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Step-Controlled VPE Growth of SiC Single Crystals at Low Temperatures

Naotaka KURODA, Kentaro SHIBAHARA, Woosik YOO
Shigehiro NISHINO* and Hiroyuki MATSUNAMI

Department of Electrical Engineering, Kyoto University, Kyoto 606
*Department of Electrical Engineering, Kyoto Institute of Technology, Kyoto 606

SiC was grown on 6H-SiC(0001)Si face substrates at 1350-1500°C by CVD method using a H_2-SiH_4-C_3H_8 system. Polytypes of grown layers changed with the control of the density of surface steps by the introduction of off orientation from (0001) face. 6H-SiC was grown reproducibly at 1400-1500°C. This temperature is 300-400°C lower compared with well known typical growth temperature. P-n junction diodes of 6H-SiC grown layers showed very good rectification. Fabricated p-n junction diodes showed blue-light emission in the forward bias region.

1. Introduction

SiC is well known as a typical example of polytypism. The most popular polytypes of SiC are 3C(zincblende) and 6H-types. Their band-gap energies are 2.2 and 3.0eV, respectively. Compared with other wide-gap semiconductors, SiC has high electron mobility and it is much more stable thermally. Hence, SiC is a promising candidate of materials for high-temperature electronic devices. 6H-SiC is also investigated for the application to blue-LED.

The largest problem which has prevented realization of SiC devices is a lack of large crystals. Usually, obtained bulk crystals of 6H-SiC are small($\simeq$1cm^2) and irregular. In the case of 3C-SiC, before our successful heteroepitaxial growth on Si[1-4], there had been no methods to obtain large crystals. Recently, we found that off orientation of Si(100) substrates was effective to eliminate antiphase domains[5-6]. In general, introduction of off orientation is known as one method to improve epitaxially grown layers. Chemical vapor deposition(CVD) growth of both 3C and 6H-SiC on 6H-SiC substrates was reported by several authors[7-9], but no one mentioned clearly about the effect of the off orientation of the substrate.

In this paper, we report that by introduction of off orientation to the substrates 6H-SiC can be homoepitaxially grown at 1400°C. This temperature is much lower than ever known standard growth temperature($\simeq$1800°C). Using this technique, we fabricated p-n junction diodes which showed good properties comparable to ever reported best data.

2. Experiment

SiC was grown using SiH_4-C_3H_8-H_2 system at ordinary atmospheric pressure in a horizontal reaction tube. Since undoped layers showed n-type conduction, TMA or TEA was introduced to obtain p-type layers. Substrates were heated by RF induction. CVD growth was carried out at 1350°C-1500°C. Growth temperature was measured using an optical pyrometer by monitoring the temperature of the hole which was made in the backside of a graphite susceptor. Polytypes of the grown layer were identified by RHEED observation, PL spectra and the shape of etch pits. Details of how to identify polytype using these methods will be described elsewhere.

Natural faces of 6H-SiC are either the (0001)Si face or the (000$\bar{1}$)C face. The (0001)Si face was used as substrates. Because, in our previous work of homoepitaxial growth of 6H-SiC by CVD and LPE methods, grown layers on the (0001)Si face had flat surfaces compared with those on the (000$\bar{1}$)C face[9,11].

The natural (0001)Si faces were polished with diamond paste to obtain mirrorlike surfaces. Off oriented substrates were prepared by angle lapping of natural faces before mirror polishing.

3. Results and discussion

3-1 Crystal growth

Figure 1(a) shows a typical surface morphology of the grown layer on a natural face. A mosaic pattern was observed. The grown layers were separated by step-like or groove-like boundaries. Such morphology was already reported[7-9]. The grown layer with such mosaic patterns was found to be twin-crystalline 3C-SiC by RHEED and etch pits observation. The boundaries were twin-boundaries. To improve crystallinity growth conditions were widely varied. However, single crystalline SiC could not be obtained on a natural face.

The (0001)Si face was lapped and polished as mentioned above to introduce off orientation. Figure 1(b) shows a typical surface morphology of the grown layers on off oriented substrates. A very smooth surface was obtained. By observation of the RHEED patterns, the grown layers were found to be single crystalline 6H-SiC. Single crystals were obtained in the range of the growth temperature from 1400°C to 1500°C. These temperatures are very low compared with an ordinary growth temperature of 1800°C for 6H-SiC. When the temperature was 1350°C, the grown layer was twin crystalline 3C-SiC. Figure 2 shows the relationship between polytypes of the grown layers and the magnitude and the direction of off orientation. When the off angle was larger than 1.5°, 6H-SiC was grown homoepitaxially.

These results are explained in relation to surface steps introduced by off orientation. We assume that fundamentally epitaxial growth takes place inheriting stacking information of atoms nearby the surface. When the polished natural face is used, the density of surface steps is very

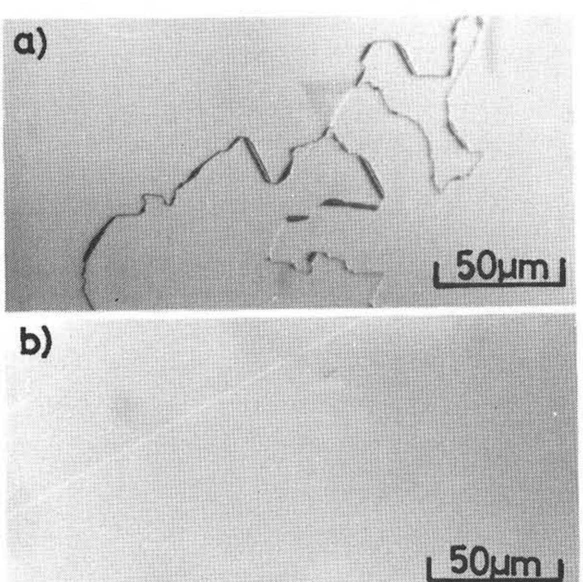

Fig.1, Surface morphology of the grown layers on (a)natural (0001) face (b)off oriented substrtaes.

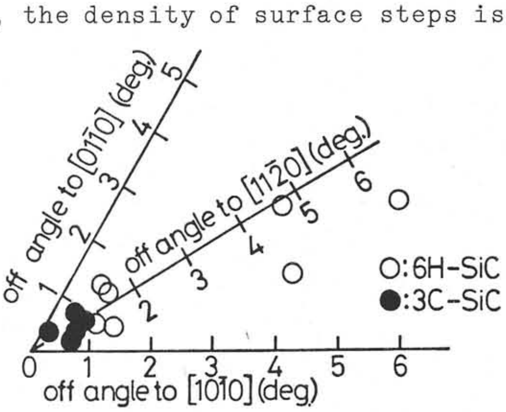

Fig.2, The relationship between polytypes of the grown layers and the magnitude and the direction of off orientation.

low. Therefore, almost growth happens on the flat surface not at the steps. Then, arrived atoms on the surface inherit the stacking information of the atoms that locate just under the surface.

Structures of all polytypes of SiC are expressed by the stacking order of the close packed planes of atoms. For example, the stacking order of 3C and 6H-SiC are ABC.. and ABCACB.., respectively. The stacking direction of the planes corresponds to the direction of the c-axis, in other words the direction of <0001>*).

Even the natural face which has a very low offset angle from (0001) there are steps in a macroscopic view point. Hence, the surface of the 6H-SiC(0001) face can be divided into two parts. In one part the surface is occupied by the atoms belonging to ABC of the former half of the stacking order of ABCACB, and in the other part by the atoms belonging to ACB of the latter half. On the ABC part 3C-SiC grows in accordance with the stacking order of ABC, and on the other part in accordance with ACB as shown in Fig.3(a). In other words on the natural face of 6H-SiC twin crystals of 3C-SiC grow.

*) 3C-SiC has cubic-structure and usually cubic-lattice Miller indices (ex. [hkl]) are used. However to avoid a confusion, in this paper, hexagonal-lattice indices(ex. $[a_1a_2a_3c]$) are used.

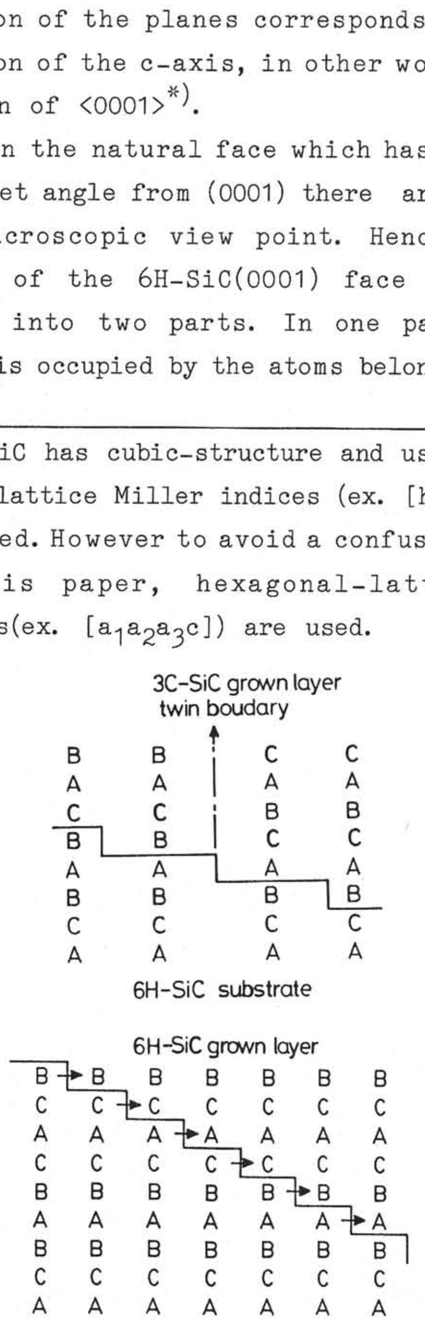

Fig.3, Model of (a)growth of twin crystalline 3C-SiC on well oriented 6H-SiC(0001) (b)homoepitaxial growth on off oriented 6H-SiC(0001).

As an offset angle becomes larger, the density of the surface steps becomes larger. Then atoms easily reach to steps by migration. In this case, epitaxial growth happens inheriting stacking information around the steps as shown in Fig.3(b). Hence, 6H-SiC layers were obtained on off oriented substrates. In our previous work 6H-SiC layers were obtained at 1800°C on a natural face. At very high temperatures surface migration becomes active. Therefore, even if the density of steps is low, atoms can reach to steps and 6H-SiC can grow epitaxially at high temperatures.

3-2 Fabrication of p-n junction diodes

Mesa-type 6H-SiC p-n junction diodes were fabricated. The structure of fabricated diodes are shown as an inset in Fig.4. An undoped n-layer and Al-doped p-layer were continuously grown on off oriented 6H-SiC substrates at 1500°C. Using reactive ion etching(RIE) technique (CF_4+O_2,

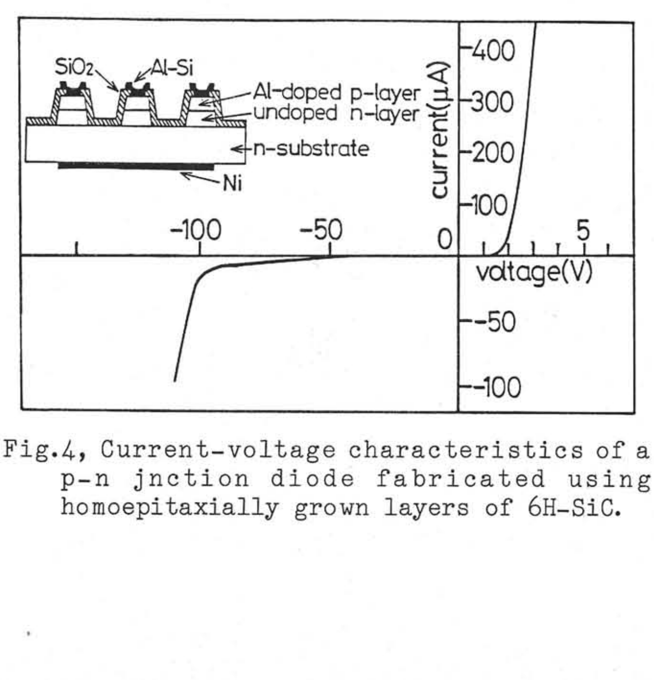

Fig.4, Current-voltage characteristics of a p-n jnction diode fabricated using homoepitaxially grown layers of 6H-SiC.

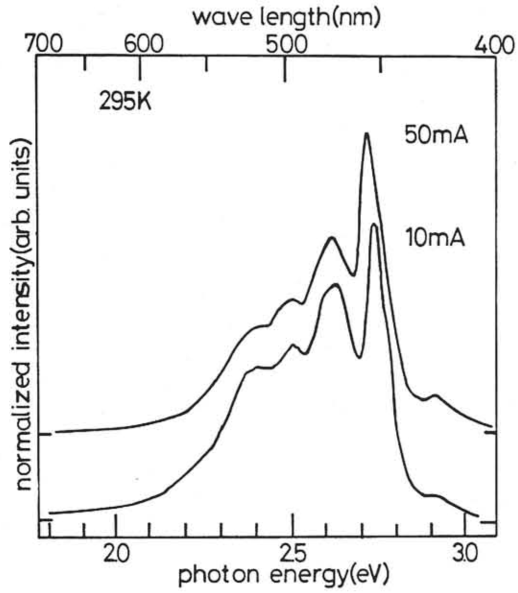

Fig.5, Electroluminescence spectra of a fabricated p-n junction diode.

Al mask) mesa structure was formed. Then, by thermal oxidation at 1050°C SiO_2 film was grown for surface passivation. For p-type and n-type ohmic contacts Al-Si and Ni were evaporated and alloyed, respectively. Figure 4 shows I-V characteristics of a fabricated p-n junction diode. Large breakdown voltage of about 100V was obtained. $1/C^3$-V characteristics showed a proportional relationship, which means that this diode had a graded junction. The breakdown electric field was estimated to be 2.4×10^6 V/cm. Muench et al. fabricated a p-n junction diode at 1800°C by CVD method and they obtained the break down field of $2\text{-}3.7\times10^6$ V/cm[11]. Thus, 6H-SiC with high quality was obtained at lower growth temperature than ordinary by 300°C. Examples of electroluminescence spectra of these diodes are shown in Fig.5. Blue-light luminescence with the main peak of about 460nm was observed at room temperature.

4. Conclusion

Crystals of SiC were grown on 6H-SiC(0001)Si faces at 1350-1500°C by CVD method. In this temperature region, 3C-SiC twin crystal was obtained on a natural face. However, 6H-SiC was grown on off oriented substrates at 1400-1500°C. This temperature is 300-400°C lower than necessary growth temperature for 6H-SiC. The change in polytypes by off orientation of substrates was explained in relation to the control of the surface step density. Fabricated p-n junction diodes showed very good rectification. This technique makes fabrication of 6H-SiC electronic devices easy.

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