

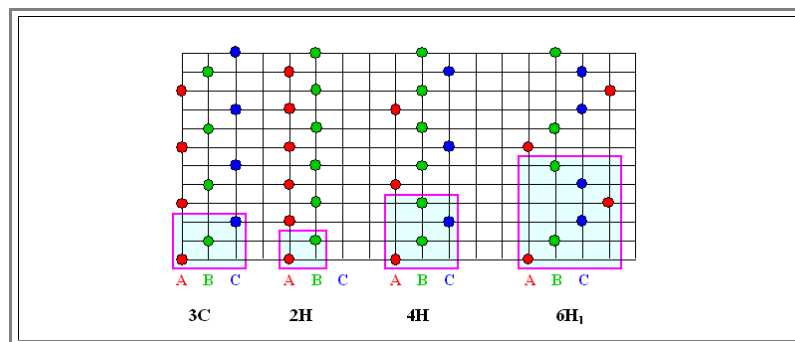
# 10. Specialities

## 10.1 Silicon Carbide

### 10.1.1 Silicon Carbide - Material Aspects

#### Structure and Basic Properties

- There is no such thing as plain **SiC**!
  - Instead, whenever you look in the literature, you will find names like **3C-SiC**, **6H-SiC**, **4H-SiC**, or **2H-SiC**. In other words: There are many different **polytypes** of **SiC**.
  - Polytypism** is a special case of **Polymorphism**, which means that a given element or compound can assume more than one crystal structure. Polytypism simply is the one-dimensional variant of polymorphism.
- SiC** (unfortunately) is sort of the paradigmatic material for polytypism. The always identical hexagonal two-dimensional **SiC** layers can form many crystal structures by different ways of stacking the layers on top of each other - that's why it is one-dimensional. See "[MatWiss I](#)" (in German) for the basics of how crystals can be formed by stacking atomic layers.
- SiC** does not just have a few polytypes, it has more than **200!** Now you have a problem: which one is the best for the application you have in mind, and if you know that, can you actually make it all by itself (and not in a mix with all the others)?
- SiC** is also the only stable group **IV - IV compound** semiconductor. No other combination of the elements **C**, **Si**, **Ge**, **Sn** exists in a defined lattice (and not just as mixed crystal like **Si-Ge**).
- All polytypes have a rather **large** indirect bandgap and other properties, which make **SiC** a very interesting material for many applications.
- As you may have guessed, **SiC** is devilishly difficult to grow as a (large) single crystal of **one** polytype with low defect density. **SiC** actually boasts a particular (and very bad) lattice defect all of its own - so-called micropipes - the likes of which have not (yet) been found in other crystals.
- The formal way of identifying polytypes, i.e. the [nomenclature of the polytypes](#), is explained in the link (basic module); here we just look at the more important variants in terms of the [familiar "ABC"](#) stacking definition. The basic building block (not necessarily a unit cell) is highlighted in light blue.



- Upon contemplation, you should be able to notice that the "**3C**" structure is nothing but the **ABC** stacking sequence of a close-packed **fcc** lattice; the **2H** is the corresponding simple **hcp** structure resulting from an **AB** stacking sequence.
- Your guess then that **C** stands for "cubic"; **H** for hexagonal, is correct. If an "**R**" comes up in variants not shown here, it stands for [rhombohedral](#).
- In some older nomenclature, cubic **SiC** is also known as  $\beta$ -**SiC**; the hexagonal phase (**6H-SiC** more or less) is the  $\alpha$ -**SiC**
- Not only the structure of **SiC** polytypes is different, but so are their **electronic properties**.
  - The always **indirect** band gap varies from **2.4 eV** for the cubic **3C-SiC** to **3,3 eV** for the simple hexagonal **2H-SiC** variant. Other relevant parameters like carrier mobility might be quite different, too. Some values (mostly adapted from the publications or presentations of Erlangen (Germany) **SiC** group) are shown below

		4H-SiC	6H-SiC	15R-SiC	3C-SiC
<b>Band Gap [eV]</b>		3.265	3.023 3.03	2.986	2.390
<b>Lattice Constant [Å]</b>	<b>a</b>	3.08 3.073	3.08	3.08	4.36
	<b>c</b>	10.05	15.12	37.70	-
<b>Effective Mass [<math>m_c</math>]</b>	<b><math>m_e</math></b>	0.37	0.69	0.53 - 0.28	0.68 - 0.25
	<b><math>m_h</math></b>	0.94	0.92	-	-
<b>Mobility (@ 300K) [<math>\text{cm}^2/\text{Vs}</math>]</b>	<b><math>\mu_e</math></b>	500	300	400	900
	<b><math>\mu_h</math></b>	50	50	-	20
<b>Thermal conductivity (RT) [<math>\text{W}/\text{cm} \cdot \text{K}</math>]</b>		3.0 - 3.8	3.0 - 3.8		

● If you look at the table long enough, you should now [actually have a question!](#)

▀ Anyway, besides the rather large bandgap, the effective masses and the mobilities are not so remarkable [compared to the more standard semiconductors](#).

● However, if you compare on a [more specific level](#), there are definite advantages. Activate the link if you are interested.

## Crystal Growth, Wafers and Defects

▀ Here we will only look at the basics; details are left to an [advanced module](#).

▀ In most cases, large single crystals are grown from a melt (e.g. [Silicon](#)) or some solution (e.g. quartz, or sugar if you leave your coffee cup around too long), but this is not a feasible option for **SiC** single crystal growth since **SiC** does not have a liquid phase under normal conditions (i.e. without applying a large pressure). **SiC** is also extremely hard (close to diamond) and therefore has a high melting point (or is it the other way around?).

● There is also, in principle, no crucible material that could contain molten **SiC** at its nominal melting point temperature of  $< 2.500 \text{ }^\circ\text{C}$ . Nevertheless, **SiC** was grown from a melt at  $2200 \text{ }^\circ\text{C}$  and  $150 \text{ bar}$  in a recent study, but this is probably not a commercially viable process.

▀ We need a basically new method of crystal growth. Some "older" techniques are described [in the link](#), the main method used nowadays is **physical vapor transport (PVT)** also known as *seeded sublimation growth* or *modified Lely method*.

● A piece of **SiC** is heated to  $(1800-2600) \text{ }^\circ\text{C}$  at low pressure. Due to the high sublimation rate, **SiC** vapor forms and deposits itself on a cooler single-crystalline seed crystal.

● Straightforward and basically simple, as shown in the schematic picture on the right.

▀ However, pondering the situation, some questions should come to mind:

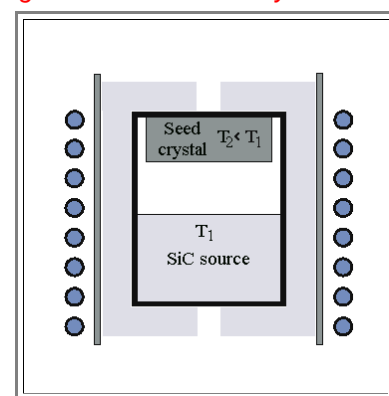
▀ What materials can you use for the crucible and everything else that gets hot? After all, not many materials can cope with temperatures above  $2000 \text{ }^\circ\text{C}$ !

● Well, you are basically stuck with graphite, and maybe a bit of **Ta** here and there. That means, of course, that you are forming **SiC** also on your crucible walls and everywhere else. If it flakes off, you will have a defect problem.

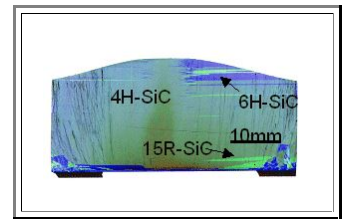
▀ What kind of *growth rate* can you get?

● Well, as you would expect: Not much! Growth rates depend on many parameters, but are in the range of  $0.2 - 2 \text{ mm/hr}$ . That's about a factor of **50** slower than the growth rates for **Si** crystal pulling and that makes **SiC** crystal growing automatically expensive

▀ What *polytype* will you get (hoping that it will not be a mixture)? What determines what you get? Can you control it and, if yes, how?



● Good question! First, you might get mixtures as shown in the picture (courtesy of the Erlangen group). Otherwise, the following parameters are essential:



- Polytype of the seed crystal (as you might have guessed).
- "Face" of the seed crystal; i.e if the surface is a **C-** or a **Si** layer. If you start with a **4H-SiC** seed crystal, for example, you tend to get **4H-SiC** if you have a **C-face**, and **6H-SiC** if you have a **Si** face. Why? Nobody really knows.
- Temperature difference and - gradient between **SiC** source and seed. Small values tend to favor **4H-SiC**, larger values **6H-SiC** growth.
- Gas composition. Whatever gas you add will influence the polytype you obtain. **C-rich** gases, for example, promote **4H-SiC** growth
- The pressure, oddly enough, seems not to have a large influence on polytype.

● Note that while the polytype **6H** is the easiest to grow, **4H** would be favored by the power electronics industry.

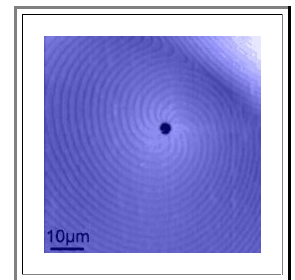
▸ Last not least: What kind of crystal quality do you get? What is the dislocation density?

● The bad news is: the dislocation density is high. The good news is, you do not worry too much about that - you worry about something weird called "**micropipe**" (and mixtures of polytypes, and all kinds of stacking faults or special boundary faults, and carbon inclusion, or **Si** inclusion, or big voids, ...).

● To quote an Internet source: "*Problems with micropipes and polytypes dominate to such a degree that the research of dislocations, vacancies and impurities still remains an academic activity*".

▸ What are micropipes? Well, micropipes are hollow channels running through the lattice; the diameter of these pipes is **(0.1 - 5) μm**.

● It is not totally clear what micropipes are, how they are formed, and why they exist at all. The probably best way to think about these defects is to consider them to be screw dislocations with a "giant" Burgers vector (violating the rather [general rule](#) that Burgers vectors always are the shortest possible lattice vectors) and a *hollow core*.



● The hollow core actually makes sense. If you accept the "giant" Burgers vector bit, it is energetically far more favorable to have the dislocation core hollow instead of extremely strained. What you pay in terms of surface energy, you easily gain in avoided elastic energy.

● But this is not gospel yet. Micropipes are at present simply not completely understood.

● Micropipes are also somehow connected to the growth mechanism of the crystal. This is neatly illustrated in the picture on the right (taken with a scanning force microscope, courtesy of H. Strunk; Uni Erlangen) where typical growth spirals are visibly centered around a micropipe.

▸ Micropipes also will definitely kill any device that contains one of them. They thus must be avoided as much as possible!

▸ Let's look at the state of the art of what is around. To quote from the product sheet of the major **SiC** supplier Cree, Inc. (located somewhat ironically in Silicon Drive 4600 in Durham, North-Carolina, **USA**):

- At present, wafer diameters are **50.8 mm** or **76.2 mm**; doping (usually with **N** for n-type and **Al** for p-type) at high levels produces resistivities in the **0.0x mΩcm** region. Or there is no doping for semi-insulating stuff.
- **4H-** and **6H-SiC** polytypes are sold; for a [more detailed look](#) of some of the products that are available use the link.

▸ The **2003** state of the art (mostly in the laboratories and not necessarily on the market) is summarized in the following table:

Diameter		100 mm "Four-inch"	For Si, 100 mm was the standard back in the late 70ties/early 80ties).
Defects	Micropipes	< 1 cm <sup>-2</sup> for 3" < 30 cm <sup>-2</sup> for 100 mm	Increasing wafer size usually dramatically increases micropipe density
	Dislocations	3 · 10 <sup>3</sup> cm <sup>-2</sup> achieved	Factor 10 reduction

Of course, in the many laboratories (university and industrial) devoted to **SiC**, some data might be even better.

## Electronic Properties

The basic electronic properties were listed [above](#) and in an [illustration module](#), here we briefly consider **doping** and **optical properties**.

First let's ask ourselves a question that should have come up by now: Why is **SiC** interesting for **optoelectronic** applications? How could [Siemens make light-emitting diodes](#) back in **1977** from an indirect semiconductor?

Well, maybe there are bound excitons as [in the case of GaP](#)? Right - maybe! To quote one of the recommended [Books](#) (published **1995**):

*"The emission (of  $\alpha$ -SiC; i.e. probably 6H-SiC) occurs in a wide band from about **400 nm - 600 nm** with a maximum at **480 nm** (blue). So far it is not clear what kind of transition causes the **SiC** emission".*

Now you should be glad: There is something left to do - for you!

The situation becomes a bit clearer, maybe, by pondering another quote (from a very good source in [Sweden](#)):

*"The viewpoint of a crystal grower differs largely from that of a spectroscopist. The work of a crystal grower is often to provide material of very high quality and sometimes also of high purity. A **PL** spectrum which may look excellent for a crystal grower (i.e. shows nothing for an indirect semiconductor), may perhaps not create any higher emotional feelings for a spectroscopist. Indeed, samples which for a crystal grower may be the outcome of failed experiments will be the samples of greatest interest for the spectroscopist".*

In other words: **SiC** crystals usually are full of defects with some energy level in the band gap. Besides the levels from the (usually heavy) doping, and all kinds of exciton levels, there are all kinds of atomic defects, spanning the range from simple vacancies to impurity atoms and clusters of atomic defects with levels in the big and roomy band gap of **SiC**.

There are thus many possible transitions or [recombination channels](#) for electron and holes, and some of those transitions might will emit light.

Some more information about the photo luminescence properties of **SiC** can be found in an [advanced module](#), here we simply note that the light emission properties of **SiC** are not so much a property of the ideal (doped) perfect material, but of crystal lattice defects in a general sense.

However: Whatever recombination events produce light - the quantum efficiency is never very good - the over-all efficiency of the early **LEDs** was **< 1%**. Nevertheless, before the advent of **GaN** in the nineties, **SiC LEDs** were the only ones emitting in the blue.