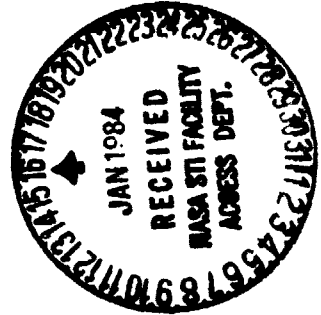


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Silicon Carbide, a High Temperature Semiconductor

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SILICON CARBIDE, A HIGH TEMPERATURE SEMICONDUCTOR

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ABSTRACT

Electronic applications are described that would benefit from the availability of high temperature semiconductor devices. Comparisons are made among potential materials for these devices and the problems of each are discussed. Recent progress in developing silicon carbide as a high temperature semiconductor is described.

INTRODUCTION

In recent years, there has been a growing need for electronic components capable of operating at high temperatures for extended periods of time.¹ The desired operating temperature in some applications approaches 600° C, which is well beyond the capability of currently available semiconductor devices. In this paper, a few of these applications will be discussed and then some potential high temperature semiconductors will be compared. Progress in the development of silicon carbide (SiC) as a high temperature semiconductor will be described.

APPLICATIONS

Since the NASA Lewis Research Center is primarily involved with aerospace R&D, applications related to this field will be emphasized in this paper.

A major potential user of high temperature semiconductors is jet (or turbine) engines.² The reasons are much the same as for automobile engines where there is a need for on-board electronics to monitor and control the engine. For turbine engines, this need can be divided into two areas: first, ground testing during the development phase of a new engine, and second, flight condition monitoring and control systems after the engine becomes operational.

During the ground testing of a new turbine engine, tests are often run with the engine heavily instrumented with sensors of many types. Of particular interest are measurements on the rotating part of the turbine. This creates a problem in that there usually is not sufficient

room to connect all these sensors to the outside world by means of wires and slip rings. So, for each test, only a fraction of the sensors can be connected. Tests must then be repeated with a different set of sensors until sufficient information is obtained from all the sensors. This repeated building up and tearing down of an engine to connect sensors is very expensive and time-consuming. This problem could be eliminated if a multiplexer could be installed on the turbine disc. Unfortunately, current electronic devices cannot operate in the 600° C environment of the turbine disc.

After an engine becomes operational, monitoring and control systems are highly desirable in order to reduce maintenance, improve engine performance and improve fuel efficiency. Such electronic systems would have to operate for long periods of time in a temperature environment that will reach 300° C in advanced supersonic engines, and the trend is to design the engine to run even hotter for sake of engine efficiency. In order to satisfy the extreme reliability requirements of flight electronics, the electronic devices will have to be capable of operating much higher than this expected 300° C environment for purposes of accelerated life testing.

We have concluded that an operating temperature of 600° C is a reasonable goal for devices that will be used for either ground testing or flight applications.

In addition to turbine engine applications, there are other applications that could benefit from high temperature electronics. In space, the thermal environment can be a problem for electronics where there is a significant amount of power dissipated. So, satellite power systems in general, and communication satellites in particular, are two potential applications. Another obvious space application would be planetary probes. Other applications on earth include down hole or deep-well drilling instrumentation, power electronics, and nuclear reactor instrumentation and control.

COMPARISON OF MATERIALS

Since the temperature limits of available devices are exceeded in many of the above applications, new semiconductor materials will have to be developed. Six materials were selected and some

Table I. A Comparison of Some Electronic Materials.

Material	Bandgap (eV)	Carrier Mobility	Physical Stability	Thermal Conductivity	Maximum Operating Temp. (°C)
Silicon	1.1	Good	Good	Good	300
Gallium Arsenide	1.4	Excellent	Fair	Fair	460
Gallium Phosphide	2.2	Fair	Fair	Fair	875
Cubic Silicon Carbide	2.3	Fair	Excellent	Very Good	925
6H Silicon Carbide	2.9	Fair	Excellent	Very Good	1240
Diamond	5.5	Good (?)	Very Good	Excellent	1100

pertinent properties of these materials are assessed in Table I. There are other materials that could have been included but the six selected are either commercially available or offer much potential for future development. They also present a wide range of operating temperature capability.

The first material listed in Table I is the most commonly used semiconductor, silicon; it provides a basis of comparison for the other materials. The next two on the list, gallium arsenide and gallium phosphide, are representative of the many III-V compounds and their alloys. Two silicon carbide crystalline forms are included because they are both potentially useful high temperature semiconductors but have significantly different electronic and optical properties. Diamond is listed because of its long-term potential.

The maximum operating temperature for a semiconductor is determined by the forbidden energy bandgap. The temperature limit is reached when the number of intrinsic carriers, thermally excited across the energy gap, approaches the number of extrinsic carriers. This temperature (when expressed as the absolute temperature) is roughly proportional to the energy bandgap. In Table I, a maximum temperature of 300° C was assumed for silicon, and based on the ratio of bandgaps, the maximum operating temperature was calculated for the other materials. Diamond is a special case in that a phase change around 1100° C determines its maximum temperature. These temperatures should be used only as a starting point since other factors also affect the maximum temperature, such as the type of device and the length of service required for a given application.

Other material properties of major importance for the operation of a semiconductor at high temperatures are the carrier mobility, physical stability, and thermal conductivity. The thermal

conductivity is of particular importance if much power is to be dissipated in a device.

In addition to the properties listed in Table I, there are other considerations in selecting a semiconductor material. For example, the technology base for silicon is so far ahead of the other materials that there must be compelling reasons for choosing any other material. In the case of the Lewis program for developing electronics for advanced turbine engines, the target operating temperature was set at 600° C. This ruled out silicon. Gallium arsenide and gallium phosphide are also commercially available, and gallium phosphide meets the Lewis temperature goal. However, the stability of this material (and the other III-V compounds) was not considered sufficient for reliable operation for long periods at 600° C.

A major disadvantage of the remaining three materials in Table I has been the lack of reproducible processes for growing the large-area single-crystal substrates that are needed for commercial production of devices. This is still a problem with diamond, but considerable progress has been made recently on the crystal growth of SiC. The remaining part of this paper will review the technology of SiC and describe this recent progress.

SOME BACKGROUND ON SiC

Silicon carbide is commonly known as a ceramic and as an abrasive material. Crystals that were a byproduct of the industrial process for making sandpaper grit have been studied for many years. These studies have shown that SiC grows in many different crystalline forms, called polytypes. The cubic and 6H are two of the most common of these polytypes. Another aspect of SiC is that it doesn't melt at any reasonable pressure and temperature, but rather sublimates at temperatures above 1800° C at one atmosphere. So, most crystal growth processes involve a vapor phase approach. In the industrial process, SiC is formed at 2500° C by the reaction of silica and coke. At these temperatures, gas pockets form within the SiC reaction product. The SiC sublimates and then condenses on the walls of pockets located at cooler parts of the reaction product. Occasionally, isolated SiC crystals are produced within these pockets during the production process. The larger and better crystals are selected for research purposes.

In 1955, Lely³ developed a laboratory version of the industrial sublimation process and was able to produce rather pure SiC crystals. Encouraged by the Lely process and support from the military and NASA, SiC research mushroomed. Justification at that time was the supersonic transport and nuclear-power systems for space applications. This research continued for a period of nearly twenty years to the extent that three international SiC conferences were held⁴⁻⁶ with many papers presented. During the late sixties and early seventies, NASA Lewis also had an active SiC research effort.

Around 1973, the programs that funded this SiC research were phased out. Unfortunately, the

Lely process and other processes had not been developed to the point where high-quality large-area crystals could be grown in any reproducible way. Since crystal substrates are crucial to device fabrication, interest in SiC waned, and from 1973 to 1980, there was very little effort in the U.S. on SiC. However, research did continue in Japan and in Europe during this period.

In 1980, because of the increased need for high temperature electronics in advanced turbine engines, NASA Lewis again embarked on a high temperature electronics program. The emphasis again has been on developing SiC.

SIC POLYTYPES

In Table II is a list of a few of the known polytypes of SiC. The only difference in the crystal structure of the various polytypes is in the sequence of stacking of double layers of silicon and carbon atoms. The relative orientations of these double layers with respect to the other double layers is the key factor. A given double layer can occupy one of three possible orientations, which are arbitrarily designated as A, B, and C. The cubic SiC polytype, frequently called β -SiC, has the stacking sequence ABCABC, and so forth. The Ramsdell notation is also commonly used to describe the polytypes. This consists of a number followed by a letter. The number designates the number of double layers in a stacking sequence before it repeats. The letter designates the crystal structure. Thus, we have 3C for cubic SiC. All of the polytypes, except the cubic polytype, are known as alpha SiC. The most common of these is 6H. Among the alpha polytypes, the H stands for hexagonal and the R stands for rhombohedral.

Figure 1 is a photo of some alpha SiC crystals that were produced by the Lely process. Most of the crystals are a mixture of polytypes, and since each polytype has its own electronic properties, the crystals are unsuitable for device fabrication. The coloration, from black to clear, is determined by the level of impurities in the crystals. Cubic SiC, with a smaller bandgap than the alpha polytypes, is intrinsically yellow in color. Until recently, available cubic SiC crystals were even smaller and poorer in quality than the alpha crystals shown in Fig. 1.

The crystal growth situation for SiC has dramatically changed within the last year. Two new reproducible growth processes have been developed: one for cubic SiC at NASA Lewis⁷ and one for 6H SiC at Siemens⁸ in West Germany. Both of these processes promise to provide the large-area single-crystals that are necessary for device production, so both will be briefly described in the following sections.

The reason for interest in both the cubic and 6H polytypes is that each may have advantages over the other in specific applications. Since the 6H energy bandgap is significantly larger than cubic, 6H has the potential for a higher maximum operating temperature. Also, blue light-emitting diodes have been fabricated from 6H,⁹ but not from cubic because of the smaller bandgap. A potential advantage of cubic SiC over 6H in some applica-

Table II. Some SiC Polytypes

	Ramsdell Notation	Stacking Sequence
(cubic or beta)	3C	ABC...
(alpha)	2H	AB...
	4H	ABAC...
	6H	ABCACB...
	15R	ABCBCACBACBCACB...

tions is based on the higher carrier mobility that has been reported for cubic.¹⁰ This may lead to particular cubic SiC devices whose performance may be superior to similar 6H SiC devices.

GROWTH OF CUBIC SiC

For many years, researchers have tried to grow cubic SiC single-crystal films on silicon single-crystal wafers because silicon wafers have the same crystal structure and are readily available. These SiC films could then serve as substrates for device fabrication. Unfortunately, the difference in atomic spacing between silicon and SiC (about 20%) usually leads to SiC layers that are polycrystalline and thus unsuitable for this purpose.

The Lewis developed process⁷ has solved this lattice mismatch problem. The approach uses chemical vapor deposition (CVD) to grow SiC on the silicon wafer. As described below, an initial layer is grown in a manner that minimizes the effects of lattice mismatch.

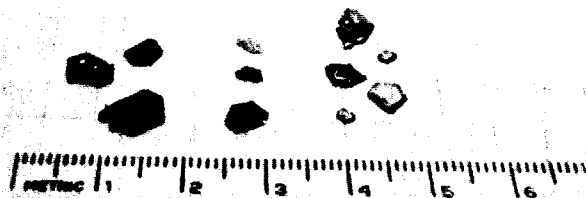


Fig. 1. Some typical Lely-grown α -SiC crystals.

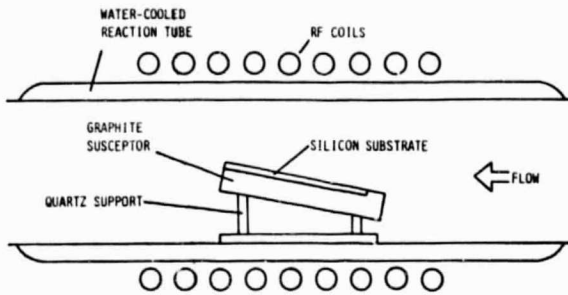


Fig. 2. Schematic diagram of reaction chamber for the cubic SiC crystal growth process.

The CVD system is of conventional design with special attention given to system cleanliness and reproducibility of growth conditions. The source of silicon and carbon are silane and propane, respectively, in a purified hydrogen carrier gas. Deposition takes place at atmospheric pressure in a horizontal water-cooled quartz reaction tube. The silicon substrate is placed on an rf-heated graphite susceptor as shown in Fig. 2.

The process of growing the SiC layer consists of three steps as shown in Fig. 3. The etching step cleans the substrate prior to growth. The initial layer step provides a 20 nm thick layer of SiC that is necessary for the subsequent single-crystal growth step. With the conditions listed for the crystal growth step, the growth rate of the SiC single-crystal layer is about 4 $\mu\text{m}/\text{h}$.

The process has consistently yielded high quality single-crystal layers with areas of several cm^2 and thicknesses up to 34 μm . The silicon substrate can be removed by chemical etching leaving a thin SiC wafer, as shown in Fig. 4.

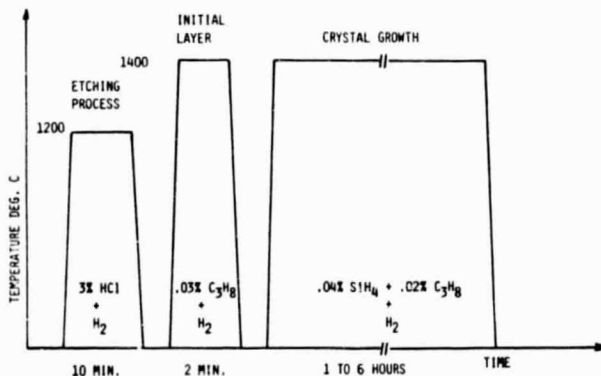


Fig. 3. Conditions for growing a cubic SiC single-crystal layer on a silicon single-crystal wafer.

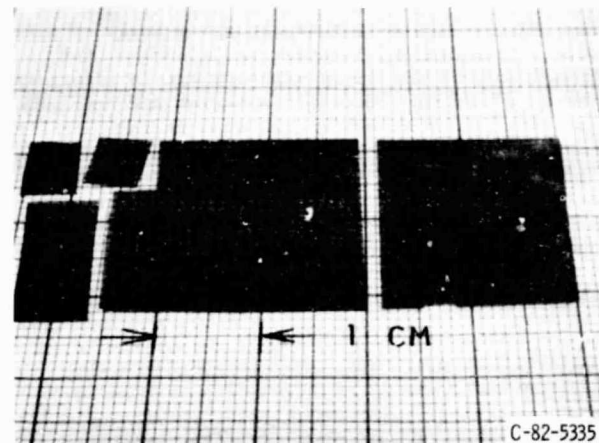


Fig. 4. A 16- μm -thick cubic SiC wafer (broken into five pieces).

X-ray diffraction measurements and electron channeling patterns obtained from the cubic SiC wafers verify that they are high quality single crystals. Hall measurements have yielded electron mobilities up to 380 $\text{cm}^2/\text{v-s}$.

GROWTH OF 6H SiC

The recently reported Siemens process⁸ can reproducibly grow large bulk crystals of 6H SiC. The technique is a modification of the Lely process and a Russian-developed process involving growth on a SiC seed crystal.¹¹ Polycrystalline SiC is sublimed at one end of a hollow growth chamber and deposited on the seed crystal located at the other end. Important parameters in the growth process are: (1) a temperature gradient with a temperature of 2400°C at the polycrystalline SiC, decreasing to 2200°C at the 6H SiC seed crystal, and (2) the chamber pressure which is reduced to 2 mbar during crystal growth. Growth rates of 4 mm/h are achieved; single crystals of 6H SiC up to 24 mm in length and 20 mm in diameter have been grown. Substrates for device fabrication can be obtained by slicing these bulk crystals. With controlled aluminum doping of these crystals, blue light emitting diodes were fabricated with the highest quantum efficiency for SiC reported so far.⁸

SiC DEVICE TECHNOLOGY

Because of the long history of SiC research, much device technology already exists.^{12,13} The technology required for device fabrication includes (1) the introduction of specific dopant elements, (2) the formation of junctions and device structures, (3) the formation of passivating and insulating layers, (4) contacting, and (5) packaging.

Silicon carbide can easily be doped either n or p type by introducing appropriate doping

material during crystal growth for either the sublimation or CVD process. For example, during CVD, p-type SiC can be grown by adding the doping gas, diborane (B_2H_6).⁷

Techniques that have been used successfully to fabricate junctions in SiC include both vapor^{14,15} and liquid phase⁹ epitaxy, diffusion,¹³ and ion implantation¹⁶. Of these three approaches, epitaxial techniques have been the most successful. As in the doping of SiC substrate material, the addition of appropriate material during the epitaxial growth is used to produce the desired doped profile (e.g., a p-n junction). Temperatures required for epitaxial techniques range from 1320°C¹⁴ to 1800°C¹⁷.

Diffusion for doping purposes in SiC requires temperatures in excess of 1800°C. At these temperatures, material stability and control of junction profiles becomes a problem, so this technique is not recommended. Ion implantation may become a useful doping technique in SiC but so far has not been used very much.

Silicon carbide surfaces can be passivated in much the same way as used for silicon. The surface can be thermally oxidized in an atmosphere of wet or dry oxygen at around 1000°C.^{17,18} The oxide layer can also be used as a mask during the fabrication of mesa-type devices, such as SiC bipolar transistors¹⁷ and blue light-emitting diodes⁹. In these processes, windows are created in the oxide using photolithographic techniques; the SiC is then shaped by gaseous etching in a mixture of Cl_2 , O_2 , and Ar at around 1000°C.

Contacting and packaging for 600°C SiC devices will probably be a difficult task. Careful selection of materials will have to be made in order to prevent harmful interdiffusion of elements over long periods of time. Ohmic contacts for both n- and p-type SiC have been developed that are suitable for lower temperatures (<400°C); these contacting materials include gold/tantalum alloys and nickel.¹²

As in the development of silicon and GaAs, SiC device technology will not mature overnight. But, considering the recent advances in crystal growth and the feasibility of practical devices that has been demonstrated, SiC finally appears to be emerging as a useful semiconductor.

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