

Current Status of Silicon Carbide and the III-V Nitrides for High Temperature Devices in Japan and USA

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Purpose: Assess the current status of Japanese and US high temperature electronics research and technology.

Laboratories Visited:

- o Kyoto University in Kyoto on 26 May, 1993.
- o Nichia Chemical Industries, LTD in Anan (close to Tokushima) on 27 May, 1993.
- o Sharp Central Research Laboratory in Nara on 28 May, 1993
- o Meijo University in Nagoya (did not visit the university; instead the panel met Prof. Isamu Akasaki at AFOSR/AOARD office) on 29 May, 1993.
- o National Institute for Research in Inorganic Materials (NIRIM) in Tsukuba on 31 May, 1993.
- o Fujitsu Limited in Kawasaki on 1 June, 1993.

Persons Visited in Japan:

- o Kyoto University in Kyoto on 26 May, 1993.
 - Prof. Hiroyuki Matsumani
 - Mr. Hisanobu Mimoto
- o Nichia Chemical Industries, LTD in Anan (close to Tokushima) on 27 May, 1993.
 - Mr. Shuji Nakamura
- o Sharp Central Research Laboratory in Nara on 28 May, 1993.
 - Dr. Akira Suzuki
 - Dr. Nobuo Hashizume
 - Dr. N. Teraguchi
 - Dr. Haruhisa Takiguchi
- o Meijo University in Nagoya (did not visit the university; instead the panel met Prof. Akasaki at the ANA Hotel in Tokyo and had meeting at AFOSR/AOARD office) on 29 May - Prof. Isamu Akasaki.
- o National Institute for Research in Inorganic Materials (NIRIM) in Tsukuba on 31 May
 - Dr. Koh Era
 - Dr. Osamu Mishima
 - Dr. Seiichiro Matsumoto
- o Fujitsu Limited in Kawasaki on 1 June
 - Dr. Yuji Furumura
 - Mr. Masaki Yamabe
 - Mr. Masafumi Nakaishi
 - Dr. Toshihiro Sugii (affiliated with Fujitsu Laboratories in Atsugi)
- o Special thanks to Dr. G. L. Witt of AFOSR for spearheading the project and to Max Yoder of ONR for many discussions.

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I. Preface

Due to the increasing need for device operation in adverse thermal environments and large power amplification, new materials with high thermal stability must be sought and developed. Recent advances in the science and art of wide bandgap semiconductors have made these semiconductors serious contenders in the field of high temperature electronics and light emitters in the blue and UV part of the optical spectrum. Among the emerging semiconductors are silicon carbide and wide bandgap nitrides. Wide bandgap nitrides and silicon carbide also possess excellent thermal properties, namely the ability to operate at high temperatures and other hostile environments. The same attributes are also essential for high power devices as well. Recent advances, particularly in SiC, have been responsible for the present surge of activity in the newly created sub field of high temperature electronics. In the area of optical emitters, silicon carbide light emitting diodes have even entered the market place with GaN on the wing. With green and red already available, all three primary colors of the visible spectrum are now available for full color displays. In addition, the shorter the wavelength the greater the density of information that can be stored in optical disks.

In this spirit, a committee consisting of Robert Davis, North Carolina State University, Kenichi Nakano, Wright Patterson AFB, and S. Joe Yakura, AFOSR/AOARD, and Hadis Morkoç, University of Illinois was assembled by Dr. Jerry L. Witt of AFOSR to assess the status of high temperature electronics in the USA and Japan via meeting scientists and engineers in Japan having internationally recognized stature in the growth, characterization and device development in silicon carbide and the III-V nitrides of boron, aluminum, gallium and indium. During the period of May 24 and June 2, 1993, members of the committee traveled to various Japanese University and Industrial laboratories. Among the laboratories visited were University of Kyoto, known for its long standing research in SiC; Nichia Chemical Co. in Anan, known for work in GaN; Sharp Laboratories, known for SiC research; National Institute for Research in Inorganic Materials, NIRIM, in Tsukuba City, known for its c-BN research; and Fujitsu-Kawasaki, known for its SiC research. The task force also visited with Professor I. Akasaki, a well known researcher of GaN, of Meijo University in Tokyo. A report inclusive of the SiC and GaN research activities, and to some extent the c-BN effort at NIRIM, was assembled during June 1993 and provided to AFOSR. Where necessary appendices are provided for detailed

description of some programs and other published material deemed beneficial. Moreover, shortly after the submission of this report a critical review of wide gap semiconductors, GaN, SiC and ZnSe for their electronics and optoelectronics applications was prepared, by Morkoç and colleagues, and provided to AFOSR separately, available upon request from Drs. Witt or Morkoç.

II. Synopsis

It is very clear to the panel that a great deal of activity in semiconductors suitable for high temperature electronics is occurring in the US, Japan and to some extent Europe. As this report will detail, the effort in Japan, particularly that in Japanese industry, is primarily geared towards displays as the blue light emitters are made possible by these wide bandgap semiconductors. The interest in Japan for devices operational at elevated temperatures appears to reside only in some of the automobile companies (Toyota and Nissan were noted by Prof. Matsunami) and the aerospace defense group. However, beyond the fact that Toyota has an apparently small effort in the growth of SiC thin films, probably with Si(100) as the primary substrate together with a few SiC wafers purchased from Cree Research in the United States, very little could be learned regarding the exact status of the interest and device accomplishments in these organizations.

In contrast the American effort is geared toward basic material and growth studies, and power and high temperature applications. There is also a definite emphasis in the US on the detector applications, particularly in the UV with applications to negative electron affinity devices spawning. This is not to say that there are no exceptions. Certainly there are. For example, the SiC research effort at Kyoto University, while primarily involved with the growth and materials issues, is soon going to include electronics devices as well. Likewise, the US's Cree Research is a very successful supplier of blue LEDs based on 6H SiC. Other SiC LED suppliers are Siemens, Sanyo, and Sunkei.

The rapidly developing digital audio and video information technology in Japan is a very strong incentive for almost all the major electronics companies to be in the thick of blue emitter activity. Naturally blue LEDs, along with the already existing green and red LEDs, complete the missing link for full color all semiconductor displays. The market for devices for displays is enormous as new uses for displays are generated on a daily basis for home, office, and factory use. Japan, particularly, is infatuated with displays of all kinds. Also under development are blue lasers with short wavelengths, half that of red lasers, that can double the density of minidisk memories. (We must mention that LEDs cannot fill this function as coherent radiation is needed.) Coupled with signal

compressing, this enables storage of several hours of high definition TV programming in a minidisk. In addition, diskettes with a several Gbit memory capability can be obtained with ease. The commercial market prospects of this technology are simply enormous, a potent lure for the Japanese industry.

In the US, the attractiveness of high temperature and high power applications of the wide bandgap semiconductors cannot be overstated. Power amplifiers based on wide gap semiconductors can replace bulky traditional vacuum device-based amplifiers in microwave transmission systems for communications and entertainment. Similarly, the potential replacement of magnetron tubes in microwave ovens, as contemplated by Sharp of Japan, is an intriguing prospect. The automotive industry is also a likely area for large scale use of electronics based on wide bandgap materials as they can be placed in engine blocks and other regions that get hot for a better and reliable control of various functions. The panel heard repeatedly that the Japanese auto industry has programs in this area, but it was not in a position to acquire information directly. Buoyant electronics based on wide bandgap electronics should also find applications in oil drilling and exploration.

Applications to UV emitters and detectors are alluring, as space-to-earth communication, uplink and downlink, can be conducted without paying the typical penalty for absorption due to water vapor. Getting sunburned on a cloudy day is a testament to this concept. With UV emitters and detectors, more precise object definition is possible owing to the short wavelengths involved. Again, with UV emitters and detectors combustion processes can be monitored and controlled for more efficient use of fuel in these environmentally sensitive times. With the recent reports that AlN surface may be a negative electron affinity surface, a plethora of applications from cold and mono-energetic cathodes, that would enhance the resolution of electron microscopes of all types, to vacuum electronics and flat panel displays with low energy deflection. An additional attribute of low energy and mono-energetic electron beams is that the voltage necessary for deflection and brightness control is very small, as little as $1/10^4$ of the conventional hot filaments, thus making it an ideal candidate for flat panel displays. These represent some of the driving forces for programs with applications to both military and civilian systems that are in place in the US.

The wide bandgap nature of these semiconductors also implies that the minority carrier generation rate is so small that permanent charge retention in MOS-like devices is possible, obviating the need for replenishing stored information. Precisely, this replenishing step is chiefly responsible for the limitation of the longevity of the present memory circuits based on the Si flash memory technology. Given the heavy use of computers in technologically advanced countries such as the USA, power consumption is also a critical concern. In automotive and aerospace technology a pressing need exists for electronic devices operating under very hostile environments and high temperatures. For example, a sizable weight load of a given aircraft is due to the hydraulic and mechanical systems for controls. Hydraulic systems also represent fire hazards. Replacing these with on spot electronics, and actuators and sensors, can save a tremendous load in aircraft. Moreover, the operation at high temperatures would reduce the need for heat removal, obviating bulky radiators in satellites.

The problems faced by the scientific community in SiC can be divided into engineering and intrinsic categories. On the engineering side we have size and cost of the wafers, polytype control, ion implantation, and high quality dielectrics and dielectric-semiconductor interfaces. Among the intrinsic properties of 6H SiC that present problems of non-permeable nature are small electron and hole mobilities, large acceptor ionization energies and resultant large ohmic contact resistances. These problems can be mitigated somewhat by using 3C SiC. The bulk of the 3C SiC research has been on films grown on Si substrates because of the obvious advantages ascribed to Si. However, the faceting problem and other crystalline defects have reduced, if not completely eliminated, the attractiveness of this approach. Bulk growth of 3C holds a glimmer of hope in that the lattice matched epitaxial layers can be grown without the deleterious effects of mismatched layers mentioned above.

The reason behind these polytypes, particularly the 3C, is that it has very attractive electrical properties. Although there is no evidence at the moment indicating that the deep impurity behavior can be assuaged with 3C, enhanced electrical properties (albeit lattice mismatched on Si) have already resulted in transconductances much larger than those available in homo-epitaxy 6H SiC. Researchers at Sharp have in fact been successful in growing 3C bulk SiC

motivated by the reasons discussed above. The rapidly expanding Japanese market for such displays inspired this particular effort's shift in emphasis to blue LEDs available with the larger bandgap 6H SiC. At the moment there are indications that bulk 4H SiC substrates can be prepared. These developments must be watched very carefully so that the opportunities presented by many different types of this material can be exploited in a timely manner. High resistivity substrates, which are not yet available, should assist FETs or other types of devices requiring electrical isolation.

Some of the problems mentioned above, such as the deep impurity levels and low electron mobilities in SiC, can be avoided by going to a different material system altogether, direct bandgap GaN. Direct bandgap GaN is also made more attractive by the availability of larger bandgap AlGaIn. Though there has been little effort, already the GaN MESFET's and MODFET's exhibit excellent transconductances. With the recent results indicating that the improved GaN can be prepared on 6H SiC, devices with much better performance should soon follow. Ohmic contacts, nemesis of any wide bandgap semiconductor, seem to be less problematic in GaN with lower specific resistivities having been achieved already, perhaps as much as an order of magnitude lower than those available in the SiC system. Unlike SiC, which enjoys the existence of a lattice matched substrate, GaN is grown on sapphire and recently, on SiC. If and when GaN substrates become available, marked improvements in epitaxial quality are to be expected. Already a group at the Polish Academy of Sciences, High Pressure Research Institute, is growing GaN in the bulk form. This effort consists of a graduate student who reacts a Ga melt with nitrogen at 1500°C and under 30 kbar pressure. So far only 2 mm size pellets have been grown. Simply stated, there is much room for improvement.

At the time that this report was prepared GaN LEDs exhibited the maximum brightness and long lifetimes of SiC and ZnSe based LEDs. This is despite the fact that the layers were grown on sapphire substrates, c axis, with considerable lattice and thermal mismatch. Using 6H SiC substrates has been shown to result in better GaN films, but the high cost of the substrates is an obstacle to widespread use. It is left to the imagination of the reader to project the performance of devices based on GaN that are grown on GaN substrates, when and if they become available, or at the very least grown on SiC substrates when

they become cost effective. Since the emitters for minidisks require coherent laser sources, the need for developing GaN based coherent sources becomes evident as the reliability of even the ZnSe based LEDs does not measure up to that offered by GaN. LEDs based on the GaN/InGaIn fabricated at Nichia are so bright that one can seriously begin considering coherent sources in the AlGaIn/GaN/InGaIn system that has the required excellent wave guiding properties.

Finally we must comment on other nitrides with even larger bandgaps, namely c-BN. The hardness and thermal conductivity of this material is second only to diamond. Its hardness and heat conductivity make this material an ideal candidate for any application for which natural diamond is suitable. This class of applications includes coating tools and passivating circuits or any other object. To a large extent, both the American and Japanese efforts appear to have this in mind. In addition to applications cited above, the effort at the National Institute for Research in Inorganic Materials in Tsukuba Science City is exploring the potential of this material for UV emitters. So far, p/n junction LED type emitters have been achieved. This effort has been detailed later in this report.

Due to lack of time and/or access the panel was unable to assess the level of high temperature electronics research in the Japanese automotive industry. The panel was repeatedly told by others that there may be programs for carburization and other applications for which SiC is contemplated and/or researched. The panel was made aware of a workshop where the high temperature electronics aspects of wide gap semiconductors are discussed on an annual basis. A copy of the proceedings of this workshop was made available by Prof. Yoshida of the University of Tokyo to Dr. S. J. Yakura of the panel. To some extent, the same lack of adequate access that the panel experienced is true for American companies pursuing high temperature electronics. This report therefore covers only those activities that have been made public. We can generally conclude that the display applications of wide bandgap materials, and high power and materials research of the wide band gap materials are prevalent in Japan and the United States, respectively.

III. Japanese Side

III a. Silicon Carbide

In certain close-packed structures such as SiC, there exists a special one-dimensional type polymorphism called polytypism. Polytypes are alike in the two dimensions of the close-packed planes but differ in the stacking sequence in the dimension perpendicular to these planes. In SiC, the stacking sequence of the close-packed planes of covalently bonded tetrahedra (either SiC₄ or CSi₄) can be described by the ABC notation. If the pure ABC stacking is repetitive, one obtains the zincblende structure. This is the only cubic SiC polytype and is referred to as 3C or β -SiC, where the 3 refers to the number of Si-C bilayers necessary to produce the periodic sequence (unit cell). The purely hexagonal (ABAB) sequence is also found in SiC. Furthermore, both occur in more complex, intermixed forms yielding a wider range of ordered, larger period, stacked hexagonal, or rhombohedral structures of which 6H is the most common. In addition, the 4H form has recently begun to receive some attention. All of these non-cubic structures are known collectively as α -SiC.

The devices produced from this material in both the 3C and the 6H polytypes have a proven and documented record of continuous operation at elevated temperatures with characteristics essentially those obtained at room temperature.

III a. i. Visit to Kyoto University

May, 26, 1993

- Prof. Hiroyuki Matsunami
- Prof. Hisanobu Kimoto

Professor Matsunami has been the director of one of the leading Japanese university laboratories for SiC electronics research for some 20 years. He is considered one of the prominent SiC experts in the world. Both bulk growth and epitaxial growth have been and are being investigated at Kyoto. Substrate cutting, lapping and polishing techniques have been developed as well as growth technology by CVD and more recently by MBE. In the past two decades, Matsunami has trained numerous graduate students. In fact, in 1982 Professor Robert Davis spent several weeks in Matsunami's laboratory observing SiC

research and has maintained good contact with Professor Matsunami by frequent visits and correspondence. During the mid-seventies Professor Matsunami spent a sabbatical year at North Carolina State University, where he worked with the present chancellor of that university. One of Professor Matsunami's students, Dr. A. Suzuki, is continuing SiC research at Sharp Corporation. Professor Matsunami now has a collaborator, Mr. Hisanobu Kimoto, who graduated from Kyoto University in 1987 and worked at Sumitomo for 2 years before returning to the University. Currently Mr. Kimoto is working on 6H SiC which involves CVD growth and growth mechanisms, and device fabrication and characterization. One student is also conducting some of the same studies with 3C SiC.

Following introductory remarks and a response to Prof. Matsunami's inquiry regarding the purpose of the panel and its background, discussion started with the debate of bulk SiC growth and properties. The panel members and the Kyoto team observed the fact that a significant developments in the evolution of SiC-based electronics has been the transfer to commercial practice of a feasible, albeit expensive, sublimation method of producing single crystal boules of the 6H polytype of this material. At this writing, the materials produced by this procedure are not perfect; they contain moderate concentrations of line and planar defects and larger micropipes. However, sufficiently good area is available for fabrication of devices and probably simple integrated circuits. As such, the development of boule growth techniques is currently a significant component of the SiC effort in Japan.

Boule growth research efforts at Westinghouse and Cree Research, Inc. are concerned with both eliminating the micropipes and scaling up the boule diameter to two inches. Micropipes and scaling up the size of the substrate material were perceived to be important problems to tackle. Micropipes have hexagonal cross sections and may traverse the entire length of the boule. Micropipes always start at the seed surface and have hexagonal cross sections. The reasons for their occurrence are currently unknown, but the Case Western group is actively looking into the micropipe problem. Seeking diversification, Nippon Steel is presently growing one-inch 6H-SiC boules from which wafers are sliced, processed, and sold. Apparently boules of the 4H polytype as well have been produced by this company. The Nissan effort began some 5 years ago

at the Yokohama First Research Center. In addition, there are apparently many other small companies who are patterning their efforts after Cree's. At this writing the bulk crystal research and quality in Japan appeared to be lagging behind the Cree Research and Westinghouse achievements.

To summarize other laboratories' efforts: the Sharp Corporation has a strong 6H boules effort similar to that by Cree Research, Inc., as discussed below. Sanyo Corporation is believed to have a similar but smaller effort, but no details could be learned. However, Sanyo is conducting major research on SiC for LEDs.

Because commercial substrates are expensive, the Kyoto group has a supporting effort in boules growth, via sublimation, primarily of the 6H polytype. The growth is by sublimation within a thermal gradient, 20°C/cm, and occurs on a seed held at 2100°C with a source temperature of 2100-2400 °C. The seed for the growth was a thin 6H-SiC (01 $\bar{1}$ 4) which was polytype-converted from 3C-SiC(001). The resultant growth rate is about 0.1-6 mm/h. The boules lengths and diameters are generally 12 mm and up to 25 mm, respectively, after 6 hrs of growth. Low temperature epitaxial growth was attempted by GSMBE (Gas source molecular beam epitaxy) on substrates from the aforementioned boules sliced orthogonal to the (01 $\bar{1}$ 4) direction. Since the growth temperature is relatively low, the grown layer is of the 3C-SiC polytype. The crystal direction of the 3C-SiC is (001) and the crystal is void of double positioning boundaries (DPB). Usually, the DPBs appear when 3C-SiC is grown on the basal plane of 6H-SiC(0001). However, it is possible that a significant portion of the other types of defects such as twins and stacking faults which are commonly found in the 3C material were also manifest in the 6H (11 $\bar{1}$ 4) material.

As is the case with any semiconductor technology, the SiC boules are cut or sliced. While the surface preparation and polishing can be improved, the present quality is almost as good as that of GaAs. The Kyoto surface polishing process involves a sequence involving SiC powder and diamond paste. No chemical polishing techniques have yet been developed in Japan. Characterization of the wafer has employed optical microscopy to determine etch pit densities (EPD) and the longitudinal optical mode of Fourier transform infrared spectroscopy (FTIR) in the reflection mode to determine the nature of the wafer surface. The

results indicate an EPD of $10^4 - 10^5/cm^2$. The width of the LO phonon at about 980 cm^{-1} is used as a figure of merit for the quality of the surface preparation.

Sharp Corporation has been successful in growing cubic 3C boules with diameters of about 10 mm at a growth rate of 0.7 mm per hour. Sharp grows the 3C SiC on Si (111) and uses the SiC (111) as seed on which to grow 6H SiC (0001). The quality of the 6H grown in this manner is comparable to that grown with a 6H seed. They have also produced 3C boules using 3C powder prepared for Sumitomo as the starting source material. The source and seed temperatures are 2200°C, and about 1700°C, respectively. If B, Al, Be - p type dopants - are introduced in high concentrations during boules growth, the formation of the 4H polytype may occur.

In Japan, smaller companies are beginning to pursue the bulk growth, and are planning to use the sublimation method, at least initially. MITI does not support them, tending instead to support the large companies. Universities, in contrast, obtain their funding from the Ministry of Education. It is the small companies that are interested in new ideas such as growth from the melt. At the moment, price is the main obstacle. Once the price is reduced issues such as cutting and polishing will have to be perfected.

In the USA, Cree Research has increased its production capability and is also working on larger area wafers. Westinghouse will not sell its substrates, and has both internal and Air Force /Naval Weapons Center support. Westinghouse is also looking into 3 inch substrates, along with lowering the process cost as is the case for Cree Research.

Sanyo substrates are intentionally p-type doped for use with n-type devices as high resistivity substrates are not available. Westinghouse samples are unintentionally doped and possess 10^5 ohm-cm resistivity, but are not yet semi-insulating. Chemical cleaning in hot KOH and other types of alkaline solutions should be explored. Etch pit densities are still around $10^4 - 10^5\text{ cm}^{-2}$. The dislocations are associated with twins and stacking faults.

Chemical vapor deposition (CVD) and gas-source molecular beam epitaxy (MBE) are being employed by Matsunami to grow SiC films. The former

technique is employed in the deposition of SiC films; the latter technique is rarely used for this purpose. It is probably fair to state that no other group in Japan is currently using MBE to deposit SiC films. Both low pressure and one atmosphere CVD are being employed in Japan for SiC thin film growth. The former is used where deposition uniformity over larger area substrates such as Si(100) is desired. However, since the use of one inch SiC wafers is growing in importance, deposition at one atmosphere is certainly adequate at this time. Prof. Matsunami has a well equipped laboratory, with both MBE and CVD deposition techniques available, as well as sufficient students and research associates to conduct his SiC efforts. Though he has a boule growth effort as noted above, he continues to use Si substrates because of their low cost, availability and excellent surface and internal character.

Matsunami continues to use "step controlled epitaxy" whereby particular off-axis substrate conditions are employed to produce selected surface terrace distances (i.e., distances between crystallographic steps on the surface) so as to eliminate either inversion domain boundaries in β -SiC(100) films deposited on Si(100) substrates or double positioning boundaries in β -SiC(100) deposited on-axis α -SiC(0001) wafers. In MBE the growth temperatures are around 1050 to 1100 °C and β (3C)-SiC is produced. There are DPBs both on on-axis and off-axis substrates. In CVD, which is closer to equilibrium growth, 6H-SiC is usually obtained on vicinal 6H-substrates.

The quality of the epilayers is better than that of the bulk. EPD counts in approximately 1 μm thick epitaxial layers are about 10^4 cm^{-2} , whereas the EPDs in substrates are about $10^5 - 10^8 \text{ cm}^{-2}$. Prof. Matsunami reported to us that in his thin films, photoluminescence studies revealed excitons bound to N. By contrast in the thicker (e.g., 30 μm) films, free excitons were observed, indicating that thicker films, especially on Si(100), were of higher quality. In 6H SiC depending on which C gets replaced with N, the N donor can have a different binding energy. Professor J. Choyke of the University of Pittsburgh and others have characterized the N donors occupying two cubic and one hexagonal sites in SiC.

Boron doping in α (6H)-SiC introduces a deep level at approximately 670 meV above the valence band and results in yellow emission. As for the films

with H_2 , Prof. Davis grows films with as high as 6% H_2 at a growth temperature of about 1200°C. The problem has not yet been well-studied.

Acceptor-type doping with Al is a recognized problem in SiC, though recently, considerable advances have been made in the US on this point. The Al is somewhat difficult to incorporate into the SiC lattice, and the electronic defects (holes) created by the addition of this species are rather tightly bound. As such high ($>10^{19} \text{ cm}^{-3}$) carrier concentrations are difficult to achieve except during high temperature growth. The Kyoto group has been successful in obtaining p-type carrier concentrations of $10^{19} - 10^{20} \text{ cm}^{-3}$ by incorporating Al using a CVD growth temperature of 1500°C and the Si face of SiC. In contrast the growth on the C face allowed hole concentrations of $10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$. Trimethylaluminum (TMA) is the commonly used dopant source for Al doping. The lowest doping obtained is about $10^{16} - 10^{17} \text{ cm}^{-3}$. For n type doping 10^{20} cm^{-3} is possible. When higher doping levels are attempted SiN forms and the crystal becomes polycrystalline.

Mobility: Electron mobility of the n-type SiC films having the lowest carrier concentration ($2 \times 10^{15} \text{ cm}^{-3}$) grown in Matsunami's laboratories were approximately 300 - 400 cm^2/Vs . Preliminary results indicate the n type background observed is attributable to nitrogen in the source material. As is well known, N forms a deep level in Si, but is a shallow donor in SiC. Thus, gas suppliers having lacked the feedback from the Si technology need to closely work with SiC researchers to reduce the nitrogen content of the source material. In addition to the possible role of nitrogen, Prof. Choyke reported transition metals to be present, such as Ti which may in part be responsible for these observation. He indicated that this mobility could be increased by interface modification, presumably by creating a 2-dimensional electron gas interface. The Erlangen group measured 370 cm^2/Vs in n type layers grown at Siemens. Hole mobilities are around 30-50 cm^2/Vs for low concentrations and about 10 cm^2/Vs for high concentrations of Al dopant.

In cubic β (3C)-SiC, the electron mobility μ is about 1000 cm^2/Vs . When grown on Si substrates the mobility is about 750 cm^2/Vs , which was obtained at ETL, whereas at Kyoto the mobility is about 550 cm^2/Vs . Prof. Ferry's early Monte Carlo calculations indicated that the saturation electron velocity in β SiC

is larger than that in α SiC. However, his new calculations indicate both to be about the same.

Devices: Matsunami believes that the major problems facing SiC devices, especially those which would be employed in high temperature applications, are those involving packaging. Encapsulation, bonding to insulators and interconnects are examples of problems in this arena. Other problems include the achievement of low resistivity ohmic contacts and the bonding of all contacts to the SiC. He is not concerned with the operation of any SiC devices at elevated temperatures.

Device work in Japan is concentrated on display applications, i.e. LEDs, although Fujitsu laboratories explore HBTs based on the SiC wide emitters. At NRL, G. Kelner obtained JFETs with transconductances of about 20 mS/mm in β SiC. A transconductance of 30 mS/mm was obtained in MESFETs at Westinghouse on 6H SiC with sub-micron gate lengths. Among the problems associated with FETs is the lack of high doping in source and drain regions. One can ion implant in the source and drain region for an increased doping levels. The group at Purdue has already conducted ion implantation work with annealing temperatures in the vicinity of 1700°C. One problem with the source resistance is the fact that the donor level is deep. Regardless of all the above, the mobility degradation with temperature is a severe problem. As for the MOSFETs, the SiO₂/Si face of the SiC interface must be improved to increase the surface mobility.

Wet oxide used for DRAM's at Cree is purported to be better than dry oxide. The Purdue results too, appear to support this, but one sample each for wet and dry oxidation was investigated and conditions other than the oxidation process were not controlled. Researchers at Kyoto will initially pursue devices such as p-n junction and Schottky diodes. Available fabrication facilities will determine which type of FET, JFET or MOSFET they will investigate, recognizing that JFETs will be easier to fabricate, although MOSFET is more attractive.

As for high temperature devices, there is a consensus that some sort of an encapsulation is needed. If integrated circuits are contemplated, one needs insulators for incorporating interconnects. Obviously, ohmic contacts with low

resistivities are essential. At the moment the best ohmic contacts have high 10^{-4} Ωcm^2 and low 10^{-3} Ωcm^2 contact resistivities for n and p type materials, respectively. Schemes must be developed to lower these resistivities. A problem related to integration which must be addressed is bonding, both wafer and wire bonding. Moreover, packaging issues are of critical importance.

Applications of SiC range from high temperature electronics, high power, and blue LEDs.

In Japan the automobile companies are interested in SiC for high power-high current operation. Electric generation companies (electric power utilities) have invested in SiC as a potential technology. Some of the Japanese companies, such as Fuji Electric, have in fact put money into the International Center for Power Electronics at NCSU under Prof. Jayant Baliga. There are also Swedish companies investing in the same center. Toyota is interested in applying SiC technology to carburation-control electronics in engine blocks, as well as brake pad loss measurements. Toyota also does research in SiC/Si heteroepitaxy, (they have a SiC laboratory). Toyota Central Research has recently opted for homoepitaxy. Nissan has an affinity toward the heteroepitaxy approach, because of the abundance of Si substrates and its familiarity with Si technology.

In Europe several consortia are in action. Among them are:

Thomson CSF	Inter-European consortium
Tych	
Linköping	Sweden
Eric Jansén	
Fraunhofer Institute	German work on ohmic contacts
	(Erlangen Institute, G. Pensl
	Siemens is tentative
	Daimler-Benz is the big player)

In Sweden many applications of SiC technology are being pursued. Among them are SiC detectors for measuring the decay of wheat to be marketed. Wheat

produces alcohol upon decay and the onset of this process can be detected with SiC devices.

In conclusion, Prof. Matsunami seemed very open to us. At Kyoto University work is being performed mostly on epilayer of SiC (substrate growth is performed only because the cost of the substrate from CREB is high). Growth equipment (CVD and MBE) was observed during a tour of the KU. Mr. Kimoto (worked on diamond devices at Sumitomo Electric before returning to KU) is going to start an electronic device effort such as that based on JFETs. The impression the panel formed about the application of SiC devices in Japan is that the effort on displays outweigh the other type of devices. Cree Research seems to be supplying most of the substrates to Japan. Nippon Steel is growing 1" wafers, whereas Cree Research and Westinghouse are growing 2" wafers and looking at 3" and 4" wafers. In fact Cree Research began offering 1 3/16 " substrates to potential customers. There is more emphasis on epilayer growth in Japan. We did not obtain detailed information about what Toyota and Nissan are doing with SiC, nor information on any of the electric power companies using SiC devices. In my opinion there are more electronic device developments (non LED) performed in the US by GE, Westinghouse and Cree than in Japan.

III a. ii. Visit to Sharp Central Research Laboratory
5/28/93

Persons visited:

Dr. Akira Suzuki
Dr. Nobuo Hashizume
Dr. N. Teraguchi
Dr. Haruhisa Takiguchi

The visit with Dr. A. Suzuki and his colleagues was important because it gave us valuable insights regarding the research directions and scientific concerns of one of the leading electronics corporations in Japan regarding SiC for electronic applications. Sharp Corporation is in the multimedia business and displays represent a significant business interest in both stand-alone configurations and within the consumer electronics items which they produce. Blue emitters, be it SiC light emitting diodes (LEDs) or any other technology, are apparently their

only device concern at this time. Compact devices, new video type magneto-optical disks for memory are among the technologies pursued which justify the research based on SiC and ZnSe. The availability of blue lasers, would allow a minimum of 2 hours of video program to be stored in a 13 mm diameter disk. This potential alone is strong motivation for developing blue laser diodes. They are not necessarily wedded to a given materials system. If GaN advances to the point of providing lasers with better performance than ZnSe, then it would be the device of choice. Displays based on liquid crystal (LC) and the electric field (EL) materials are of interest with an emphasis on research in new materials and new modes for LCD operation. The brochure details other areas of interest. Sharp has also explored the applications of SiC to blue LEDs—in fact we saw a full color display at the exhibition hall with SiC providing the blue emitter. The LED was mounted in an inverted fashion with a reflector mirror bending the beam 180° for normal emission. Sharp has also explored (it seemed like a past interest) SiC for high temperature and/or high power applications. Personal cellular communication will most likely employ GaAs/AlGaAs Power HBTs operating at 1-1.5 GHz.

Also under development are organic photo materials for copying machines to replace Se or a-Si, because the organic materials are inexpensive and simple to make. One simply dips the cylinder tube in the liquid and pulls it out to obtain the film. The lifetime is about 10,000 hours, which is respectable. The III-V laser diodes are considered classical but no less important. Sharp needs low power, low jitter (noise) small lasers. These requirements would be operative on potential GaN lasers as well.

Presently laser diodes for compact disk (CD) applications operate at 50-60 mA, whereas Sharp's lasers operate at 30 mA. The power requirement needs to be decreased more by using, for example, V-groove stripe lasers. The main concerns with laser diodes are reduced power, and low noise level. Self-pulsating laser diodes are less noisy.

SiC applications at Sharp:

A long range application of SiC that the management, motivated by the systems people, would like to see is the replacement of magnetrons with SiC oscillators/FETs in microwave ovens. Not seriously considered and perhaps even farfetched at the moment, power FETs based on SiC are popular with the systems people. A few years are needed to assess the potential of SiC in microwave ovens. The challenge is formidable because magnetrons are inexpensive, several tens of dollars, very rugged, and reliable. Obviously the SiC devices must be small and less expensive if they are to be used in this application. The efficiency for magnetrons is about 70-80%, and costs about ¥ 1000 for a 60-80 Watt version. The overall efficiency for a microwave oven is 40-50%. SiC substrates are expensive, which makes SiC on Si attractively cost-effective, but the quality is insufficient. Displays and microwave ovens comprise the only interests on Sharp's part. The most immediate application of SiC for Sharp is blue emitting LEDs, but recent advances in II-VI's have taken away the edge from SiC as the present emphasis of Suzuki appeared to be ZnSe. As will be discussed later, Drs. Suzuki and Takiguchi, department managers, are interested in observing GaN up close. Significant concern was again expressed about the cost of substrates and the necessity of 2 inch wafers. Size and cost effectiveness of SiC on Si was used as a paradigm.

Some automobile companies, such as Toyota (Central Research) and Nissan may be working on SiC, but the effort is small, 2-3 people. Teraguchi indicated that Nissan has a collaboration with some group(s) which is included in the list Dr. Teraguchi prepared for Morkoç while at Illinois. Dr. Hashizume heard from a source that Nippon Steel has a SiC research effort. Nippon Steel is producing SiC wafers, a point that the panel heard from Prof. Matsunami also, with no interest in devices. Fuji Electric is carrying out SiC research for power generator sensor applications. Toyota Central Research has a limited effort on SiC devices. Nissan appears to be collaborating with one company on SiC.

Westinghouse has prepared 2" substrates as outlined in a paper discussing that effort published in *J. Crystal Growth*. At Sharp, particularly in the past three years, II-VI materials have gained more interest for display and memory applications; however, Suzuki astutely seemed to recognize the shortcomings of the II-VI's and is interested in nitrides. He and his immediate boss repeatedly talked about Nakamura's results and wanted to know our views on the nitrides.

The problems with II-VI's were summarized in the context of the lack of flux control, particular to solid source MBE (MOCVD is purported to be better in that regard by Professor Fujita at the University of Tokyo): low growth temperatures coupled with instabilities; lack of p type doping as the S and Mg concentrations are increased; and lack of facet stability due to problems such as the formation of MgO at the facets. Sharp has a laboratory in England where GaN research is being carried out (Dr. Geoff Duggan is one of the scientists on the project). In fact Teraguchi is hoping to be sent to England to work there.

There were some discussions of the nitrides because both Suzuki and his immediate supervisor showed considerable interest. They justified their curiosity and interest in nitrides because of the problems with ZnSe as will be outlined below and the successful results reported independently by Mr. Nakamura and Prof. Akasaki. We should mention here that the problems associated with ZnSe have been known for decades. Many now believe that the remaining problems, outlined below, are engineering problems, implying that they will definitely be solved with the expenditure of sufficient time and effort. According to A. Suzuki, Akasaki announced 100-200 mCd at 20 mA in GaN diodes. The efficiencies of blue LEDs based on nitrides and SiC are:

0.01% for SiC

0.1% for GaN are the kinds of figures available.

The II-VI ohmic contacts are problematic as outlined below:

1. p type doping at best low to mid 10^{18} cm^{-3} are achievable. This is with very low S and Mg concentrations. When S and Mg concentrations are increased to about 30%, needed for lattice matched quaternary cladding layers, the p doping problem becomes a major problem.

2. Stability of the II-VI device structure was discussed in some detail. For example, the growth temperature of ZnSe is about 250 °C. Consequently, the contacts must be formed below 250 °C, but they need to be alloyed at 300 °C. Morkoç is not necessarily concerned about the growth temperature being below the annealing temperature as surface phase diagrams and bulk phase diagrams are two different entities. In addition, there are other problems which hinder, if not bring into question, the long term prospects for ZnSe based blue emitters.

3. Control of the composition. Zn and Se have a sticking coefficient of 1 at 250 °C. In contrast, Mg and S have a sticking coefficient of about 0.1.

MOCVD is better in this sense. Professor Fujita at the University of Tokyo, conducts research using MBE and MOCVD and he feels that MOCVD is better in terms of the compositional control.

4. Sulfur % in lattice matched quaternary is about 30% and with increased S comes the problem that the maximum p type doping is reduced.

5. Magnesium % in lattice matched quaternary is about 30% as well. As Mg and S concentrations are increased the N activation as a p type dopant becomes less effective and the series resistance goes up.

Problems associated with SiC:

Dr. Suzuki also expressed several concerns regarding the further development of SiC devices. He voiced Matsunami's concern that high temperature ion implantation and activation of p-type dopants, e.g., Al, were difficult and represented a major problem to device development.

a) Ion implantation, especially p type doping and activation present formidable obstacles.

b) All the p-type dopants thus far investigated, namely Al, B, Ga and Sc have deep acceptor levels and are difficult to activate unless post-implantation high temperature annealing is also conducted. The deep acceptor energy levels also create a situation in which the concentration of holes changes rather dramatically with temperature. This is also somewhat true for n type layers as well. The Al acceptor is deep with an activation energy of 0.2-0.3 eV. Nitrogen (n type) donors are not so shallow either. For N, 3 different crystallographic sites and thus 3 possible energy levels may be possible, see Pensl and Choyke, *Physica B*, Vol. 185, p. 264, 1993 for a thorough review of N donor and Al acceptor levels in SiC.

c) Dr. Suzuki appeared to espouse the opinion that the MESFET is not a promising device for high temperature applications. Not everyone would agree with this comment if the temperature range of use is 350°C or less. This comment is valid for truly high temperature ($T > 500^\circ\text{C}$) applications over an extended period of use where metals form rectifying contacts. The result is extensive chemical reactions between metals and SiC to form carbides of the metal. Likewise the contacts intended for rectification may form silicides.

Another problem is that the surface Fermi level is pinned; thus the barrier height between the metal contact and the SiC remain virtually the same regardless of the work function of the metal employed (assuming it is high). The Schottky barrier height measured is $\phi_b \geq 1$ eV for Au or Pt on SiC. Pseudomorphic Ti Schottky barriers with low leakage and an ideality factor of $\eta = 1.01 - 1.04$ have already been obtained by Bob Davis using the metals Ti, Pt, Hf, and Co ($\phi_b \approx 0.9$ eV). For Ti, ϕ_b should be around 1.2 eV or higher. For FET applications β SiC on Si is attractive but will not be used because of the much inferior material quality. The main problem is the 5 independent slip systems which allow twinning and faulting along (111) $\langle 110 \rangle$. In contrast, in 6-H SiC, there is only one type of slip direction. Bulk β SiC material, however, may be very attractive because it avoids the heteroepitaxy problems. In fact Dr. Suzuki and company obtained β SiC bulk material, on which one can already grow β SiC epitaxial layers for devices. Even ion implanted layers can be considered too.

d) Another problem with which Dr. Suzuki was concerned was the need for additional studies in the chemistry and technology of dry etching of SiC including the use of ECR to produce anisotropic microstructures in the (0001) surface. Some minuscule dry etching activity exists with RIE with CF_4 and SF_6 chemistry.

e) The attainment of a complete understanding of the residual donor species which produce the background impurity in all SiC wafers and films is another concern of Dr. Suzuki. The determination of low resistivity ohmic contacts and their bonding to the SiC surface and their soldering to metal lead wires is also of some concern.

f) Thermal oxidation is another problem that must be explored. There are some reports of dry and wet oxidation of the Si face of SiC, but a more fundamental understanding is a must before MOS devices can reliably be fabricated. SiC has a large band gap so the minority carrier generation rate, particularly at room temperature, is very low. This requires the CV measurements to be performed at high temperatures, such as 300°C. Only then can one obtain equilibrium and meaningful capacitance values.

Dr. Suzuki iterated the well known fact that inversion SiC MOSFET have not functioned well. The background in SiC is n type and the level is 10^{15} cm^{-3} . This may be due to residual N impurity atoms or some other defects. The mobilities at the SiC/SiO₂ interface are $\leq 100 \text{ cm}^2/\text{Vs}$ in a 3C, β SiC MOSFET. The bulk Hall

mobility range in 3C SiC is $\mu_{\text{bulk}} = 500\text{-}200 \text{ cm}^2/\text{Vs}$. It is quite possible that the background doping level can be reduced to 10^{14} cm^{-3} which is sufficient for devices. Purity of the gases used may be responsible for the somewhat large background doping. Nitrogen used for n type doping too must be purified.

In short, SiC LEDs comprise Sharp Corporation's near-term priorities. Sharp is contemplating initiating a research in GaN for blue emitters and seems to have put a hold on high temperature and power device development. Dr. Suzuki was very interested in obtaining information on GaN development as Sharp feels that the urgency for power and high temperature devices is not yet there. Sharp is a consumer oriented company that is unlikely to put its effort into development until there is a need or product in sight. The issue of the high cost of 6H SiC substrates was raised both at Kyoto and Sharp. This and the capital already invested in Si technology, in addition to better electrical properties of 3C SiC, are the driving forces behind the hetero-epitaxy of SiC on Si. The near-term availability of such wafers from Nippon Steel and possibly Sharp corporation (unless all are used for internal consumption) may reduce this problem to some degree, and drive down the cost of Cree wafers to competitive levels. However, the cost will still far exceed that of Si and remain beyond the reach of most university investigators. This will slow the progress in SiC research and induce some reluctance to enlarge the scale of one's efforts until the SiC wafers become available at a much lower cost.

For the time being, the blue LED whether from SiC or some other material has become a viable product of international commerce which is important to several of their commercial lines involving displays. Sharp has made the prototype blue LEDs using their own SiC wafers as a base. Because of the importance of this device to their business, they will concentrate on this product in the near term.

III a. iii. Visit to Fujitsu, Kawasaki,
June 1, 1993
Persons visited:
Dr. Yuji Furumura

Mr. Masaki Yamabe
Mr. Masafumi Nakaishi
Dr. Toshihiro Sugii

Presentations by:

Dr. Yuji Furumura:	SiC growth by LPCVD
Mr. Masaki Yamabe:	X-ray membrane, processing
Dr. Toshihiro Sugii,	Atsugi SiC Emitter in Si HBTs
Dr. Morkoç	GaN Research
Mr. M. Nakaishi	Observer/Participant, processing/ etching

Dr. Furumura began his presentation by stating that he was at one time interested in electronics applications of SiC, which explains his early involvement with 3C SiC on Si. His most recent interest is the high volume growth by low pressure CVD of SiC layers on Si substrates for x-ray masks. LPCVD has been chosen to achieve multi-wafer growth at reduced cost. The orientations attempted are (100) and (111), the latter working better for him in terms of the quality of the SiC films. Dichlorosilane is used for the Si source at a pressure of 200 Pa and a substrate temperature of 1000 °C is used for growth. On (111) surface he saw the typical stacking faults and on (100) substrates there were regions of hillocks. Backed by experiments with bacteria-contaminated water, Dr. Furumura argues that the no growth regions are caused by bacteria. In fact, experiments run with water-treated wafers indicated the presence of C, H, and P. With C present, for example, reaction between Si and C leads to SiC formation, a bad layer, which prevents further growth.

The solution was an obvious one, UV exposure to kill the bacteria. In experiments involving the deliberate addition of bacteria, and UV ozone treatment to remove the bacterial contamination, voids in the grown SiC or Si epitaxial films were prevented. SIMS analyses were also performed confirming the above conclusions.

In the second approach, Dr. Furumura used C_3H_8 for C, SiHCl_3 for Si, H_2 carrier gas at 200 Pa pressure. To heat the SiC coated graphite susceptor, he used 8 kHz RF induction. Heating of the substrate was through a 8 kHz RF induction heating scheme. Dr. Furumura tried eight substrates grown at the same time in parallel. The susceptor actually has 20 slots for substrates with wafers being

loaded on both sides. Dr. Furumura's growth procedure is as follows: After a 10 min. hydrogen flow at 25 °C, the substrates are subjected to a 1000°C heat treatment in H₂ environment, the 1000°C temperature being very important. The purity of the H₂ carrier gas used is also critical. This is followed by growth at 1000°C for the necessary duration using SiHCl₃ and C₃H₈ in H₂ carrier gas. Upon the completion of the growth, the samples are cooled in H₂ to room temperature. A roots blower pump together with a rotary vane pump are used on the deposition vessel. A cleaning cycle in high purity H₂ is very important. If H₂ is not very pure, the surface turns out very hazy. Si is delivered to the surface of the substrate by bubbling H₂ through SiHCl₃. The system is capable of handling 5 inch wafers; Dr. Furumura used 4 inch wafers on which to grow SiC. The 1000 Å films on 4" wafers are violet in color, and the 250 Å thick films on 5" wafers are yellow in color.

The SiC film growth rate at 1000°C increases as the propane, C₃H₈, flow rate is increased. For a C₃H₈ flow rate at 60 cc/min, the growth rate is about 30 nm per minute. This growth rate is comparable to that of Si for the particular SiHCl₃ flow. The 3C SiC films were also measured in terms of their IR absorption. The results reveal a single absorption line at 800 cm⁻¹ indicating a pure SiC film.

Dr. Furumura employs both (100) and (111) Si substrates, the latter are tilted 4° towards (1̄ 1̄ 2), which is the standard orientation used in the epitaxial growth of bipolar transistor structures. The morphological differences in SiC on (100) and on tilted (111) are markedly different. On Si-(100), the surfaces are generally hazy. The surfaces on tilted (111), in contrast, are shiny with some surface features. X-ray diffraction measurements in SiC on the tilted Si (111) show only (111) SiC diffraction. But the SiC films on Si(100) point to the presence of small (111) and (200) peaks, the latter associated with (100) orientation. Based on these results Furumura decided to employ (111) surfaces as X-ray masks. In fact even with their problems, the films on (100) surfaces are acceptable for X-ray masks. On the (111) face the 6 fold symmetry in electron diffraction is observed. Rotational twins were not observed in TEM. In TEM cross sectional samples the dark regions are caused by strain. For additional information the reader is encouraged to study the paper by Furumura appearing in JES. The process

developed can produce, as it stands, 10 wafers per hour with 2 μm thick SiC epitaxial layers.

Applications: X-ray membrane by Mr. Yamabe

For DRAM circuits one needs the following design rules:

64 Mbit	0.35 μm	pilot production by optical lithography.
256	0.2 μm	X-ray, already accomplished.
1 GBit	0.15 μm	X-ray, not yet but would like to show.

Requirements for the control of critical dimensions, CD, etc.

For 40x40 mm² exposure area in step and repeat aligner.

CD control	1/10 of CD,
Distortion	1/10 of CD ,
Optical transparency	50%
Alignment tool	HeNe laser
X-ray transparency	70%
Lifetime	> 100 MJ/cm ³

Typical materials used for X-ray masks at various organizations

	<u>Membrane</u>	<u>Location</u>
	BN	AT&T Bell Laboratories(USA)
	Boron Nitride Carbide(BNC)	Fujitsu (Japan), Nagoya Univ. (Japan) B
doped Si	(FRG)	MIT (USA), IBM (USA), IMT
	Silicon-Nitride (SiN)	NTT (Japan), NEC (Japan)
	Silicon-Carbide (SiC)	Philips (FRG), Fujitsu (Japan), NTT (Japan), HOYA, (Japan)

Property	Required	Si	Si ₃ N ₄	SiC
Transparency at 0.834 μm	> 70%	76%	58%	68%
Optical Transparency at 632.8 nm	50	25	70	50
Stress, dyn/cm ²	> 10 ⁹	8 x 10 ⁸	5 x 10 ¹⁸	6 x 10 ⁹
Young's Modulus dyn/cm ²	2 x 10 ¹²	1.8 x 10 ¹²	1.5 x 10 ¹²	4.7 x 10 ¹²
Radiation Durability J/cm ²	> 10 ⁸	depends on	depend on deposition	OK

Stress and Transparency vs. Absorbed Energy, J/cm³, must be within the acceptable figures. The SiC masks produced by Fujitsu did not show any change after 94 MJ/cm³. The exposure times contemplated are about a second or so. The 94 MJ/cm³ represents several days of exposure to the X-ray source. Companies working on x-ray lithography are Sumitomo, NTT and Matsushita (SORTEC consortium for x-ray in Japan in Tsukuba City)

Process:

1. The process begins with the growth of 2μm SiC.
2. Removal of SiC from the back of the substrate in CF₄.
3. Deposition of 0.8 μm Ta and ion implantation of Ar to compensate for the thermal difference.
4. Install the ceramic grade SiC frame by a heat and press process.
5. Etch Si away from back in a solution of HNO₃ + HF (1:3)
6. Pattern Ta by e-beam exposure and subsequent RIE as the mask in chlorine, chloroform chemistry by RIE. Ta was selected because the differential etch rate between SiC and Ta as well as undercutting are favorable. Additionally, strain and stress issues for minimum distortion as well as the density against X-rays.

The diameter of the mask opening for exposure is about 60 mm. Distortion depends on the Ta stress. If the stress is 1.68 X 10⁹ dyn/cm² and tensile, distortion in the mask will result. If it is -0.17 x 10⁹, meaning compressive, distortion is only 30 nm as determined by a Nikon 3M instrument, within the resolution of the instrument. Distortion is only 30 nm as determined by Nikon 3m system, within measurement error.

NTT has an in house X-ray source and Sumitomo Heavy Industry manufactures sources for commercial use. Matsushita's X-ray ring belongs to a consortium, SORTEC for X-ray lithography in Tsukuba Science City.

SiC is the best material next to diamond, as it holds up to X-ray exposure well. Since uniform diamond films are not easily grown in large areas, SiC is the best practical solution for X-ray masks. BN is problematic in that under radiation it interacts with atmospheric H₂O, resulting in the formation of B₃OH and B(OH)₃; both are water soluble. In addition, O₂ penetrates into BN.

- All the SiC produced so far has sufficient durability.
- High volume production of SiC by CVD, 10 wafers/batch

Dr. B. Tobey, is in charge of marketing the product in the USA. While the panel members were at Fujitsu Kawasaki, Dr. B. Tobey was visiting IBM and Motorola. Motorola is interested but wants the back side polished. Motorola's X-ray experiments are conducted at Brookhaven.

Optical lithography achieves below 0.5 μm using Kr-F excimer lasers and phase shifting. Obviously, X-ray lithography competes with optical lithography. Currently, this competition favors optical lithography as Fujitsu management has decided to discontinue the project unless a market can be found. We must also mention that the spacing between the mask and the sample surface is about 5 μm. Because He has favorable cooling characteristics, He gas is passed through this spacing for cooling.

Dr. Sugii who is associated with the nearby Atsugi Laboratory met the panel at the Kawasaki plant and gave a presentation on the SiC wide emitter HBT research. The panel was informed that the Fujitsu Atsugi Laboratory employed about 1050 people. After elucidating on the limitations of polycrystalline Si emitter HBTs, he described the Fujitsu effort on the SiC wide gap emitter

transistors. The topics of discussion according to the outline of his presentation were:

- GSMBE and LPCVD growth of SiC
- Single crystal SiC BJTs
- Fluorine doped amorphous SiC emitter HBTs

ECL ring oscillator delays in time for Si BJTs have progressed from 300 ps in 1978, to 20 ps in 1982. At least in theory, one can do better with SiC/Si wide emitter HBTs where the base can be made thinner and base doping larger.

If the propagation delay time as a function of the extrinsic base resistance over the current gain cut off frequency is plotted, one obtains a linear relation, increasing with resistance. The data were plotted between 25 and 100 ps. By using self aligned base contacts, which eliminates the extrinsic base resistance, and HBT, which allows higher base doping levels to be used, the intrinsic base resistance can be lowered.

Previously used 1360 °C	Atmospheric Pressure	SiH ₄ C ₃ H ₈
Presently using 1000 °C	LPCVD	SiHCl ₃ C ₃ H ₈

For the emitter, a P doped SiC layer was used and the SIMS profile indicated both P and C to be sharp at the interface and flat, and the n/p junction is at the heterointerface between n SiC and p Si. Heterojunctions HBT on Si(111) were fabricated using B implant for the base at a dose of $5 \times 10^{14} \text{ cm}^{-2}$, 30 keV base implant $\sim 1000 \text{ \AA}$. Following the base implant, a P doped SiC layer growth was carried out at 1000 °C, and the resultant device exhibited a current gain, β , of 20 with the Early voltage being 50V. For lightly doped base B: $5 \times 10^{12} \text{ cm}^{-2}$, $\beta = 800$, despite the fact that the emitter concentration was also lowered. However, the growth temperature of 1000 °C causes the B to diffuse out into the emitter and down into the collector. This is particularly troublesome when small transit times need a base of 50 nm. Thus an investigation of low temperature growth was launched.

Study of Low Temperature Growth

CSMBE: Effective in lowering T_s and 800 °C surface cleaning temperature is sufficient. Si is provided by e-gun evaporation and the C source is C₂H₆. The dopant source for P is provided TMP. The growth is initiated by carbonizing the Si surface to form SiC. Carbonization is carried out at 900 °C tried of 4° off, 2° off and 0° off 1-2 nm of carbonized layer is commonly employed. After the 900 °C carbonization, the temperature is lowered to 500 - 600 °C to observe the RHEED patterns. 6th order streaks can be seen after lowering the temperature to 500-600 °C. Obviously 900-950 °C is not for the reconstruction, after heating the surface.

Good quality SiC, determined from TEM images, is obtained when the growth takes place at $\sim 900^\circ \text{ C}$. Lowering the temperature further can cause non-crystalline SiC which is acceptable providing that the dangling bonds are tied. This is accomplished by adding SiH₂F₂ gas to the process much like H in a-Si. The growth temperature can then be lowered to 700 °C, which also alleviates the out-diffusion problem. The band gap of this fluorinated SiC grown at 700 °C as determined from absorption, is 1.8 eV. This SiC may not be stoichiometric but the SiC_x/Si pn junctions exhibit much lower leakage currents and larger breakdown voltages than polycrystalline Si/Si junctions.

HBTs with polycrystalline Si and SiC_x have about the same collector current for the same base emitter voltage; however, the base current in the SiC_x HBTs is much smaller. In addition, the current gain in SiC_x HBTs is about 75 whereas devices with polycrystalline Si emitter exhibit current gains of about 20-25. The base doping in SiC_x