Epitaxial Growth II

Bending of Basal Plane Dislocations in the VPE Grown 4H-SiC Epitaxial Layers
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Aluminum Doping of Epitaxial Silicon Carbide grown by Hot-Wall CVD, Effect of Process Parameters
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Investigation of Residual Impurities in 4H-SiC Epitaxial Layers Grown by Hot-wall Chemical Vapor Deposition
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Fast Growth and Doping Characteristics of Alpha-SiC in Horizontal Cold-wall CVD
S. Nakamura, T. Kimoto, H. Matsunami
Kyoto University, Japan

Growth, Characterization and Properties of SiC Quantum Well Structure s
A. Fissel, U. Kaiser, B. Schrer, J. Grillenberger, W. Richter,
W. Witthun, F. Bechstedt
Friedrich-Schiller-Universität Jena, Germany

Delta-Doped Layers of SiC Grown by "Pulse Doping" Technique
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Bending of basal plane dislocations in the VPE grown 4H-SiC epitaxial layers

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The propagation of basal plane dislocations from the off-cut SiC substrate into the epilayer has been investigated by KOH etching, optical microscopy, and transmission electron microscopy (TEM). It is well known that in homo-epitaxial growth, dislocations intersecting the growth surface replicate into the overgrowth. The Burgers vector of individual dislocations remains unchanged across the interface. It is also assumed that the dislocation line direction stays the same. In the case of hexagonal SiC polytypes, this implies that screw and edge dislocations propagating along the c-axis thread through the epilayer almost perpendicular to its surface, while the basal plane dislocations should form a shallow angle with the layer surface. The results presented below indicate that this is not the case.

The samples examined in this study were 4H-SiC wafers oriented 8° from the [0001] toward the $<11\bar{2}0>$ direction with the 10 μm thick epitaxial layers grown by vapor phase epitaxy (VPE) at low pressure (~100 mbar). Epilayers were etched in molten KOH to reveal the locations where dislocations intersect the (0001) Si surface of the epilayer. After etching, the epilayer was removed by polishing and the bare substrate was etched to reveal the dislocations present in the

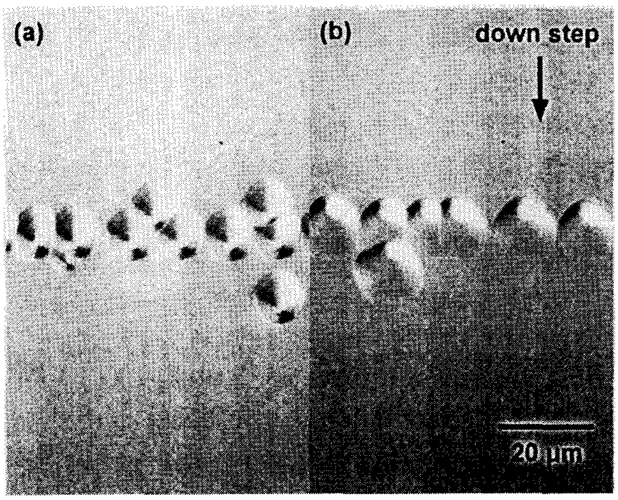

Fig. 1 Dislocation etch pits revealed by molten KOH etching of (0001) Si surfaces.
(a) On top surface of the epitaxial layer
(b) 10 μm below the epitaxial layer

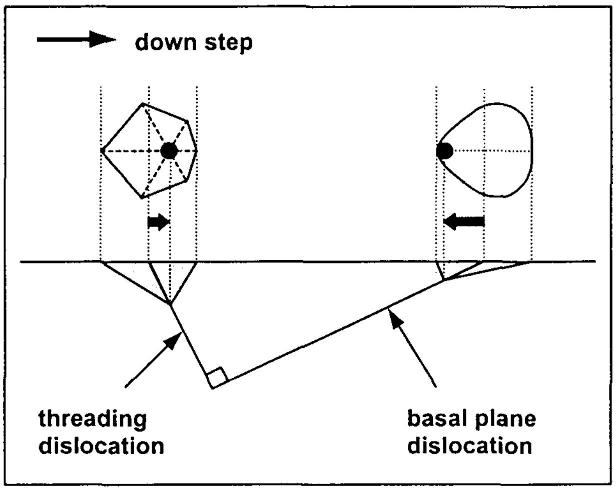

Fig. 2 Formation scheme of the two different etch pits shown in Fig. 1. Note that the point bottoms marked with large solid circles are shifted in the opposite directions.

substrate prior to growth of the epilayer. The shape and distribution of etch pits were analyzed by optical microscopy. Specifically we have analyzed etch pits in the slip bands of basal plane dislocations. In the substrate, the etch pits making up the slip bands have an oval shape characteristic of basal plane dislocations. On top of the epilayer, the same pits have a form of hexagons indicating that the dislocation line is almost normal to the surface (Fig. 1 and 2). This is a direct experimental evidence of a conversion of basal plane dislocations into a threading edge dislocation. This behavior was confirmed by conventional TEM (Fig. 3) and by gradual polishing of the wafer/epilayer structure and etching in molten KOH. The conversion was interpreted as a result of the image force in epilayers grown in the step flow mode. It is argued that this mechanism can cause the increase of the threading edge dislocation density in PVT growth and can lead to an apparent improvement in x-ray reflection width of epilayer.

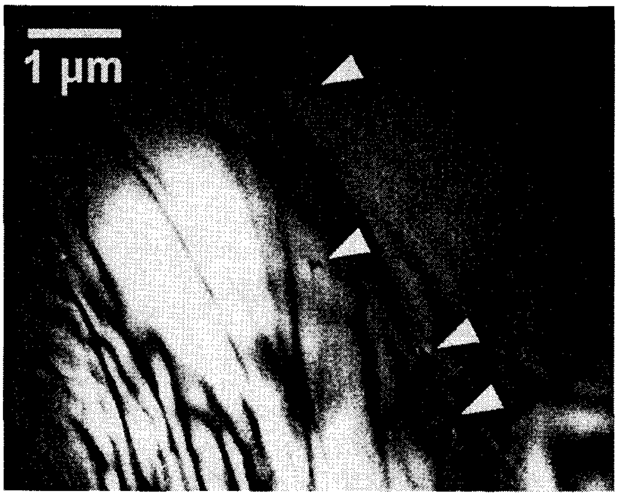

Fig. 3 Plan-view conventional TEM micrograph showing four threading dislocations corresponding to a basal plane slip band in a VPE layer.

Aluminum Doping of Epitaxial Silicon Carbide grown by Hot-Wall CVD, Effect of Process Parameters

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Aluminum is the most common p-type dopant in SiC. The incorporation of aluminum in epitaxial SiC grown by hot-wall CVD is strongly connected to the chosen growth parameters. Common process parameters such as C/Si ratio, trimethylaluminum (TMA) flow, pressure, temperature and growth rate influence the aluminum incorporation.

A detailed study of the aluminum incorporation in 4H- and 6H-SiC epitaxially grown layers for both Si- and C-faces has been performed including both thermodynamical calculations and growth runs. The calculations have been made on a H_2-SiH_4-C_3H_8-$Al(CH_3)_3$ system using a commercially available code CFD-ACE+ and typical growth conditions where consideration has been taken to whether solid phases are allowed to be formed or not. We will present results from growth runs and calculations on aluminum incorporation and its dependence on the process parameters as mentioned above. All materials have been characterized with second ion mass spectrometry, SIMS.

The incorporation of aluminum is strongly connected to the creation of available lattice sites. The calculations have shown that the highest concentration of aluminum is found in the Al, AlH, AlH_2, AlH_3 and $AlCH_3$ species which indicates that we are not dependent on dissociation of larger molecules, as in the case of nitrogen incorporation [1]. In the case of aluminum incorporation, the bonding at the surface of the aluminum atoms is more important. Aluminum, with three available bonds, will bond strongly to the three different carbon atoms at the Si-face, assuming ideal bulk terminated surface during typical growth conditions. On C-face there is only one available bond to one carbon atom on the surface. Consequently, C-face material suffers more easily from reevaporation of adsorbed aluminum containing species.

Our investigation shows that the aluminum atoms are relatively immobile on the surface. The incorporation is more related to the carbon coverage on the terrace. High carbon coverage creates more available stable sites for aluminum species to bond to. In the case of increased growth rate the aluminum incorporation increases, as shown in fig. 1a and 1b. The increased precursor flow (maintaining C/Si ratio constant), resulting in an increased growth rate, creates more available lattice sites for the aluminum species due to the increased carbon coverage. Although the silicon coverage increases at the same time it does not seem to out compete the aluminum atoms. At very high growth rates the aluminum incorporation saturates and the incorporation becomes diffusion limited. The C-face suffers from reevaporation of aluminum species but very high growth rate could reduce this effect.

The thermodynamical calculations have shown that reduced pressure increases the C/Si ratio. The increased C/Si ratio will enhance the aluminum incorporation [2]. At low growth rate the Si-face suffers from reevaporation of aluminum species due to the low carbon coverage. Consequently, at low growth rate, the aluminum incorporation increases with reduced pressure due to the increased C/Si ratio. At a critical pressure of 300 mbar the aluminum incorporation has its maximum and a further decrease of the total pressure reduces the aluminum incorporation due to reduced partial pressure of the aluminum containing species, as can be seen in fig. 2a. At high growth rate and at atmospheric pressure (diffusion limited incorporation) all aluminum species are incorporated and the aluminum incorporation decreases with reduced pressure which is due to reduced partial pressure of the aluminum containing species, see fig. 2b. Although the C/Si ratio increases, which creates more available lattice sites, all aluminum species are already bonded to the surface and the incorporation becomes C/Si ratio independent.

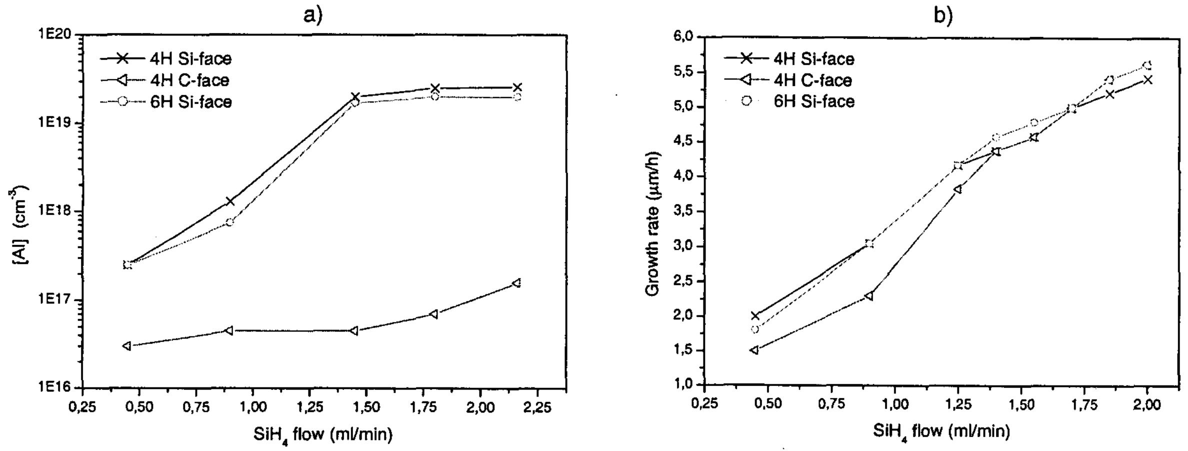

Fig.1 a) The aluminum incorporation dependency of silane input flow b) the growth rate versus silane input flow. The C/Si ratio was kept constant at 3.5, the growth temperature was T=1600 °C and the reactor pressure was P=1013 mbar.

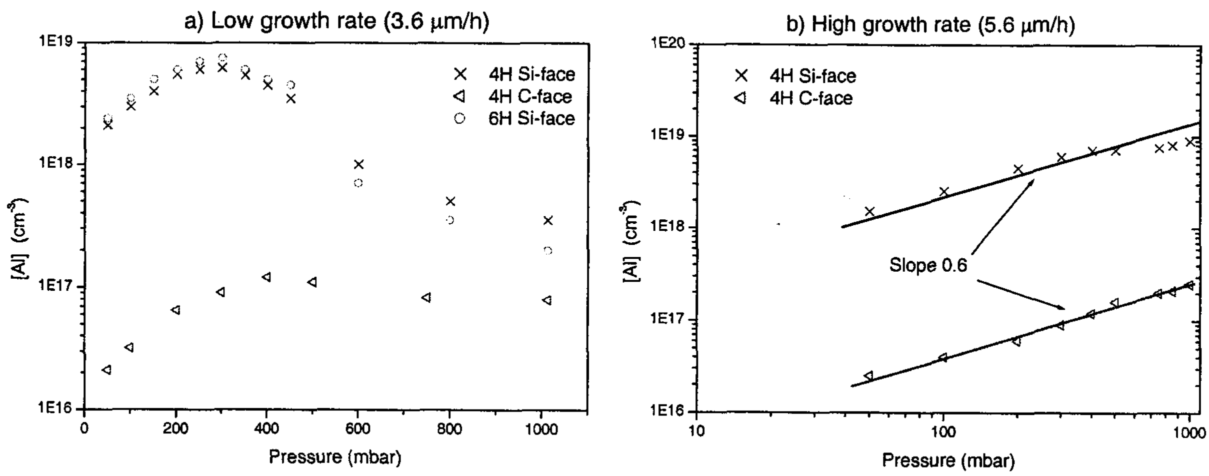

Fig. 2 The aluminum incorporation versus pressure presented at a) low growth rate and b) high growth rate. The C/Si ratio was kept constant at 3.5 and the growth temperature was T=1600 °C.

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Investigation of residual inpurities in 4H-SiC epitaxial layers grown by hot-wall chemical vapor deposition

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Introduction

A lot of work has been concentrated to realize higher growth rate in CVD at higher growth temperature. Therefore, next to the crystal imperfection, reduction of residual impurities in epitaxial layers becomes the most essential issue to be focused. There are some reports that consider graphite susceptor as a source of the contamination to the epitaxial layers [1,2]. There has been, however, no precise study on the cause and effect of residual impurities thus far.

In this work, the effectiveness of the SiC coating and the change in various impurity contamination has been investigated.

Experimental

The epitaxial layers without intentional impurity-doping were grown by using a horizontal hot-wall CVD reactor. Precurser gases used were monosilane and propane in hydrogen atmosphere. Growth pressure was around 250 mbar. Growth duration time was about 4 hours for each run. Temperature dependence on residual impurity concentraion was studied between 1500 and 1600 °C. Effect of run number was also studied. Impurity concentration was determined by SIMS analysis for B, Al, Ti, V, Cr, and Fe. Nitrogen concentration in the epitaxial film was estimated by photo luminescence [3]. Minority carrier lifetime was measured by the microwave photo conductivity decay method.

Results and discussion

It was found that when the temperature gets higher, both nitrogen, aluminum, and boron concentrations in the epitaxial layers increase. Nitrogen was the most abundant species than any other impurities studied.

On of the most important approach to reduce the contamination from the graphite susceptor has been SiC coating. Even this widely employed technique cannot be the complete answer to the prohibition from contamination at higher temperature [4]. In Fig. 1, growth run number dependence on nitrogen is shown. The dependence on aluminum and boron is depicted in Fig. 2. Also, the dependence on the transition metals is shown in Fig.3. In the present study, the coating layer became something like peeled-off after about only 4 runs. After degrading the coating layer, nitrogen concentration increases rapidly whereas aluminum and boron slowly. Effective carrier lifetime is shown as a function of growth run number in Fig. 4. The tendency of the lifetime decrease might suggest that lifetime determining impurity might be transition metals.

Summary

When the growth temperature is higher, it has been found that nitrogen is the most abundant species to contaminate the epitaxial film. We have concluded that SiC coating is not reliable for the use in this temperature range. In order to realize extremely pure epitaxial layers for high voltage device application, further development of purifying graphite is indispensable.

Acknowledgement

This work was performed under the management of FED as a part of the METI NSS Program (R&D of Ultra-Low-Loss Power Device Technologies) supported by NEDO.

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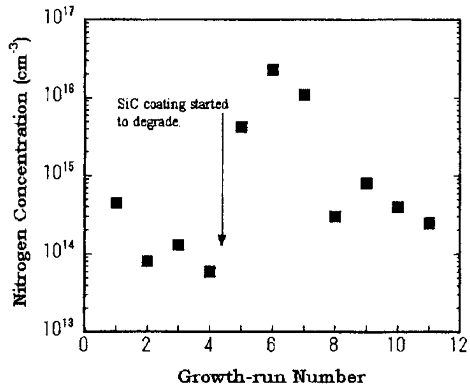

Fig. 1 Growth-run number dependence of nitrogen concentration.

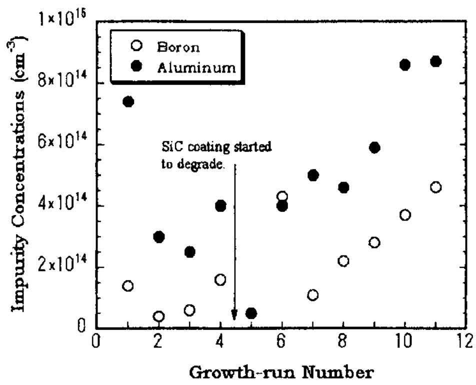

Fig.2 Growth-run number dependence of aluminum and boron concentrations.

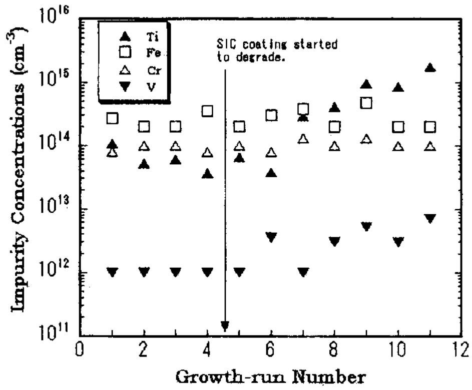

Fig. 3 Growth-run number dependence of transition metal concentrations.

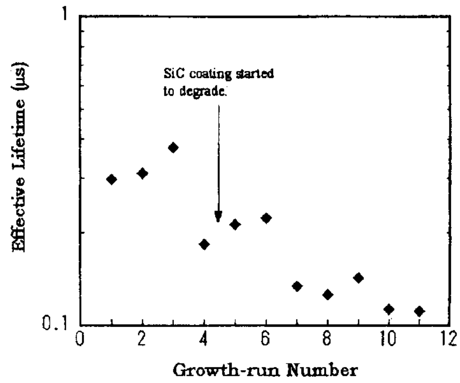

Fig.4 Effective lifeteime dependence on growth-run number

Fast Growth and Doping Characteristics of α-SiC in Horizontal Cold-wall CVD

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To consider device application of SiC, requirements for homoepitaxial growth are good surface morphology, uniformity of film thickness, uniformity and controllability of impurity doping, and high growth rate for thick epilayers. For the last requirement, hot-wall CVD, both horizontal and vertical, have been proposed and developed. In contrast, atmospheric-pressure horizontal cold-wall CVD can be carried out with a simple system, and can produce good uniformity and controllability of impurity doping. However, few has been reported on homoepitaxy at high growth rates. In this study, high-speed homoepitaxy by horizontal cold-wall CVD was investigated.

The substrates used in this study were commercially-available off-axis n-type 4H-SiC (0001) and p-type 6H-SiC (0001), and the epilayers were grown simultaneously. Source gases were SiH_4 and C_3H_8, and carrier gas was H_2 (typical flow rate: 3 slm). The typical SiH_4 flow rate was 0.85 $\sim$ 1.5 sccm and the C/Si ratio was 2 $\sim$ 3. The growth temperature was typically 1500 °C, and the growth time was 2 $\sim$ 6 hours.

Previously, it was reported that the growth rate was proportional to the SiH_4 flow rate [1], but a high SiH_4 concentration over 200 ppm degraded surface morphology [2]. However, by improvements of initial growth condition, good surface morphology as shown Fig. 1 was obtained at a high SiH_4 flow rate of 1.5 sccm (500 ppm).

Figure 2 shows the relationship of the growth rate and the SiH_4 flow rate. The growth rate was found to saturate at about 6 μm/h. The saturated growth rate seemed to be independent of C/Si ratio within 2 $\sim$ 4, growth temperature within 1500 $\sim$ 1600 °C, and carrier gas flow within 3 $\sim$ 10 slm, whereas another group reported an increase of growth rate under a high carrier gas flow [3]. The saturation of growth rate should be attributed to polymerization of SiH_4: once SiH_4 polymerizes to form clusters, the clusters are exhausted from the reaction system.

Some runs of six-hour growth were carried out to produce about 30 μm-thick epilayers. With a SiH_4 flow rate of 1.0 sccm the surface of epilayers showed severe macro-step bunching. Reducing the SiH_4 flow rate to 0.85 sccm and the C/Si ratio to 2, macro-step bunching was alleviated. In spite of low C/Si ratio of 2, the residual donor concentration was within low 10^{14} cm^{-3} as already reported for long-time growth with a lower SiH_4 flow rate [4], and was tend to decrease with increasing SiH_4 flow rate. With a SiH_4 flow rate of 0.85 sccm or above and a C/Si ratio of 3, the epilayers showed p-type conduction with a net acceptor concentration below 10^{15} cm^{-3}. These results support SiH_4 exhaustion at a high SiH_4 concentration, because the SiH_4 exhaustion leads to the increase of effective C/Si ratio, which causes the decrease of donor incorporation and the increase of acceptor incorporation.

In photoluminescence (PL), relatively strong free-exciton peaks were observed. L_1 line, which is often observed in the epilayers grown at high growth rates, were hardly observed. Figure 3 shows the relationship of PL intensities and growth conditions, with corresponding impurity concentrations. The PL intensities are normalized with the free exciton peak marked as I_{LA}. The intensity of neutral nitrogen-bound exciton Q_0 decreases with decreasing donor concentration, and is very small in the p-type epilayer. The latter is because of ionization of nitrogen donors due to compensation with acceptors.

Schottky diodes were fabricated on the thick n-type epilayers. Schottky contacts were nickel and their diameters were $300 \sim 1500\,\mu$m. No edge termination technique was employed. Figure 4 shows typical *I-V* characteristics. The maximum breakdown voltage was 3.6 kV, about two thirds of ideal parallel-plane blocking voltage (5.3 kV). Using these Schottky diodes, deep levels were analyzed and will be discussed briefly.

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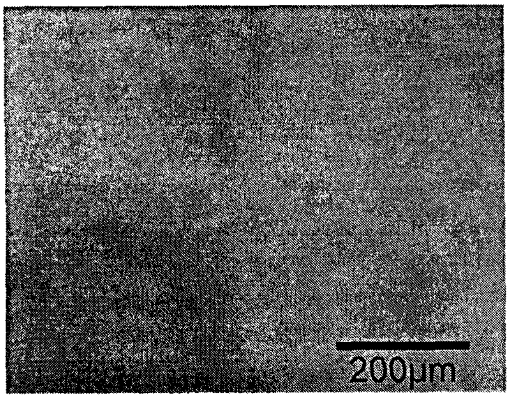

Figure 1: Surface morphology of 4H-SiC epilayer grown with SiH_4 flow rate of 1.5 sccm.

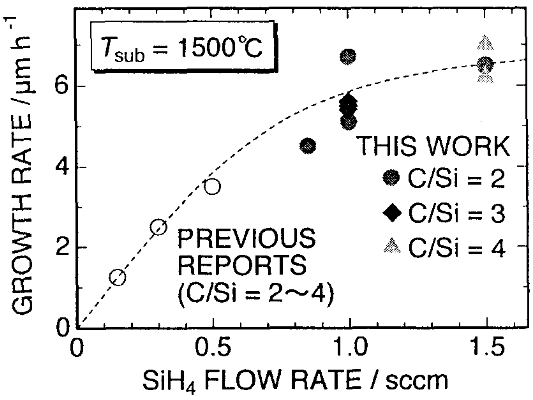

Figure 2: Relationship of growth rate and SiH_4 flow rate.

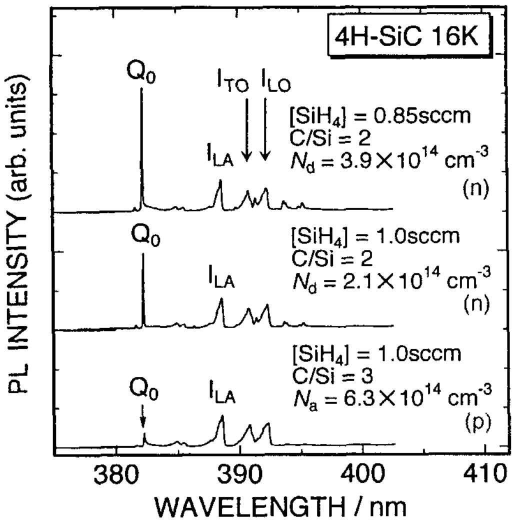

Figure 3: Relationship of PL intensities and growth conditions, with corresponding impurity concentrations.

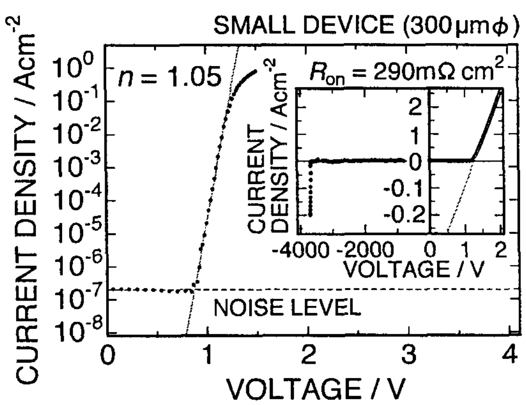

Figure 4: Typical *I-V* characteristics of a Ni Schottky diode on 31 μm-thick epilayer. Donor concentration of the epilayer was about $2 \times 10^{14}\,\mathrm{cm}^{-3}$.

GROWTH, CHARACTERIZATION AND PROPERTIES OF SiC QUANTUM WELL STRUCTURES

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Semiconductor heterostructures and superlattices are of increasing interest in various applications. But investigations of such structures have been focused on mostly on systems consisting of different chemically materials such as GaAs/AlAs. However, in recent years also new types of heterostructures are under discussion consisting of only one material with different types of crystal structures, such as wurtzite/zinc-blende heterostructures. In such structures, for example effects due to different chemical constituents can be avoided. Therefore, by changing the crystal structure during the growth in a controlled manner, it is possible to prepare heterostructures maintaining a completely defect-free, lattice matched, and coherent interface.

In this field silicon carbide is the most promising candidate because SiC crystallizes in more than two different stable structures with different physical properties, in particular variations of the energy gap of about 1 eV. This is what makes SiC especially interesting for semiconductor application in comparison for example to AlGaN/GaN heterojunction devices.

In this work we like to present results of the growth and the investigation of multi quantum well (MQW) structures of SiC. The growth of MQW structures consisting of some dozens of hexagonal SiC barriers and of 3C-SiC wells has been performed by solid-source molecular beam epitaxy on hexagonal off-axis substrates.

In a first step, wire-like 3C-SiC was grown selectively on some wider terraces of the substrates at lower temperatures (<1500 K), where the number if wires is determined by the width of the terraces and the temperature. In a second step, SiC was grown via a step-flow growth mode of both the hexagonal matrix material and the 3C-SiC wires at higher temperatures (1600 K) resulting in the formation of multi-heterostructures of SiC polytypes (upper figure). The thickness of the 3C-SiC layers (2.3 nm in average) is determined by the 2-3 nm heights of the steps on the substrate surface.

Photoluminescence investigations of the MQW structures reveal additional signals, which were not obtained for thick homoepitaxial layers consisting of one polytype (lower figure). This new signals can be explained within the model of a triangular electron quantum well in 3C-SiC. Furthermore, the electrons in the MQW structure should be localized in the 3C-SiC layer at one heterointerface, whereas holes may occur on the other side of the heterostructure in the hexagonal material near the second interface. This seems to be supported by capacity-voltage (C-V) measurements in which a modulation of the electron concentration was detected.

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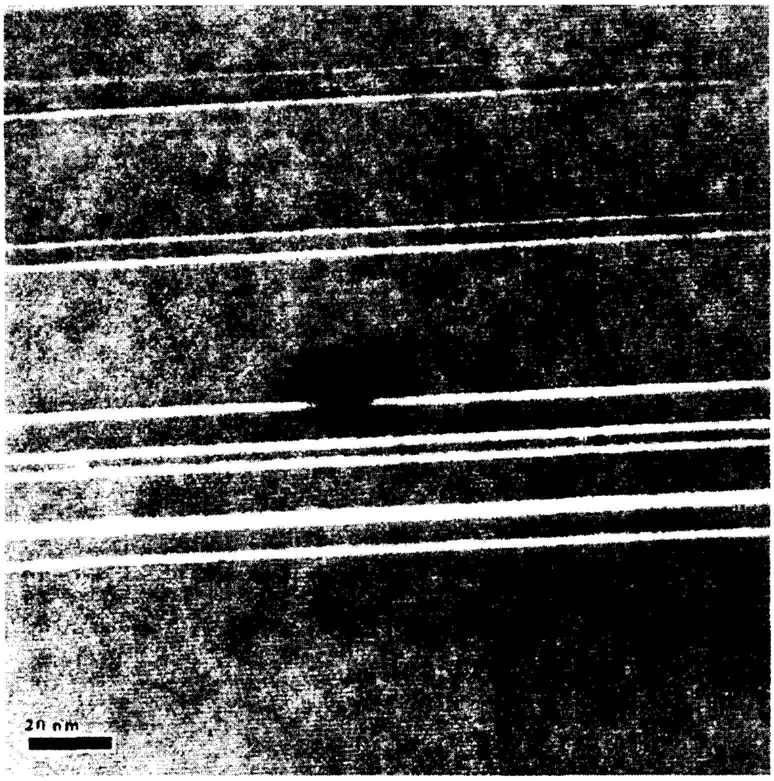
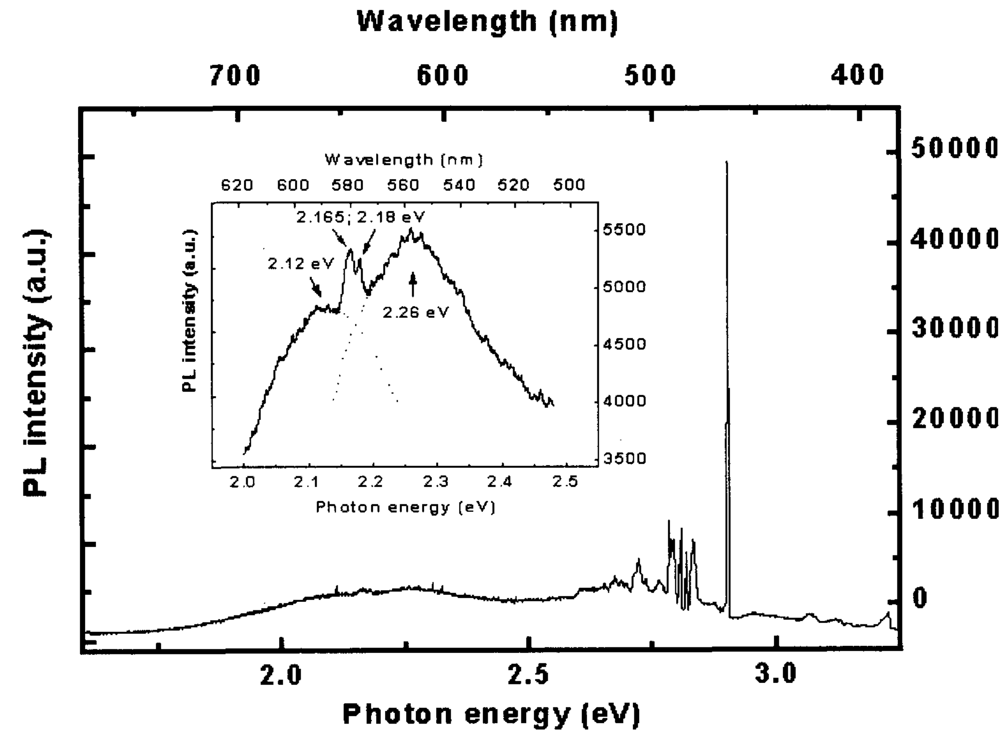


High-resolution TEM micrograph of a multi quantum well structure with 3C-SiC wells (light stripes) between 4H-SiC barriers grown on 4H-SiC.



LTPL spectrum of a 3C/4H-SiC multi quantum well structure grown on 4H-SiC(0001). The inset shows the low energy region between 2 and 2.5 eV in a higher magnification.

Delta-Doped Layers of SiC Grown by "Pulse Doping" Technique

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It is expected that the delta-function doped structures have a great potential for realizing high-performance SiC devices. In this study, delta-doped layers of SiC were investigated by our original "pulse doping" technique during epitaxial growth in the hot wall type CVD system.

The vertical hot wall type CVD system equipped with the pulse valve was described elsewhere in detail.[1] Commercially available 4H-SiC wafers with n-type doping in $10^{18}cm^{-3}$ range were used for the substrates. Typical epitaxial growth temperature and pressure were 1600°C and 90kPa, respectively. The flow rates of SiH_4, C_3H_8 and H_2 carrier gas were set to 3.0sccm, 0.5sccm and 2slm, respectively. The N_2 gas was selected as n-type dopant. Typical growth rate was about 2μm/hr under the conditions described above. The pulse valve, which is a solenoid valve, can open and close within <10μs. In this study, the dopant gases were intermittently introduced and managed utilizing the pulse valve without mass flow controller. It has been derived that the carrier concentrations of the doped layers were increased from 10^{15} to $10^{18}cm^{-3}$ with increasing the on period of pulse valve from 90 to 120μs with its off period of 4ms during "pulse doping".[1]

"Pulse doping" technique enabled formation of very abrupt interface between doped and undoped layers. 10nm-thick doped (delta-doped) layer of SiC was grown utilizing "pulse doping" for 20 sec during continuous epitaxial growth. The doping profiles of the delta-doped layers were analyzed by capacitance-voltage (C-V) measurement and secondary ion mass spectroscopy (SIMS). The peak carrier concentration is $1x10^{18}cm^{-3}$ surrounded by the undoped layers with the impurity concentration of the order of $10^{15}cm^{-3}$. The full width at half maximum (FWHM) of the delta-doped layer is measured to be less than 12nm. Furthermore, it is noted that the stratified structures of the delta-doped layers are achieved in the SiC epitaxial films for the first time. Consequently, it is possible to completely shut off the supplied dopant gas within a very short term by "pulse doping", so that the delta-doped layers can be formed in the hot wall type CVD system even at higher temperature region.

In conclusion, delta-function doped layers of SiC were successfully formed by "pulse doping" technique in the hot wall type CVD system. "pulse doping" technique leads novel SiC devices, such as MESFET and MOSFET (DACFET) based on the delta-doped layered structures.[2-4]

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