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Research in Silicon Valley
Forschung im Silicon Valley

(Akademievorlesung am 30. Mai 1996)

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Die Gegend südlich von San Francisco in Kalifornien wird heute das "Silicon Valley" genannt, weil dort die entscheidende Entwicklung der Mikroelektronik mit dem halbleitenden Material Silizium stattfand. Das Silizium löste erst spät das viel leichter handhabbare Germanium ab, mit dem im Jahre 1947 bei den Bell Laboratories die erste Demonstration des Transistors erfolgt war. Die folgende Publikation berichtet über persönliche Erfahrungen in der Forschung dieser frühen Zeit der Siliziumtechnik im Laboratorium von William Shockley. Sie ist eine erweiterte, englischsprachige Fassung des Akademievortrages am 30. Mai 1996 in Berlin.

Introduction

The transistor invention in the *warm Christmas Eve atmosphere* (1) of 1947 has shaped our daily lives in a truly profound manner. A huge industry with a wide gamut of applications has developed from this first demonstration of transistor action in a semiconducting material (2–6). In retrospect, this glorious success story appears like an inevitable, almost logical chain of events. Such a view is, however, far from being a correct historical interpretation. Many decades of often frustrating attempts to understand semiconducting materials preceded the transistor demonstration. Decades of struggle followed before the transistor gained acceptance in industrial applications. Vexing detours had to be traveled before the seemingly so simple and obvious idea of a field-effect transistor was finally put into practice.

This paper opens with a description of the background information, on which the transistor development was based. Next, the early research work is covered, especially the competition between germanium and the eventually victorious silicon.

The main part then reports upon the materials research work in the early years of this most famous industrial region, carrying the name of a semiconducting element: silicon.

Pristine Semiconductor Foundations

Grapplings of a Century Ago

Our scientific forefathers of the nineteenth century performed remarkable amounts of empirical work, documenting the physical properties of all sorts of materials. Metals were quite easy; the bronze age and the iron age were based on this wisdom. Ohm's law was established and seemed – eventually – convincing and useful for the oncoming age of electricity. Yet there were strange classes of naturally occuring minerals, many sulfides and oxides in particular, which disobeyed the simple rules; they were neither good metals nor could they be classified as insulators. The parameters for these materials were almost impossible to be obtained uniquely and reproducibly for handbook listings. External influences and deviations from chemical purity were apparently of significance. Such irreproducibility disqualified these materials from proper scientific attention. Out of sheer desperation, the disparaging term *semiconductor* was adopted.

Ferdinand Braun, a young high school teacher at Leipzig, Germany (4, 7) provided the first definitive report in 1874 on the rectifying properties of a metallic point contact on crystalline sulfides (8). A nonlinear and polarity-dependent current flow was demonstrated in an experimental lecture in the November of 1876 (4, 7), a truly revolutionary violation to the contemporary paradigm of Ohmic linearity! Suspicions arose, especially against the artificiality of the low-dimensional contact. The physics community dared not to tread on such dangerous grounds. A comparatively much better defined area of investigations arrived with the evacuated tubes, where individual electrons could be isolated and studied. Braun himself deserted solids for the tube; he invented the cathode-ray tube (*Braunsche Röhre)* in 1897. The Nobel Prize in physics of 1909, however, acknowledged his solid-state contributions. Guglielmo Marconi, who shared the prize, and Braun had laid the foundations for simple and cheap radio receivers of that age. Although it was yet totally unclear how these needle-detectors worked, they were still useful to rectify and demodulate radio waves, although in a noisy and instable fashion (7).

The systematic search by last century's chemists for completing the periodic table encountered substantial difficulties with the elements in the center of the table. The slot below silicon in the fourth column remained mysteriously empty until Clemens Winkler, a chemist in the "Bergbauakademie" in Freiberg, Sachsen, Germany identified a new element (4, 9) in 1886, which he baptized *germanium*, patriot that he had to be in the nationalistic European era of his days. By the end of last century, synthesis of elemental silicon and germanium was well documented, and it seemed irrefutable to at least a minority of scientists that these elements plus selenium and an extensive number of compounds, especially copper oxide or cadmium sulfide, were neither metals nor insulators. These materials were all quite remarkable photoconductors. Embarrassing was the analysis by the Hall effect: several samples indicated transport by some sort of positive charge carrier, certainly *not* an ion.

Primitive Device Suggestions

Those accepting that semiconductors were indeed a separate class of materials, were almost forced to consider applications. These materials had charge carrier volume densities much below those of real metals. It became clear – especially via photoconductance – that external influences could modulate the carrier densities, apparently by incredibly large variations over many decades; unthinkable for metals! This wide variation of the resistance of a strip of semiconductor should be controllable to act as a switch for current flow. The simplest arrangement would be a parallel-plate condenser. One plate would be the semiconductor, whose conductivity ought to be "influenced" (in the electrostatic sense) by the voltage of the other plate, made of a metal. We now know that this idea forms the basis for a field-effect-transistor (10). The many attempts of those days a century ago, mostly undocumented, all failed. Materials control remained inadequate (10, 11).

Device usage of semiconductors was therefore restricted to primitive applications. Large-area rectifiers made of selenium or copper oxide conquered good market shares because they were cheap. Engineers suspected that the rectification originated from the interface between a contact metal and the semiconductor. It seemed necessary to "form" these interfaces somehow by an annealing treatment, often with a voltage applied. These techniques were so completely heuristic and non-scientific that people spoke of the "*shame of the rectification – problem*" (12). Nevertheless, semiconductors existed in symbiosis with the regally reigning electron vacuum tubes, but merely in a lowly, humble slavery of ancillary passive functions.

The other usage was photoconductivity, remarkably optimized by empirical efforts and utilized in applications of measurements and control, such as in exposure meters for cameras or in light-activated sensors and switches. Studies of photoconductance by Russell Ohl (13) evidenced two types of silicon with *p*ositive and *n*egative carriers, leading to early distinction betwen *p*- and *n*-type materials and first inklings about junctions. Semiconductor applications were henced restricted to just two-terminal functions. A realization of a three-terminal device with amplification, oscillation, and modulation was still impossible; one relied on tubes, however complicated, expensive, far from thermal equilibrium these evacuated devices were (4, 14).

The Basis of Quantum Theory

Quantum theory, first succeeding with atoms and molecules, expanded to the solid state with the simplifying notion of periodic atomic arrangements in a crystal. The glaring difference between a many-electron metal and a few-electron semiconductor was suddenly clarified: semiconductors had an energy gap between the low-lying valence electrons and the higher states of conduction electrons. The idea of localized electronic states inside the forbidden gap explained many features, including selective photoexcitation of conductance. Theorists such as Felix Bloch, Max Born, Léon Brillouin, or Rudolf Peierls all helped to elevate solids, especially semiconductors, to presentable, tractable objects of quantum physics (4–6, 14). It was no longer demeaning to devote oneself to semiconducting materials, an important fact to attract good young reasearchers! In 1912, quantitative X-ray analysis became available by Laue's discovery (4), and the crystal was finally an accepted, even respectable target of physics. The ideal solid as a perfect, infinitely extended regular spatial array with unperturbed translational symmetry, free of impurities was, however, just an elegant concept, useful for group theory. The real solids were very far removed from this lofty ideal.

Single crystals, as idealized in theory, had to become available for practice. Early work was performed with alkali halides, which are easy to be pulled as single crystals out of a melt. Spiro Kyropoulos in the attic of Robert Pohl's labs at Göttingen University (4, 15) succeeded to grow large and quite perfect crystals to serve as model solids in color center research (16); Johan Czochralski did similar work on metals (17); his name is perpetuated in today's growth technology for semiconductors. Silicon and germanium, however, were too difficult to be grown in the twenties and thirties, there also seemed no need to attempt it as yet.

A small theorists' community began to tackle first the metal-semiconductor interface; an appropriate topic, as we can judge today. Nevill Mott (18) and Walter Schottky (13, 19) made the most significant contributions. A model was developed for the interface between a metal – with its Fermi level at the top of its electron energy distribution – and a semiconductor, with the Fermi level inside the gap and fixed by the doping. At equilibrium, those Fermi levels must coincide; an applied voltage removes this constant behavior. The essential junction features of polarity-dependence and nonlinearity were therefore at least plausible.

Quantum theory also prescribed the treatment of the electrons, especially the dependence of their energies E as functions of their wave vectors k. The Schroedinger equation had to be solved for the idealized periodic potential, yielding an energy dispersion E(*k*), the "band structure". With it came the realization that electrons in a solid also have *antiparticles,* unoccupied states in the valence bands, the *holes.* The present generation is so used to this vital semiconductor feature that it is hard to explain how uneasy many people felt about this seemingly artificial concept. When Shockley wrote his book (20), his publisher did not accept the author's suggestion to mention "holes" first in the title – it was even difficult to keep them in the book's title at all!

Another, very significant realization occurred in those days: space charge layers appear in semiconducting materials. The small electron densities and the requirement of neutrality lead – via Poisson's equation – to regions of spatially fixed electric charge. A very helpful recipe was handed to the experimentalists: the geometric extension of such space charge layers is measurable via its capacitance (19)!

The thirties of our century thus provided basic tools and ideas to understand the novel phenomena of semiconductors, which truly sprang from quantum mechanics as applied to idealized crystal lattices. In retrospect, it may seem somewhat surprising that experimental realizations were so sluggish in keeping up with theory. The extreme difficulties in preparing, modifying, measuring these materials as definitive samples are the reasons for this delay. Materials reproducibility still presented an immense hurdle. Patents were filed, especially for the evident idea of a field-effect transistor (10), in particular by Julius Lilienfeld in 1926 (21), by Oscar Heil in 1935 (22), and by William Shockley in his patent notebook in 1939 (6, 23) – but any reduction to practice with their contemporary materials was totally unattainable – what frustration!

Wartime Semiconductor Detectors

Radar was a decisive weapon in the Second World War, especially in anti-aircraft strategy (4, 24). Huge efforts started in Britain and Germany, but on even bigger scales in the US MIT Radiation Laboratory. Detector diodes handling high radar frequencies were urgent for mixer applications. The only available solutions for this need were the elemental semiconductors Ge and Si, mounted in reasonably stable packages – with the *cat's whisker* of a metal spring contact to reduce capacitance for high-frequency operation. Frederick Seitz, active in this field, describes these events in a symposium (25). Figure 1 shows a typical rectifier diode arrange-

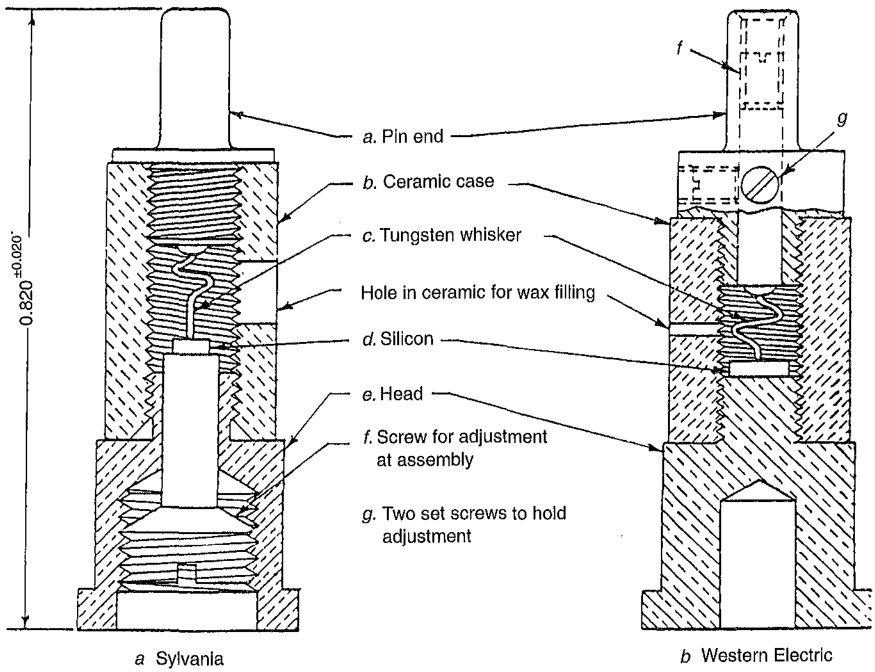


Figure 1
Radar detector diodes, USA of World War II, see Ref. (26)

ment; the illustration stems from a remarkable book on detectors of the "Radiation Lab Series" (26).

Empirical trial-and-error prevailed in the haste of this defense work. Recognition of admixing foreign elements, such as aluminum, to Ge and Si was considered more like traditional metallurgical alloying. Nevertheless, remarkable attention was paid to the theoretical foundations (25, 26). Hans Bethe (27) explained the low ionization energies of "donators" and acceptors, as compared to this energy of hydrogen, with the reduced masses of holes and electrons and with the screened attraction inside the dielectric medium, today taught as *effective-mass-theory*. Basic understanding thus also continued to expand during the war years.

Universities were also involved in scientific war service. Best known are the US activities at Penn State (28) and at Purdue, where Karl Lark-Horovitz and his doctoral students, in particular Ralph Bray, performed intensive studies on Ge – and were later surpassed by the massive research at Bell Labs (29). Even more tragic was the fate of Josef Stuke, who autopsied Ge diodes from British bombers, shot down by German *flak* guns. He measured the intrinsic and extrinsic conductivities of Ge for his thesis; his advisor Robert W. Pohl did not accept his – correct – interpretations (6, 30) and therefore severely delayed publication. Most of the European, especially the German, academic establishment did simply not acknowledge the existence of semiconductors.

Orchestrated Efforts at Bell Labs

The Transistor Demonstrated

When the war ended, an extensive body of knowledge existed – both empirical and fundamental – on semiconductors, especially for germanium and silicon. Mervin Kelly, director at Bell Labs, rehired Shockley, who had been on duty for military "*Operations Research*" (31). Kelly and Shockley were convinced that a solid-state replacement for mechanical telephone switches was possible. The elemental semiconductors, prototypes for simple and defined materials, were selected as the

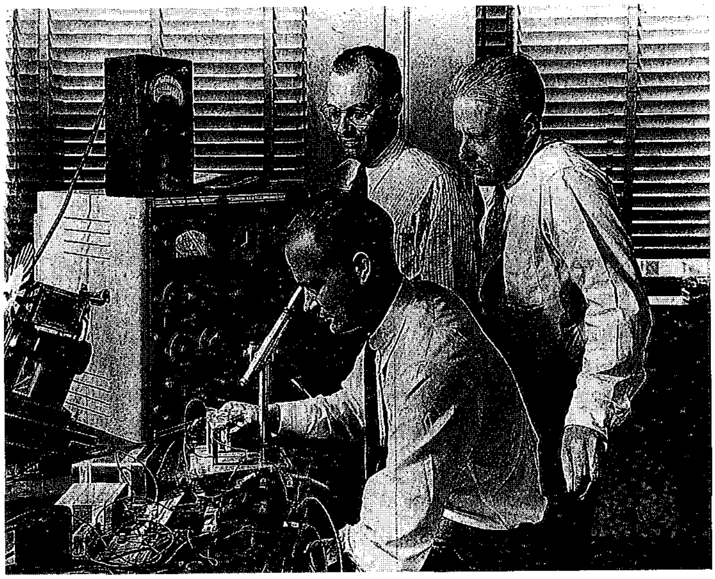


Figure 2
The transistor inventors of 1947 and Nobel laureates of 1956: William B. Shockley, looking through the microscope, John Bardeen (left), and Walter H. Brattain

objects of concentrated research. This mission was critized by the applications engineers of the Bell System, who just demanded improvements and cost reductions for devices based on selenium and copper oxide, which were already heavily used in the network. The independence and the copious finances of Bell Labs, then being part of a regulated monopoly, provided the foundations for continuous, professional interdisciplinary research, delving deeply into the scientific base. The details of this work are profusely recorded in a historical book series of Bell Laboratories (32) and will not be repeated here. Shockley, group leader for the semiconductor effort, and his colleagues, especially John Bardeen and Walter Brattain, – shown in Figure 2 – related the story of the transistor invention on several occasions (33), such as in their Nobel speeches in 1956 (34). A highly personal account by Shockley is Ref. (35). December 23, 1947 has been officially decreed as the birthday of the *transistor,* because of the properly documented and verified reduction to practice on that day. The shaky germanium device is shown in Figure 3. On a piece of polycrystalline germanium, properly called *base*, two contact needles are seen, one injects minority carriers, the *emitter,* while the other needle collects them, obviously called the *collector.* Bell Labs colleague John Pierce suggested the name, where the prefix *trans* indicates the carrier transfer from one needle to the other.

Hardly Any Competitors

Bell Labs faced little competition in their semiconductor research. Universities could match neither the orchestrated teamwork by physicists, chemists, crystal growers, engineers nor the financial resources. Traditional US electrical companies, such as General Electric and Westinghouse, however, also got involved. Hopes to replace tubes in radios and in those fancy new computing machines or for improved telecommunication were not so much the driving forces for their research engagements. In the earlies fifties, it was more a straightforward continuation of their striving for better rectifiers for high-power applications. The wartime experiences, on silicon in particular, promised stable and temperature-tolerant large-area rectifier diodes to become achievable and to replace selenium and those unwieldy mercury-vapor rectifier vessels.

European efforts right after the war were scarce. Hardly anything happened in France; Britain and Holland started work only later. Strangely, it was war-devastated Germany, where many radar-experienced people remained and quickly returned to peaceful work (36, 37). Silicon was not put on the list of research forbidden in Germany by the US military government (OMGUS); Si was apparently not considered to be as significant as was, for example, magnesium – a strategic

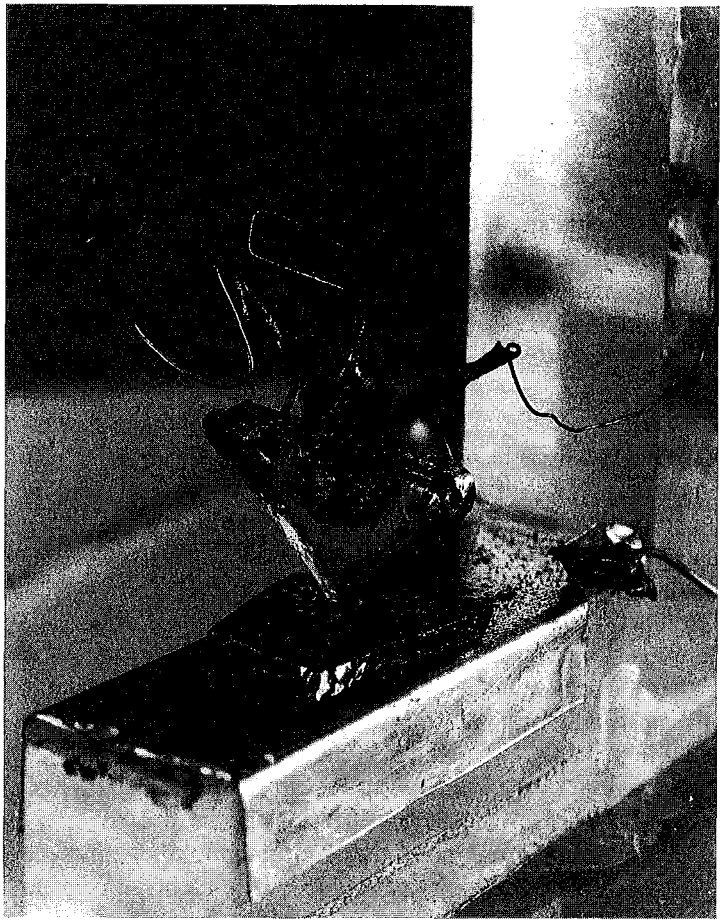


Figure 3
The early germanium point-contact transistor, demonstrated in the December of 1947 at Bell Laboratories, Murray Hill, New Jersey

aircraft metal. The wartime research on silicon and other semiconductors, however, was summarized in several of the so-called FIAT reports (36) for the Allies. The great advantages of the German electrical and chemical industries in synthesizing ultrapure silicon were effectively utilized, such as for basic patents of the *Siemens Process* (38). The Siemens-Schuckertwerke, being the high-power division of Siemens, had massive interests in getting better rectifiers for high currents and large voltages. The Siemens und Halske division, responsible for low-power

applications, such as telephony and radio, actually started a germanium device line in Berlin as early as 1945!
An old castle in Northern Bavaria, at Pretzfeld, served as home for silicon research by Eberhard Spenke and Walter Schottky (39), whose office was in a converted horse stable. The so-called *C-Prozeß* was finally victorious; here $SiHCl_3$ is dissociated near an inductively heated Si rod in a hydrogen atmosphere. This process became the world-wide standard and provided pretty license money for Siemens (38). Heinrich Welker, who had filed a field-effect device patent during the last week of the war, went to Siemens in Erlangen, where he later discovered the $A^{III}B^{V}$ – compound semiconductors, such as gallium arsenide (40). Serious Japanese semiconductor efforts, so charmingly related by Makoto Kikuchi (41), started in the fifties and then accelerated tremendously in the sixties.

Hardly a Device Breakthrough

Sad disappointments emerged after the glorious Christmas days of 1947. Bell's press conference for the transistor provoked no excitement, hardly any attention (4). Vacuum tubes continued unassailed. The wobbly dual-needled polycrystalline germanium transistor was essentially neglected. Neither industry nor the military dared to shift to these unreliable devices (2). New inventions do take longer times to succeed than usually anticipated by proud researchers. This sober realization also held for the transistor, although it initially seemed such an advantageous replacement for vacuum tubes (which reacted with sharply lowering prices).
Most people at Bell Labs, of course, were fully aware that the preset goal had *not* been achieved. The device of 1947 was certainly not the convincingly simple field-effect-transistor at all. The point-contacts were clumsy, makeshift arrangements. Shockley was particularly dissatisfied (35, 6) with the entire course of events, also deeply hurt in his typical, zealous pride, that his collaborators Bardeen and Brattain had achieved this ouright deviatory invention and were the two authors for the scientific paper (42). In addition, the Bell System had to yield to a *patent consent decree* (2); the monopoly of the telephone network was kept with the consent that the transistor knowledge and the patent treasures be made widely available to all those interested in learning and using the new technology. This judgment proved to be most favorable for the development of modern microelectronics. The pride of the inventing team at Bell Labs, however, was certainly diminished.
What was actually demonstrated 50 years ago? Semiconductor materials were proven controllable and useful to amplify current! *Minority carrier injection* was experimentally verified, if only with those little aiguille contacts. Nonequilibrium

excess holes in electron-rich, n-type, germanium were proven to be achievable by external contacts. Bardeen had painstakingly elucidated that the adversity of the *surface* endangered transistor action. Most unexpected and truly promising was the observation that minority carriers had such astoundingly *long lifetimes*, before they recombined (43) at the surface or inside the defect-ridden material. The convincing beauty of the Haynes-Shockley experiment demonstrated this asset (44). Semiconductors now earned their important distinction to be materials, where non-equilibria could be achieved and maintained over substantial times and therefore also through substantial geometrical separations. Similar effects can never happen in metals, where the sea of the many electrons immediately reestablishes equilibria. The measurable minority carrier lifetime now ruled as the essential, merciless yardstick for crystal quality. This quantitative figure of merit eventually forced everybody to appreciate the need for high-quality single crystals as the only acceptable device material. Shockley and most of his colleagues initially argued vociferously for a polycrystalline technology; single crystals would be too expensive to be accepted by the production-line colleagues. Later they all agreed with their opposition, with Gordon Teal being the main spokesman (45). The stage was set for materials research, supplying excellent crystal quality, maintaining purity, enabling defect control.

Respectability Achieved

Those irreproducible mavericks of semiconductors had now been elevated to respectable objects of physics, finally, after centuries of cinderella humiliation. The idiosyncracy against foreign admixtures had been converted into a viable, predictable doping technology. When Shockley's suggestion of carrier injection by a *p-n* junction – instead of a point contact – succeeded in practice, junctions could be quantitatively described without any artificial fitting parameters (20), linking current I to applied voltage V by

$$I = I_0 (\exp \langle qV/kT \rangle - 1), [1]$$

this *ideal rectifier equation* was strictly obeyed by junctions in germanium. A rapidly rising forward current with positive values for V contrasts with an essentially constant reverse current for negative V. Thermally activated transmission over a potential barrier was proven with the dependence on temperature T. The prefactor I_0 was shown to be calculable with the input of carrier parameters, such as densities and lifetimes.

The glory of this early transistor-related research hence resided not in the device itself, which failed to quickly expel the tubes from their sockets; it was rather the success in materials understanding by the *scientific approach to a practical prob-*

lem, a gospel incessantly preached by Shockley to his teams of collaborators. The recalcitrant, unpredictable semiconductors were proven to be reproducible and domesticable materials, in spite of the actually disappointing first device realization!

Germanium versus Silicon

The teams at Bell Laboratories were devoted to germanium and silicon, since both elements had been proven useful in the radar development. It was soon clear that silicon would present some major advantages. In particular, the intrinsic density n_i, given by

$$n_i = (N_c N_v)^{1/2} \exp(-E_g/2kT), [2]$$

where N_c and N_v are effective densities of state in conduction- and valence-band. The exponential dependence on the energy gap E_g indicated quite drastically that the much smaller gap E_g (Ge) = 0.66 eV would cause problems. Even at merely slightly enhanced temperatures, the intrinsic density rapidly rises and overwhelms any doping-induced, deliberately determined carrier density. The semiconductor then is out of control and just thermally dominated. Silicon, with E_g (Si) = 1.12 eV is a better choice for stable operation. Yet, germanium was chosen for the first transistor, and for good reasons. With its melting point at 937 °C, Ge is so much easier to be prepared than Si with T_m = 1.415 °C. Silicon binds chemically so strongly to oxygen that its elemental synthesis is difficult. Germanium also has valuable properties, which were significant in the birthday on December 23, 1947: a markedly higher electron mobility μ_e(Ge) = 3.900 cm^2/Vs than that of silicon, being only μ_e(Si) = 1500 cm^2/Vs. With the Einstein relation

$$D = \mu\,(kT / q), [3]$$

linking diffusion coefficient D to drift mobility μ, germanium evidently provided a much better chance for an injected carrier to penetrate deeply into the bulk, to reach a collector and thus enable transistor action.

Germanium had such nice, convenient properties, that the production engineers loved this material. Highly automated lines, such as the one at Philco Corp., where the young Robert Noyce did his apprentice years (46), or the European production lines, like those of Siemens in Munich, used alloying and clever etching techniques for profitable mass production. No wonder that by 1965 – when Fairchild, TI, and others had already been offering silicon transistors for some time (47) – germanium devices with 334 million units annual sales still outsold silicon transistors with only 275 million pieces (2). Germanium devices populated hearing aids, pacemakers, and radios; they also gradually invaded the computer markets with diodes and transistor logic (3).

Enticing Silicon Anomalies

The competition among the group-IV elements shifted only slowly toward the more temperature-resilient Si (2). Bell Labs continued basic studies as well as device development; so did, for example, General Electric, where William Dash was a successful crystal grower (48); he used a "*neck*" to drive dislocations out of the seed to achieve dislocation-free Si. The new ventures in the Western USA, especially at Texas Instruments (45), devoted more attention to silicon, in part as a reaction to military demands for sturdier transistors.

A quirkish anomaly of silicon initiated its colonization in Mountain View and Palo Alto of Santa Clara County in Northern California. Shockley stated that he had seen his "*name often enough in Physical Review, now was the time for the Wall Street Journal!*" (49). Mervin Kelly's old guideline was not forgotten: create a simple, cheap solid-state telephone switch! Silicon with its decidedly non-ideal current *versus* voltage relation could be advantageously utilized to create such switches. The deviations in Si from Eq. [1] are

$$I_0 \rightarrow I_0' \text{ and } \exp(qV/kT) \rightarrow \exp(qV/n\,kT). \quad [4]$$

The currents described by Eq. [4] greatly exceed those of the ideal rectifier because carrier recombination and generation provide efficient competitive paths against pure thermal activation. The slope of log I against applied forward voltage V is sharply reduced by the factor n in the exponential, again because of the extra current paths via recombination of electrons and holes at centers within the junction's space charge layer. These effects are particularly pronounced for low applied voltages; at higher bias, thermal activation dominates. The parameter n approaches 2 asymptotically. (This parameter, unfortunately, carries a misnomer: *ideality factor*, although the higher n, the less ideal the junction.)

These deviations from ideal junction behavior make many features a function of junction current, such as for transistor current gain $\alpha(I)$. This fact produces a pronounced bistability in a four-layer *p-n-p-n* two-terminal diode (50). The detailed story of Shockley's hope in a now defunct device is presented in a symposium by Kurt Hubner, who contributed much development work to this four-layer-diode in Shockley's little company (50). Shockley had left Bell Laboratories, spent some time as a government consultant on weapons systems evaluation first and at that time published a controversial, irritating study on the statistical distributions of human creativity (51). Then, he received the support of his school-mate Arnold O. Beckman (6) in setting up his own little silicon-oriented company in an old apricot storage barn on 391 South San Antonio Road in Mountain View (52), as seen in Figure 4 – plus some facilities for production in the so-called *Spinco-Building* of the Beckman Instruments Corporation in Palo Alto (6, 50). Silicon had established its foothold in California!

Figure 4
The laboratories of the Shockley Transistor Corporation, located on 391 South San Antonio Road in Mountain View, California – a former fruit storage barn, see Ref. (52)

The risky venture with the bistable diode floundered (4–6, 50). Silicon had now been advanced sufficiently to be applied to traditional silicon mesa transistors. This alternative was suggested by Shockley's hand-picked elite crew – but Shockley rejected this rebellious plan. Bob Noyce, Gordon Moore, Jay Last, Vic Grinich, Murray Siegel, Sheldon Roberts, Jean Hoerni, and Eugene Kleiner, condemned by Shockley as the *Traitorous Eight* seceded and formed Fairchild Semiconductors with help of financier Hayden Stone. This fateful rebellion of 1957 (4, 6), often repeated as division and multiplication, stimulated growth of *Silicon Valley*. The Fairchild team contributed tremendously to silicon technology: planarization and use of silicon's greatest asset: its stable, strong oxide – a story retold by Bruce Deal (47) – finally the integration and connections of so many functions in the crystal interior, as related by Jack Kilby (53).

Stubborn Continuation: Materials Research

Strategy of Fundamental Studies on Silicon

Shockley did not capitulate, in spite of a serious breakdown after the secession (6). The four-layer switch remained the goal, and intensive materials research had to show the way. He hired a number of new scientists, many of them from Europe, who were not exactly "*slaves*" to master Shockley (54), but less experienced with ventures in the USA, hence less likely to secede. I was one of them, joined in 1959 with the task to look at defects in silicon. Thin layers were a definite goal, which appeared endangered by dislocations causing short circuits to diffusions as well as to carrier currents. Point defects had to be understood and prevented, since they exercised strong control of junction currents. Surfaces had to be clean and protected. Shockley's sales of four-layer-diodes could not support extensive basic and applied research. However, the *sputnik shock* had come, and money was suddenly available from government agencies to catch up with Soviet space technology. Shockley applied for these grants and was quite easily successful. Fairchild, on the other hand, did not rely on such outside money; proprietary techniques were sought with internal financing and with handsome profits from selling the first planar Si transistors to the military customers (47).

Solar Cells with Silicon

The solar cell, a large-area Si device, was invented at Bell Labs by D. M. Chapin, Calvin Fuller, and Gerald Pearson (55), but found little use in the Bell System (trials for battery replacement at Americus, Georgia (56) failed because of coverage by opaque pigeon excrements!) nor by the US Armed Forces, who saw no interest in this feeble power-supply. The cold-war archenemy Soviet Union, however, paid serious attention. The US situation was altered after the launching of *Sputnik* on October 4, 1957 with its *p on n*-Si solar cell, which Soviet scientists had made after the Bell recipes (57). Air Force (at Dayton, OH) and Army (at Ft. Monmouth, NJ) were particularly active in solar cell work and as contract sources. I worked for both these agencies in my initial projects at Shockley's little barn in Mountain View. Shockley's interest was not in a new, additional product; he took the money (less than 50.000 $, imagine!) to enhance silicon methodology. Many space-experts deemed semiconductor solar cells inferior sources; a compact, low-weight nuclear reactor seemed the candidate to beat for unmanned missions (58).

Large-area Si sheets, to be pulled (like glass) from a Si/Pb melt, were proposed by Shockley (59). Such sheets ought to support many cells, connected in series

for enhanced output voltage. In anticipation, we made a multicell from a very thin, 60 µm piece of silicon. Masking with sprayed-on black wax and with Kodak photoresist provided for double-diffused structures, as shown in Figure 5. I struggled days and nights, succeeded in getting half a dozen devices, which actually delivered up to six volts output through the series connections of *p-n* junctions (60). I gave a report in Palo Alto at Rickey's Hotel on El Camino Real (a small room sufficed) in a local IRE chapter semiconductor meeting (61). Bob Noyce came just for my talk, asked no questions and left. I was surprised to have this silent auditor from Fairchild. Now it seems more understandable, in view of the ideas and the patents on integrated circuit ideas at that time (62). We had achieved a somewhat bizarre, but certainly a working *integrated circuit*! We should have published it, applied for some sort of patent claims. But at that time, Shockley and his people had other worries; we were just being sold off from Beckman to Clevite Corporation (63), barely surviving. The tournament of patents was ceded to Noyce and Kilby (62).
My second project was more theoretical. The limiting efficiency for solar cells was not clarified. Only empirical estimates existed, hence it was also not firmly established which was the optimal material for solar energy conversion – as determined by the band gap energy for best matching to the solar spectrum. Silicon was con-

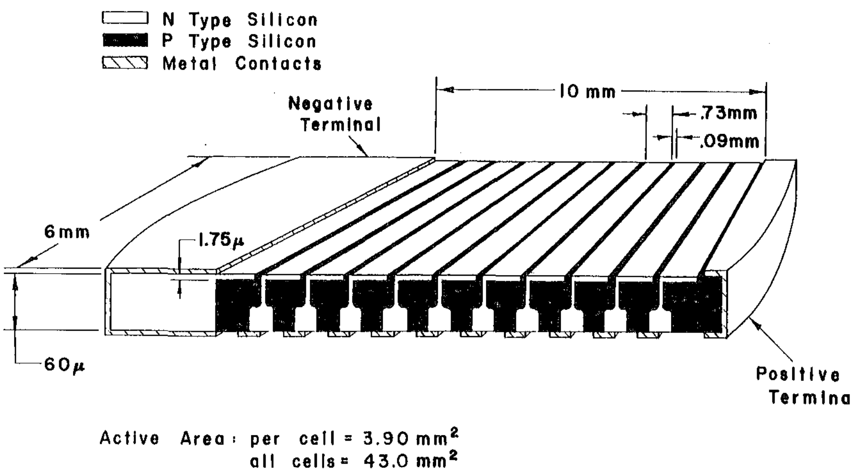


Figure 5
Multicell Solar Battery, produced at the Shockley Transistor Corp. in 1960, see Ref. (60)

venient; yet others, especially the very active group at RCA (64) and the Clevite people in Cleveland (65), favored higher gaps E_g, as in $A^{III}B^{V}$ or $A^{II}B^{VI}$ compounds. We proposed a thermodynamic theory, based on the idea that an ideal material would be one having only radiative recombination as required by the principle of detailed balance. Our paper was eventually accepted (66) after struggles with the referees, it now seems to have been recognized and has been reprinted several times (8). Silicon came out very close to the optimum (67).

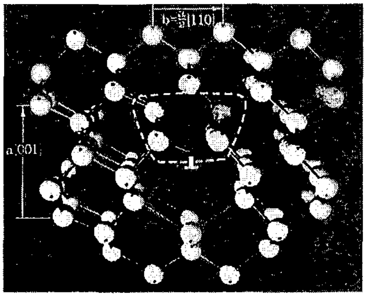
Dislocation Fears and Follies

I was supposed to work on defects, a topic related to my thesis at Göttingen. Dislocations were extremely worrisome then. These line defects were thought to consist of a series of dangling bonds, which were hypothesized to be acceptor states. A *p*-type short circuit would thus traverse a narrow base from emitter to collector; horrible threat for high-frequency devices! My studies on junctions with and without dislocations gave relief (68). Dislocations by themselves were not necessarily harmful. Impurities, especially heavy metals, however, tend to precipitate out around dislocations – and those precipitates badly deteriorate junctions (69). Oxygen also precipitates at dislocations of a grain boundary and may actually invert the polarity of a photovoltage originating at the junction (70). Metals and oxygen in Si had thus to be monitored and to be kept under tight control, just as the donors and acceptors had to be controlled.

Diffusion, nowadays recognized as a decisive step forward from simple alloying of dopants, was a vivid topic already in the late fifties. Again, dislocations gave worries, since they might provide a path for more rapid diffusion and junction advancement than in the undislocated bulk. We made arrays of dislocations by growing bi-crystals out of the melt and then studied junction profiles (71). Indeed, as seen in Figure 6, sharp spikes are observed; dopants diffuse much more rapidly near grain boundaries! Figure 6 is really a job offer advertisement, published in a series in *Physics Today*. Shockley tried to lure researchers with examples of this scientific, yet applicable work towards Mountain View.

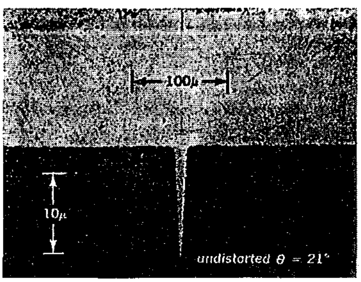
Multiple diffusions of donors and acceptors near grain boundaries gave me some rather fancy structures, some with very narrow-looking base layers. They failed as good transistors with high cutoff frequencies, the junctions were soft and not under sufficient control (68). There was a motive behind our work. Shockley had filed a patent in which he claimed that a material with a "non-zero Burgers vector" ought to be useful for high frequency transistors. A cylinder of, say, *p*-type doping would constitute the smallest possible base region. The dislocation should help to make functional structures of atomic dimensions – a dream eventually realized in

DIFFUSION DOWN DISLOCATIONS

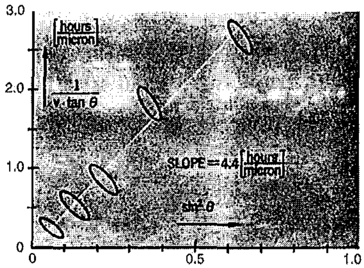


What is the core of a dislocation in silicon like? Does it have unpaired electrons in dangling bonds, or do the electrons pair up as in the model we constructed to illustrate Hornstra's[1] theory? Impurities diffuse down dislocations faster than through the bulk. Is the cause an extra concentration near the dislocation-core of impurities or vacancies or both? Are dislocations good or bad for semiconductor device development? Can they be used as guides for diffusion to produce new and useful structures?

We are trying to get answers to these questions by studying diffusion down small-angle grain boundaries in silicon composed of spaced edge dislocations. We have found a simpler way[2] of measuring the constants describing diffusion on the boundary by making p-n junctions through phosphorus diffusion into p-type silicon. The p-n junction is a phosphorus isoconcentration line that can be revealed by staining. The velocity v and the angle θ of the advancing spike are measured and the accompanying graph is made. The value of the slope of the straight line can be combined with Cottrell's theory[3] of atmospheres around dislocations to reach the conclusion that most of the grain boundary diffusion current flows down the enclosed two atomic columns of maximum compression, the diffusion current density being 400,000 larger there than in the bulk.



We expect to achieve bigger current concentrations by using atoms like gallium or bismuth which have larger misfit factors in silicon than phosphorus has. We also expect to make transistors of various sorts using diffusion structures built on grain boundaries.



If increasing the fund of knowledge of atomic phenomena in silicon and at the same time helping get new devices to our customers challenges you, please let us know. We hope you have worked on semiconductors, but more important is your ability, general level of experience, and attitude.

For employment opportunities where this grain boundary work is being done, address your inquiries to:

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CLEVITE CORPORATION

1. J. Hornstra, J. Phys. Chem. Solids 5, 132 (1958).
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H. Queisser, K. Hubner and W. Shockley (to be submitted to Phys. Rev.).
3. A. H. Cottrell, *Dislocations and Plastic Flow in Crystals*, (Clarendon, Oxford, 1953), p. 56.

(Publications of reference 2 describe results obtained under contract with the Air Force Cambridge Research Laboratory.)

Figure 6
Job offer advertisement: Spike of a diffusion performed in a silicon bicrystal, see Ref. (71)

the nineties with quantum wires. Technology in the sixties was much too crude, but we tried.

I wanted to do some surface etching of my bicrystals and asked my colleagues in the Shockley barn under what conditions such etching arose. Heavy boron diffusions seem to do so, was the answer. I looked into it, indeed there appeared strange crosshatch patterns, which followed crystallographic directions, as I clearly saw through the difference of orientations in the two grains. I soon found that those heavy doses of undersized B acceptor atoms inside the Si lattice created so much strain that slip arose: dislocations moved into the lattice to relieve the mechanical strain. People did not believe this idea at first; again we fought with referees and eventually my paper was accepted (72). The real proof for dislocations came through a nice transcontinental cooperation with Gunter Schwuttke, then at General Telephone Corp. in Bayside, NY, expert in defect identification through X-ray diffraction topography (73); for reviews, see also Refs. (68, 74).

Punctilio in Point Defects

Foreign atoms are difficult to avoid in silicon devices, especially after oxidation and diffusion treatments became essentials in processing. The hot furnaces would inevitably contaminate the crystal, however purely it might have been grown. Silicon junctions, with their no longer neglectable junction space charge layers, are sensitively affected by even very small amounts of such impurities with their deep electronic levels, which facilitate carrier generation and recombination. The first outstanding scientific publication out of early Silicon Valley explained the irregular features of silicon junction, see Eq. [4]. The non-ideal junctions were quantitavely explained by Sah, Noyce, and Shockley (72). A few days after this paper had appeared in print, Robert Noyce and his colleagues left the luckless Shockley company and started with Fairchild (4, 76). C.-T. Sah still stayed for a little while in the old barn on San Antonio Road.

Combat had to be declared to the metallic contaminations. How had the vacuum tube producers cleaned their active volumes? By "gettering" the residual gases! Fortunately, similar recipes work inside the silicon crystal. Impurities bind strongly to dislocations, to precipitated oxygen, to surface damage, to glassy phases near the surface. Gettering was studied judiciouly by Adolf Goetzberger and proven useful in hardening "soft" junctions, meaning that very low reverse currents and sharp avalanche breakdowns could be obtained by confining the metals to regions outside the active crystal portions (77). The forward characteristics are similarly affected (78). Figure 7 shows a drawing, again taken from a job offer advertisement in *Physics Today*, with the proof of excess currents flowing through the

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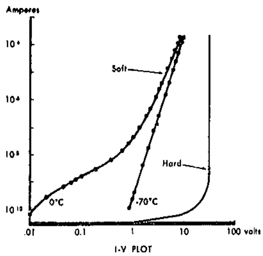
Basic or Applied?



Why did our p-n junctions sometimes come out "soft"? This was a practical question. But it also interfered with research on avalanche breakdown processes and on studies of thin diffused layers. The quantitative form of the current voltage characteristics suggested tunnelling or Zener currents rather than secondary ionization or avalanche. What could produce the necessary high field? Perhaps metal precipitates like those Dash observed on dislocations.[1] This hypothesis was confirmed by deliberately introducing metals. Furthermore, the "soft" current of the I-V plot flows only in a small region of the mesa diode, as shown by probing.[2]

Once it was known that metal precipitates cause the soft current, ways were found to get rid of them[3].

This is an example of the type of research we are trying to do more of. It is both basic and applied.

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(Publications 2 and 3 describe research on contract with the Air Force Cambridge Research Center.)

So are the activities of our research and development leaders. Most of them split their time between publishable research and new device development.

If increasing the fund of knowledge of atomic phenomena in silicon and at the same time helping get new devices to our customers challenges you, please let us know. We hope you have worked on semiconductors, but more important is your ability, general level of experience, and attitude.

By the way, we are not through with the metal precipitates. How big are they? What is their shape? Are they wholly in the space charge layer or do they stick in from one side? Can we control them and use them? Do they reduce the efficiency of solar cells? We could use more scientific manpower on these problems.

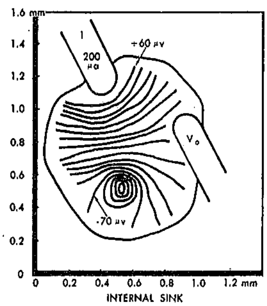

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Figure 7
Job offer advertisement: the physics of "soft" junctions

precipitates. Gettering with its scientific foundations has remained an important and active field of current research. Of utmost significance is the gettering via oxygen precipitates, which creates a denuded, clean zone near the wafer surface for housing the elements of dynamic random-access memories. Present technologies still heavily rely on this somewhat embarrasing, yet pragmatically successful processing trick.

Errors in Epitaxy

Much useful knowledge still flowed from the big East Coast laboratories, especially from Murray Hill and Allentown, toward Silicon Valley. Shockley had some licensing and know-how arrangement with Bell Labs, he and his staff went there for regular snooping and enlightenment. Much quantitative information was acquired, such as solubilities and energy levels of dopants, diffusion coefficients and dopant profiles, mobilities as functions of doping levels, measurement methods. Of special importance to us were crystal growth techniques, epitaxy above all, first reported for a device by Henry Theuerer and his colleagues (79). Myself being the materials person in the now much more presentable Shockley Labs on Page Mill Road in the Stanford Industrial Park, I had set up the equipment to grow epitaxial layers for the power transistors, now explicitly expected from us by our Clevite mother organizations in Waltham, Mass. and Freiburg, Germany.

Epitaxy brought new defects, new problems. The interface was difficult to control, the materials quality initially quite poor. Desperation led Richard Finch and myself to invert the process, making heavily doped layers for the collector portion and then mechanically polishing the lowly doped substrate down to a few microns thickness (80). This "inverse epitaxy" is quite similar in spirit to today's wafer bonding technique; our unwieldy makeshift method overcame a serious bottleneck until epitaxy became better controlled.

New, beautiful-looking triangular defects cropped up in epitaxy on (111) – surfaces. They grew in size with increasing layer thickness. By that time, I had learnt enough about defects in solids to identify these tetrahedral defects as stacking faults (81). Special dislocations, some even bearing the name of the boss as "Shockley partials", mark the intersections of the (111) planes. We found with electrical measurements and with direct visual microscopic observations of soft-glowing microplasma breakdown (82) that the faults themselves were harmless, just as I had previously seen on coherent grain boundaries in Si (83), but precipitates of metals at these "stair-rod" partial dislocations were – once again – culprits for damaging the *p–n* junctions.

Everyboy, myself included, constantly searched for new methods to identify and characterize defects in Si. Ours was a small lab with limited budgets for equipment. We used an old loudspeaker to construct a pretty Kelvin probe for studying ion motion above junctions (84). I liked electron microscopes, since I had been a technician (4) with Ernst Ruska in Berlin, inventor of this microscope and later a Nobel laureate. I realized we could never buy our own, but also knew that experts at UC Berkeley had some Siemens microscopes, so I went there with 15 neatly etch-thinned Si samples and begged Jack Washburn and Gareth Thomas to inspect them. Nothing to be seen, silicon is just so much more perfect than the metals – people had already warned me. But sample number 13 graciously presented us the beautiful triangle of a stacking fault – actually the first high-resolution image of any defect in Si, suggesting us a model to explain fault growth as initiated by surface oxide (85). Figure 8 gives an example. We also investigated my favorite foes, those diffusion-induced slip dislocations (86). Electron microscopy is today a routine tool, indispensable to check crystal integrity; thus it pleases me a little to remember these still crude, but very first observations in our Cal-Stanford collaboration (87).

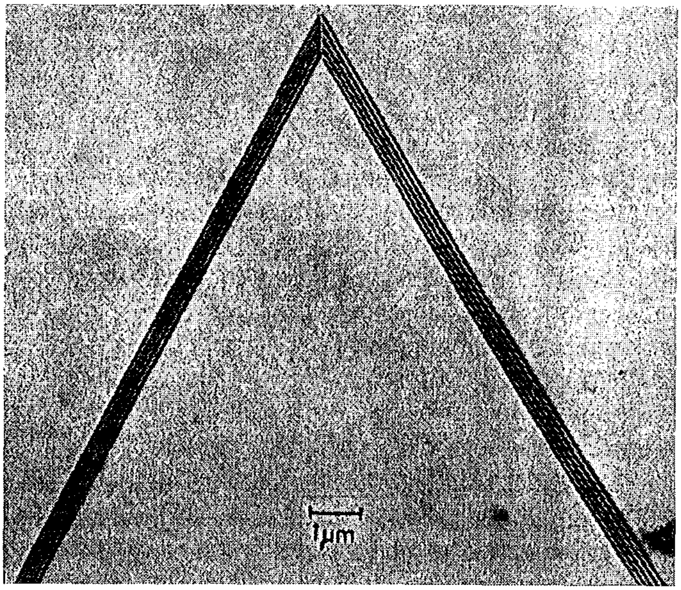

Figure 8
Early transmission electron microscrope view of an oxidation – induced stacking fault, compare Refs. (85, 86)

Finale

Understandably grateful I am to have had a chance to participate in this awe-inspiring development of silicon microelectronics. Had anybody offered me a bet that one day we would have millions of transistors, yes: field-effect transistors, in circuits, fabricated with yields close to 100 per cent, I would have laughed unbelievingly. But Shockley always admonished us, as he had done to our predecessors then at Fairchild, not to be too discouraged by the grim reality of daily lab disappointments. He insisted that ideas can be realized by proper engineering unless physics principles – such a thermodynamics or quantum theory – are violated. If economic incentives suffice, things can eventually be miniaturized within silicon.
At an American Physical Society meeting in Pasadena, around Christmas 1959, Shockley introduced me to a former outstanding student of his, Richard Feynman, who encouraged us with his charming after-dinner speech under the now famous motto "*There is Plenty of Room at the Bottom!*". Indeed, semiconductor crystals do provide plenty of room for electronic functions, ever more miniaturized (88).
Materials research was – and still is – probably the most essential part of the finally successful story of microelectronics. The materials resisted so often the seemingly straightforward device concepts. Martin Lepselter's perpetual dictum over the lunch tables in the Murray Hill and Allentown cafeterias still rings in my ears: "*The materials people's concern is materials, but the device people's concern is ... materials*!" The retrospective of 50 years of transistors lends some credence to this axiom. The *silicon age* differs from the stone age, the bronze age, the iron age. For us it was a strict, relentness scientific approach, not busy empirical attempts, which paved our way. Shockley demanded "*scientific aspects for practical problems*", but sometimes obviously and tragically neglected economic reality. Frederick Seitz honors his tragic role in calling him the "*Moses of Silicon Valley*", showing the way to a promised land but not reaching it himself.
Modern semiconductor technology and business were achieved by great armies of researchers and engineers, and also financiers, who followed the mere handful of pioneers fifty years ago. Maturing technologies always become anonymous affairs, while the early forefathers are personally basking in glory. This natural course of events should not be construed as unfair; we all belong to a family of scientists working for a remarkable, a useful and peaceful, a demanding and rewarding cause. This quest will continue, maybe as lively for the next fifty years as in the previous half century.

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