I. INTRODUCTION

As our ancestors abandoned stones and adopted bronze, human beings are always seeking new materials to satisfy personal curiosities and ambitions and social desires. An invention of a triode vacuum tube in 1906 gave rise to electronics. However, soon peoples found the limitation of size, reliability and power of the vacuum tube. After triode action of Ge in 1948[1], semiconductors, especially Si, have held a leading part of evolution of industries and our lives. Nowadays, we are living surrounded by uncountable semiconductor-devices and computer-aided technology. Needless to say, Si dominates electronics and semiconductor fields. At the same time, other semiconductors hold important parts. Now microwave and optical communications are supported by III-V semiconductor devices. And beside us CD(compact disk) players which need semiconductor lasers can be easily found. Even in the field of a super computer which is one of the symbol of Si technology, a product which uses GaAs IC's(integrated circuit) for its CPU(central processing unit) is announced to ship in 1989[2].

However, still there are many fields where new materials are expected to satisfy needs. Wide-bandgap semiconductors are necessary for high-temperature operation of devices and blue light-emitting devices. IV-IV compound semiconductor SiC treated in this thesis is one of the most hopeful candidates for such uses.

SiC is well known as an example of polytypism. Structure of every polytype of SiC is described by stacking sequence in the [0001] direction*). Atoms occupy one site out of three in the close packed structure. Three sites of A, B and C have the relative arrangement shown in Fig.1. Stacking sequences and bandgaps of popular polytypes are listed in Table 1. Each polytype is described by a number of layers in the repeat distance of a primitive cell and three types of crystal structures. The crystal structures are expressed by H for

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*): See notes at P.7.

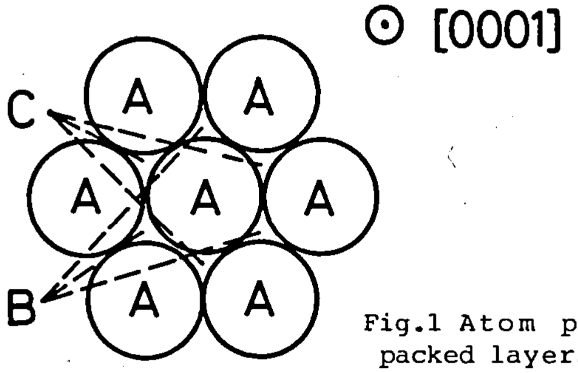

Fig.1 Atom position in close-packed layers.

polytype	stacking sequence	exciton bandgap(eV)
2H(wurtzite)	AB	3.330
3C(zinc blende)	ABC	2.390
4H	ABAC	3.265
6H	ABCACB	3.023
15R	ABCACBCABACABCB	2.986

Table 1 Stacking sequences and bandgaps of popular polytypes.

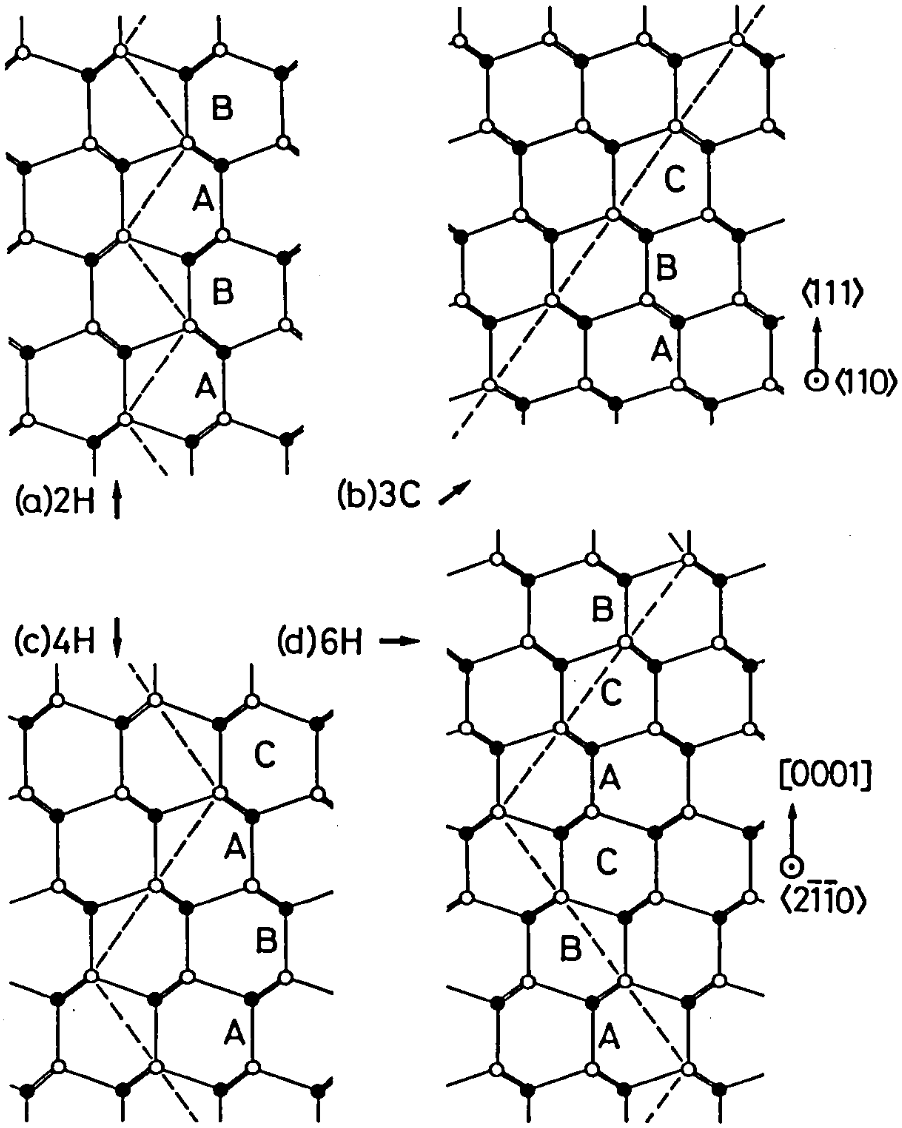

Fig.2 Crystal structures of (a)2H-, (b)3C-, (c)4H- and (d)6H-types.

	band structure	E_g (eV)	μ (cm^2/Vs)	v_s (cm/s)	E_b (V/cm)	λ (W/cm°C)	lattice constant(Å)	crystal structure
3C-SiC	I	2.4	1000	2.7×10^7	–	–	4.36	ZB
6H-SiC	I	3.1	600	2×10^7	5×10^6	5.0	$a_0=3.09$ $c_0=15.1$	6H
Si	I	1.12	1500	1×10^7	2×10^5	1.5	5.43	DI
GaAs	D	1.42	8500	2×10^7	3×10^5	0.5	5.65	ZB

I:indirect D:direct E_g:energy gap μ:electron mobility at 300K

v_s:saturated electron drift velocity E_b:break down field

λ:thermal conductivity at 300K ZB:zinc blende DI:diamond

Table 2 Physical properties of 3C-SiC, 6H-SiC, Si and GaAs.

hexagonal, R for rhombohedral and C for cubic. 3C-type is the only cubic structure. Generally its structure is known as a zinc-blende structure. 3C-SiC is often called β-SiC and others are called α-SiC. The structures of 2H-, 3C-, 4H- and 6H-SiC are shown in Figs.2(a)-(d). There are many polytypes except for those shown here. As far as the author knows, the longest repeat distance of a primitive cell corresponds to 594 layers[3]. Off course usually, easily obtainable several polytypes are used and investigated. In this thesis the most popular two polytypes of 3C- and 6H-types are mainly treated.

Physical properties of 3C-SiC, 6H-SiC, Si and GaAs are listed in Table 2[5-11]. As mentioned above both 3C- and 6H-SiC are expected as materials for electronic devices which operate under harsh (high temperature and high radiation) circumstances. 3C-SiC has high electron mobility of 1000cm^2/Vs[5] in spite of its wide bandgap of 2.4eV. Therefore, potentiality for active devices of 3C-SiC is superior to that of 6H-SiC. SiC has higher thermal conductivity[6], higher saturated electron drift velocity[7,8] and higher breakdown electric field[9] than Si and GaAs as listed in Table 2. These features are desirable for high-power microwave electronic devices such as IMPATT(impact ionization avalanche transit time) diodes. 6H-SiC is also a promising material for blue LED's(light-emitting diode) in spite of its indirect bandgap structure. Because both p and n-type conduction are easily obtained for SiC different from other wide-bandgap semiconductors.

After an invention of synthesizing method by Acheson in 1892, SiC has been utilized in industry. SiC is very hard and it is well known as polishing powder named carborundum. SiC is very stable even at high temperature, and it is also used as a heat-resistant material and a heater. Recently its ceramics is used as package for VLSI. Because its ceramics simultaneously can realize high thermal conductance, high resistivity and the same thermal expansion coefficient as Si[12]. FRM(fiber-reinforced metal) using SiC whisker is utilized for a cylinder of a motorcycle engine. Composite materials using fiber and whisker of SiC are actively investigated for the aerospace industry.

By the Acheson method 6H-SiC is mainly obtained. Therefore, 6H-SiC was used in industry and sometimes it was investigated as a semiconductor material. In 1907[13] and 1923[14] electroluminescence was reported. SiC was used as a crystal detector at the time. And utilizations for a varistor and a surge absorber are known. However, investigation for other electronic devices was difficult. Because crystals obtained by the Acheson method were not adequate for electronics use. In the Acheson method, SiC is synthesized in an electric furnace using silica, carbon and some additional sources. Such crystals usually contain many impurities and they are small and irregular in shapes. Usually usable area for the investigation is smaller than 1cm^2. In 1955, Lely invented a growth method of pure crystals utilizing sublimation[15]. By this method 6H-SiC was mainly obtained. This innovation motivated investigation for ingot growth of 6H-SiC and its electronic devices. Since in the Lely method nucleation for crystal growth takes place randomly, the problems of size and shapes were not solved. Based on the Lely method some modification was carried out. By the introduction of a seed crystal, growth of large crystals became possible[16,17]. Recently growth of 6H-SiC ingots which were 30mm in diameter and 13mm in height was reported[18]. However, the technology of ingot growth still stays at research level.

Epitaxial growth technique was utilized to fabricate electronic devices of 6H-SiC. By sublimation technique impurity control of thin layers is difficult. And diffusion technique is hard to apply for device fabrication because of very low diffusion coefficient of impurities in SiC[19]. Fabrication of blue LED's with 6H-SiC was investigated by CVD(chemical vapor deposition)[20,22] and LPE(liquid phase epitaxy)[21,22] methods. Recently investigation continues to achieve higher efficiency using the LPE method[23] in the aim of marketing. P-n junction diodes[7,9], FET's(field effect transistor)[19] and bipolar transistors[24] were fabricated to investigate properties of 6H-SiC as semiconductor materials and potentiality of high-temperature use. However, recently investigation for such purpose is not active. Difficulty in preparation of substrates with good quality and high epitaxial-growth temperature are probably main reasons. Typical growth-temperatures are higher than 1650°C and 1800°C for LPE and CVD, respectively. Success of growth of 3C-SiC on Si is also a reason.

In the case of 3C-SiC, crystals are obtained by sublimation and solution growth methods. However, such crystals are too small for investigation as electronic materials. Typical area usable for investigation is smaller than several mm^2. Rising of trend for investigation began in 1980's by the success of heteroepitaxial growth of 3C-SiC on Si[25] by Nishino, Matsunami and co-wokers. They were members of the laboratory where now the author belongs. 3C-SiC is considered to be stable at lower temperatures(<1600°C) compared with other polytypes. Therefore, heteroepitaxial growth of 3C-SiC by CVD has been attempted by many investigators[26]. Si is the most popular substrate for heteroepitaxial growth of 3C-SiC. Since Si wafers are cheap and they have controlled high quality. However, lattice mismatch between Si and SiC reaches 20% and reproducible growth of thick single crystals was impossible. To overcome the large lattice mismatch, Matsunami et al.[27] proposed introduction of an intermediate thin layer between a substrate and a grown layer which was called as "a buffer layer". They tested several methods to form a buffer layer[27,28] and chose a carbonization method[25,29]. By carbonization of Si surface using C_3H_8 before CVD growth, single crystalline SiC was reproducibly obtained. However, the role of "a buffer layer" is not clear and investigation as a semiconductor material just started. Since 3C-SiC has higher potential for active devices than 6H-SiC and single crystal with large area is easily obtained by this method[30], many groups began to take part in the investigation.

In the former part, features, history and present situation of SiC were explained. Based on this knowledge the following subjects are listed as the purpose of this thesis.

To establish growth technique of 3C-SiC on Si,

(1)Characterization of carbonized layers and grown layers;
(2)Optimization of factors concerning crystal growth

are investigated. Based on the results, if necessary,

(3)Improvement of grown layers

is attempted. And to apply 3C-SiC for electronic devices,

(4)Impurity doping;
(5)Fabrication of devices

are attempted. And to seek future of SiC the next subject is added:

(6)Growth on 6H-SiC(0001) under 1500°C.

CVD growth under 1500°C was not well investigated. This subject includes two meanings. One is to know whether 6H-SiC(0001) is usable for a lattice-matched substrate of 3C-SiC or not. The other is to investigate whether control of polytypes is possible or not by changing the growth conditions.

*)Note: Usually for 3C-SiC, Miller indices (e.g. (hkl)) for a cubic lattice are used. However, in chapter VI to treat both 3C-SiC and 6H-SiC at the same time, hexagonal-lattice Miller-Bravais indices[4] are also used. This notation explicitly expresses symmetrical relationship between various faces. Popular faces such as (0001), $(2\bar{1}\bar{1}0)$ and $(10\bar{1}0)$ are idiomatically identified by this notation. However, to discuss diffraction phenomena of various polytypes, vector calculation is necessary and Miller indices for hexagonal lattice is convenient for all polytypes. In this thesis from chapter II to chapter V, faces of 3C-SiC and Si are identified by Miller indices for cubic lattices. In chapter VI and APPENDIX, diffraction phenomena are explained by Miller indices for hexagonal lattices, and Miller-Bravais indices are used to identify popular faces. Correspondence between these notations are shown in APPENDIX.

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