FUNDAMENTAL INVESTIGATIONS FOR FABRICATION OF SILICON CARBIDE LIGHT-EMITTING DEVICES BY LIQUID-PHASE EPITAXIAL GROWTH

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—— PHOTOLUMINESCENCE STUDIES OF RADIATIVE CENTERS AND FABRICATION OF BLUE-LIGHT-EMITTING DIODES ——

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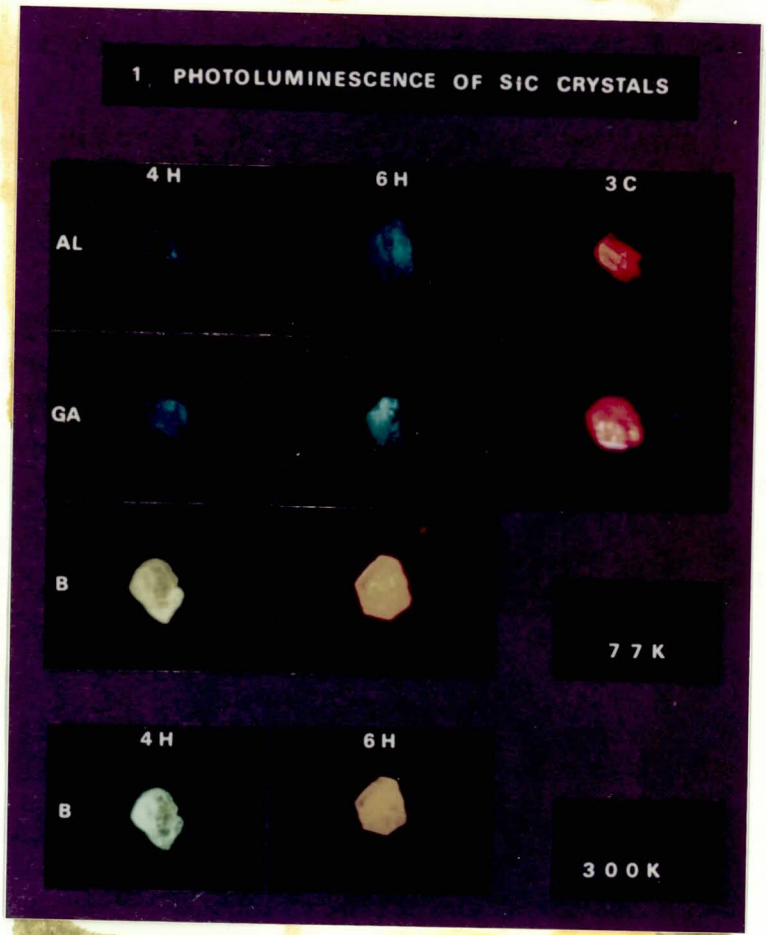
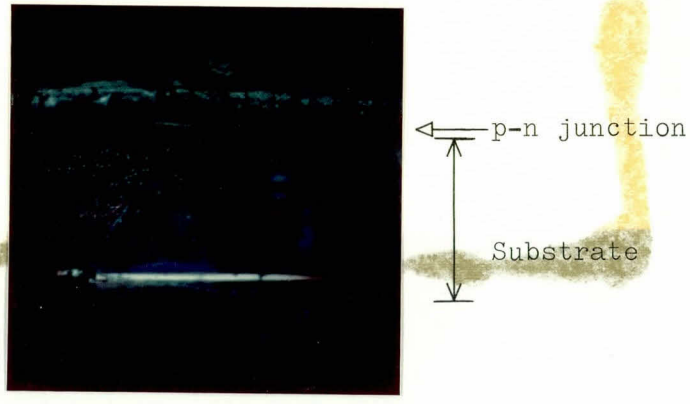


(1) Photoluminescence due to Al, Ga, and B of 4H-, 6H-, and 3C-SiC crystals grown from a Si melt (See text p. 20).

ELECTROLUMINESCENCE OF SiC DIODE

(2) Blue electroluminescence of 6H-SiC diode (300 K) prepared by liquid-phase epitaxial growth (See text p. 80).



(3) Side view of the electroluminescence under the microscope (See text p. 80).

PREFACE

Although investigations on SiC as a new material for semiconductor devices have long been made for almost twenty years, SiC electron devices or optoelectronic devices have not yet been developed to practical use. But a large number of lectures and lively discussions at the international conference on SiC which has been held three times since 1959 have shown that SiC has incessantly been drawing much attention of a lot of researchers to its attractive properties.

The present investigation was carried out during the Doctor's course on the basis of the author's previous investigation (for the degree of Master) on the crystal growth of SiC from a silicon melt. The original purpose of the previous investigation was a fundamental study for the fabrication of 3C-SiC optoelectronic devices. (3C-SiC crystals, which has the smallest energy gap, usually grow by the silicon melt method.) But in the course of the investigation, 4H- and 6H-SiC, which have much larger energy gaps, have been found to grow under certain growth conditions, and even undoped crystals showed intense visible photoluminescence at room temperature (which was found to be due to boron acceptors later). Especially, 4H-SiC emitted brilliant green luminescence. Being charmed with its fascinating color, the author has been moved to start the present investigation on luminescent centers in 4H- and 6H-SiC and on liquid-phase epitaxial growth to utilize the centers in light-emitting devices.

The present investigation is a fundamental one for the fabrication of various SiC light-emitting devices by liquid-phase epitaxial growth in the future, and has shown fairly satisfactory results. The procedures of the photoluminescence measurements used in the investigation were ordinary ones, and the measurement systems did not have any special high sensitivity. Nevertheless, detailed studies were able to be done owing to the very intense luminescence. Moreover, the blue electroluminescence of the SiC diode was successfully observed even from the first trial sample,

and the blue-light-emitting diodes were able to be fabricated quite reproducibly and relatively easily. From these results, the author believes that the liquid-phase epitaxial growth in the present investigation has a bright future for the preparation of SiC light-emitting devices.

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October, 1976

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CONTENTS

I. INTRODUCTION

Silicon carbide (SiC) is one of the oldest semiconductors historically. Its physical hardness and chemical inertness have long been utilized as a material for abradant, refractory, heater, and resistor. But the physical and chemical stableness makes the crystal growth and the device fabrication very difficult. It was when J. A. Lely reported a new crystal growth method utilizing the sublimation of SiC in 1955[I.1)] that researches on SiC as a material for semiconductor electron devices were substantially initiated. By this method, relatively large and pure single crystals have been able to be obtained. Electrical and optical properties of the crystals have been studied by a number of researchers. Alloy, grown, and diffused p-n junctions were prepared using the crystals by the Lely method.[I.2)] The electrical characteristics and the electroluminescence of the junctions were measured.

At first, SiC had attracted considerable attention as a potential semiconductor for high-temperature and high-power electron devices because of its stable properties even at high temperatures. Later, SiC optoelectronic devices, especially light-emitting diodes in the visible-light region, have been expected, because SiC has a wide energy gap. SiC exists in a large number of different crystal structures referred to as "polytypes". Since each polytype has a different energy gap (2.3-3.3 eV), optoelectronic devices over a very wide wavelength range will be able to be fabricated.

However, although semiconductor technology for Si and III-V compounds has achieved a remarkable development, and light-emitting diodes of GaAs, GaP, etc. are used practically, the researches for developing SiC devices have shown quite slow progress. And they are as yet in a preliminary experimental stage.

One of the predominant causes is that any crystal growth

method and device fabrication technique suitable for systematic researches for the SiC device development are not yet established. The crystal growth by the Lely method and the device fabrication by the alloying (scarcely used recently because of the poor junction characteristics) and the diffusion techniques have great disadvantages. The Lely method uses extremely high growth temperature (2300°-2500°C) and utilizes spontaneous nucleation without any seed or substrate crystal, which raises considerable difficulties in controlling the crystal growth and the impurity doping. The diffusion of dopants to these crystals also requires high temperature near 2000°C and long diffusion time around an hour. But since any other fabrication technique in place of the Lely method and the diffusion technique is not established, they are mainly used for the fabrication of SiC devices even now.

Recently, epitaxial growth of SiC on appropriate substrates has been carried out by several researchers, mainly to fabricate light-emitting diodes. The vapor-phase epitaxial growth has been done using silicon chloride and carbon chloride or hydrocarbon,[I.3-I.6] and the liquid-phase epitaxial growth with a Si melt [I.7] (or a Si + Ti melt [I.8]) in a graphite crucible. Since the growth temperature is low (about 1600°C), and the crystal growth, the impurity doping, and the device fabrication are controlled more easily, these epitaxial growth methods are much expected to promote the development of SiC technology rapidly.

The liquid-phase epitaxial growth with a Si melt which was carried out successfully by Brander et al.[I.7] to fabricate visible-light-emitting diodes has been regarded as a promising method that will approach the techniques used for III-V semiconductors practically. But their experiments were concerned only with the epitaxial growth of n-SiC (6H) on a p- SiC (6H) substrate prepared by the Lely method, and p-type epitaxial layers were not grown. Since their several reports in 1969, the work has not made any further progress, and any other successful work has

not been reported. One reason may be that their technique used for the epitaxial growth was inconvenient to manage and unsuitable for systematic studies of epitaxial growth and device fabrication. Moreover, there have been very few studies on visible-luminescence centers in SiC grown from a Si melt. (Recently, boron centers in 3C-SiC grown from a Si melt have been studied in detail,[I.9,I.10] but the emissions were near-infrared.)

From these standpoints, the author has initiated fundamental investigations for fabricating SiC visible-light-emitting devices by liquid-phase epitaxial growth with a Si melt. The purposes of the present investigation are the following two: 1) detailed studies of radiative recombination processes of visible-luminescence centers in SiC grown from a Si melt (Chapter II, III, and IV); and 2) preparation of SiC blue-light-emitting diodes by liquid-phase epitaxial growth with the dipping technique (Chapter V).

In the luminescence studies, photoluminescences from violet to near-infrared due to Al, Ga, and B centers in 4H-, 6H-, and 3C-SiC bulk single crystals are described (Chapter II). Especially, the photoluminescences due to Al and Ga in 4H-SiC (which has the largest energy gap of 3.2 eV among the three polytypes) are studied in detail under continuous and pulsed excitations. The recombination processes are discussed, and the energy levels of the luminescent centers are determined (Chapter III). The differences of luminescence spectra and energy levels of Al, Ga, and B centers among the three polytypes are discussed (Chapter IV).

One of the original features of the present investigation is that liquid-phase epitaxial growth is done by the dipping technique in order to avoid the inconvenience encountered in Brander's experiments (Chapter V). The dipping technique has already been successfully used for the liquid-phase epitaxial growth of GaAs and GaP.[I.11, I.12] By this technique, the procedures of epitaxial growth will be carried out more easily, and systematic studies for the establishment of epitaxial growth

conditions and device fabrication techniques will be able to be done. In the present investigation, both p- and n-type 6H-SiC epitaxial layers are grown, and growth conditions suitable for preparation of light-emitting diodes with high quantum efficiency are obtained. Using Al as luminescent centers, blue-light-emitting diodes are fabricated, and the diode characteristics are measured.

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II. SOLUTION GROWTH OF 4H-, 6H-, and 3C-SiC FROM A Si MELT, AND VISIBLE PHOTOLUMINESCENCE DUE TO Al, Ga, AND B ACCEPTORS

1. Introduction

SiC exists in a large number of different crystal structures referred to as "polytypes". Since each polytype has a different energy gap (2.3-3.3 eV), SiC will be a useful semiconductor for various visible-light-emitting devices by a combination of polytypes and luminescent centers. A considerable number of SiC light-emitting diodes have been fabricated up to date, but their luminescent efficiencies have been low.[II.1] One of the predominant causes is a high temperature process used for the crystal growth and the impurity doping (above 2000°C), which makes it difficult to obtain crystals of good quality and to control impurity doping.

The method of solution growth from a Si melt has the advantage of low growth temperature (1550-1800°C).[II.2] By this method 3C-SiC is usually obtained, which has the smallest energy gap. But Brander et al. succeeded in liquid-phase epitaxial growth of 6H-SiC by the immersion technique using a substrate of the same polytype.[II.3] The author has carried out liquid-phase epitaxial growth of 6H-SiC by the dipping technique as described in Chapter V. Both Brander et al. and the author prepared p-n junctions by each own epitaxial technique, and fabricated blue-light-emitting diodes with efficiencies up to 1×10^{-5} photons/electron at room temperature using aluminum as luminescent centers.[II.3]

In this chapter it will be described that single crystals of 4H-type and 6H-type, which have large energy gaps, in addition to 3C-type can be obtained without a substrate crystal

under certain growth conditions. And it will also be shown that aluminum (Al), gallium (Ga), and boron (B) acceptors in these crystals act as luminescent centers of intense visible photo-luminescences at low temperatures. The color of the luminescence varied from violet to red depending on the acceptor and the polytype.

2. Crystal Growth

The method of solution growth from a Si melt in a graphite crucible has been used for the preparation of 3C-SiC crystals by several researchers.[II.2,II.4] But the author has found that single crystals of 4H- and 6H-SiC in addition to 3C-SiC were obtained without any seed crystal when the following two conditions were satisfied. 1) The temperature of the Si melt should be higher (about 1800°C) than usually used for the growth of 3C-SiC. 2) The temperature gradient of the melt was kept as small as possible (less than 5°C/cm). In order to realize the condition 2, the temperature of the bottom of the crucible was set slightly higher than that of the upper part, because the bottom was apt to be cooled by thermal conduction through the graphite support.

The arrangement for the growth is shown in Fig. II.1. The crucible was made of dense and high-purity graphite (apparent density 1.60 g/cm^3, ash content 0.02 %). Its size was 40 mm in depth and 25 mm in inner diameter. A graphite lid was used to avoid evaporation of silicon. The crucible was baked at about 1850°C for 2-3 hours by induction heating under the flow of pure argon gas before the growth. It was filled with a 26 g charge of pure polycrystalline silicon and maintained at about 1300°C for 20 minutes. Then, the temperature was raised to the growth temperature of 1800°C in no more than 15 seconds to

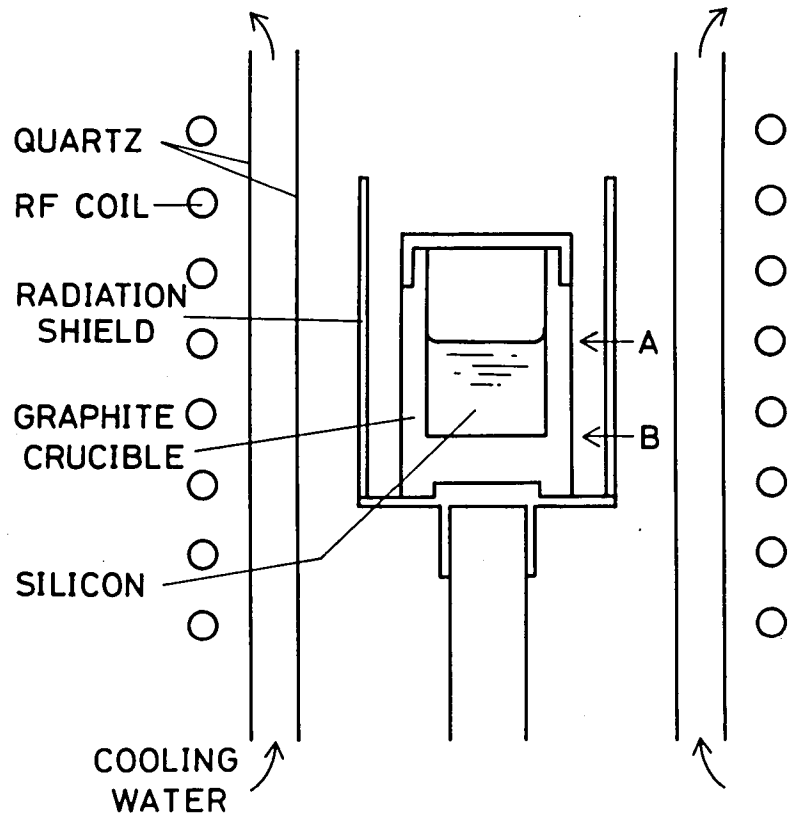
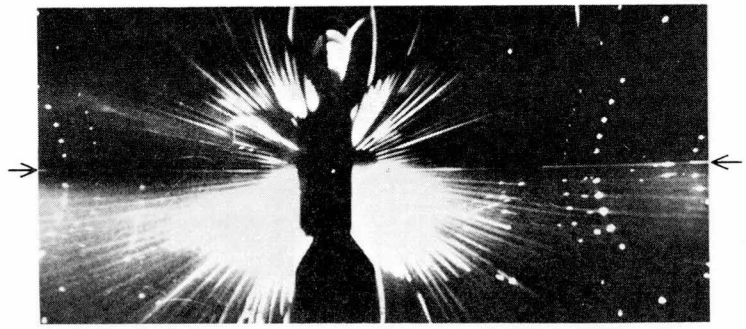


Fig. II.1. Arrangement for the solution growth of 4H-, 6H-, and 3C-SiC single crystals from a Si melt.

(a)



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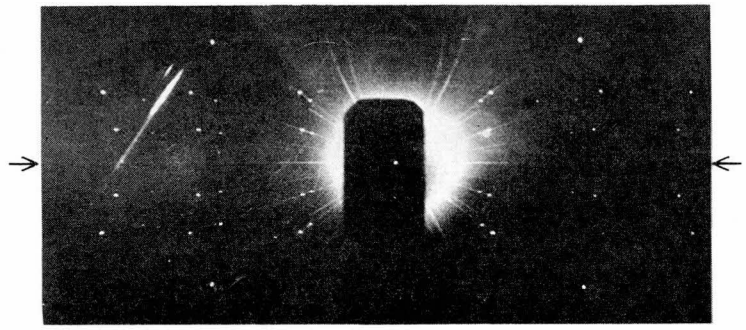

(c)

Fig. II.2. X-ray oscillation photographs about the <0001> axes of SiC bulk crystals, (a) 4H, (b) 6H, and (c) 3C polytypes. (The arrows indicate the center lines.)

avoid cracking of the crucible around the melting point of silicon, and the Si melt was kept at that temperature for 8 hours. (The temperature at point B in Fig. II.1 was set 10-20° C higher than that at point A.) The gas ambient during the growth was pure argon at about 150 cm^3/min.

After the growth, the silicon was removed with a 1:1 mixture of HF and HNO_3. A large number of single crystals of SiC grew on the inner wall of the crucible. The typical crystal size was 0.8x0.8x0.2 mm^3. The inner wall near the bottom was found to be dissolved away slightly.

The polytypes of the crystals in the crucible were identified by X-ray oscillation photographs about their <0001> axes.[II.5] They were found to be single crystals of 4H-, 6H-, and 3C-type. Some examples of the photograph are shown in Fig. II.2. The quality of 6H-SiC crystals seemed to be poorer than those of 4H- and 3C-SiC, because every spot in the photograph of 6H-SiC was somewhat diffused.

Nine kinds of samples were prepared for the photoluminescence measurements, that is, 4H-, 6H-, and 3C-SiC doped with Al, Ga, and B. Al-doped and Ga-doped crystals were grown from the Si melt with 0.025-0.25 at. % Al metal and 1 at. % Ga metal in excess, respectively. B-doped crystals were obtained using B-doped ($2x10^{-3}$ at. %) silicon as a source material.

The impurities of Al, Ga, and B act as acceptors in SiC, but all the crystals were n-type containing unknown donors of the order of 10^{19} cm^{-3}. The donors were probably nitrogen introduced unintentionally from the ambient during the growth.

The author prepared some crystals adding Be, Zn, or In to the silicon by 1 at. %, but they did not show any remarkable photoluminescence at 77-300 K.

3. Photoluminescence

Table II.1. Colors of photoluminescences from SiC of three polytypes. Each value is the wavelength of the maximum peak at 77 K (unit: nm).

Polytype	Luminescence center		
	Al	Ga	B
4H	Violet 419	Blue 431	Green-yellow 542
6H	Blue 465	Green 488	Yellow-orange 621
3C	Orange 612	Red 646	Infrared 870

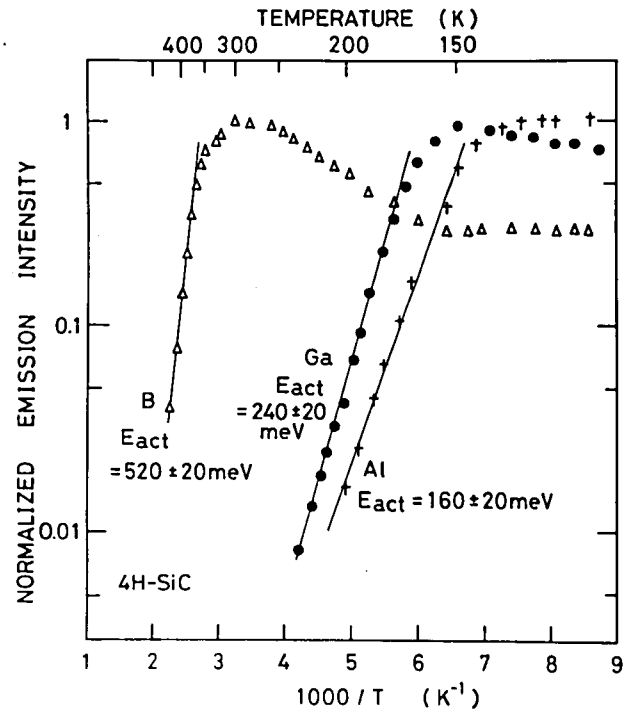

Fig. II.3 Temperature dependence of the emission intensities of the Al-doped, the Ga-doped, and the B-doped 4H-SiC.

By the excitation of UV light (365 nm) from a high-pressure mercury lamp, photoluminescences of these nine kinds of crystals were observed. At low temperatures, all the samples emitted intense photoluminescences of various colors from violet one of 4H-SiC:Al to red one of 3C-SiC:Ga (Color frontispiece 1). Only 3C-SiC:B emitted near-infrared photoluminescence. The color of each luminescence and the wavelength of its maximum emission peak at 77 K are shown in Table II.1. The luminescences of the Al-doped and the Ga-doped samples were quenched below room temperature. But the B-doped samples showed intense luminescence even at room temperature, and the colors were much the same as at low temperatures.

The temperature dependence of the luminescence intensities of the 4H-SiC crystals is shown in Fig. II.3 as a function of reciprocal temperature. The emission intensities of 4H-SiC:Al, 4H-SiC:Ga, and 4H-SiC:B decreased exponentially above 150 K, 175 K, and 350 K, with activation energies of 160 ± 20, 240 ± 20, and 520 ± 20 meV, respectively. The emission intensity of 4H-SiC:B considerably increased with increasing temperature before the thermal quenching occurred. The luminescences of 6H- and 3C-SiC also showed similar temperature dependences.

The luminescences of the Al-doped and the Ga-doped 4H-SiC will be studied in detail in Chapter III. The luminescence spectra and recombination processes of all the samples including 4H-SiC:Al and 4H-SiC:Ga will be discussed in Chapter IV.

4. Summary

Single crystals of 4H-, 6H-, and 3C-SiC were grown from a Si melt in a graphite crucible. Visible photoluminescences due to Al, Ga, and B acceptors in these crystals were observed at low temperatures. The luminescence color varied from violet

to near-infrared depending on the acceptor and the polytype.

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III. RADIATIVE RECOMBINATION PROCESSES IN Ga-DOPED AND Al-DOPED 4H-SiC

1. Introduction

It has been known that acceptors such as Be, Sc, B, Al, Ga, and In act as radiative centers of visible photoluminescences in SiC.[III.1-III.3] Properties of Al acceptors as luminescent centers have been investigated in detail for 3C-, 6H-, and 4H-SiC doped with N and Al.[III.4-III.9] These SiC crystals were prepared by vapor-phase growth. Recently, the luminescence due to B acceptors has been studied for 3C-SiC grown from a Si melt saturated with carbon.[III.10,III.11] These studies have shown that the emissions at low temperatures were due to donor-acceptor pair recombination between the N donors and the B or Al acceptors. They also showed that the emissions at higher temperatures were attributed to the recombination of free electrons with bound holes at the acceptors. Analyzing the luminescence spectra, they have determined the ionization energies of the donor and the acceptors. The values obtained for the Al acceptor were 193 meV,[III.5] 250-260 meV [III.4, III.6] for 3C-SiC, and 150-180 meV + E_x [III.8,III.9] for 4H- and 6H-SiC. E_x is the exciton binding energy of 4H- and 6H-SiC, which is considered to be of the order of 10 meV.[III.12] On the other hand, Hall-effect measurements have given 230-250 meV for the Al acceptor in 4H- and 6H-SiC,[III.9,III.13] which did not agree with those obtained by the luminescence measurements. The ionization energies of the N donor given by Hall-effect measurements were 33 meV for 4H-SiC and 95 meV for 6H-SiC,[III.14] but those by the luminescence measurements were 45-120 meV independent of the polytype.[III.5,III.6,III.8,III.9,III.11]

About the properties of Be, Sc, Ga, and In as luminescent centers, very little is known, and their energy levels in the

forbidden gap remain unknown.

Ga-doped and Al-doped 4H-SiC crystals prepared in Chapter II showed intense blue and violet photoluminescences at low temperatures, respectively. The purpose of this chapter is to find recombination processes of these luminescences and to determine the ionization energies of the Ga and the Al acceptors by measuring luminescence spectra under continuous excitation and time-resolved spectra after pulsed excitation. The ionization energy of the N donor which seems to participate in the recombination process will also be given.

Properties of donor-acceptor pair emissions were investigated in detail by Thomas et al.[III.15] Their theory agreed well with their experimental results obtained for GaP. According to their theory the author summarizes the features of donor-acceptor pair emissions here. When the energy level of either of a donor or an acceptor is shallow and hydrogenic, the transition probability W(R) for pairs with the separation R is given by

$$W(R) = W_0 \cdot \exp(-2R/R_B), \qquad \text{(III.1)}$$

where W_0 is a constant and R_B is the Bohr radius of the carrier bound at the shallower impurity. Equation (III.1) shows that W(R) increases exponentially with decreasing pair separation R. The energy E(R) of the emitted light is expressed by

$$E(R) = E_g - (E_d + E_a) + e^2/\varepsilon R, \qquad \text{(III.2)}$$

where E_d and E_a are the ionization energies of the donor and the acceptor, respectively, e is the electron charge, and ε is the static dielectric constant of the material.

As a result, donor-acceptor pair emissions show the following features in the spectra. 1) Emissions from the pairs with very small separations appear as discrete sharp lines. 2) Emissions from the pairs with relatively large separations produce a non-discrete broad peak. 3) The broad peak observed under

continuous excitation shifts towards higher energies with increasing excitation intensity. 4) The broad peak becomes narrower and shifts towards lower energies during luminescence decay after excitation. 5) The total emission intensity decays non-exponentially owing to the distribution of R and, therefore, of W(R).

2. Experimental Procedures

Ga-doped and Al-doped 4H-SiC crystals were prepared as described in Chapter II.

For continuous excitation a 250 W high-pressure mercury lamp was used as a light source. The UV light of 365 nm was suitably filtered and focused on a sample. The photon number on the sample surface was estimated to be about 5×10^{16} photons/$cm^2 \cdot sec$.[III.16] (Electron-hole pairs of about $7 \times 10^{18}/cm^3 \cdot sec$ will be generated since the absorption coefficient of 4H-SiC is about $4 \times 10\ cm^{-1}$ for the excitation light.[III.20]) Luminescence from the sample was passed through a grating spectrometer (Ritsu MC30) and detected by a photomultiplier (HTV R592).

For time-resolved spectroscopy and luminescence decay measurements after pulsed excitation, a xenon flash lamp (Ushio US190) was used to provide an excitation light. It was operated at a repetition rate of one or ten pulses per second using the stored energy in a 1500 pF condenser charged to 10 kV. The emitted light had a half-width of about 1 μsec. The photon number per flash on the sample surface was about 7×10^{12} photons/cm^2.[III.16] (Electron-hole pairs of about $3 \times 10^{14}/cm^3$ will be generated per flash pulse.) The output signals of the photomultiplier were analyzed by means of a boxcar integrator (NF BX530-A) to obtain time-resolved spectra and decay curves.

3. Experimental Results

3.1. Emission spectra under continuous excitation

Under continuous excitation at low temperatures, blue and violet photoluminescences were observed from the Ga-doped and the Al-doped samples, respectively. Luminescence spectra at 2 K are shown in Fig. III.1. These two spectra were very similar in shape, but that of the Ga-doped sample appeared on the lower energy side. Both consisted of several peaks. The highest-energy peak B_0 (at 2.990 eV for the Ga-doped sample and at 3.067 eV for the Al-doped sample) was relatively sharp. The photon energies of the other peaks B_i (i=1,2,---,5) are given in Table III.1. Each peak energy of the Ga-doped sample was smaller than the corresponding one of the Al-doped sample by an almost constant value: 77 ± 5 meV. Undoped samples showed the same luminescence as that of the Al-doped sample since they contained a small amount of unintentional Al impurities*. But the luminescence intensity was much lower.

The similarity of the two spectra of the Ga-doped and the Al-doped samples may suggest that both emissions originated from similar recombination processes. In Section 4, it will be shown that they are due to donor-acceptor pair recombination between an unknown donor and the Ga or Al acceptor. The B_0 peak will be explained as a zero-phonon peak and the other peaks as its phonon replicas. The energy difference of 77 ± 5 meV between the two spectra is due to the difference in ionization energy of the two acceptors. In Table III.1 the energy difference between the B_0 and the B_i peaks also is shown, from which one can find what kind of phonons contributed to each B_i peak, as will be described in Section 4. The following experiments will be concerned mainly with the B_0 peaks. The other B_i peaks can reasonably be expected to behave in the same manner as the B_0 peaks.

With decreasing excitation intensity down to 1/100 at

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* By spectroscopic analysis.

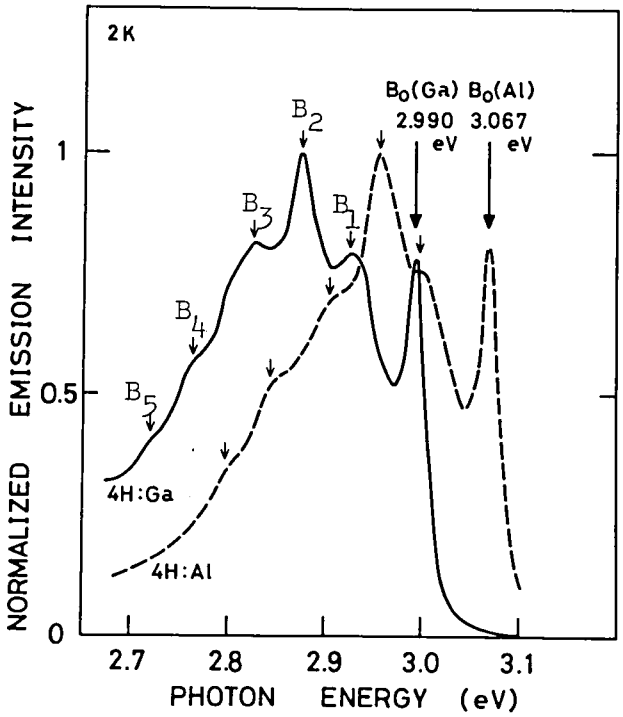

Fig. III.1. Photoluminescence spectra of Ga-doped and Al-doped 4H-SiC under continuous excitation at 2 K. (The B_0 peak is a zero-phonon peak.)

Table III.1. Emission peaks of the luminescence spectra at 2 K.

Peak	Peak energy		Contributing phonon
	4H-SiC:Ga	4H-SiC:Al	
B_0	2.990eV	3.067eV	
B_1	2.924 (66meV)	2.996 (71meV)	LA
B_2	2.873 (117)	2.954 (113)	LO
B_3	2.824 (166)	2.904 (163)	LA + LO
B_4	2.762 (228)	2.843 (224)	2LO
B_5	2.718 (272)	2.798 (269)	LA + 2LO

Numbers in parentheses are energy differences between the B_0 peak and the other peaks.

2K, both B_0 peaks in Fig. III.1 shifted to lower energies by a few meV as shown in Fig. III.2 for the Ga-doped sample. This is one of the evidence of pair recombination.

At higher temperatures a new peak A_0 appeared on the higher energy side of the B_0 peak. Figure III.3 shows the change in the spectrum of the Ga-doped sample with increasing temperature. While thermal broadening of the B_0 peak occurred, the new A_0 peak was found at 3.025 eV at 150 K. The energy difference between the A_0 and the B_0 peaks was about 35 meV. In the spectrum of the Al-doped sample, the A_0 peak seemed to appear above 140 K, but each peak could not be distinguished because of thermal broadening. On the other hand, the spectrum due to Al in the undoped sample changed remarkably with temperature as shown in Fig. III.4. The A_0 peak appeared at 118 K and became dominant with increasing temperature. It was located at 3.101 eV at 129 K. The width of the A_0 peak was narrower than that of the B_0 peak. The energy difference between the A_0 and the B_0 peaks was about 30 meV.

When the excitation intensity was decreased to 1/100, the spectrum at 118 K in Fig. III.4 (due to Al in the undoped 4H-SiC) changed as shown in Fig. III.5. The B_0 peak shifted towards lower energies as at 2 K, while the energy of the A_0 peak did not change. The two peaks of the Ga-doped sample in Fig. III.3 also behaved in the same manner. The A_0 peaks, therefore, are believed to be due to some other recombination process than donor-acceptor pair recombination. As will be described in Section 4, the A_0 peaks are attributed to the recombination of free electrons with bound holes at the acceptors.

The temperature dependence of the luminescence intensity is shown in Fig. III.6 as a function of reciprocal temperature. The luminescence intensity of the Al-doped sample decreased exponentially with a quenching activation energy of 160 ± 20 meV above 150 K, while that of the Ga-doped sample decreased with 240 ± 20 meV above 175 K.

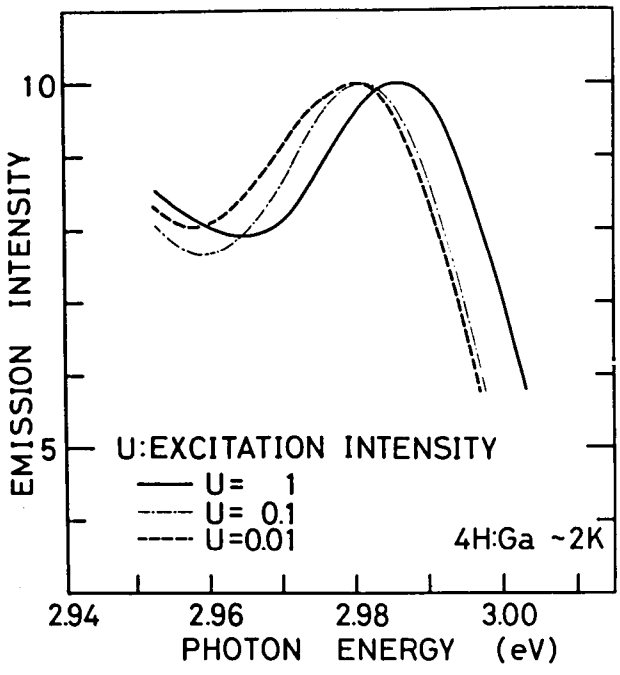

Fig. III.2 Energy shift of the B_O peak of the Ga-doped 4H-SiC with increasing excitation intensity at 2 K.

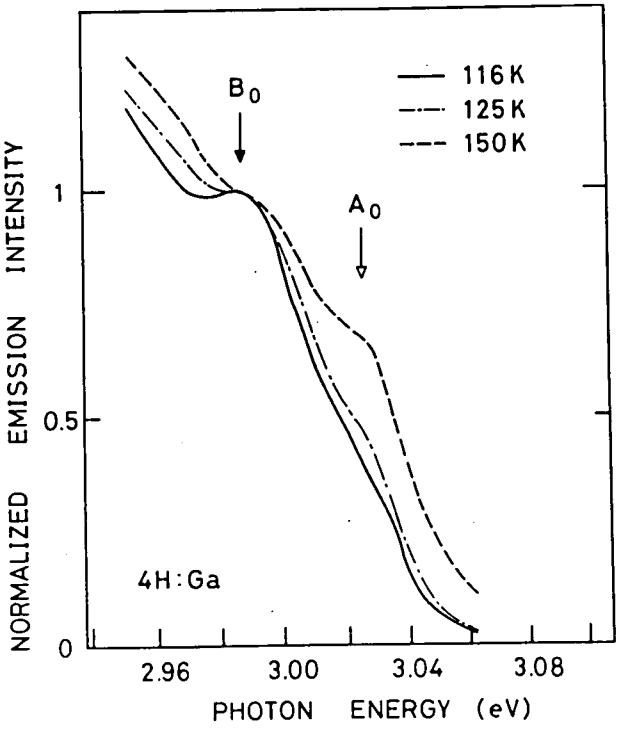

Fig. III.3. Spectral change of the A_O and the B_O peaks of the Ga-doped 4H-SiC with increasing temperature.

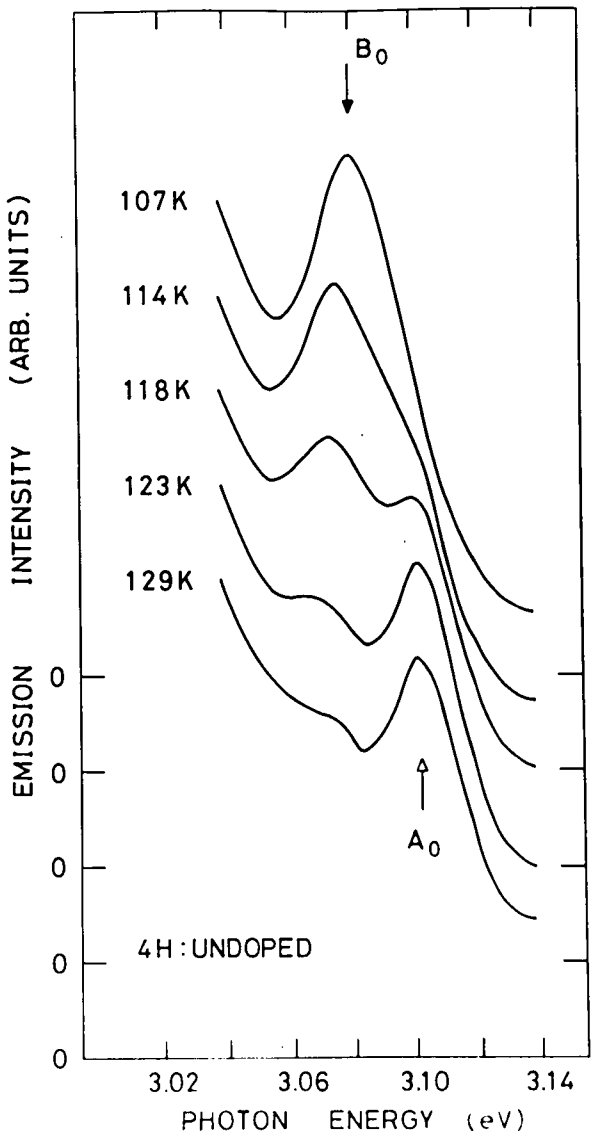

Fig. III.4. Spectral change of the A_0 and the B_0 peaks due to the Al center of the undoped 4H-SiC with increasing temperature.

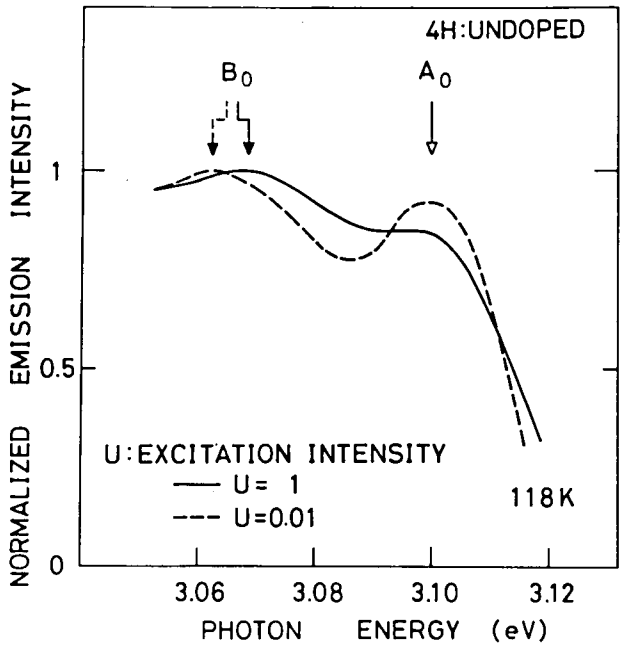

Fig. III.5. Spectral change of the A_0 and the B_0 peaks due to the Al center of the undoped 4H-SiC with excitation intensity at 118 K.

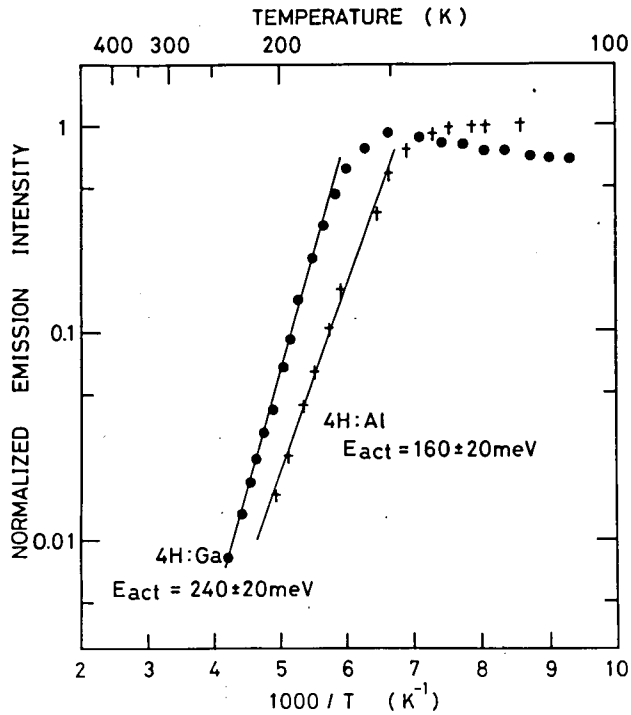

Fig. III.6. Temperature dependence of the emission intensities of the Ga-doped and the Al-doped 4H-SiC samples.

3.2. Time-resolved spectra and decay curves

Figure III.7 shows time-resolved spectra of the B_0 peak of the Ga-doped sample observed at different delay times (t) after pulsed excitation. They were measured at 2 K, 77 K, and 135 K. At 2K, the B_0 peak was very broad at 10 μsec delay. With increasing delay time, it shifted to lower energies and the peak width decreased gradually (Fig. III.7(a)). These features also show another evidence that the B_0 peak is due to pair recombination. The origin of a peak appearing at 2.96 eV at 7 msec remains unknown.

At 77 K, the B_0 peak behaved in the same manner as at 2 K, and a new emission was observed on the higher energy side of the B_0 peak at longer delay times than 500 μsec (Fig. III.7(b)). With increasing delay time it became a distinct peak and its peak height reached to 2/3 of that of the B_0 peak at 7 msec. It was located at 3.021 eV at 7 msec. At 135 K, this new peak appeared as a hump even at 50 μsec (Fig. III.7(c)). It was located at 3.024 eV at 7 msec and its intensity exceeded that of the B_0 peak. From the photon energy, this new peak is considered to be the same A_0 peak that was observed at 150 K under continuous excitation (Fig. III.3). The feature that each A_0 peak had much the same energy at any delay time also shows that it is not due to pair recombination.

In the spectra at 135 K (Fig. III.7(c)), another new peak A_1 appeared at 2.961 eV at 7 msec. Since the energy difference of 63 meV between this peak and the A_0 peak almost agrees with 66 meV between the B_1 and the B_0 peaks (Table III.1), it may be the first phonon replica of the A_0 peak.

Time-resolved spectra of the Al-doped sample at 2K and 77 K are shown in Fig. III.8. The B_0 peak showed the features of donor-acceptor pair recombination. The same A_0 peak observed under continuous excitation was found at longer delay times at 77 K as in Fig. III.8(b). Its peak energy was 3.106 eV at 4 msec.

It should be noted that at 77 K, the A_0 peak of both

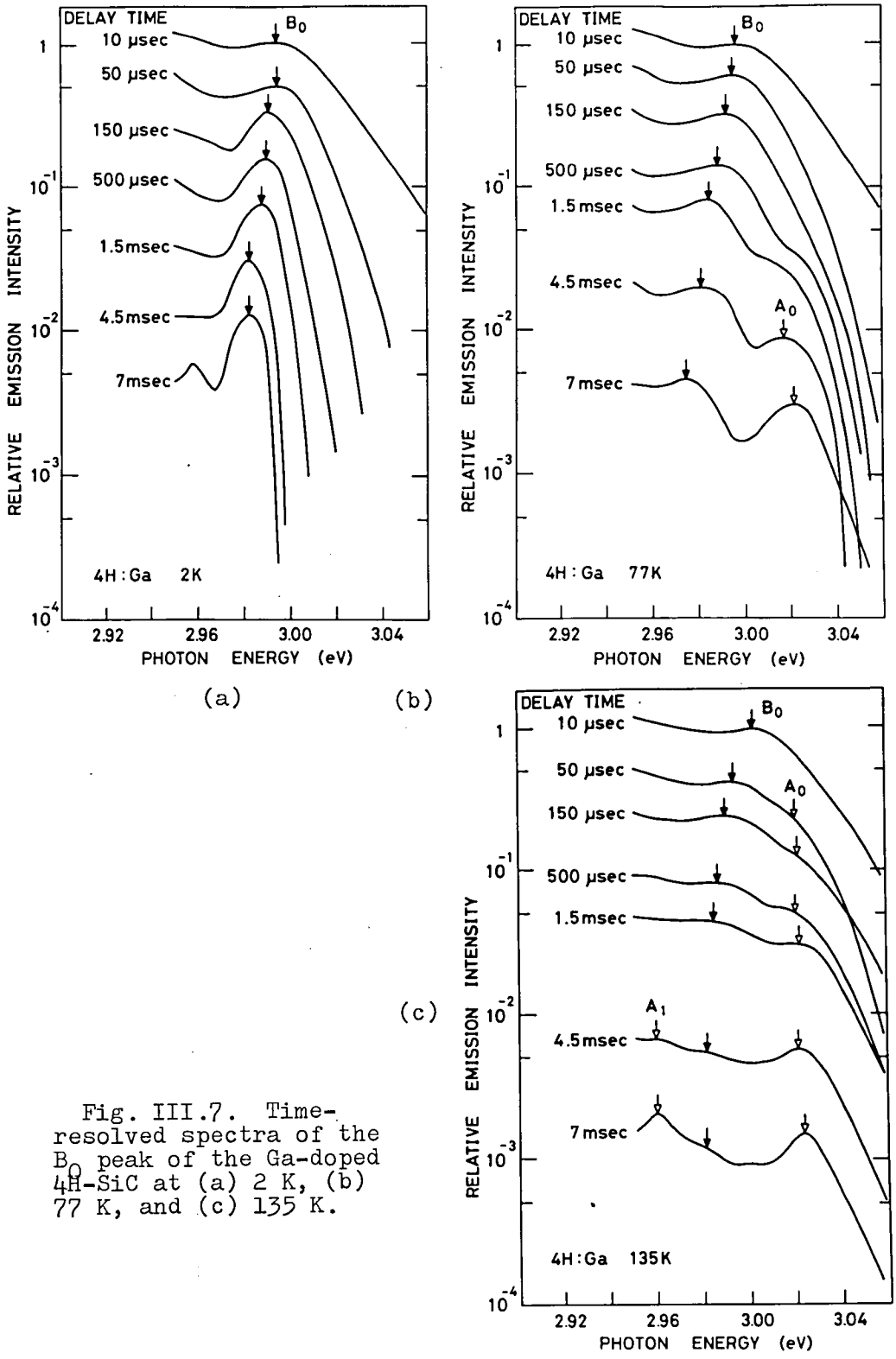

Fig. III.7. Time-resolved spectra of the B_0 peak of the Ga-doped 4H-SiC at (a) 2 K, (b) 77 K, and (c) 135 K.

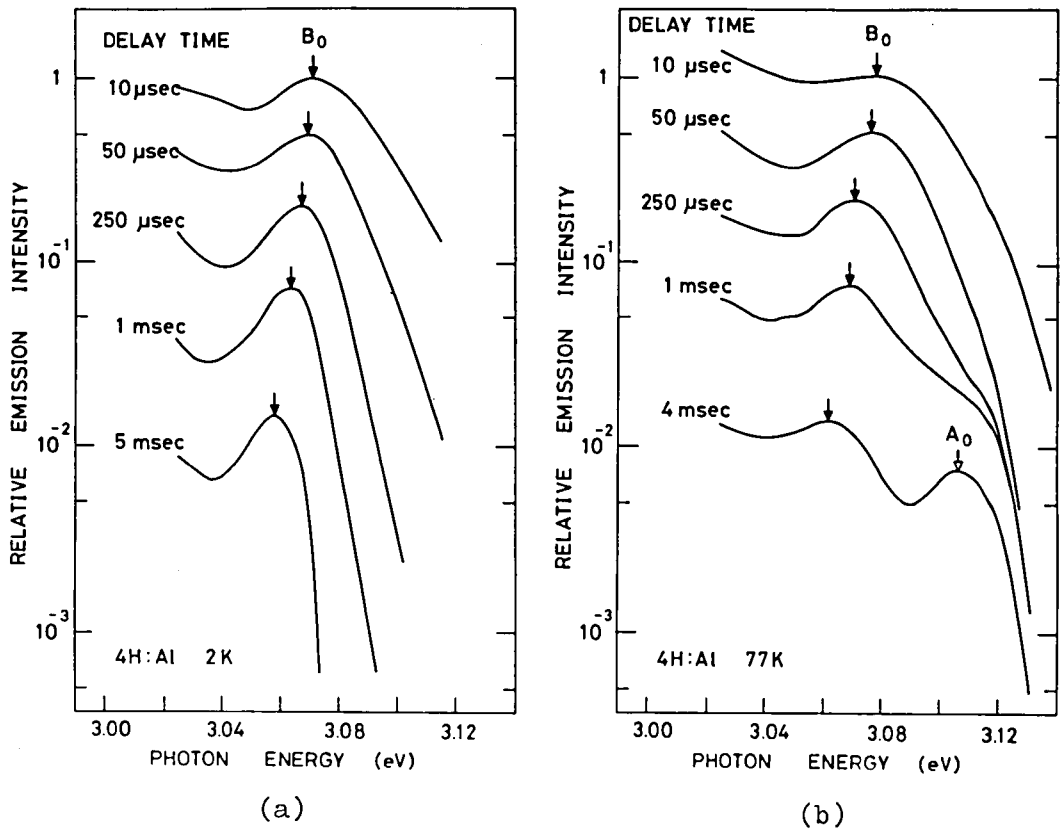

Fig. III.8. Time-resolved spectra of the B_0 peak of the Al-doped 4H-SiC at (a) 2K and (b) 77 K.

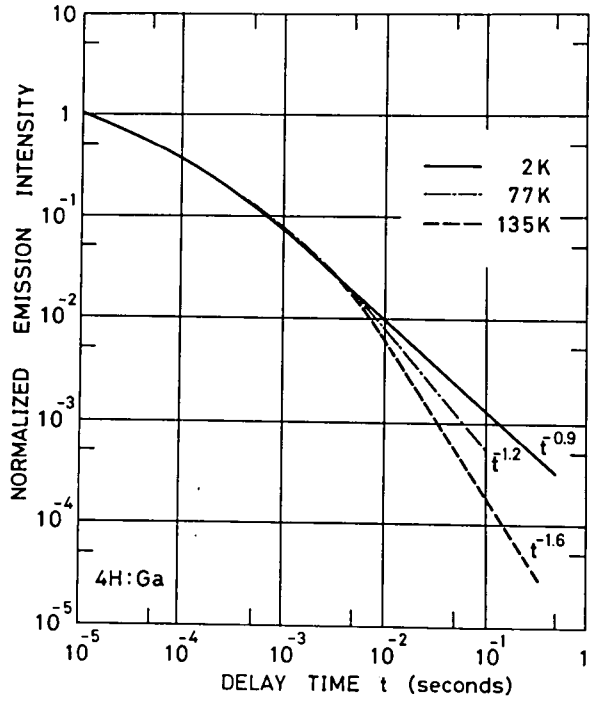

Fig. III.9. Normalized decay curves of the luminescence of the Ga-doped 4H-SiC at 2 K, 77 K, and 135 K.

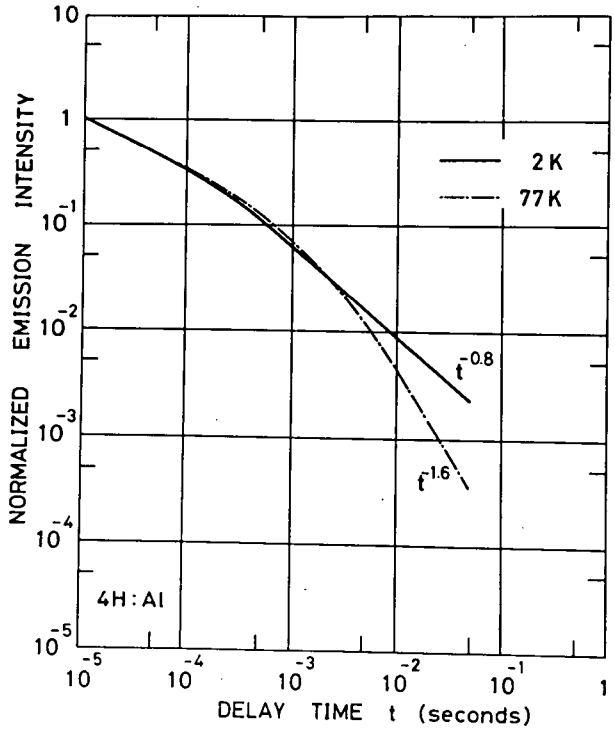

Fig. III.10. Normalized decay curves of the luminescence of the Al-doped 4H-SiC at 2 K and 77 K.

Ga-doped and Al-doped samples were not found in the spectra under continuous excitation, but they appeared in the time-resolved spectra.

Decay curves of the total luminescence intensity are shown in Figs. III.9 and III.10 for the Ga-doped and the Al-doped samples, respectively. They are normalized at the delay time of 10 μsec. All the decay curves at 2 K, 77 K, and 135 K were non-exponential. At longer delays than 5-10 msec they varied as t^{-n}. The value of n is given on each curve. The values were 0.90 and 0.84 at 2 K for the Ga-doped and the Al-doped samples, respectively. They increased with increasing temperature, and the luminescence decayed more rapidly.

4. Discussion

4.1. Donor-acceptor pair recombination

The B_0 peak of the luminescence spectrum of the Al-doped sample showed the features of donor-acceptor pair emissions described in Section 1. Since the excitation intensity was not high enough, discrete emission lines peculiar to pair recombination were not observed. The other B_i peaks on the lower energy side behaved in the same manner as the B_0 peak. Luminescence from SiC crystals containing N donors and Al acceptors has been investigated by a number of authors.[III.4-III.9] They have shown that at low temperatures it was attributed to pair recombination, and the spectrum consisted of a zero-phonon peak and its phonon replicas. The photon energy of the B_0 peak of the Al-doped sample in the present study almost agreed with that of a zero-phonon peak of 4H-SiC reported by Gorban' et al.[III.8] and Hagen et al.[III.9] Unknown donors of the order of 10^{19} cm^{-3} in our samples are probably nitrogen introduced unintentionally from the ambient during the growth (as will be described in Chapter V)*. Consequently,

* Nitrogen is very apt to be introduced into SiC. Oxygen might be introduced unintentionally from the ambient, but how it acts as a donor or a luminescent center in SiC has not yet been studied.

the B_0 peak of the Al-doped sample is a zero-phonon peak of the pair recombination between the N donors and the Al acceptors, and the other B_1-B_5 peaks are its phonon replicas.

Hagen et al reported the presence of another different zero-phonon peak at about 50 meV lower energy than the aforementioned one. But Gorban' et al. did not find such a peak. Hagen et al. explained the two zero-phonon peaks as being due to two kinds of N donors: at the "hexagonal" and the "cubic" lattice sites of 4H-SiC. The Al-doped 4H-SiC in the present study showed much the same spectral shape as Al-doped 3C-SiC prepared in the same growth run (Chapter IV). Since 3C-SiC has only one kind of lattice sites, it is improbable that some of the B_1-B_5 peaks of the Al-doped 4H-SiC may be another zero-phonon peak and its replicas.

The luminescence of the Ga-doped sample also was found to be due to pair recombination at low temperatures. The B_0 peak can be regarded as a zero-phonon peak of the pair recombination between the N donors and the Ga acceptors. As compared with the luminescence of the Al-doped sample, the spectrum appeared on the lower energy side by 77 ± 5 meV. This can be explained by the assumption that the ionization energy of the Ga acceptor is larger than that of the Al acceptor by such a quantity.

Since the spectra of the Ga-doped and the Al-doped samples resembled each other in shape, the same kind of phonons may contribute to the corresponding phonon replicas of the two spectra. The energies of phonons of 4H-SiC have been reported by other authors.[III.17] They obtained 75.6 meV for LA phonon at the zone boundary, while 119.5 meV and 103.9 meV for LO phonons at the zone center and at the zone boundary, respectively. Comparing these values with the energy difference between the B_0 and B_i peaks given in Table III.1, the B_1 and the B_2 peaks are found to be LA and LO phonon replicas, respectively. The B_3, B_4, and B_5 peaks may be explained as LA + LO, 2LO, and LA + 2LO phonon replicas, respectively.

4.2. Recombination between free electrons and bound holes

Emissions due to the recombination of free electrons with bound holes at Al acceptors were found in 3C-SiC doped with N and Al by Zanmarchi.[III.4] Recently, Gorban' et al. have reported the presence of such emissions in 4H-SiC doped with N and Al.[III.8] Similar emissions were observed from 3C-SiC doped with N and B in addition to donor-acceptor pair emissions.[III.10, III.11] These emissions appeared on the 35-40 meV higher energy side than the pair emissions.

The A_0 peaks of our samples are thought to be caused by the recombination of free electrons with bound holes at the Ga or Al acceptors by the following reasons. 1) The A_0 peaks appeared in place of the B_0 peaks at higher temperatures for both samples. 2) The energy difference between the A_0 and the B_0peaks was 30-35 meV. 3) The A_0 peaks did not show the features of donor-acceptor pair recombination. Since at higher temperatures electrons trapped at the donors are ionized thermally into the conduction band, the A_0 peaks become dominant.

The result that the A_0 peak due to the Al acceptor of the undoped sample was observed at relatively low temperatures under continuous excitation may be explained as follows. Under continuous excitation, electrons and holes are generated ceaselessly, and they recombine through the pairs with small pair separations on account of their large transition probabilities. The number of such pairs is probably much smaller in the undoped sample because of the small number of the Al acceptors. Therefore, even at relatively low temperatures, electrons trapped at the donors are ionized thermally before they recombine. Such free electrons can recombine with bound holes at the acceptors.

The thermal quenching of the luminescence intensity shown in Fig. III.6 is not caused by thermal ionization of electrons at the donors but by that of holes at the acceptors. The reasons are that 1) even at the temperature where the A_0 peak began to be dominant, the quenching did not occur yet, and

2) the quenching of the Ga-doped sample began at higher temperature and showed larger activation energy than that of the Al-doped sample. The probability of thermal ionization of bound holes at the acceptors may be expressed as $s \cdot \exp(-E_a/kT)$, where s is a constant and E_a is the ionization energy of the acceptor. Then, the quenching activation energy can be regarded as E_a.[III.18] Therefore, the activation energies of 160 ± 20 meV for the Al-doped sample and 240 ± 20 meV for the Ga-doped sample may be around the ionization energies of the respective acceptors. When the probability of the radiative transition for the A_0 peak and the constant s do not differ between the Ga-doped and the Al-doped samples, the temperature where thermal quenching begins is in proportion to E_a.[III.18] The result that the luminescence of the Ga-doped sample began to quench at higher temperature (175 K) than that of the Al-doped sample (150 K) shows such a tendency.

4.3. Time-resolved spectra and decay curves

This section will discuss the result that the A_0 peaks appeared at longer delay times in the time-resolved spectra at 77 K and 135 K. Such a phenomenon had been observed at 77 K in 3C-SiC doped with N and Al by Long et al.[III.7] They explained it as the recombination of free electrons with bound holes at the acceptors which were isolated or entered the donor-acceptor pairs with large separations. On the basis of their idea, the result obtained is explained as follows. Since the photon number of the excitation light was not large enough, all the excited electrons and holes may be bound by the donors and the acceptors. At 2 K, the bound electrons and holes are not ionized thermally before they recombine to generate pair emissions. Since electrons and holes at the pairs with larger separations recombine more slowly, long decay curves characteristic of pair recombination were observed at 2 K as shown in Figs. III.9 and III.10. At

higher temperatures, bound electrons and holes with smaller pair separations recombine in shorter delay times, but electrons largely separated from the holes are ionized thermally before they recombine. (The ionization energy of the donor is much smaller than that of the acceptor as described in the following section.) These free electrons recombine with bound holes and produce the A_0 peak at longer delay times in the time-resolved spectra even at such low temperatures as 77 K. With increasing temperature, the electrons begin to be ionized in shorter delay time as in Figs. III.7 and III.8.

The normalized decay curve at higher temperature falls more rapidly at longer delay times as in Figs. III.9 and III.10, because electrons largely separated from the holes are ionized much faster. At 135 K, only the A_0 peak and its phonon replicas may be observed at longer delay times than 7 msec from the spectra at 135 K in Fig. III.7(c), but the luminescence intensity did not decay exponentially but as t^{-n} during these delay times at 135 K. This suggests that the thermal ionization and the recombination processes of the electrons are not simple.

Under continuous excitation, electrons and holes are generated ceaselessly, and they recombine through rapid recombination processes, that is, through the pairs with small separations at low temperatures such as 77 K. Therefore, the A_0 peaks, which appeared in the time-resolved spectra at longer delay times owing to the pairs with large separations, were not observed in the spectra under continuous excitation.

4.4. Ionization energies of the N donor and the Ga, Al acceptors

From the energy $h\nu_A$ of the A_0 peak, the ionization energy of the acceptor can be obtained by the following relation III.19):

$$E_a = E_{gx} + E_x + kT - h\nu_A, \qquad \text{(III.3)}$$

where E_{gx}, E_x, and kT are the exciton energy gap, the exciton binding energy, and the thermal energy of the free electron respectively. The sum of E_{gx} and E_x is the energy gap E_g. Using the values of $h\nu_A$ obtained under continuous excitation and in the time-resolved spectra (E_{gx} is given by Ref. III.20), Eq. (III.3) gives

$$E_a = 168 \pm 3 \text{ meV} + E_x \qquad \text{(III.4)}$$

for the Al acceptor, and

$$E_a = 249 \pm 3 \text{ meV} + E_x \qquad \text{(III.5)}$$

for the Ga acceptor.

The ionization energy of the Al acceptor given by Eq. (III.4) almost agrees with 180 meV + E_x by Gorban' et al.[III.8] and 150 meV + E_x by Hagen et al.[III.9] When 13.5 meV is used for E_x (reported for 3C-SiC [III.12]), 182 ± 3 meV is obtained as the ionization energy. This value is smaller than 230-250 meV obtained by Hall-effect measurements.[III.9,III.13]

The ionization energy of the Ga acceptor has been found to be 249 ± 3 meV + E_x by the present study for the first time. The energy is 81 meV larger than that of the Al acceptor. When 13.5 meV is used for E_x, the ionization energy is 263 ± 3 meV.

Both ionization energies of the Al and the Ga acceptors are found to be almost in agreement with the activation energies of the thermal quenching of the luminescence in Fig. III.6 (160 ± 20 meV and 240 ± 20 meV, respectively), as has been expected in Section 4.2.

The photon energy $h\nu(R)$ of the pair emission with the separation R is expressed by

$$h\nu(R) = E_{gx} + E_x - (E_d + E_a) + e^2/\varepsilon R, \qquad \text{(III.6)}$$

where E_d is the ionization energy of the donor, and e and ε are

the electron charge and the static dielectric constant of the material.[III.15] Then, from the photon energy $h\nu_\infty$ due to the pair with extremely large separation, one can obtain $E_d + E_a$ by Eq. (III.6):

$$E_d + E_a = E_{gx} + E_x - h\nu_\infty. \qquad \text{(III.7)}$$

The energy $h\nu_\infty$ can be estimated from the peak energy $h\nu_B$ and the half-width δE of the B_0 peak (the zero-phonon peak) under continuous excitation as described in Ref. III.21. Since the excitation intensity was not high enough, our experimental condition corresponds to the unsaturated limit in Ref. III.21. Thus,

$$h\nu_\infty = h\nu_B - (1/0.76)\,\delta E. \qquad \text{(III.8)}$$

Using the values of $h\nu_B$ and δE given in Table III.2 and 3.265 eV for E_{gx} at 2 K,[III.20] Eqs. (III.7) and (III.8) give

$$E_d + E_a = 227 \text{ meV} + E_x \qquad \text{(III.9)}$$

for the Al-doped sample, and

$$E_d + E_a = 300 \text{ meV} + E_x \qquad \text{(III.10)}$$

for the Ga-doped sample. Using the values previously determined for E_a (Eqs. (III.4) and (III.5)), one obtains

$$E_d = 59 \pm 3 \text{ meV} \qquad \text{(III.11)}$$

for the Al-doped sample, and

$$E_d = 51 \pm 3 \text{ meV} \qquad \text{(III.12)}$$

for the Ga-doped sample. Since the donors in both samples are

Table III.2. $E_d + E_a$, $h\nu_\infty$, and R_p calculated from the peak energy $h\nu_B$ and the half-width δE of the B_0 peak at 2 K.

Sample	$h\nu_B$ (eV)	δE (eV)	$h\nu_\infty$ (eV)	R_p (Å)	$E_d + E_a$ (meV)
4H-SiC:Ga	2.990	0.019	2.965	58	$300 + E_x$
4H-SiC:Al	3.067	0.022	3.038	50	$227 + E_x$

probably the same nitrogen, the ionization energy of the N donor is determined to be 55 ± 7 meV from Eqs. (III.11) and (III.12). This value may be compared with 65 meV from the luminescence data by Gorban' et al.[III.8] and 33 meV by Hall-effect measurements.[III.14]

The pair separation R_p making the most contribution to the B_0 peak is derived from Eqs. (III.6) and (III.7) by $h\nu(R) = h\nu_B$:

$$R_p = e^2/\varepsilon(h\nu_B - h\nu_\infty). \qquad \text{(III.13)}$$

Using 10 as ε,[III.22] 50 Å and 58 Å are obtained for the Al-doped and the Ga-doped samples, respectively.

4. Summary

In order to find the recombination processes of the blue and the violet photoluminescences from the Ga-doped and the Al-doped 4H-SiC, luminescence spectra under continuous excitation were observed at various temperatures and excitation intensities, and the temperature dependence of the total luminescence intensity was measured. In addition, time-resolved spectra and decay curves after pulsed excitation were observed at different temperatures. As a result, the luminescences at 2 K were found to be donor-acceptor pair emissions between the N donors and the Ga or Al acceptors. The luminescence spectra of the two samples resembled each other in shape, and consisted of a zero-phonon peak and its phonon replicas. The contributing phonons were found to be LA, LO phonons and their combinations. At higher temperatures another emission due to the recombination of free electrons with bound holes at the Ga or Al acceptors was observed.

From the energies of the zero-phonon peaks of these two kinds of emissions, the ionization energies of 55 ± 7 meV, 249 ± 3 meV + E_x, and 168 ± 3 meV + E_x were determined for the N donor, the Ga acceptor, and the Al acceptor, respectively. When the value of 13.5 meV obtained for 3C-SiC is used as the exciton binding energy E_x, the latter two are 263 ± 3 meV and 182 ± 3 meV, respectively. The ionization energy of the Ga acceptor was determined by the present study for the first time.

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IV. COMPARISONS OF THE PHOTOLUMINESCENCE SPECTRA DUE TO Al, Ga, AND B ACCEPTORS IN 4H-, 6H-, AND 3C-SiC

1. Introduction

As has been described in Chapter II, Al, Ga, and B acceptors in 4H-, 6H-, and 3C-SiC acted well as visible-photoluminescence centers at low temperatures (Table II.1). SiC crystals doped with B showed intense luminescence even at room temperature (Fig. II.3). The color of the luminescence was found to depend on the acceptor and the polytype. Radiative recombination processes involving Al and Ga in 4H-SiC have been described in detail in Chapter III, and the ionization energies of the N donor and the Al, Ga acceptors were determined.

In this chapter, recombination processes of the photoluminescences due to the three acceptors (Al, Ga, and B) in the three polytypes (4H, 6H, and 3C) will be discussed in terms of the luminescence spectra. The ionization energy of the B acceptor in 4H-SiC will be estimated in addition to those of the Al and the Ga acceptors. Differences in ionization energy among the three polytypes will be discussed for the three acceptors and the N donor.

2. Photoluminescence Spectra

Photoluminescence spectra were measured using a high-pressure mercury lamp, a spectrometer (Ritsu MC30), a photomultiplier (HTV R636), and a lock-in amplifier (NF LI-572B).

Figure IV.1 shows luminescence spectra due to the three

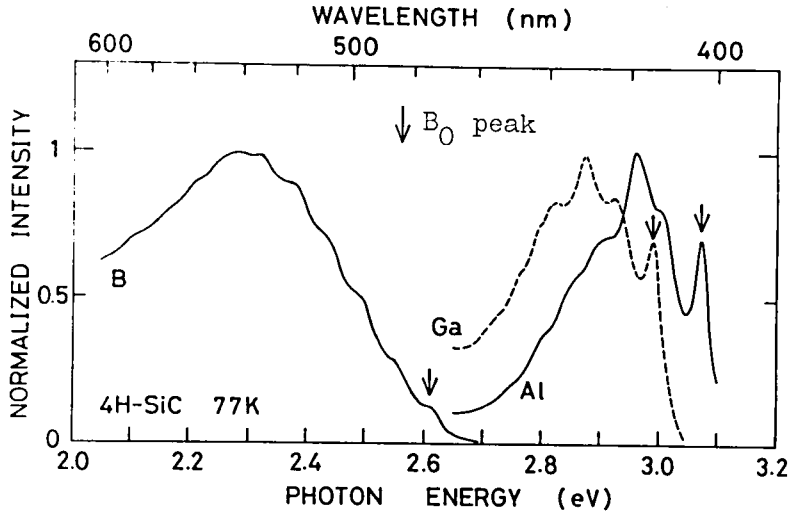

Fig. IV.1. Luminescence spectra of the Al-doped, Ga-doped, and B-doped 4H-SiC crystals at 77 K.

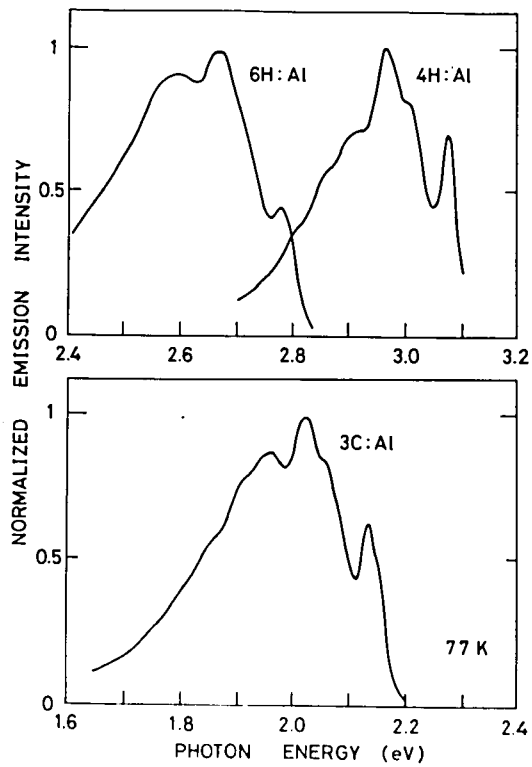

Fig. IV.2. Luminescence spectra of the Al-doped 4H-, 6H-, and 3C-SiC at 77 K.

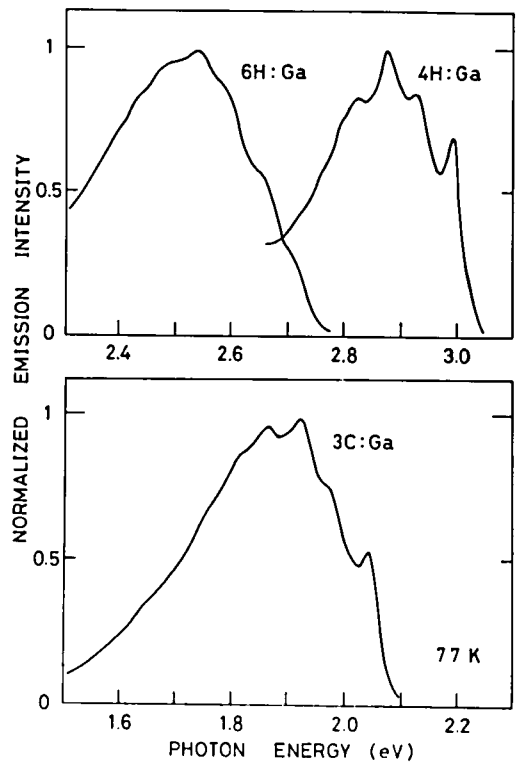

Fig. IV.3. Luminescence spectra of the Ga-doped 4H-, 6H-, and 3C-SiC at 77 K.

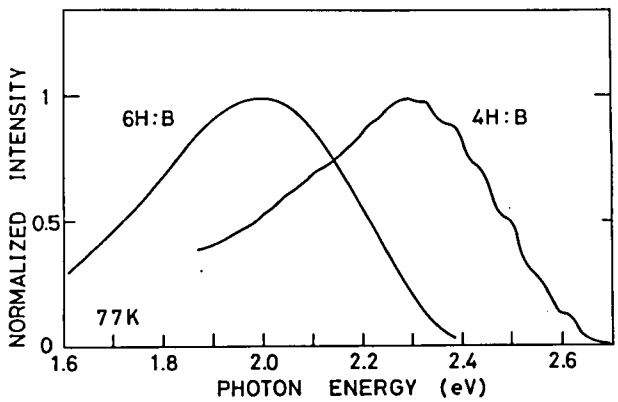

Fig. IV.4. Luminescence spectra of the B-doped 4H- and 6H-SiC at 77 K.

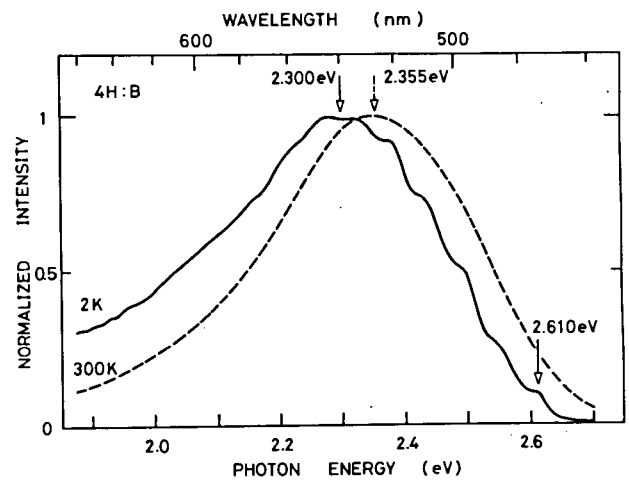

Fig. IV.5. Luminescence spectra of the B-doped 4H-SiC at 2 K and 300 K.

different centers (Al, Ga, and B) in 4H-SiC at 77 K. Comparisons of the spectra due to the same center in the three different polytypes (4H, 6H, and 3C) are shown in Figs. IV.2, IV.3, and IV.4. The spectrum of the B-doped 4H-SiC at room temperature is shown in Fig. IV.5 as compared with that at low temperatures. From these spectra, the following six features may be pointed out. 1) The spectra of 6H- and 3C-SiC due to the same kind of centers were on the lower energy side than that of 4H-SiC by 250-300 meV and 850-950 meV, respectively (Figs. IV.2, IV.3, and IV.4). 2) The spectra due to Ga and B were on the lower energy side than the spectrum due to Al by 50-100 meV and 500-700 meV, respectively, for the three polytypes (Fig. IV.1). 3) All the spectra due to Al and Ga, except 6H-SiC:Ga, almost resembled in shape. Each spectrum had several peaks, among which the highest-energy one (B_0) was relatively sharp (Figs. IV.2 and IV.3). 4) The spectra due to B were "bell-shaped" ones with a very broad spectral width. That of 6H-SiC:Ga resembled these spectra (Fig. IV.4). 5) The spectrum of 4H-SiC:B at room temperature was observed at higher energy than at low temperatures by about 60 meV (Fig. IV.5). 6) Each peak in the spectra of 6H-SiC was a little broader than that of 4H-SiC and 3C-SiC.

Luminescence spectra observed at 2 K were much the same as at 77 K, but each peak was a little sharper. The spectrum of 6H-SiC:B showed two humps on the higher energy side at 2 K like the spectrum of 4H-SiC:B at 77 K shown in Fig. IV.4.

The energy of the highest-energy peak or hump (B_0) of each spectrum, and the energy differences between the B_0 peak and the other peaks on the lower energy side (B_1-B_6) are given in Table IV.1 from the data at 2 K. The peak with an underlined value in Table IV.1 had the maximum height in each spectrum. The peaks B_3 and B_4 of 6H-SiC:Al could not be resolved. The peak of the broad spectrum of 6H-SiC:B may correspond to the peak B_6 as shown in Table IV.1. (For 3C-SiC:B, the data reported by Yamada and Kuwabara [IV.1,IV.2] were adopted. Their crystals

Table IV.1. Photon energy of the zero-phonon peak B_0, and energy differences between B_0 and its phonon replicas B_i (i=1,2,-----,6) at 2 K.

Peak	Al			Ga			B			Contributing phonon
	4H	6H	3C	4H	6H	3C	4H	6H	3C	
B_0	3.067 (eV)	2.774	2.133	2.990	2.725	2.040	2.610	2.334	(1.635*)	
B_1	71 (meV)	64	72	66	61	68	60	59	(69*)	LA
B_2	112	117	114	118	125	120	115	116	(116*)	LO
B_3	162	208	179	167	187	185	177			LA + LO
B_4	223		217	229	239	234	231			2LO
B_5	268	270		273	299	292	286			LA + 2LO
B_6					339	346	335	354		3LO

_____: Maximum peak, (*): by Yamada et al.(Ref.1V.1)

Table IV.2. Photon energy of the A_0 peak.

Sample	Photon energy (eV)	Temperature (K)
4H-SiC:Al	3.101	129
4H-SiC:Ga	3.025	148
4H-SiC:B	2.644	126
6H-SiC:Al	2.801	132
3C-SiC:Al	2.150	120

were prepared by a similar method to that was used in the present study.)

Above 77 K, another peak (A_0) appeared on the higher energy side of the B_0 peak, and it became dominant with increasing temperature (which has already shown in Figs. III.3 and III.4 for 4H-SiC:Ga and 4H-SiC:Al.). The energies of the A_0peaks obtained for several samples are given in Table IV.2.

3. Discussion

3.1. Comparisons of the luminescence spectra

The unknown donors contained in the crystals may be nitrogen introduced unintentionally from the ambient during the crystal growth. The violet and the blue luminescences from the Al-doped and the Ga-doped 4H-SiC have been investigated in detail in Chapter III. At low temperatures, they were found to be due to donor-acceptor pair recombination between the N donors and the Al or Ga acceptors. At higher temperatures, the emissions due to the recombination of free electrons with bound holes at the Al or Ga acceptors were found. Each spectrum due to these two recombination processes consisted of a zero-phonon peak and its phonon replicas.

Luminescence from 3C-SiC doped with N and Al has been investigated by several authors.[IV.3-IV.6] The spectra obtained by them almost agreed with that of 3C-SiC:Al in this study. Recently, studies on the luminescences from 4H- and 6H-SiC doped with N and Al have been reported.[IV.7,IV.8] These luminescences from these three polytypes were explained as donor-acceptor pair emissions between the N donors and the Al acceptors at low temperatures. Yamada and Kuwabara observed near-infrared

luminescence from 3C-SiC doped with N and B at low temperatures.[IV.1,IV.2] They also showed that it was due to pair recombination between the N donors and the B acceptors, but the zero-phonon peak was weak as compared with that of the luminescence due to Al. At higher temperatures, in both luminescence spectra due to Al and B, different emission peaks were found owing to the recombination of free electrons with bound holes at the Al or B acceptors, and they became dominant with increasing temperature.

The six features of the luminescence spectra mentioned in the preceding section offer some properties of the three acceptors in the three polytypes. From the feature 3, all the luminescences due to Al and Ga may be donor-acceptor pair emissions between the N donors and the Al or Ga acceptors. Each relatively sharp peak (B_0) on the highest energy is a zero-phonon peak and the others (B_i) are its phonon replicas. Since the spectra due to B resembled that of 3C-SiC doped with N and B reported by Yamada and Kuwabara, they also may be pair emissions between the N donors and the B acceptors. The first hump (B_0) on the highest energy can be regarded as a zero-phonon peak. All the A_0 peaks which were observed on the higher energy side of the B_0 peaks at higher temperatures are thought to be due to the recombination of free electrons with bound holes.

The energy differences among the spectra of the three polytypes (the feature 1, Figs. IV.2, IV.3, and IV.4) are accounted for by the difference of the energy gap. (The energy gaps at 2 K are 2.390 eV + E_x, 3.023 eV + E_x, and 3.265 eV + E_x for 3C-, 6H-, and 4H-SiC, respectively,[IV.9] where E_x is the exciton binding energy of the order of 10 meV.[IV.10])

The energy differences among the spectra due to the three acceptors (the feature 2, Fig. IV.1) may be attributed to the different energy levels of the acceptors. Therefore, the ionization energy of the Ga acceptor is a little larger than that of the Al acceptor, while that of the B acceptor is

much larger.

Each peak of 6H-SiC was somewhat broader than that of 4H- and 3C-SiC (the feature 6). This might be related to the relatively poor quality of 6H-SiC crystals as shown in Fig. II.2.

3.2. Spectra due to the B acceptors

The bell-shaped spectra with a very broad spectral width of the B-doped samples (the feature 4, Figs. IV.4 and IV.5) are presumably caused by the deep energy level of the B acceptor. It had been shown by Keil [IV.12] that when a localized center participates in an optical transition, the spectrum is composed of a weak zero-phonon peak and a number of its phonon replicas with simultaneous emissions of multiple phonons because of the strong lattice-impurity interaction. Recently, Tajima et al.[IV.13,IV.14] have successfully explained the spectrum of donor-acceptor pair emissions in GaP involving a deep center such as Ge or Bi on the basis of the theoretical model of Keil. They have shown that for a deeper impurity level the lattice-impurity interaction was stronger and replicas emitting larger numbers of phonons were dominant in the spectrum. The spectra of 4H-SiC:B and 6H-SiC:B shown in Fig. IV.4 can be regarded as a case of a strong lattice-impurity interaction, because the energy level of the B acceptor has been found to be located deeply in the forbidden gap. It is due to this strong interaction that the maximum emission peaks of the B-doped samples were the B_6 peaks, while those of the Al-doped and the Ga-doped samples were the B_2 or B_3 peaks as in Table IV.1.

SiC has two kinds of lattice sites, namely, Si-sites and C-sites. Analyzing the discrete line-spectra of pair emissions from 3C-SiC, Choyke et al.[IV.4] and Yamada et al.[IV.1] have shown that N and B substitute the same kind of sites,

while Al the other one. According to the relative atomic sizes, N and B probably occupy the C-sites (which has been confirmed by ESR studies [IV.15]), while Al and Ga the Si-sites. This may be related to the result that the B acceptor has much larger ionization energy than the Al and the Ga acceptors.

The spectrum of 4H-SiC:B at room temperature (300 K) appeared at higher energy than that at low temperatures (2 K and 77 K) by about 60 meV (the feature 5, Fig. IV.5). Since the forbidden gap at room temperature is 30-40 meV smaller,[IV.9] the peak shift of 90-100 meV occurred toward higher energies. The shift is accounted for partly by the change in the recombination process from pair recombination to that between free electrons and bound holes.

Luminescence decay curves of 4H-SiC:B after pulsed excitation were measured by the method mentioned in Chapter III. The curves at various temperatures are shown in Fig. IV.6. They are normalized at 10 μsec delay. The luminescence at 2 K and 77 K showed extremely slow decays. The emission was visible over several seconds after the application of an excitation pulse. (The pair emissions between the N donors and the Al or Ga acceptors showed more rapid decays as in Figs. III.9 and III.10). The decay curves at 200 K and 300 K differed considerably from those at 2 K and 77 K. The normalized intensity at earlier than 5 msec was larger at the higher temperatures (200 K and 300 K) than at the lower temperatures (2 K and 77 K). Moreover, the absolute intensity at 10 μsec delay increased with increasing temperature above 150 K. From these results, rapid radiative recombination is found to increase at higher temperatures.

Although the decay became rapid gradually with increasing temperature, it was fairly slow even at 300 K. The curves at 200 K and 300 K were non-exponential, and at longer than 5 msec they varied as $t^{-0.6}$ and $t^{-1.2}$, respectively.

The total emission intensity of 4H-SiC:B under continuous excitation increased gradually with increasing temperature from 150 K to 300 K as shown in Fig. II.3. This may be caused

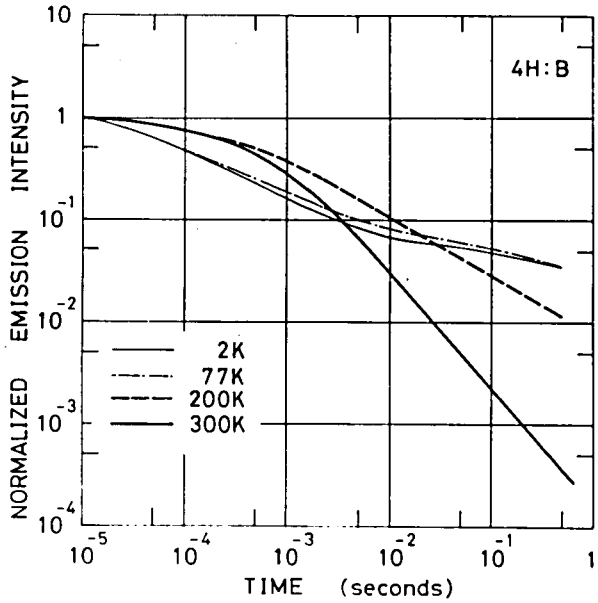

Fig. IV.6. Normalized decay curves of the luminescence of the B-doped 4H-SiC at 2 K, 77 K, 200 K, and 300 K.

by the increase of rapid recombination processes shown by the decay measurements, because under continuous excitation electrons and holes are generated ceaselessly, and they recombine through rapid recombination processes.

3.3. Phonon replicas

Much the same dispersion curves have been reported for the same mode of phonons of every polytype.[IV.20,IV.21] In Table IV.1, the same B_i peak of every polytype is separated from each zero-phonon peak B_0 by an almost constant value independent of polytypes and acceptors. This may indicate that the same mode of phonon contributes to the same B_i peak of every sample. From the values in Table IV.1 and the phonon energies of SiC, the B_1 and the B_2 peaks are found to be LA and LO phonon replicas, respectively. The other replicas may be due to combinations of these two modes as given in Table IV.1. The phonon energies of the B_1 replicas are a little smaller than the value of LA phonon at the zone boundary (75-80 meV), while those of the B_2 replicas are near the value of LO phonon at the zone center (119-121 meV) rather than at the zone boundary (102-105 meV).

3.4. Ionization energies of the donors and the acceptors in the three polytypes

In Chapter III, from the detailed investigation on the luminescences of 4H-SiC:Al and 4H-SiC:Ga, the ionization energies of 55 ± 7 meV, 168 ± 3 meV + E_x, and 249 ± 3 meV + E_x were determined for the N donor, the Al acceptor, and the Ga acceptor, respectively.

It has already been described that from some of the other samples the emission peaks attributed to the recombination

of free electrons with bound holes at the acceptors were observed at higher temperatures. In the same manner as in Chapter III, from the photon energy $h\nu_A$ of the zero-phonon peak A_0, the ionization energy E_a of the acceptor can be obtained by the following relation:[IV.16]

$$E_a = E_{gx} + E_x + kT - h\nu_A, \qquad \text{(IV.1)}$$

where E_{gx}, E_x, and kT are the exciton energy gap, the exciton binding energy, and the thermal energy of the free electron respectively. The sum of E_{gx} and E_x is the energy gap.

The photon energy $h\nu_B$ of the zero-phonon peak of donor-acceptor pair emission is expressed by

$$h\nu_B = E_{gx} + E_x - (E_d + E_a) + E_c, \qquad \text{(IV.2)}$$

where E_d is the ionization energy of the donor and E_c is the Coulomb energy term.[IV.17] From Eqs. (IV.1) and (IV.2), one gets

$$E_d = h\nu_A - h\nu_B - kT + E_c, \qquad \text{(IV.3)}$$

where T is the temperature at which the A_0 peak is observed. Using the values of $h\nu_A$ in Table IV.2, $h\nu_B$ in Table IV.1, and E_{gx} given in Ref. IV.9, one obtains E_a and E_d by Eqs. (IV.1) and (IV.3). The results thus obtained are shown in Table IV.3 in addition to the values obtained for 4H-SiC:Al and 4H-SiC:Ga in Chapter III.

Since the value of E_x is 13.5 meV for 3C-SiC,[IV.10] the ionization energy of Al in 3C-SiC is obtained as 262 meV, which is in good agreement with 260 ± 15 meV obtained from the detailed luminescence study by Long et al.[IV.5] (Their crystals were prepared by vapor-phase growth.) The value of 168 meV + E_x for Al in 4H-SiC may be compared with 150 meV + E_x by Hagen et al.[IV.8] and 180 meV + E_x by Gorban' et al.[IV.7]

Table IV.3. Ionization energies of Al, Ga, and B acceptors and N donor (unit: meV).

	4H	4H	4H	4H	6H	3C
	Al	Ga	B	Al	Al	Al
E_a	$168 + E_x$	$249 + E_x$	$628 + E_x$	$168 + E_x$	$231 + E_x$	$248 + E_x$
E_d	59	51	$23 + E_c$	59	$16 + E_c$	$7 + E_c$

E_a, E_d: the ionization energies of the acceptor and the donor, respectively.
E_x: the exciton binding energy.
E_c: the Coulomb energy term.

(Their crystals were also prepared by vapor-phase growth.) Precise values of E_x for 4H- and 6H-SiC are unknown. When E_x is assumed to be of the same order in the three polytypes, the ionization energy of Al in 4H-SiC is 60-80 meV smaller than those in 6H- and 3C-SiC. It is quite possible that E_x differs substantially among the three polytypes. But since E_x does not probably exceed E_d (55 ± 7 meV), the difference of 60-80 meV cannot be accounted for only by the difference in E_x. When E_a is obtained from Eq. (IV.1), the value of the exciton energy gap E_{gx} is used. So long as E_{gx} for various polytypes obtained by Choyke et al.[IV.9] is used, the smaller ionization energy of Al may be essential to 4H-SiC. The Ga and the B acceptors in 4H-SiC also seemed to show somewhat smaller ionization energies than those in 6H- and 3C-SiC.

There have been very few reports about Ga acceptors in any polytype up to date. Precise electrical measurements about Ga acceptors have not been carried out, either. The ionization energy of the Ga acceptor in SiC was obtained by the present study for the first time. The ionization energy of the B acceptor has been found to be 390 meV for 6H-SiC by Hall-effect measurements.[IV.18] Kuwabara et al. have reported much larger ionization energy of 735 meV for B in 3C-SiC by luminescence studies recently.[IV.2] The value of 628 meV + E_x for B in 4H-SiC by the present investigation almost coincides with their result.

The Coulomb energy term E_c obtained for 4H-SiC:Al and 4H-SiC:Ga were 29 and 25 meV, respectively (in Section 4.4 in Chapter III). If these values are used as E_c in Table IV.3, 48-52 meV is obtained as E_d for 4H-SiC:B. This value is in agreement with 59 and 51 meV for 4H-SiC:Al and 4H-SiC:Ga, respectively. Therefore, one kind of donor with the ionization energy of 55 ± 7 meV, namely, nitrogen participates in the recombination processes of the three kinds of 4H-SiC samples with the different acceptors. Similarly, 41-45 meV for 6H-SiC:Al and 32-36 meV for 3C-SiC:Al are obtained as E_d. These are a

little smaller than the value for 4H-SiC. Since 6H-SiC and 3C-SiC have larger absorption coefficients for the excitation light owing to their smaller energy gaps, the excitation is possibly done in a smaller volume near the sample surface. This may produce the same effect that is brought about by the increase of excitation intensity. Then, the pair separation making the most contribution to the pair-emission peak B_0 becomes small, and the Coulomb energy term E_c becomes large (Eqs. (III.6) and (IV.2)). [IV.17] Therefore, E_d for 6H- and 3C-SiC will be able to approach the value for 4H-SiC.

The value of 55 ± 7 meV for the N donor in 4H-SiC can be compared with those obtained by other researchers, that is, 118,[IV.4] 46,[IV.5] 55 meV [IV.2] for 3C-SiC, 65 [IV.7] and 80 meV [IV.8] for 4H-SiC, and 100 meV [IV.8] for 6H-SiC. Hall-effect measurements gave the ionization energies dependent on the polytype, that is, 95 meV for 6H-SiC and 33 meV for 4H-SiC.[IV.19] The results in the present study did not show such a tendency. It should be noted that E_{gx} and E_x are not used when E_d is obtained by Eq. (IV.3).

3.5. Thermal quenching of the luminescences

The thermal quenching shown in Fig. II.3 may be brought about by the thermal release of bound holes at the acceptors into the valence band, because the luminescences due to the three acceptors began to be quenched at different temperatures with different activation energies. The probability of thermal ionization of bound holes at the acceptors may be expressed as $s \cdot \exp(-E_a/kT)$, where s is a constant and E_a is the ionization energy of the acceptor. Then, the quenching activation energy can be regarded as E_a.[IV.11] The activation energies of 160 ± 20, 240 ± 20, and 520 ± 20 meV obtained for the luminescences due to Al, Ga, and B in 4H-SiC (Fig. II.3) almost agree with the ionization energies of the respective acceptors determined

above (Table IV.3). Moreover, if the probability of the radiative recombination between free electrons and bound holes at the acceptors, and the constant s do not differ among the three different samples of 4H-SiC, the temperature where the quenching begins is in proportion to E_a.[IV.11] The temperatures of 150 K, 175 K, and 350 K obtained for the three samples are almost in such relationship to the ionization energies.

4. Summary

In 4H-, 6H-, and 3C-SiC grown from a Si melt, Al, Ga, and B acceptors were found to act as visible-luminescence centers at low temperatures. The luminescence color varied from violet to near-infrared depending on the energy level of the acceptor and the energy gap of the polytype. The luminescences at low temperatures were due to donor-acceptor recombination between the N donor introduced unintentionally and the Al, Ga, or B acceptor. Each spectrum consisted of a zero-phonon peak and its phonon replicas. The contributing phonons were LA, LO phonons and their combinations. At higher temperatures, another emission appeared owing to the recombination of free electrons with bound holes at the acceptors.

From the luminescence spectra and the temperature dependence of the emission intensity due to the three acceptors, the ionization energy of Ga was found to be a little larger than that of Al in the three polytypes, while B had much larger ionization energy. The ionization energies of Al, Ga, and B in 4H-SiC were 168 meV + E_x, 249 meV + E_x, and 628 meV + E_x, respectively, where E_x is the exciton binding energy of the order of 10 meV. The ionization energy of the N donor was 55 ± 7 meV.

Owing to the deep level of the B acceptor, the spectra

were different from those due to Al and Ga, and phonon replicas emitting larger numbers of phonons were dominant because of the strong lattice-impurity interaction. The luminescence due to B began to be quenched above room temperature, while those due to Al and Ga did below room temperature.

The ionization energies of the Al acceptor in 6H-SiC and 3C-SiC were 231 meV + E_x and 248 meV + E_x, respectively. Even if the difference in E_x among the polytypes is taken into consideration, the value for Al in 4H-SiC was smaller than those in 6H-SiC and 3C-SiC.

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V. LIQUID-PHASE EPITAXIAL GROWTH OF 6H-SiC BY THE DIPPING TECHNIQUE FOR PREPARATION OF BLUE-LIGHT-EMITTING DIODES

1. Introduction

Although light-emitting diodes of GaP, GaAlAs, and GaAsP have been used practically as red and green lamps, blue-light-emitting diodes with high quantum efficiencies have not been realized yet. Wide forbidden gaps (more than 2.5 eV) are necessary for semiconductors to emit blue light. Successive efforts have been made to obtain blue-light-emitting diodes of GaN, ZnS, and ZnSe with high efficiencies. But these semiconductors have the disadvantage that p-type crystals are not easily obtained owing to the self-compensation effect. The maximum external quantum efficiencies for MIS structures were 2×10^{-4} and 5×10^{-4} photons/electron at room temperature for GaN [V.1] and ZnS,[V.2] respectively.

Since SiC has a wide forbidden gap (3.0 eV for 6H-polytype) and both p- and n-type crystals can be obtained by appropriate impurity-doping, considerable attention has long been given to SiC as a material for blue-light-emitting diodes. The diodes have been fabricated mainly by diffusion technique using crystals prepared by the Lely method.[V.3, V.4] But their quantum efficiencies have been low ($<1\times10^{-5}$ photons/electron at room temperature). One of the predominant causes may be a high temperature process (above 2000°C) used for crystal growth and impurity diffusion, which makes it difficult to obtain good crystals and to control impurity doping.

Liquid-phase epitaxial growth of 6H-SiC from a Si melt in a graphite crucible was carried out successfully by Brander et al.[V.5, V.6] Their method is more useful for preparation of

light-emitting diodes with high efficiencies, because the lower growth temperature (1600°-1700°C) can easily control growth processes, impurity doping, and polytypes.

Using aluminum as a luminescent center, they fabricated blue-light-emitting diodes with external quantum efficiencies up to 1×10^{-5} photons/electron at room temperature.[V.5, V.6] Since they fixed the substrate crystal on a stock in the Si melt, they had to take out the grown crystals by cutting the crucible and etching the silicon after the growth. Moreover, they mentioned that grown crystals tended to be damaged by induced stresses when the molten silicon solidified.

In order to solve these problems, the author has attempted liquid-phase epitaxial growth by dipping a substrate crystal into the Si melt. The conditions of epitaxial growth and impurity doping for preparation of blue-light-emitting diodes are described in this chapter. Current-voltage characteristics, luminescence spectra, and external quantum efficiencies of blue-light-emitting diodes fabricated by this dipping technique also are presented.

2. Liquid-Phase Epitaxial Growth

2.1. Procedures of the dipping technique

The arrangement for the growth is shown in Fig. V.1. The crucible was made of dense and high-purity graphite (apparent density 1.60 g/cm^3, ash content 0.02 %). Its size was 53 mm in height and 40 mm in depth. The outer and inner diameters were 35 mm and 25 mm, respectively. In order to avoid evaporation of silicon, a graphite lid with a center hole of 10 mm was used. The crucible was heated inductively, and the temperature of its wall was measured with an optical pyrometer.

SiC crystals used for substrates were prepared by the

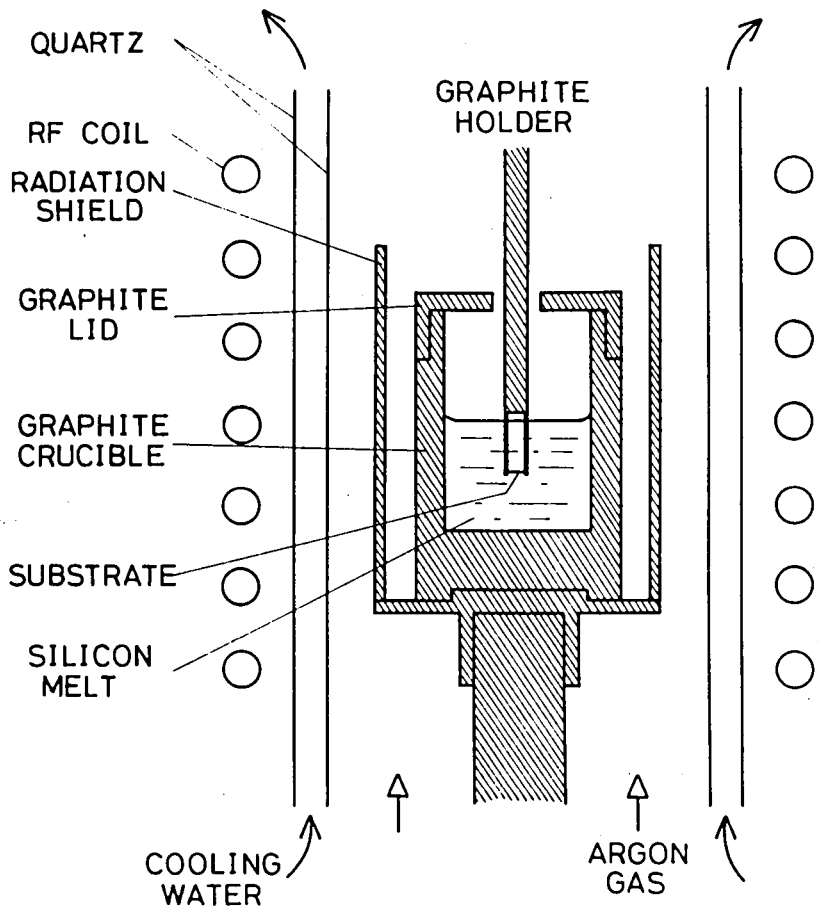


Fig. V.1. Arrangement for liquid-phase epitaxial growth by the dipping technique.

Acheson method. They were identified as single crystals of 6H-polytype by X-ray oscillation photographs about their <0001> axes. The two {0001} faces (the Si face and the C face) of the crystal were lapped with SiC powder and polished with diamond paste. It was cut into pieces of 1x7 mm^2. (The thickness was 0.2-0.4 mm.) The surface polarities were examined by etch pits of H_2 gas at 1550°C for 20 minutes. After being rinsed with trichloroethylene and deionized water, the substrate was put into the slits on the end of the graphite holder. The {0001} faces were set parallel to the surface of the Si melt.

The crucible and the substrate holder were baked at about 1800°C for 2 hours under the flow of pure argon gas before the growth. Then, the crucible was filled with a 26 g charge of pure polycrystalline silicon. After being maintained at 1300°C for 15 minutes, it was heated up to a growth temperature of 1500°-1650°C. (The temperature was raised rapidly around the melting point of silicon to avoid cracking of the crucible.) The substrate was dipped into the Si melt and kept at that temperature for 5 hours. The gas ambient during the growth was pure argon at about 200 cm^3/min.

After the growth, the substrate was pulled up from the Si melt before the melt was cooled. Residual silicon on the grown layers was removed with a 1:1 mixture of HF and HNO_3. By this dipping technique, the crucible and silicon could be used several times.

Since the purpose of the present investigation is to prepare light-emitting diodes with high efficiencies by this method, a series of experiments has been done to obtain epitaxial layers satisfying the following conditions. 1) The polytype of the grown layer should be the same 6H-type as the substrate. 2) The surface of the grown layer is flat and smooth. 3) The growth temperature is as low as possible.

2.2. Results of epitaxial growth

At first, the substrate was fixed to the holder with

the {0001} faces perpendicular to the Si melt. Epitaxial layers of 6H-SiC 20-140 μm thick were grown on the {0001} faces after 5 hours growth at 1550°-1750°C as shown in Fig. V.2. But the grown layers were not flat, that is, much thicker near the surface of the Si melt. Therefore, the {0001} faces were set parallel to the surface of the Si melt as shown in Fig. V.1.

In every experiment, two substrates made from the same crystal were put side by side on the holder. One of them was set with the Si face upward, while the other with the C face upward. But no considerable difference between the upward and the downward grown layers was found.

Epitaxial growth was carried out at 1500°-1650°C for 5 hours with the substrate at the middle of the Si melt and without temperature gradient of the crucible. Grown layers up to 100 μm thick were obtained almost uniformly over the substrate. The layer on the C face was thicker than on the Si face with every growth. Growth rates obtained are shown in Fig. V.3 as a function of growth temperature. The growth rate increased with increasing growth temperature. Between 1550°C and 1650°C, it varied as $c \cdot \exp(-E/RT)$, where c was a constant and E was about 140 kcal/mole. At 1500°C, the growth rate was considerably larger for the C face, and very little deposition was found on the Si face.

The appearance of the grown layers was quite different between the Si and the C faces as shown in Fig. V.4. The former was relatively smooth and showed a wavy pattern, whereas the latter was composed of many growth steps. With increasing growth temperature from 1500°C to 1650°C, flatness and smoothness of the grown layers on both faces were improved. Especially, those on the Si faces at 1600°C and 1650°C were fairly good as shown in Fig. V.4. All the layers were transparent with a bluish color.

The reason why SiC deposited on the substrate without any temperature gradient and any cooling process may be that the temperature around the substrate was probably lower owing to thermal conduction through the holder. Carbon dissolving in the

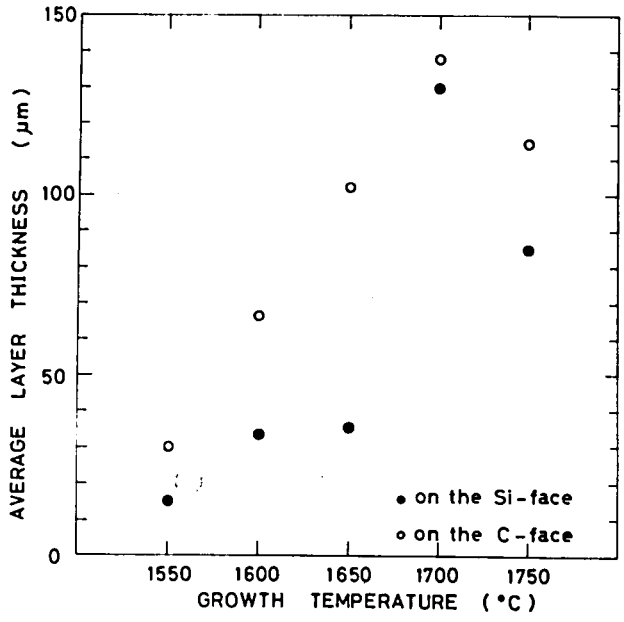


Fig. V.2. Average layer thickness grown on the {0001} faces of the substrate, which was set perpendicular to the surface of the Si melt (5 hours growth).

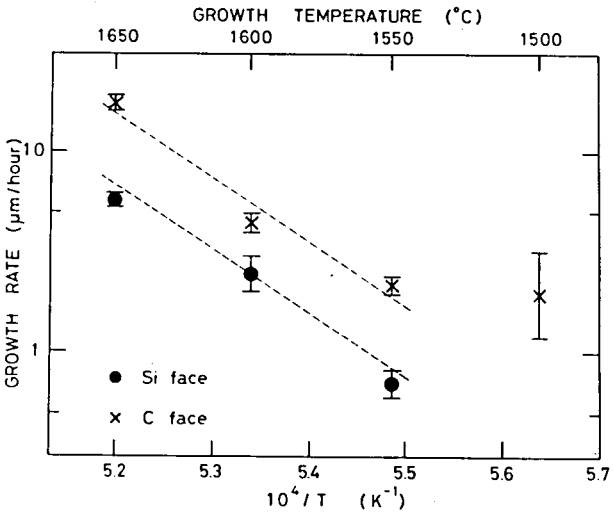
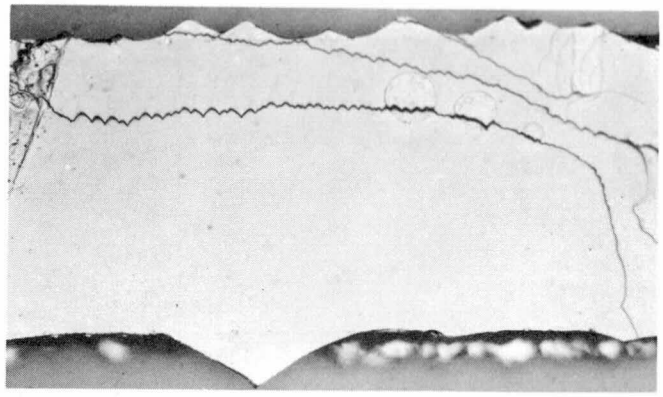
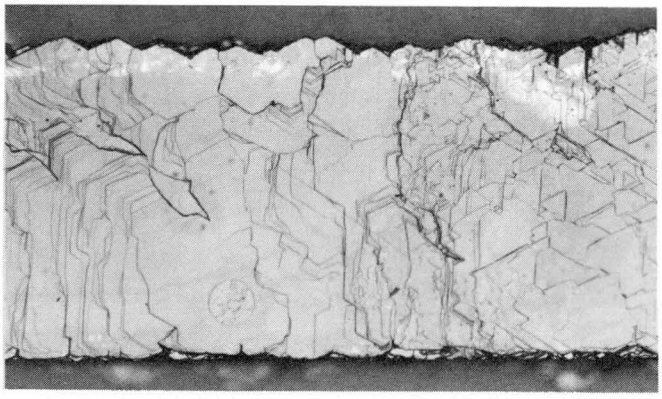


Fig. V.3. Growth rate as a function of growth temperature (5 hours growth, with the {0001} faces of the substrate parallel to the surface of the Si melt.)



(a)



(b)

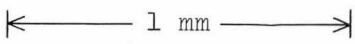


Fig. V.4. Grown layers on the {0001} faces after 5 hours growth at 1600°C, (a) Si face, (b) C face.

Si melt from the crucible wall travelled to the substrate. There, the Si melt was supersatulated with carbon owing to the lower temperature, and SiC was crystallized. The increase in growth rate at higher growth temperature shown in Fig. V.3 may be due to the increase of solubility of carbon in the Si melt.

To identify the polytypes of the grown layers is important, because when a substrate crystal is not used, SiC crystallizes in only 3C-type (which has the smallest energy gap) by this solution method at these growth temperatures.[V.7] The author determined the polytypes by taking X-ray oscillation photographs about the <0001> axes of the grown layers [V.8] and measuring photoluminescence spectra of the layers at 77 K. As a visible-luminescence center, a slight amount of pure aluminum metal (about 10^{-2} at. %) was added to the silicon in the crucible before the growth. Aluminum acts very well as a visible-luminescence center at low temperatures and the photon energy of the luminescence depends on the polytype, as has been described in Chapter IV. By these analyses, the grown layers at 1550°-1650°C were found to be 6H-type single crystals grown epitaxially on the {0001} faces of the substrates. At 1500°C a certain part of the deposited layer was 3C-SiC. This seems to have caused the deviation from the straight line of the growth rate at 1500°C in Fig. V.3.

Then, some experiments were done in order to find how the position of the substrate in the Si melt influenced grown layers. Figure V.5 shows growth rates at 1600°C for 5 hours growth as a function of the position of the substrate. Temperature gradient of the crucible was set as small as possible again. The numbers indicating the positions are the distances from the surface of the Si melt. The depth of the Si melt was about 20 mm. The growth rate thus obtained was larger near the surface of the Si melt (at the distance of 2 mm) and the bottom of the crucible (17 mm) than that at the middle of the Si melt (8 mm). But flatness and smoothness of the grown layers for the former two cases were considerably poorer.

Figure V.6 shows the changes in growth rate when some

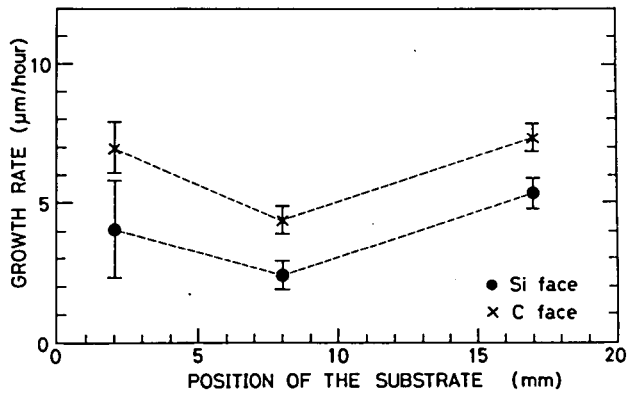


Fig. V.5. Growth rate as a function of the position of the substrate in the Si melt (5 hours growth at 1600°C). The numbers indicating the positions are the distances from the surface of the Si melt.

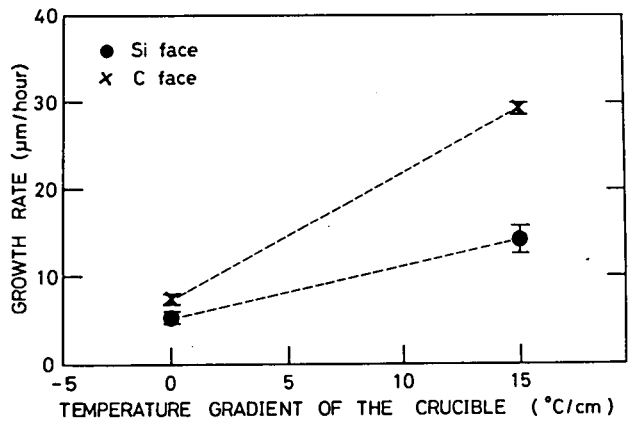


Fig. V.6. Growth rate as a function of temperature gradient of the crucible (5 hours growth at 1600°C). Positive gradient means higher temperature at the upper part of the crucible.

temperature gradient was set on the crucible. The substrate was maintained at the middle of the Si melt. When the temperatures of the crucible were 1600°C near the surface of the Si melt and 1570°C at the bottom (the temperature gradient of 15°C/cm), the growth rate increased by a factor of three to four. But the surfaces of the grown layers were found to lose flatness and smoothness.

As a result of all these experiments, it was concluded that epitaxial layers satisfying the aforementioned three conditions were obtained on the Si face at 1600°C when the substrate was set at the middle of the Si melt without any intentional temperature gradient. All epitaxial layers used for electrical measurements, impurity-doping studies, and preparation of light-emitting diodes described in the following sections were prepared under this growth condition (with the Si face upward).

2.3. Impurity doping

In blue-light-emitting diodes described in the following sections, aluminum was used as acceptors and luminescent centers, and nitrogen as donors. Aluminum-doped epitaxial layers were obtained by the addition of pure aluminum metal to the silicon in the crucible. Nitrogen-doped ones were prepared with pure nitrogen gas added to the flow of argon gas. The resistivity, carrier concentration, and mobility of undoped, aluminum-doped, and nitrogen-doped layers were measured at 80-340 K by Hall-effect measurements using van der Pauw's method.[V.9)] Ohmic electrical contacts were made by alloying of a gold-tantalum alloy (99:1) for n-type layers and an aluminum-silicon alloy (89:11) for p-type layers. The alloying was carried out at 1220°C for a few minutes in pure argon or nitrogen atmosphere for the former and at 930°C for a few minutes under the vacuum lower than 10^{-5} Torr for the latter. Thickness of the epitaxial layers were 15-30 μm, and the measurements were carried out with the substrate

behind them. Since all the substrates were n-type crystals, every n-type layer for the measurements was grown on a p-type layer 15-30 μm thick which was prepared on the substrate.

At first, undoped layers prepared by the procedures described in Section 2.1 were n-type with a high carrier concentration of about 5×10^{19} cm^{-3} at 300 K. Main donors may be nitrogen introduced unintentionally from the ambient during the growth, because it is known to be very apt to enter SiC as a donor*. (The air in the growth system shown in Fig. V.1 was exhausted to a vacuum level only obtained by a rotary pump ($\gtrsim 10^{-2}$ Torr) before the introduction of pure argon gas.)

In order to decrease a carrier concentration of an undoped layer, the following procedures were taken. 1) Before the growth, the crucible and the substrate holder were baked at 1800°C for 2 hours under the vacuum of 10^{-5} Torr or less. 2) The substrate crystal which was rinsed with trichloroethylene and deionized water were immersed in HF acid for more than 8 hours before the growth. 3) Surfaces of source Si crystals were cleaned by etching with a 1:5 mixture of HF and HNO_3.(Aluminum also was etched with HCl acid.) 4) The crucible filled with the silicon (and aluminum) was heated at about 600°C for an hour under the vacuum of 10^{-5} Torr or less before pure argon gas was introduced and the crucible was heated up to the growth temperature of 1600°C.

As a result, the carrier concentration of undoped layers was decreased to 6.3×10^{17} cm^{-3}. Mobilities up to 130 $cm^2/Vsec$ at 300 K were obtained. The procedures 1 and 4 seemed to be most effective. Results of Hall-effect measurements for several typical samples including aluminum-doped and nitrogen-doped ones are shown in Table V.1 ((a) 300 K, (b) 80 K). The temperature dependences of the resistivity, carrier concentration, and mobility of a typical undoped layer with a carrier concentration of 1.4×10^{18} cm^{-3} at 300 K (sample U2) are shown in Fig. V.7. The carrier concentration increased exponentially with decreasing reciprocal temperature between 150 K and 340 K. The activation energy was 66 meV, which agreed with the ionization energy of

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* Whether oxygen is introduced into SiC from the ambient or not and how it acts as a donor or a luminescent center have not yet been studied.

Table V.1 (a). Electrical properties of epitaxial layers at 300 K.

Sample	Conduction type	Added impurity Al (ato%)	Added impurity N_2 (vol%)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vsec)	Resistivity (Ωcm)
U1	n	0	0	6.3×10^{17}	1.3×10^{2}	7.6×10^{-2}
U2*	n	0	0	1.4×10^{18}	4.8×10	9.5×10^{-2}
N1	n	0	0.1	5.1×10^{19}	1.2×10	1.0×10^{-2}
N2	n	0	0.2	9.0×10^{19}	2.2×10	3.2×10^{-3}
A11	n	0.01	0	3.9×10^{17}	9.4×10	1.7×10^{-1}
A12	p	0.6	0	———	———	———
A13	p	2.5	0	1.6×10^{18}	1.3×10	3.1×10^{-1}
A14	p	5.0	0	4.5×10^{18}	1.0×10	1.4×10^{-1}
A15	p	10.0	0	5.2×10^{18}	7.0	1.7×10^{-1}

* The vacuum prepared before the growth was rather poor (3.4×10^{-4}Torr).

Table V.1 (b). Electrical properties of epitaxial layers at 80 K.

Sample	Conduction type	Carrier concentration (cm^{-3})	Mobility (cm^2/Vsec)	Resistivity (Ωcm)
U2	n	1.4×10^{16}	3.0×10^{2}	1.5
N1	n	4.6×10^{19}	1.2×10	1.2×10^{-2}
A13	p	2.2×10^{16}	8.7	3.3×10

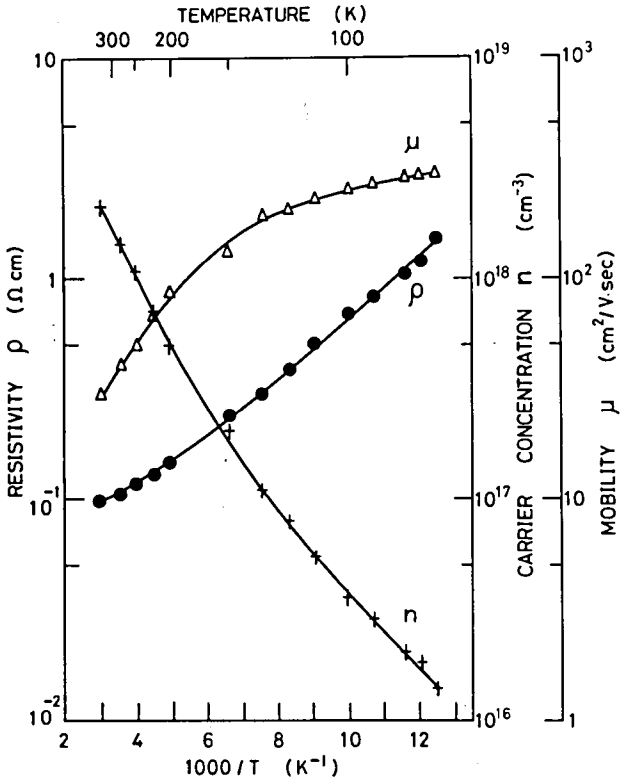

Fig. V.7. Temperature dependences of the resistivity (ρ), carrier concentration (n), and mobility (μ) of a typical undoped sample (sample U2).

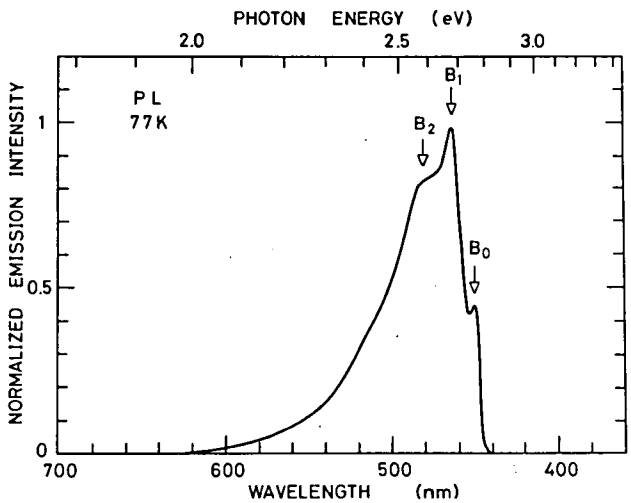

Fig. V.8. Typical photoluminescence spectrum of aluminum-doped layers at 77 K.

50-70 meV for the nitrogen donor reported by other researchers.[V.10, V.11]

Nitrogen gas of 0.1-0.2 vol. % added to the argon gas brought about highly-doped n-type layers with carrier concentrations of $(5.1\text{-}9.0)\times10^{19}$ cm^{-3} as in Table V.1. By the addition of more than 0.5 at. % aluminum metal to the silicon, p-type epitaxial layers were obtained. The layers showed carrier concentrations up to 5.2×10^{18} cm^{-3} at 300 K as in Table V.1. Mobilities of the p-layer were 7-13 $cm^2/Vsec$ at 300 K and changed little with decreasing temperature.

The growth rate and appearance of the undoped and nitrogen-doped layers were the same as described in the preceding section. But the growth rate of the aluminum-doped one on the Si face increased with increasing aluminum, while that on the C face did not change. Consequently, the difference in growth rate between both faces became very little. The p-type layers obtained by the addition of more than 5 at. % aluminum had poor transparency and surface flatness. A number of defects also were found on the surfaces. Therefore, those layers were unsuitable for light-emitting diodes.

Aluminum-doped layers showed intense blue photoluminescence at 77 K by the excitation with UV light (365 nm) from a high-pressure mercury lamp. Its typical spectrum is shown in Fig. V.8. This luminescence is thought to be due to donor-acceptor pair recombination between nitrogen donors and aluminum acceptors from detailed luminescence studies about bulk crystals of 6H-SiC by the author (described in Chapters III and IV) and other researchers.[V.12, V.13] As compared with the spectrum of 6H-SiC:Al in Fig. IV.2, the peak B_0 of 448 nm is explained as a zero-phonon peak. The other peaks and humps on the lower photon-energy side, including B_1 (462 nm) and B_2 (478 nm), are its phonon replicas.

3. Light-Emitting Diodes

3.1. Diode fabrication

The blue pair-emissions between nitrogen donors and aluminum acceptors shown in Fig. V.8 were utilized for blue-light-emitting diodes prepared by liquid-phase epitaxial growth by the dipping technique. By an overcompensation procedure, p- and n-layers of the diode were grown continuously in one growth run.

The diode structure is shown in Fig. V.9. Since substrate crystals obtained by the Acheson method were all n-type, a p-type layer (P_1) for attaching an electrical contact was first grown on the Si face of the substrate in the Si melt with 5 at. % aluminum. After the grown layer was polished slightly, it was partially covered with a small piece of SiC and fixed to the holder. In the Si melt with 2.5 at. % aluminum, the second p-layer (P_2) was grown epitaxially. Then, without changing the temperature and moving the holder, nitrogen gas less than 0.1 vol. % being introduced into the flow of argon gas to over-compensate aluminum acceptors, the last n-layer (N) was grown on the second p-layer continuously. Each layer was grown at 1600°C for 5 hours. Thickness of each layer is given in Fig. V.9. In order to remove n-SiC slightly deposited under the SiC cover, the surfaces of the sample were etched at 500°C for half a minute with a 1:1 molten mixture of Na_2O_2 and $NaNO_2$. Then, the sample was cut into the size given in Fig. V.9.

Results of Hall-effect measurements for each layer are given in Table V.2. The second p-layer (P_2) showed much higher carrier concentration than was anticipated from the data in Table V.1. As a result, under the forward bias, free holes in the p-layer are expected to be injected into the n-layer and to recombine with electrons in the n-layer. This may be favourable for the donor-acceptor pair emissions because a large number of

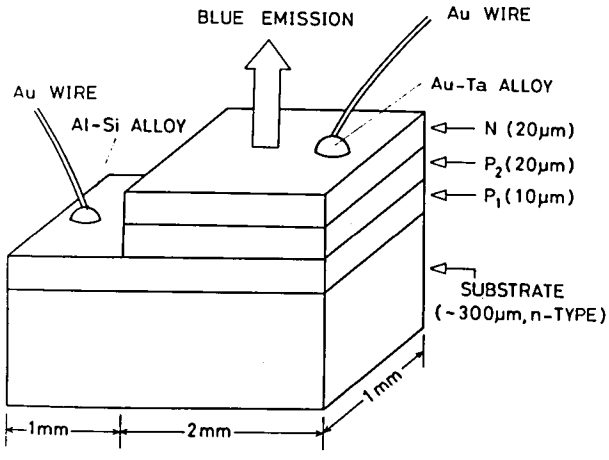

Fig. V.9. Diode structure.

Table V.2. Electrical properties of each layer of the diode at 300 K.

Layer	Conduction type	Added impurity Al (ato%)	Added impurity N_2 (vol%)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vsec)	Resistivity (Ω cm)
N	n	2.5	<0.1	5.1×10^{18}	7.0	1.8×10^{-1}
P_2	p	2.5	0	3.3×10^{19}	3.0	6.4×10^{-2}
P_1	p	5.0	0	4.5×10^{18}	1.0x10	1.4×10^{-1}
Substrate	n	——	——	10^{17}~10^{18}	——	——

aluminum acceptors are compensated by nitrogen donors in the n-layer and may act as luminescent centers.

Ohmic electrical contacts with low resistance were made by alloying of a gold-tantalum alloy (99:1) for the n-layer and an aluminum-silicon alloy (89:11) for the p-layer. The alloying was carried out at 1220°C for the gold-tantalum alloy and at 930°C for the aluminum-silicon alloy for a few minutes in pure argon atmosphere.

3.2. Electroluminescence

Current-voltage characteristics and electroluminescence of the diode were studied at 300 K. Electroluminescence spectra were measured using a grating spectrometer (Ritsu MC30) and a photomultiplier (HTV R636). External quantum efficiencies of the luminescence were obtained by an integrating sphere method.

A current-voltage curve in the low applied voltage range is shown in Fig. V.10. The rectification characteristic was rather poor, and considerable leakage currents were observed in the reverse bias region.

By the application of pulse voltages (frequency 1 KHz, pulse width 100 μsec), electroluminescence was measured at forward currents ranging from 10 mA (applied voltage 3.5 V) to 600 mA (32 V). The forward current increased almost in proportion to the square of the applied voltage. At the current of 10 mA (3.5 V), blue luminescence was observed at the junction near the aluminum-silicon contact (see Fig. V.9). The area emitting the luminescence spread from the left to the right in Fig. V.9. Above 200 mA (20 V) the luminescence was emitted from the whole junction area, and had enough brightness under room light (Color frontispiece 2). Polishing one side of the diode and observing the luminescence from the side with a microscope, the emission was found to originate from the p-n junction (Color frontispiece 3). At reverse currents no luminescence was observed.

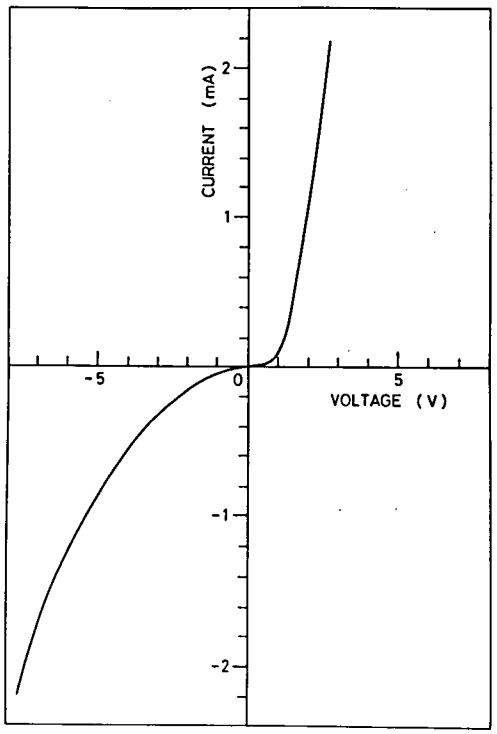

Fig. V.10. Current-voltage characteristics of the diode.

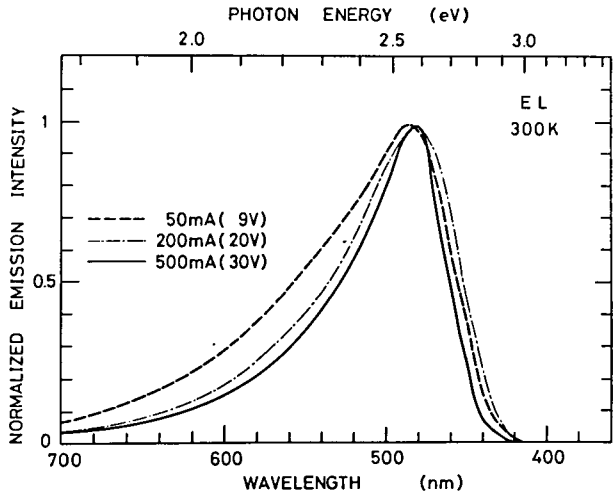

Fig. V.11. Electroluminescence spectra at various currents (300 K).

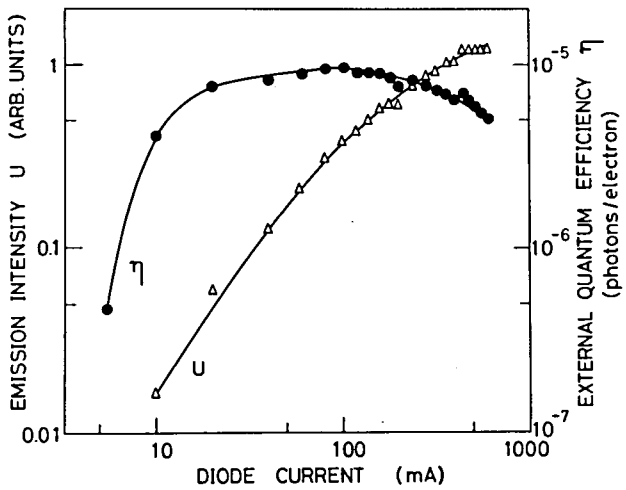

Fig. V.12. Emission intensity and external quantum efficiency of the electroluminescence at 300 K as a function of diode current.

The luminescence spectra at 300 K are shown in Fig. V.11. The spectral width decreased with increasing current. The spectra well resembled that of the photoluminescence of aluminum-doped epitaxial layers shown in Fig. V.8 though thermal broadening of each peak occurred. At low temperatures (100-150 K), several humps appeared corresponding to the peaks in the photoluminescence spectrum, and the spectrum shifted towards higher photon-energies with increasing current. Therefore, the luminescence was probably the same pair emission between the nitrogen donors and the aluminum acceptors. At 300 K, it may include the emission due to the recombination of free electrons with bound holes at the aluminum acceptors.

Figure V.12 shows emission intensity and external quantum efficiency of the electroluminescence at 300 K as a function of diode current. The maximum efficiency of 1.0×10^{-5} photons/electron was obtained at 100 mA (15 V). At 77 K, the same luminescence intensity as at 300 K was obtained at the current of one tenth or less, and the efficiency was 1.5×10^{-4} photons/electron at 5 mA (65 V) and 2.0×10^{-4} photons/electron at 0.15 mA (13 V). The whole resistance of the diode increased by two to three orders at 77 K.

4. Summary

Blue-light-emitting diodes with considerable brightness under room light at room temperature were able to be prepared by liquid-phase epitaxial growth with the dipping technique by an overcompensation procedure. The external quantum efficiency of 1.0×10^{-5} photons/electron at 300 K was one of the highest values for SiC blue-light-emitting diodes reported up to date. For comparison, some diodes with a p-n junction prepared by two growth runs instead of the overcompensation procedure were fabricated. But their emission intensities were lower by two orders.

The following two points for the improvements are pointed out. 1) Although the blue luminescence was emitted from the whole junction area, its intensity was not uniform over the area. This may be due to the uneven distribution of the nitrogen donors and the aluminum acceptors. A rotation of the substrate holder during the growth will reduce this unevenness. 2) The complicated diode structure probably caused the considerable leakage currents under the reverse bias and the large applied voltages (above 20 V) to obtain the luminescence from the whole junction area. The emission only from the part near the aluminum-silicon contact at low voltages may be due to the large sheet resistance of the lower thin p-layer (P_1 in Fig. V.9). This diode structure was employed for lack of p-type substrate crystals. If a p-type substrate is used, a diode can be prepared in only one growth run by an overcompensation procedure, and the electrical contact for the p-layer can be attached to the substrate.

A considerable increase of the efficiency will be obtained by the well-controlled impurity-doping in addition to these improvements, and the diode will be operated at much lower applied voltages.

The substrate crystals in the present investigation were prepared by the Acheson method. This method is usually used for preparation of raw materials for abradant SiC. The crystals obtained by this method contain a great number of unknown impurities, and are not suitable for the substrate crystals of epitaxial growth. Much purer crystals prepared by any other method should be used. But the result that blue-light-emitting diodes with considerably high efficiency were able to be fabricated even using such impure substrate crystals may suggest that liquid-phase epitaxial growth from a Si melt by the dipping technique is a promising method for SiC light-emitting device fabrication.

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VI. CONCLUSIONS

The following conclusions were obtained by the present investigations.

1) In 4H-, 6H-, and 3C-SiC grown from a Si melt, Al, Ga, and B acceptors act as efficient centers of visible luminescences at low temperatures. The luminescence color varies from violet to red depending on the energy level of the acceptor and the energy gap of the polytype.

2) The luminescences at low temperatures are donor-acceptor pair emissions between the N donor and the Al, Ga, or B acceptor. (The N donor is introduced unintentionally during the crystal growth.) Each spectrum consists of a zero-phonon peak and its phonon replicas. The contributing phonons are LA, LO phonons and their combinations. At higher temperatures, another emission due to the recombination of free electrons with bound holes at the acceptors appears in place of the pair emission.

3) In the three polytypes, the ionization energy of Ga is a little larger than that of Al, while B has much larger ionization energy. Owing to the deep level of the B acceptor, the spectra are different from those of Al and Ga, and phonon replicas emitting larger numbers of phonons are intense because of the strong lattice-impurity interaction. Moreover, the luminescences due to B are quenched above room temperature, while those due to Al and Ga below room temperature.

4) The ionization energies of Al, Ga, and B in 4H-SiC are 168 ± 3 meV + E_x, 249 ± 3 meV + E_x, 628 meV + E_x, respectively, where E_x is the exciton binding energy of the order of 10 meV. (The ionization energy of the Ga acceptor has been unknown till the present investigation.) The ionization energy of the N donor is 55 ± 7 meV. The ionization energies of the Al acceptors in 6H-SiC and 3C-SiC are 231 meV + E_x and 248 meV + E_x, respectively. Even if the differences in E_x among the polytypes

are taken into consideration, the ionization energy of Al in 4H-SiC is smaller than those in 6H- and 3C-SiC.

5) By liquid-phase epitaxial growth with the dipping technique, epitaxial layers of 6H-SiC up to 100 μm thick are deposited on the {0001} faces of 6H-SiC substrate by 5 hours growth at growth temperatures between 1500 °C and 1650 °C. At 1500 °C, a certain part of the deposited layer is 3C-SiC. Layers grown on the Si faces at 1600 °C and 1650 °C have fairly flat and smooth surfaces. Undoped layers show n-type conduction with a typical carrier concentration of 6.3×10^{17} cm^{-3} and mobility of 130 $cm^2/Vsec$ at 300 K. N- and p-layers of higher carrier concentrations are obtained by the doping of nitrogen and aluminum, respectively.

6) A p-n junction prepared in one epitaxial growth run by an overcompensation procedure using Al as a luminescent center shows blue electroluminescence under the forward bias, which has enough brightness under room light at room temperature. (The peak wavelength is 485 nm.) The external quantum efficiency is 1.0×10^{-5} photons/electron at 300 K, which is one of the highest values for SiC blue-light-emitting diodes reported up to date.

As a result of the present investigations, liquid-phase epitaxial growth from a Si melt by the dipping technique has been found to be an extremely useful method for preparation of visible-light-emitting devices over a wide wavelength range. The quantum efficiency of the 6H-SiC blue-light-emitting diodes fabricated in the present investigation will be increased by the several improvements described in Chapter V and the well-controlled impurity-doping. The diode will be operated at much lower applied voltages. In the present diode, Al has played two roles, that is, of a p-type dopant and of a luminescent center. But, though Al (or a shallower acceptor) serves well as a p-type dopant, a deeper center, Ga or B, is better as a luminescent center, because the photoluminescence due to Al is entirely quenched below room temperature. In order to obtain short-wavelength light, such as green or blue, light-emitting

diodes with Ga centers are strongly desired to be fabricated by this epitaxial method.

One of the major problems yet to be solved in the future is how to prepare much purer substrate crystals suitable for the epitaxial growth. It is no exaggeration to say that the development of SiC electron devices and light-emitting devices depends on whether a new method of the well-controlled growth (including the control of polytypes and impurities) of pure and large single SiC crystals for the substrate is established or not. Though it may not be easy to devise a new growth method, the author emphasizes that the solution method using a Si melt will be a very potential one by suitable modification, because 4H-, 6H-, and 3C-SiC single crystals have been found to grow up to a relatively large size without any seed or substrate crystals. A pure and large single crystal of a desired polytype among these three will be obtained using an appropriate seed crystal.

4H-SiC has been reported to grow epitaxially on a 4H-SiC substrate by liquid-phase epitaxial growth with a Si melt.*) The epitaxial growth of 3C-SiC will be able to be done on a 3C-SiC substrate at relatively low growth temperature less than 1600°C. Since 4H-SiC has a wider energy gap than 6H-SiC, blue luminescence will be obtained even using Ga acceptors as luminescent centers in light-emitting diodes. When pure substrate crystals of these polytypes can be easily supplied, a wide variety of investigations on SiC light-emitting devices over the whole visible-wavelength region will start to make a great advance.

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*) W. F. Knippenberg: Private communication. The technique was considerably different from the dipping technique.

THE AUTHOR'S PAPERS RELATED TO THIS THESIS

Papers

1. "Liquid-Phase Epitaxial Growth of 6H-SiC by the Dipping Technique for Preparation of Blue-Light-Emitting Diodes" by A. Suzuki, M. Ikeda, N. Nagao, H. Matsunami, and T. Tanaka, to be published in J. Appl. Phys., 47, (1976).
2. "Photoluminescence Spectra of Ga-Doped and Al-Doped 4H-SiC" by A. Suzuki, H. Matsunami, and T. Tanaka, to be published in J. Phys. Chem. Solids.
3. "Photoluminescence Due to Al, Ga, and B Acceptors in 4H-, 6H-, and 3C-SiC Grown from a Si Melt" by A. Suzuki, H. Matsunami, and T. Tanaka, to be published in J. Electrochem. Soc.

Short Notes

1. "Photoluminescence of 4H-SiC Single Crystals Grown from Si Melt" by A. Suzuki, H. Matsunami, and T. Tanaka, Japan. J. Appl. Phys., 12, 1083 (1973).
2. "New Blue Photoluminescence of Ga-Doped 4H-SiC Grown from Si Melt" by A. Suzuki, H. Matsunami, and T. Tanaka, Japan. J. Appl. Phys., 14, 891 (1975).
3. "Liquid-Phase Epitaxial Growth of 6H-SiC by Vertical Dipping Technique" by A. Suzuki, M. Ikeda, H. Matsunami, and T. Tanaka, J. Electrochem. Soc., 122, 1741 (1975).
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1. "Photoluminescence of 4H-SiC Single Crystals Grown from Si Melt" by H. Matsunami, A. Suzuki, and T. Tanaka, in "Silicon Carbide-1973" (Proceedings of the 3rd International Conference on Silicon Carbide, Miami, 1973), University of South Carolina Press, Columbia, 1974, p. 618.