2 Silicon: the Semiconductor Material

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2.1 Introduction

Fifty years of silicon for semiconductor device applications is the milestone at which this series of articles has been written, which will present the many-faceted development of all the technologies that are connected with it, their present status, and recognizable future trends. The individual articles will cover topics such as:

- growth of single crystals and its reproducibility in industrial applications
- polycrystalline and amorphous silicon
- epitaxial technologies and thin films
- crystal defects, impurities, and doping
- various processes for micro- and nano-structuring
- materials requirements from the vantage point of the users in the fields of microelectronics, power electronics, optoelectronics, and micromechanics
- interfaces to other materials such as III–V compounds, as well as the whole area of bioelectronics.

Since this series is about silicon it is taken as self-evident that all these contributions will emphasize the material aspects.

This undertaking is justified and useful because silicon has, like no other material, dramatically changed our world. Especially, the whole of information and communication technology would have developed completely differently without the availability of silicon. Thus, we can with all justification talk of a silicon era, just like one talks of a stone, copper, bronze, or iron age, where a specific material that predominantly characterized the advancements made during that time was chosen for the name of that era. Even more than with iron and steel, we have to deal here with a multitude of individual technological advances which ultimately made the material as we know it today. The variety of the topics mentioned above attests to this. Last but not least, it has to be mentioned that silicon, because of the intense technological interest in it, belongs to the small group of solids that have been exhaustively studied and where, during its study, significant contributions to materials science have been made.

We were invited to write an introductory paper to this series of articles because we belong to those few people that have lived through this development from its very first beginnings – originally as technical–scientific researchers and later in responsible managerial positions. One of us (WH) was at Siemens, initially involved in the materials research and subsequently in device application. The other (KZ) was at RCA Laboratories in Princeton, NJ, USA, where he devoted his research efforts solely to silicon device technology. We have the indisputable advantage of a personal understanding of the various problems and an involvement in the sometimes dramatic happenings. On the other hand, there exists also the danger of a one-sided opinion. We believe that the advantage outweighs the disadvantage and that we can be rather objective; and so we have accepted this task.

In our discussion we want to show that silicon – during all of its developmental stages – in no way ever looked clearly to be the obvious solution to the various problems as we so easily see it in retrospect today. On the contrary, silicon's march forward was often an adventurous path that had many individual successes, but also erroneous paths and fallacious assessments, as is common in all research- and development activities.

The silicon semiconductor technology formed the basis for the development of the information society, a society which is characterized by the mental achievements of humankind. This partially virtual world – broken down into bits or built up from them – seems sometimes only a product of the human brain, a world made by humans. But still, where would this world be without silicon?

Silicon does not appear as a free element in nature, because of its high chemical affinity, especially for oxygen. It can only be produced by chemical reduction. Is it then also a product of man's creativity, custom tailored for his purpose? Or is it – with its special properties – still nothing else but a wonderful present of nature?

2.2 Early History

When, in this contribution to *Silicon*, we talk about making silicon available for semiconductor applications, it is not just for history's sake. No, we also want the readers to understand how this development was possible, what parts were targeted goals, and what was simply serendipitous discovery? Here we immediately come to the age-old question of humanity: Can man create his own world – as often described or shown in some science fiction of our time – or is he still just embedded in this nature and creation that was given to us as a present?

Despite some fundamental work carried out in the 1920s and 1930s on the band structure, and theoretical attempts concerning rectifier effects and several patents concerning the unipolar transistor in that period, the real semiconductor era began only with the proof of the bipolar transistor effect in germanium by Bardeen and Brattain at the end of 1947 [1]. On the basis of the rapidly increasing industrial interest, the procedures for crystal growth, purification, and doping – still important even today – were then developed in the 1940s and 1950s, but initially just for germanium.

At the same time, an increased interest in other semiconductor materials appeared. Were there perhaps materials other than germanium that would be even more suitable for specific applications? This question could only be answered by first understanding the transistor effect. The extremely high carrier mobilities in germanium, about 10^3 higher than those of oxide semiconductors, were fascinating here. Achieving even higher mobilities was then one of the goals of the pioneering work in the field of III–V compounds by Heinrich Welker and his research team at the beginning of the 1950s [2].

Research on silicon began at about the same time, but rather in the background. Sensational discoveries and/or advances were hardly expected unless one considered the proof of the semiconducting character of silicon – still in doubt in the 1940s – as such. The metallic shine and relatively high conductivity of the (highly impure) samples, similar to that in the so-called hard metals, led to this erroneous conclusion. For example, in the 1953 edition of Linus Pauling's book *General Chemistry* [3], silicon is still called a semimetal. On the other hand, Pearson and Bardeen [4] had discovered in 1949 the high-temperature transition to intrinsic conduction and, thus, presented the proof of the semiconducting character of silicon. The samples used were, however, not single-crystal, so that the conductivity below this transition did not show the typical temperature dependence of extrinsic semiconductor conductivity. This caused some irritation amongst the various researchers [5, 6].

The experiments of Pearson and Bardeen showed that the bandgap was 1.12 eV. The carrier mobility could also be determined at the beginning of the 1950s by use of Hall and drift measurements. With a value of $1200\,\mathrm{cm^2/V\,s}$ for electrons and $300\,\mathrm{cm^2/V\,s}$ for holes, it was about a factor of three lower than that of germanium. All this did not seem to be very exciting, and thus, there were only a few researchers who devoted themselves to silicon and its crystal growth.

Because of the increasing importance of microwaves in the mid-1940s various semiconductor detectors, based partially polycrystalline silicon, were used in microwave applications to replace microwave tubes because of their small dimensions and high cut-off frequencies. So even at that time, silicon was making inroads into communication technology. This was also where the newly discovered transistor was of special interest, because a higher carrier mobility is a definite advantage for achieving higher cut-off frequencies. So, a theoretical comparison – since the transistor effect in silicon was not yet experimentally proven at that time – clearly indicated the advantage of germanium for use in communication technology, and the limit on the thermal stress of 80°C, caused by the bandgap of only 0.7 eV, was considered acceptable. Only in cases of elevated heat production were these limitations serious, but it was hoped that they could be overcome by use of other semiconductors such as the III–V compounds already mentioned or by silicon. The high degree of adaptability, the high carrier mobility (in GaAs, for example), and a lower melting point favorable for processing, were all strong arguments for the III–V compounds. In silicon, on the other hand, one had to deal only with one kind of atom, which eliminates various kinds of lattice defects and guarantees a good lattice thermal conductivity.

So much for the theoretical considerations. In the reality of the technological world of the early 1950s one was far away from a general use of silicon as a semiconductor material. As already mentioned, because of silicon's high chemical aggressiveness at the elevated temperatures required for its preparation, all silicon samples were highly impure. Their level of purity was, as Pearson and Bardeen's samples showed, in the range of several ppm. Despite this, research groups, especially that of G.K. Teal at Bell Laboratories, were not discouraged. Teal devoted himself, in addition to his main task of germanium, to silicon crystal growth until he went to Texas Instruments in 1952. But even there he built up a silicon research team which had the goal of developing power transistors. The move to TI required time, and that significantly reduced the original advantage he had over possible competitors.

2.3 Competition and Cooperation in the Silicon Race

At the beginning of the 1950s, but at first entirely in a clandestine mode, another competitor came onto the scene: the Siemens Group, of which WH was a member. Despite entering late, Siemens definitely wanted to compete in the important, newly blossoming area of semiconductor physics and technology, having already its own manufacturing facility for selenium rectifiers, located in its power group; there was also a production facility for transistors, using its own experience base in high-frequency rectifiers and following Bell Laboratories as far as germanium was concerned. With regard to additional research, it had one of the best-known semiconductor pioneers, Walter Schottky, within its own ranks. For new semiconductors, Heinrich Welker, with his pioneering ideas and experience in III–V semiconductors, was appointed as department head for the new research laboratories of Siemens-Schuckert.

In this technological environment, the materials research laboratory of Siemens and Halske also entered the semiconductor area, and started in 1951 to work mainly on trial-and-error experiments on silicides such as Mg_2Si. The purification of silicon was included as a prerequisite in these fundamental studies. To achieve this, two approaches were pursued: on the one hand the classical metallurgical preparation of pure silicon powder via magnesium or zinc reduction of pure quartz (the so-called B-process), and on the other hand the reduction of $SiHCl_3$ by hydrogen in an electrical discharge according to the method of van Arkel. This second approach was carried out in collaboration with Wiberg and Amberger of the University of Munich and was called the A-process.

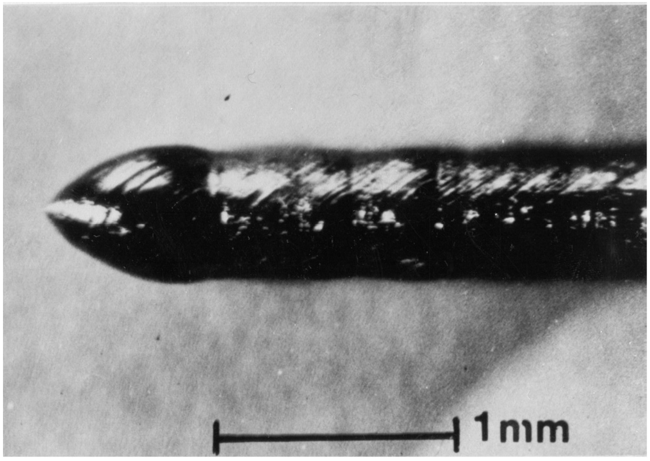

Fig. 2.1. First "high-purity" silicon rod from Siemens grown by the so-called A-process in 1953

While experiments were being carried out with this latter procedure a great surprise happened, namely, on one of the electrodes a thin silicon rod had grown (Fig. 2.1) which, in its single-crystal part, showed a purity that was orders of magnitude higher than that of all samples obtained by the B-process [7].

The specific resistance was 20 ohm cm, whereas the others had less than 0.1 ohm cm. The breakdown voltages of needle electrodes were about 100 V and exhibited the polarity of an n-type semiconductor. So, with one step, the purity was increased by at least three orders of magnitude and was in the sub-ppm region. These first results could be reproduced, and subsequently the purity, the diameter of the needles, and the size of single-crystal areas could be improved even further. Our group could compare itself now with its international colleagues, and concentrated its efforts on the crystal growing and purification of silicon *as its only goal*.

Fortunately, the aforementioned laboratory for power rectifiers, under the leadership of E. Spenke in Pretzfeld, still working on selenium, also joined the silicon work. Spenke had, at that time, already recognized the importance of silicon for power applications and stated, "Silicon is, just like germanium, an elemental semiconductor and therefore does not have many of the defects that are possible with compound semiconductors because of imperfect stoichiometry and elemental dislocations. It has a sufficiently large band gap and a carrier mobility that is definitely acceptable for power applications. Thus, we will bet on it." It is obvious that, with this decision, the internal competition with Welker's research group working on III–V compounds for the same applications was preprogrammed.

In Spenke's remarkable prognosis, made in 1953, one important characteristic of silicon is understandably not mentioned, namely the long carrier lifetime. This is a result of the specific band structure of silicon, which it shares with germanium, but was not yet known at that time, namely that the minimum of the conduction band – contrary to the original assumption – does not occur at the wave vector $k = 0$ but, rather, near the edge of the Brillouin zone. This prevents a direct optical recombination of electrons and holes, which would occur in a time on the order of magnitude of 1 microsecond (as, for example, in GaAs). This, of course, prevents, on the one hand, the technological use of silicon in the area of active light generation but allows, on the other hand, the achievement of long carrier lifetimes (just as in germanium) for high purity and perfect crystallinity. This gift of nature was a crucial (at that time of course unknown) precondition for the discovery and development of the bipolar germanium transistor, because it is the means for achieving the required diffusion lengths of minority carriers. High diffusion lengths are important factors for the I–V characteristics not only of bipolar transistors but also of all power devices such as rectifiers and thyristors.

With these comments, we have got a little bit ahead of ourselves, because these fundamental characteristics of the band structure were only discovered step by step towards the end of the 1960s beginning with the work of Herman et al. [8]. So, let us return again to the year 1953 and to the then newly discovered levels of purity in the silicon samples produced by the von Arkel method. These results were quite encouraging but the limitation of sample diameters to a few mm made the samples unsuitable for practical application, especially in the power area. The question now arose of whether or not the electrical discharge, which was concentrated on small electrode areas in the van Arkel method, really was the key to the high-purity effect, or could the thermal reduction of the $SiHCl_3$/hydrogen mixture on a hot, glowing silicon surface ("CVD, chemical vapor deposition" as it is called today) be sufficient? In order to answer this question, thin needles were heated in a specially developed reactor by sending current through them and could thereby be covered with a thick layer, which was, however, polycrystalline. To be able to assess the purity of these polycrystalline samples by resistance measurements, they had to be transformed into crystalline material, preferably into a single crystal. This had to be achieved without addition of more impurities, as would be caused for example by touching of the wall of the crucible. To achieve this, the vertical zone melting method was invented in 1952 almost concurrently by K.H. Theuerer at Bell Laboratories and K. Siebertz and H. Henker at Siemens. In this procedure a molten zone, produced by high-frequency (HF) heating, is carried by the original ingot or, as in the case of Fig. 2.2, by the already solidified new monocrystal below the glowing molten zone.

The molten zone is held stable by surface tension, as well as by the electromagnetic forces of the HF heating. The new crystal then grows out of the molten material. This zone melting method was further improved in Spenke's

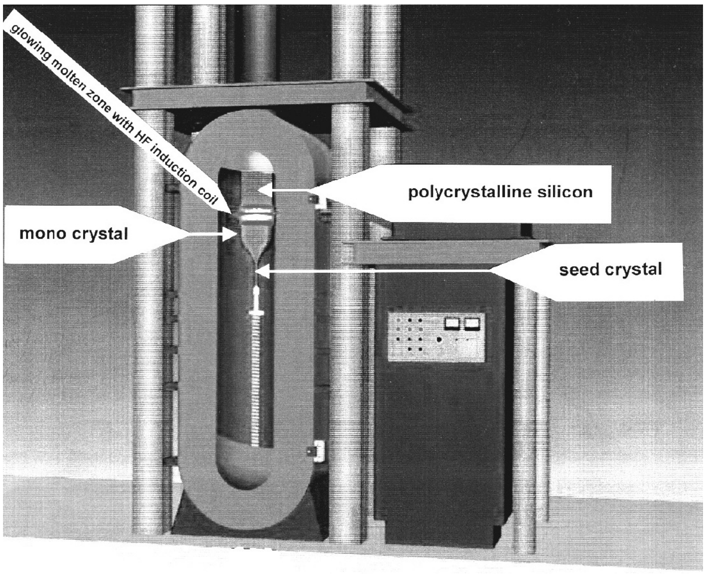

Fig. 2.2. Vertical zone melting (courtesy Wacker Chemitronics)

laboratories so that the newly forming crystal rod was not rigidly connected to the original rod that was to be melted. Using different pulling speeds for the upper and lower rods, one could arbitrarily achieve different diameters for the newly formed part of the crystal. This was used in the example of Fig. 2.2 for the transition from the small diameter of the seed monocrystal to the desired final diameter of the growing rod. In the early stages Spenke's group used this procedure for the growing of thin rods, which could then be thickened by the CVD method. A cross section of such a thickened sample can be seen in Fig. 2.3.

By this means, a closed procedure – independent of the A-process – had been achieved for wall-free production of high-purity single-crystal silicon from the gaseous phase, which, after a number of additional technological improvements, was also suitable for mass production. With this complete method (now simply called the C-process), it was possible to produce silicon rods with a diameter of a few cm and a length of more than 1 m. The maximum diameter of these rods was, however, restricted owing to the physical limitations set by the vertical zone melting itself. Thus, because of the ever-increasing demand for larger-diameter silicon wafers, and after some years of further technological development concerning oxygen and other contaminants as well as crystal quality, the vertical zone melting procedure was pushed aside again by the classical pulling from a crucible according to the method of Czochralski. A picture of such a crucible-grown rod when it just has been drawn out of the crucible is shown in Fig. 2.4.

Fig. 2.3. Cross section of a thickened silicon rod. The monocrystalline center is surrounded by a polycrystalline CVD layer

Fig. 2.4. Crucible-grown modern dislocation-free silicon monocrystal (courtesy Wacker Chemitronics)

Nevertheless, the development of the vertical zone melting process was, at that time, an absolutely necessary step for the industrial breakthrough of silicon as a semiconductor material. The complete C-process had opened the way to industrial mass production.

During the time of its development, vertical zone melting was the key for thoroughly investigating the purity, properties, and crystal quality of all our silicon samples. This may be illustrated by the following story. When increasing the diameter of thin crystals by CVD layers we found, after deposition and transformation into single crystals, an unexpectedly high conductivity of the final single-crystal rod. This was found to be due to a donor concentration that was close to 1 ppm. However, tests in an A-reactor using the same $SiHCl_3$ samples had shown a prevalence of acceptors with a concentration of about 0.01 ppm. Where did the high donor concentration come from? Were the donors impurities from the reactor? Were the samples contaminated by inadequate handling? Was this a problem of the deposition process itself? A lot of questions had to be answered simultaneously in the sub-ppm regime. A first positive result was that the impurities could be removed by multiple zone-pulling. But that was obviously cumbersome.

What kind of impurities were these anyway? This question could not be answered easily, because of their small concentration. So, normal chemical-analysis methods were way too insensitive. A suspicion concerning phosphorus could not be confirmed by a radiotracer method with neutron activation. The results were confusing. Furthermore, we measured the segregation coefficient for the desegregation during the zone melting. It did not fit anything. Thus, one talked about the donor X. Only the joint efforts of Honrath and Ziegler [9] produced clarity: during the radiotracer analysis, the neutron radiation not only activated the phosphorus but also created Si-31 from the Si-30 isotope which is contained in natural silicon. This transforms, through a gamma-process, into phosphorus. This additional phosphorus was then activated in a second step and consequently, depending on radiation dose and exposure time, resulted in erroneous results. In the zone-pulling procedure, on the other hand, one had to take into account not only the segregation coefficient of phosphorus between the molten material and the silicon crystal but also evaporation, which depended on the diameter of the molten zone.

With this knowledge – simple only *a posteriori* – it was possible to identify phosphorus as the critical n-impurity. And then it became possible to reduce its concentration and thereby solve the problem.

The story of the donor X may be considered representative of the problems we were confronted with in this early phase. Penetrating this region of ultra-high purity required thinking in new dimensions. The problems could only be solved by interdisciplinary cooperation: novel chemical means and equipment for the purification of the starting chemicals; measuring by overcoming oxide barriers and blocking layers; clarification of donor–acceptor compensation; radiotracer analysis; thermodynamics of crystal growth, including phase diagrams; interactions between the various contaminants and with lattice defects; etc. Thus, it is obvious that a close cooperation had to be developed between the different Siemens groups on the one hand and the suppliers of the chemical substances on the other hand. This mainly concerned the metal–organic compounds of the Si–H–Cl system. There was a continuous exchange of samples and data between our different groups on the one hand and Wacker (later on Wacker-Chemitronics) on the other hand. This cooperation had, at first, developed open-mindedly but then it was formalized and, finally, it led to a licensing agreement for the entire production and test process.

Two special results of this early company cooperation should be mentioned:

- The boron problem: boron is an acceptor dopant still in use for device production. In contrast to phosphorus, it cannot be removed by zone refining or evaporation, because of its chemical similarity to silicon. Thus we had to rely entirely on Wacker's purification process and reliability.
- The carbon problem: chemically, carbon is homologous to silicon and does not act as a donor or acceptor; it cannot be detected by resistivity measurement. But, through the formation of SiC precipitates, it prevents monocrystalline crystal growth. These SiC precipitates were the result of $SiHCl_2CH_3$ contamination of $SiHCl_3$. Again, we depended here entirely on the capability and quality control of Wacker.

There was also some work on silicon at IBM in Schwuttke's group. However, it did not result in many pivotal advances in the field of very pure silicon. The contributions were more along the lines of crystal defect analysis by x-ray topography.

These few examples from the early cooperative efforts may underline again that the development process described above was an expedition into the unknown that could have easily gone astray. But high-purity, perfect silicon crystals are not a purpose in themselves; they represent a crucial precondition for the proper functioning of semiconductor devices, which, in turn, are a result of proper doping, structuring, contacting, etc. All of this forms a separate set of problems, which had to be gotten under control through relevant research and development. These topics will be treated in separate contributions within the framework of this series, so that we do not have to go into details in this introduction.

2.4 Initial Device Applications

It seems significant to us that the Texas Instruments and Siemens groups, which worked independently on silicon, had also set themselves different goals. The main goal of Teal was the development of bipolar silicon transistors. He showed initial results at the 1954 IRE Conference in Dayton during his presentation "Some recent developments in silicon and germanium materials and devices." But, as he stated himself in 1976 in his survey article [10], he could hardly overcome the existing reservations concerning the reproducibility and stability of silicon transistors. In addition, there was a lower cut-off frequency due to the lower carrier mobility for comparable geometries. This did not, however, deter him from continuing to pursue this approach, especially for military applications that had higher power requirements.

Concerning the application of silicon in communication and information technology Siemens (at that time Siemens & Halske) remained sceptical despite the advances in the development of the highest-purity silicon – following the philosophy of Bell Laboratories. Only at Siemens-Schuckert (responsible for power technology) did Spenke and his group devote themselves consistently to the development and technical improvement of silicon for commercial application in high-power rectifiers in order to replace the old selenium technology. This new approach, including device technology, was ready in 1956 for application and was used at first for power rectifiers in Siemens locomotives [11]. Obviously, the total internal Siemens power-electric market was immediately available for the application of these rectifiers – an advantage not to be underestimated. Contrary to other companies, Siemens did not pursue a policy of a monopoly in the silicon market, but rather gave licenses for the total high-purity silicon manufacturing process not only to Wacker in Germany but also to other chemical companies, mainly in the USA and Japan. These licensing agreements also included cooperation, so that further improvements could be exchanged, and some kind of worldwide cooperation developed. This had the consequence that one can say today that the total world production of silicon semiconductor material was initiated by the so-called Siemens Process. An example of a modern silicon rod can be seen in Fig. 2.4 and should be compared with the mini-rod of half a century ago (Fig. 2.1).

As far as commercial power applications were concerned, Siemens obviously did not stop with the development of silicon rectifiers; transistors and thyristors were also developed. Here, they encountered the same problem of instability in the I–V characteristics that Texas Instruments had already seen. One of the important concerns was related to the trapping problem, i.e. the time-limited presence of charge carriers at defect sites. Bell Laboratories had already encountered this problem in 1953 during the examination of their silicon [12]. Was this trapping effect possibly due to "natural" defects that were intrinsic to silicon and therefore unavoidable, for example, lattice defects? We also attacked this problem and thoroughly examined various trapping effects in the silicon that was produced in Spenke's laboratories and also elsewhere [13,14]. The most important result of those investigations was that the trap density in the silicon produced by the Siemens process was below $10^{11}/\mathrm{cm}^3$ and, therefore, caused no problem at room temperature. The reason for that was the absolutely wall-free preparation of this silicon – an advantage not planned but nevertheless crucial.

2.5 MOS Technology and Integration

Despite all these above-mentioned encouraging results at Texas Instruments and Siemens, the breakthrough for the use of silicon instead of germanium in the communication and information area was not at all guaranteed yet. Even at the end of the 1950s, higher cut-off frequencies seemed to be the determining factor. The higher carrier mobilities found in Ge and GaAs were far more attractive. The breakthrough of silicon came only with two innovations which were unexpected to most semiconductor specialists:

1. The discovery that thermally grown SiO_2 films passivate (stabilize) the surface of the silicon substrate was the turning point in semiconductor technology resulting in the change from germanium to silicon, since germanium surfaces could not be stabilized in a similar manner. This passivation was due to a significant reduction of the surface states (dangling Si surface bonds) by forming Si-surface–O bonds and made possible the control of charge carriers via the oxide layer. The low density of surface states in Si–SiO_2 structures opened up the way for developing the metal–oxide (SiO_2)–semiconductor (Si) field-effect transistor (MOSFET), which, in its basic concept, utilizes ideas that were already known in the 1920s (e.g. [15]), but which were at that time miles away from being able to be realized. In the development of this technology, which is today the basis for microchips, especially those used in computers, the properties of the SiO_2 film as a dielectric and mechanical layer also played an important role.

   The first realization of an MOS transistor was achieved in 1960 by Kahng and Atalla at Bell Laboratories [16] and was followed in 1961 by Zaininger at RCA Laboratories [17]. But it still required a large amount of additional developmental work until the MOS transistor technology was under control and reproducible. This will be treated in detail in one of the following articles. Therefore we shall limit ourselves to simply pointing out that, before the development of the MOS technology, it was a downright statement of faith that stable semiconductor devices had to avoid or at least to fight the detrimental influence of the surface.
2. The second innovation is also related to the surface. It is the concept of device integration within a single silicon chip, which, at its beginning, seemed to many rather limited in its possibilities. One has to remember that the yield for single transistors at that time was about 30%. Thus, by simple deduction one would expect the yield for two hard-wired transistors to be 0.3×0.3, i.e. about 10%, for three transistors about 3%, and so on. It was Kilby's brilliant mind [18] which realized that it is really the metal wire connection that is the main source of failures and that avoiding it by "integrating" could lead to higher yield and reliability. Indeed, he built the first functioning integrated circuits, initially a phase shift oscillator and then a few flip-flops, in the summer of 1957 by connecting

> about 25 transistors that were on a 5 inch germanium wafer. But who at that time would have seriously thought of the high levels of integration that are characteristic of today's microelectronics? These developments would not have been imaginable without the specific masking properties of the silicon dioxide layer. Since this question, together with the many required research topics and technological developments, will be discussed in detail in the following articles, we shall limit ourselves to just this one question. Which properties of silicon are crucial for the role of the silicon oxide layer?

One property is pretty obvious. It is the high purity. Only on a pure material is it possible – provided that additional subsequent procedures are also clean – to grow a defect-free oxide in which, for example, no ions are contained that could move when an electric field is applied to the oxide and thereby change the I–V characteristics. Another property, at least as important as the first, is the chemical stability of the initial oxide layer. A clean, undisturbed silicon surface is unstable, as was shown, for instance, through investigations with LEED (low energy electron diffraction) on free silicon surfaces in high vacuum [19]. For example, a normal (111) silicon surface clearly shows the sixfold symmetry of the uppermost layers, as expected from this crystal structure. However, this changes during annealing in ultra-high vacuum into a much more complicated symmetry in which the dangling bonds satisfy each other (Fig. 2.5).

But this "pure" state is only stable in high vacuum and eagerly attracts atoms of other elements. Important for our considerations here is the fact that these are preferably oxygen atoms, which then can form an initial oxide layer. This stable and atomically dense first layer is a crucial advantage of silicon and does not exist in other competing semiconductor materials. This is possible because of a fortunate situation, namely that the distance between the silicon atoms in the Si–O–Si bond coincides with the distance between two silicon atoms in the diamond structure of the basic lattice. Only this makes the growth of the dense and defect-free initial oxide layer explainable and the avoidance of undesirable surface and interface states possible. The atomically dense transition of the monocrystalline silicon substrate to the grown-on SiO_2 layer is shown in Fig. 2.6.

In spite of the atomic fit, the oxide layer is amorphous because of the differing crystal symmetries of silicon and silica. Provided that we are dealing with a perfect stabilization of the silicon surface by oxygen saturation of all dangling bonds, to suppress all undesirable interface states, the only requirements which have to be fulfilled by the follow-up silica layer are stability and atomic density. This is necessary so that no contaminating ions are able to penetrate or migrate, since even minor migrations would cause instabilities of the device characteristics.

Furthermore, we recognize that the amorphous silica layer on top of the stabilized interface can be replaced by other layers provided the stability

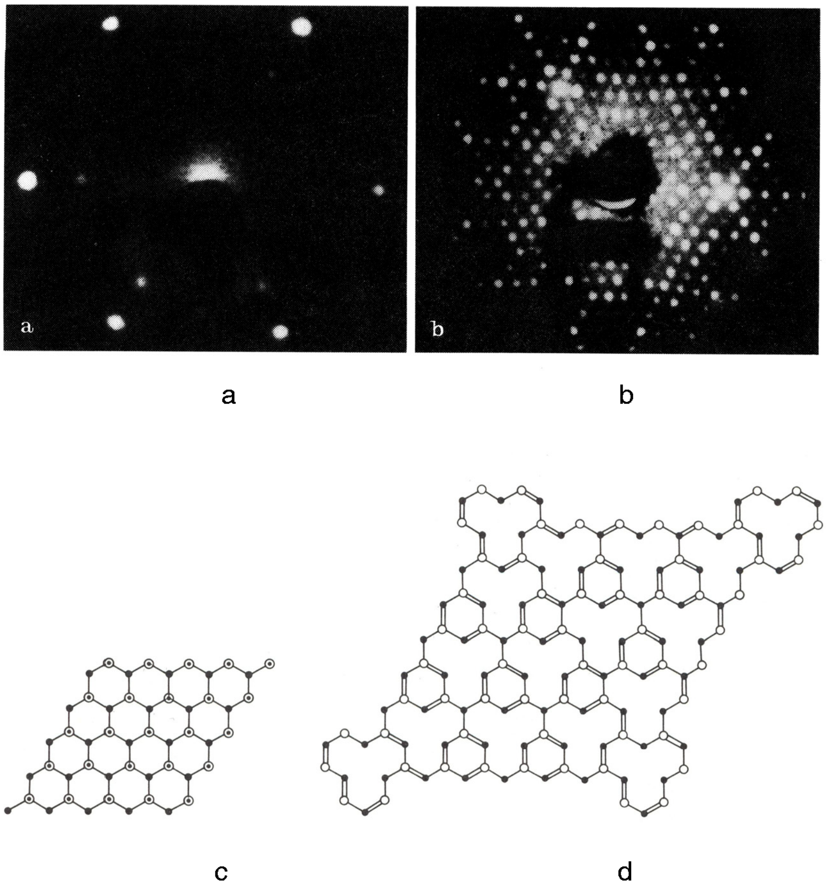

Fig. 2.5. Silicon surface, crystal structure. (a) LEED pattern of oxygen-stabilized (111) surface; (b) LEED pattern of oxygen-free (111) surface; (c) crystal structure of a (111) silicon surface with vertical dangling bonds, which have to be saturated by atoms of the next (not shown) layer; (d) self-saturation of dangling bonds, only stable in a vacuum that is better than 10^{-9} torr: ○ atoms of the top layer with dangling bonds, ○ atoms of the top layer without dangling bonds, ● atoms of the second layer from top

requirements mentioned above are fulfilled. This degree of freedom is used, for example, in the case of Si_3N_4 passivation and wherever else silica is to be replaced by low-*k* or high-*k* materials for improving speed or integration density in modern IC technology.

In summary, through this interface stabilization, nature has helped us again in the development of IC technology, including the modern varieties we are working on today. This is an effect which nobody thought of when the work on the use of silicon for semiconductor purposes began, especially at

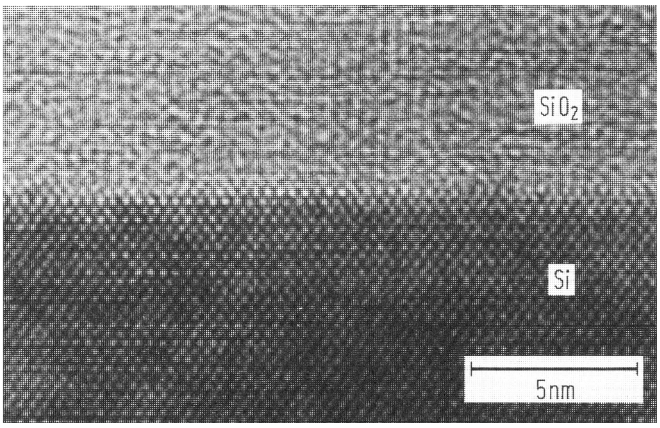

Fig. 2.6. Interface between silicon substrate and SiO_2 surface layer in atomic resolution

a time when there were so many other problems connected with the always present oxide layer during measurements and contact making.

Finally, the following fact, which was crucial for the victorious advance of silicon into information technology, has to be pointed out. Advanced MOS Technology and very large-scale integration (VLSI) – both based on the extraordinary properties of the Si–SiO_2 system – opened the way for a cost-effective digital technology, which then, in turn, opened the way for the necessary mass market in silicon integrated circuits for use in information technology.

2.6 Conclusion

With these remarks, which already reach into the heart of the silicon era, we want to conclude this review of the pioneering times of silicon, *the* semiconductor material. We hope that this description of the whole development of pure, single-crystal silicon makes three things clear:

1. Silicon, with all its positive basic attributes, had first to be made readily available for large-scale common use. This was an often difficult path into the unknown, where only the human pioneering spirit had a chance to overcome all the difficulties that were encountered. It certainly was not a straightforward development – as it might appear to someone in retrospect and as extrapolations such as Moore's Law might make one believe – but rather one that was characterized by many, often extremely complex individual developments. It was an outstanding achievement of the human spirit in research, as well as of interdisciplinary cooperation between material researchers, device developers, designers, and technologists.

2. Most importantly, it is obvious that a uniform, high-purity, perfect single-crystal piece of silicon material alone would be of extremely limited technological use. It is only when this material is suitably altered and structured through controlled, reproducible processes and then made into useful devices that it becomes valuable. All of these requirements could not have been achieved were it not for the fact that nature provided us with an extraordinary gift, through suitable physical properties and constants, etc. – an abundance of wonderful, often crucial properties and characteristics of silicon, silicon dioxide, and the Si–SiO_2 interface that, together, make modern integrated silicon technology possible at all. Let us just quickly enumerate the most important properties and characteristics:

2.6.1 Silicon

- Abundant: easy to obtain, low cost.
- Single crystal: with ever larger rod diameters (30 cm). Defects can be eliminated or selectively utilized for advantage.
- Not brittle: can easily be handled and is an excellent mechanical substrate for individual devices and integrated circuit chips.
- Adequate thermal conductivity to take away the electrically generated heat in chips.
- Can be microstructured by a combination of suitable optical and chemical methods (lithography), even breaking through the 0.1 micron barrier.
- Thin crystalline silicon films with different electrical properties can be grown onto silicon substrates via epitaxy.
- Thin crystalline silicon films with various electrical properties can be grown onto insulators (sapphire, etc.) to provide improved isolation and speed, and lower capacitance.
- Thin crystalline germanium films and, probably, novel films of III–V compounds containing quantum dots, offering different electrical and optical properties, can be grown onto silicon substrates via chemical vapor deposition or molecular-beam epitaxy.
- Buried thin films of SiO_2 can be created under the silicon surface by oxygen ion implantation and subsequent annealing (SIMOX structures).
- Has a very useful energy gap (1.12 eV).
- Conductivity can be tailored (n-type, p-type, value) by doping using diffusion and/or ion implantation.
- As an elemental semiconductor, it does not have the multitude of materials problems and chemical behavior that compound semiconductors have.
- Annealing works very well.
- Carrier mobility is good for both electrons and holes (important in CMOS circuits).

- Carrier lifetime for both electrons and holes is good because of special band structure properties and low density of traps (important for bi-polar devices).
- Not light-sensitive (stable operation of devices under various light conditions).

2.6.2 Silicon Dioxide [20]

- Can be thermally grown as a native oxide by a simple, inexpensive and reliable (oxidation) process.
- Can be deposited via chemical vapor deposition and other methods.
- Is stable up to very high temperatures (important for annealing).
- Films can be very thin (100 Å) (necessary for ultrasmall MOS devices).
- Acts as a chemical barrier during etching of selected silicon areas,
- Can act as a diffusion barrier for certain materials, especially most of the common dopants.
- Acts as a barrier during ion implantation.
- Is chemically stable but can be microstructured by a combination of suitable optical and chemical methods (lithography), even breaking through the 0.1 micron barrier.
- Metal patterns, deposited on it by various methods, adhere very well.
- Is mechanically strong and can act as a protective layer (physical and ionic protection).
- Can be polished to planarize the surface.
- Is transparent.
- High electrical breakdown strength.
- Useful dielectric constant (but here there is a need for new insulating materials to replace SiO_2 in certain areas: high-k materials for the gate and low-k materials for insulating the wiring).

2.6.3 Si–SiO_2 Interface [21]

- Has an extremely low density of interface states when properly prepared.
- Very stable.

Had this been different – either through a quirk of nature or a dispensation of providence – the development would have taken a different path, and the enormous advances we see today, especially in microelectronics and information technology, would hardly be imaginable.

3. As outlined in item 2 above, silicon is a unique gift of nature, so that we are justified in speaking of *the* semiconductor material. It cannot be supplanted in its importance to our technology and will continue to dominate the core of semiconductor electronics. Important complementary technologies can only be expected in areas where silicon encounters its

natural limits, for instance in optoelectronics, large display technologies, sensor technology, or modern bioelectronics. In these areas one also needs new materials and material combinations which might partially contain silicon.

However, significant new applications may still be discovered for this unique gift of nature, making it then one of the most significant if not the most significant material in the world today.

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