl. Phys. Lett.* **30**, 561 (1971).
218. F. F. Fang and B. L. Crowder, *Technical Digest of the 1970 International Electron Devices Meeting*, Washington, DC, p. 80; F. F. Fang and H. Rupprecht, *IEEE J. Solid State Circuits* **SC-10**, 205 (1975).
219. B. L. Crowder and F. F. Morehead, *Appl. Phys. Lett.* **14**, 313 (1969).
220. (a) K. N. Tu, P. Chaudhari, K. Lai, B. L. Crowder, and S. I. Tan, *J. Appl. Phys.* **43**, 4262 (1972); (b) L. D. Glowinski, K. N. Tu, and P. S. Ho, *Appl. Phys. Lett.* **28**, 312 (1976).
221. S. M. Hu, *J. Vac. Sci. Technol.* **14**, 17 (1977).
222. S. M. Hu, *J. Appl. Phys.* **46**, 1465 (1975); *J. Appl. Phys.* **46**, 1470 (1975); *Appl. Phys. Lett.* **31**, 139 (1977).
223. S. M. Hu, *J. Appl. Phys.* **45**, 1567 (1974).
224. S. M. Hu and S. Schmidt, *J. Appl. Phys.* **39**, 4272 (1968).
225. S. Mader and A. E. Michel, *J. Vac. Sci. Technol.* **13**, 391 (1976).
226. T. N. Morgan, B. Welber, and R. N. Bhargava, *Phys. Rev.* **166**, 751 (1967).
227. T. N. Morgan and H. Maier, *Phys. Rev. Lett.* **27**, 1200 (1971).
228. T. N. Morgan, *Phys. Rev. Lett.* **40**, 190 (1978).
229. P. Y. Yu, in *Current Topics in Physics*, Vol. 14: *Excitons*, K. Cho, Ed., Springer-Verlag, Berlin, 1979, pp. 211–253.
230. G. H. Schwuttke and J. M. Fairfield, *Solid-State Electron.* **11**, 1175 (1968).
231. G. H. Schwuttke, J. Howard, and R. F. Ross, U.S. Patent No. 3,585,088, 1971.
232. R. A. Laff and G. L. Hutchins, *IEEE Trans. Electron Devices* **ED-21**, 243 (1974).
233. R. A. Ghez and R. A. Laff, *J. Appl. Phys.* **46**, 2103 (1975).
234. E. J. Yoffa, *Phys. Rev. B* **21**, 2415 (1980).
235. J. A. Van Vechten, R. Tsu, F. W. Saris, and D. Hoonhout, *Phys. Lett. A* **74**, 417 (1979); J. A. Van Vechten, R. Tsu, and F. W. Saris, *ibid.*, p. 422.
236. G. A. Sai-Halasz, F. F. Fang, T. O. Sedgwick, and Armin Segmüller, *Appl. Phys. Lett.* **36**, 419 (1980).
237. M. I. Nathan, R. T. Hodgson, and E. J. Yoffa, *Appl. Phys. Lett.* **36**, 512 (1980).
238. Raphael Tsu, Rodney T. Hodgson, Teh Yu Tan, and John E. Baglin, *Phys. Rev. Lett.* **42**, 1356 (1979).
239. A. B. Fowler and R. T. Hodgson, *Appl. Phys. Lett.* **36**, 914 (1980).
240. D. E. Eastman and W. E. Grobman, *Phys. Rev. Lett.* **28**, 1378 (1972).
241. F. J. Himpsel and D. E. Eastman, *J. Vac. Sci. Technol.* **165**, 1297 (1979).
242. T. C. Chiang, J. A. Knapp, D. E. Eastman, and M. Aono, *Solid State Commun.* **31**, 917 (1979).
243. T. C. Chiang, J. A. Knapp, M. Aono, and D. E. Eastman, *Phys. Rev.*, in press.
244. K. C. Pandey, *IBM J. Res. Develop.* **22**, 250 (1978).

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The authors are located at the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598.