Simulation of Electrical Properties of Recrystallized SiC

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再結晶 SiC 電気特性のシミュレーション
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The height of the potential barrier originating at the grain boundaries of recrystallized SiC was experimentally controlled by varying the nitrogen pressure during sintering. The variation in electrical properties with respect to the variation of the potential barrier height was simulated using a computer. There are two conduction mechanisms for recrystallized SiC. One is thermal excitation conduction over the potential barrier and the other is tunnel conduction through the potential barrier. The WKB (Wentzel, Kramers, Brillouin) approximation was applied to calculate the number of carriers that pass through the potential barrier by the tunnel effect. The variation of electrical properties was calculated by varying the height of the potential barriers, and the result corresponded fairly well with the experimentally determined variation of these properties. This simulation method will be useful in designing the electrical properties of recrystallized SiC.

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1. Introduction

SiC is a IV-IV compound semiconductor that has a wider band gap than that of Si or Ge, and is chemically stable up to higher temperatures. Therefore, SiC is expected to be applicable in high-temperature electronic devices.1-3 The author studied the electrical properties of recrystallized SiC, especially the temperature dependence of its specific resistance using the band theory of semiconductors, and reported that the band model having potential barriers originating at the grain boundaries was able to account for the electrical conduction mechanism of recrystallized SiC. The height of its potential barrier was determined by the amount of doped impurity (the amount of doped nitrogen) and the matching between each crystal grain (grain boundary energy).4

Although it is difficult to control the matching due to the influences of many factors, the amount of doped impurity seems to easily be controlled, because the recrystallized SiC contains a certain amount of nitrogen as an impurity which was dissolved from the atmosphere during sintering and which can be adjusted by varying the nitrogen pressure. Therefore, the adjustment of nitrogen pressure during sintering is a convenient method of controlling the height of the potential barrier.

Understanding the variation of electrical properties in relation to the variation of the potential barrier height will be useful in the application of recrystallized SiC for electronic devices. Formulation of its electrical properties will enable the design of such devices by computer simulation. On the basis of the above idea, the recrystallized SiC was sintered by varying the pressure of nitrogen atmosphere to obtain samples having various heights of the potential barrier. The temperature dependence of specific resistance was measured for the samples and the relationship between the electrical properties and the height of the potential barrier was experimentally defined. Then, it was determined whether or not the computer calculation based on the conduction mechanism can simulate the experimentally determined behavior described above.

2. Experimental

2.1 Samples

The test samples were prepared by casting a slurry of commercial green SiC powder (supplied by Pacific Rundum Co., Ltd.; α-SiC powder, average grain diameter: 8 μm, main impurities: Fe 250 ppm, Al 150 ppm, SiO2 0.18%, free carbon: 0.38%) mixed with water into a gypsum mold to obtain bars 20 mm in diameter. To prevent the inclusion of impurities, approximately 3 mm of the surface of the cast samples was stripped and the resulting samples were used for sintering. These processes were performed in the same way as previously reported.4 With respect to the sintering conditions, the nitrogen atmosphere pressure was varied from 0.133 kPa to 1060 kPa. All samples were kept at a constant temperature of 2100°C for a constant holding time of 1 h.

Sintered SiC samples were not appreciably densified by the recrystallization method. The bulk density of sintered samples was about 2.3 10³ kg/m³ which was almost the same as that of green bodies. Powder X-ray diffraction indicated the crystal phases of samples to be mostly α-H6 and partly 15R. The amount of doped nitrogen in the samples was measured with an oxygen-nitrogen simultaneous analyzer (TC-436, made by Leco). A higher nitrogen pressure resulted in a higher amount of doped nitrogen, as expected.

The samples were subjected to a positive-negative discrimination test by a thermoelectric method.5 All samples were discriminated as negative types because nitrogen was doped as a donor. Table 1 shows the properties of the samples. Scanning electron microscope (SEM) observation of microstructures showed that nitrogen negligibly affected crystal grain growth. However, a slight

Table 1. Sintering Conditions, Bulk Density, Type of Crystal, Amount of Doped Nitrogen, and Electrical Conduction Type for Each Sample

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>N₂ pressure at sintering*¹, kPa</th>
<th>Bulk density / 10³kg/m³</th>
<th>Type of crystal</th>
<th>Amount of doped nitrogen / %</th>
<th>Electrical conduction type P or N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.133</td>
<td>2.3</td>
<td>6H+15R</td>
<td>0.005</td>
<td>N</td>
</tr>
<tr>
<td>2</td>
<td>13.3</td>
<td>2.3</td>
<td>6H+15R</td>
<td>0.027</td>
<td>N</td>
</tr>
<tr>
<td>3</td>
<td>132</td>
<td>2.3</td>
<td>6H+15R</td>
<td>0.061</td>
<td>N</td>
</tr>
<tr>
<td>4</td>
<td>608</td>
<td>2.3</td>
<td>6H+15R</td>
<td>0.106</td>
<td>N</td>
</tr>
<tr>
<td>5</td>
<td>1080</td>
<td>2.3</td>
<td>6H+15R</td>
<td>0.150</td>
<td>N</td>
</tr>
</tbody>
</table>

* Sintering temperature was 2100°C, holding time was 1 hour.
inhibition took place at higher pressures. Therefore, the grain boundary energy seems to be almost the same, or becomes slightly higher, with increasing nitrogen pressure. Figures 1 (a)-(e) show SEM micrographs of the fractured surface of samples.

Fig. 1. SEM micrographs of fractured surface area of the samples. (a) Sintered under 0.133 kPa, (b) Sintered under 13.3 kPa, (c) Sintered under 132 kPa, (d) Sintered under 608 kPa, (e) Sintered under 1060 kPa. Crystal grain growth was slightly inhibited by increasing nitrogen pressure. Reference bar indicates 10 μm.

3. Results and discussion

3.1 Control of the potential barrier by adjusting nitrogen pressure during sintering

Figure 2 shows the temperature dependences of the specific resistance of the recrystallized SiC samples sintered under various nitrogen pressures from 0.133 to 1060 kPa. The specific resistance of samples at room temperature depended greatly on the nitrogen pressure, i.e., an increase in the values of the specific resistance was observed with a decrease in the nitrogen pressure. Therefore, the specific resistance of the sample sintered under 0.133 kPa was up to the order of 10 Ω·m. The temperature dependence of the specific resistance of each sample was also dependent on the nitrogen pressure during sintering. The specific resistances of samples sintered under higher nitrogen pressures were relatively stable with temperature variations. The temperature dependence of the specific resistance changed from NTC (negative temperature coefficient) to PTC (positive temperature coefficient) at low temperatures. The samples that were sintered under 0.133 kPa or 13.3 kPa pressure showed only the NTC temperature dependence.

It was also confirmed that the height of the potential barrier was controlled by adjusting the nitrogen pressure from analyzing the temperature dependence of the specific resistance of the specimens. The author reported elsewhere on the temperature dependence of the specific resistance for recrystallized SiC sintered at various temperatures and for single-crystal SiC. It was concluded that the electrical conduction mechanisms of recrystallized SiC can be explained in terms of a band model having potential barriers originating at the grain boundaries. Moreover, it was shown that the conduction due to thermal excitation over the potential barriers was dominant at higher temperatures, and the conduction passing through the barriers due to tunnel and bulk conduction was dominant at lower temperatures. On the basis of these concepts, the height of the potential barrier was calculated from the temperature dependence of the specific resistance, as described below.

From the band theory, the analysis of the temperature dependence of the specific resistance of SiC, which has the donor level formed by doped nitrogen, could be carried out as follows:

\[
\ln \left( \frac{\sigma}{T^{3/2}} \right) = \left( \frac{-E_d}{k} \right) \cdot \ln \left( \frac{1}{T} \right) + \ln \left( N \cdot e^{a} \right) \quad (1)
\]

Fig. 2. Temperature dependences of specific resistance for recrystallized SiC samples which were sintered under 0.133–1060 kPa nitrogen pressures.
where $\sigma$: electric conductivity, i.e., reciprocal of the specific resistance, $T$: temperature, $E_d$: donor level formed by doped nitrogen, $k$: Boltzmann's constant, $N$: concentration of doped nitrogen, $e$: carrier charge (constant; $1.6 \times 10^{-19}$ C), $\mu$: constant related to mobility.

Equation (1) indicates that the temperature dependence of the resistance can be represented by a plot of $\ln(\sigma \cdot T^{3/2})$ vs $1/T$ (Arrhenius plot).

The conduction mechanism of single-crystal SiC, which does not have any grain boundary, is caused simply by electronic excitation from the donor level to the conductive band. Thus, the Arrhenius plot was a simple straight line, and the donor level can be given as the slope of the line. However, there are two conduction mechanisms for polycrystalline SiC, such as recrystallized SiC. One is thermal excitation conduction over the potential barrier and the other is tunnel and bulk conductions passing through the potential barrier. In this case, the Arrhenius plot shows a kinked line consisting of two populations having different slopes in low and high temperature ranges. The slope of any recrystallized SiC at low temperatures corresponds to that of single-crystal SiC. This is because the tunnel and bulk conductions are independent of the potential barrier. Therefore, the slope at low temperatures indicates the donor level formed by doped nitrogen. On the other hand, the slope at high temperatures indicates the contribution of the donor level and the potential barrier. This is because the conduction over the potential barrier due to thermal excitation is dominant at high temperatures. Accordingly, the height of the potential barrier can be calculated from the difference in the slopes (higher minus lower).

Figure 3 shows the plots of $\ln(\sigma \cdot T^{3/2})$ vs $1/T$ for samples sintered under various nitrogen pressures. For all samples, the slopes at low temperatures are the same, and it is clear that conduction is independent of the potential barriers, i.e., tunnel and bulk conductions are dominant in low temperature range. On the other hand, the slopes at high temperatures clearly become reclining with the increase of sintering pressure. It can be deduced that the height of the potential barrier becomes lower. This experiment confirms that the height of the potential barrier can be controlled by adjusting the nitrogen pressure during sintering.

Meanwhile, the height of the potential barrier can be determined from the amount of doped nitrogen as well as the grain boundary energy. The SEM observation (Fig. 1) showed that the nitrogen pressure during sintering negligibly affected the crystal grain size. It was noted that the grain boundary energies for all samples were almost the same. Therefore, the height of the potential barrier depended simply on the amount of doped nitrogen, which could be controlled by adjusting the nitrogen pressure during sintering. Figure 4 shows the relation between the nitrogen pressure and the height of the potential barrier. Solid lines in the figure indicate the effect of the amount of doped nitrogen and the grain boundary energy on the potential barrier height.

3.2 Simulation of electrical properties

As mentioned above, the height of the potential barrier could be controlled by varying the nitrogen pressure. The variation of electrical properties, related to the change in the potential barrier height, could be confirmed experimentally. Therefore, the simulation of the variation of such properties was then performed using a computer.

Specific resistance is defined as the reciprocal of the product of following: number of carriers, carrier charge, and carrier mobility. The carrier charge is constant at $1.6 \times 10^{-19}$ C. The mobility is simply in proportion to $T^{-3/2} (T$: temperature) because it will decrease due to the thermal lattice vibration. Therefore, the calculation of the number of carriers that participate in the conduction is important for the simulation.

Recrystallized SiC has two conduction mechanisms. At higher temperatures, the conduction mechanism of climbing over the potential barrier due to thermal excitation is dominant. At lower temperatures the conduction mechanism of passing through the potential barrier, mainly due to the tunnel effect, is dominant. Based on the aforementioned assumptions, the electrical conduction mechanism was modeled as shown in Fig. 5. In this figure, $\Phi$: potential barrier height, $w$: width of potential barrier, $E_d$: donor level, $N$: number of carriers at the donor level, $N_b$: number of carriers able to climb over the potential barrier by thermal excitation, $N_T$: number of carriers able to pass through the potential barrier by tunnel effect.

The calculation of $N_b$ was easier. It was performed using the following fundamental thermal excitation formula:

$$N_b = N \cdot \exp \left( \frac{- (E_d + \Phi)}{kT} \right)$$

(2)

The calculation of $N_T$ was more involved. The number of carriers that climb up to the conduction band by thermal ex-

![Fig. 3. Arrhenius plots that were modified from the temperature dependence of specific resistance for samples which were sintered under varying nitrogen pressures.](image)

![Fig. 4. Relationship between nitrogen pressure during sintering and the height of the potential barrier (with the effect of the amount of doped nitrogen and the grain boundary energy on the potential barrier height).](image)
The fundamental equation of effective mass:  
\[ m^* = \left( \frac{1}{3m_a} + \frac{1}{3m_b} + \frac{1}{3m_c} \right)^{-1} \]  
where \( m^* \): average effective mass, \( m_{a,b,c} \): effective mass of each axis.

Each effective mass of electrons in 6H-SiC is \( m_d/m_0 = 0.35 \), \( m_b/m_0 = 0.35 \), and \( m_c/m_0 = 1.3 \), as reported by Lomakina.  

Using these values, \( m^*/m_0 = 0.46 \) was calculated, where \( m_0 \): free electron mass.

There are two conduction mechanisms at low temperatures: tunnel conduction and bulk conduction. Carriers which pass through the potential barrier by bulk conduction, due to the hopping between localized levels, were significantly fewer than the carriers which pass through by tunnel conduction. Therefore, the carriers transported by bulk conduction were neglected in the simulation.

The temperature dependence of the specific resistance was simulated through the following procedure. (1) The number \( (N) \) of carriers at the donor level was calculated from the amount of doped nitrogen. (2) The number \( (N_D) \) of carriers that could climb over the potential barrier from the donor level by thermal excitation was calculated. (3) The number of carriers that could potentially climb up from the donor level to the conductive band but were not able to climb over the potential barrier by thermal excitation was calculated. (4) Some carriers calculated in procedure (3) could pass through the potential barrier by the tunnel effect. Their number \( (N_T) \) was calculated using the WKB approximation described previously. (5) The number \( (N_P) \) of carriers that climb over the potential barrier, and the number \( (N) \) of carriers that pass through the potential barrier were summed. The sum was then multiplied by the carriers' charge and the mobility. The mobility of \( 40T^{-3/2}m^2/Vs \), as described in the literature, was used for this calculation. Then the specific resistance was calculated as the reciprocal of the resulting product. (6) The number of each carrier and the mobility depended on temperature. Thus, these variables must be calculated at each temperature.

Figure 6 shows the Arrhenius plots of the simulated and the experimental results, in term of the values reflecting the temperature dependence of the specific resistance of recrystallized SiC sintered under 132 kPa nitrogen pressure. The simulated result corresponds fairly well to the experimental one. The simulated result is represented by two straight lines having different slopes for low and high temperatures. It can be concluded that the conduction...
model discussed previously is valid. The height of the potential barrier used in the calculation must be corrected to fit the experimental data. Table 2 shows a summary of $N_T$, $N_E$, and $NT/NE$. It also shows the calculated ($R_{cal}$) specific resistances. It is clear from the table that the dominant conduction mechanism changes from the tunnel effect to thermal excitation as temperature increases.

According to the result described above, it is clear that the temperature dependence of the specific resistance can be simulated. Finally, the temperature dependences of the specific resistance were simulated by varying the height of the potential barriers, and these simulated results were compared to the experimental results obtained previously.

Figure 7 shows the simulated temperature dependences of the specific resistance in the range of the potential barrier height from 0.1 eV to 0.5 eV. The slopes of the lines in the high temperature range increase as the height of the potential barrier increases. On the other hand, the slopes of the lines at low temperatures were constant because the tunnel conduction is dominant in the low temperature range. The kinked line of the Arrhenius plots reclined as the height of the potential barrier decreased. This was due to the contribution of the above two factors. A parity was observed between the simulated behavior (Fig. 7) and the experimental behavior (Fig. 3). Therefore, it is postulated that the simulation method is appropriate and useful for the design of the electrical properties of recrystallized SiC.

The height of the potential barrier used in the calculation must be corrected by multiplying the height, which was experimentally obtained from the slope at high temperatures, by 1.5. Figure 6 shows that there is only a small difference between the experimental result and the simulated result. In other words, the height of the potential barrier obtained from the slope of simulated Arrhenius plot is nearly equal to that determined experimentally. The slope at high temperatures became low due to a tunnel effect in the initial stage, even in the temperature range where thermal excitation is dominant. Thus, it was conceivable that the true values of the heights of the potential barriers were higher than those obtained experimentally.

### Table 2. Results of the Calculated Data Compared with the Experimental Data

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$N_T$ / m$^{-3}$</th>
<th>$N_E$ / m$^{-3}$</th>
<th>$NT/NE$</th>
<th>$R_{cal}$ / $10^{-2}$Ω m</th>
<th>$R_{exp}$ / $10^{-2}$Ω m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.57 x 10$^{10}$</td>
<td>1.39 x 10$^{12}$</td>
<td>25.7</td>
<td>0.190</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>5.55 x 10$^{10}$</td>
<td>5.14 x 10$^{12}$</td>
<td>10.6</td>
<td>0.150</td>
<td>0.151</td>
</tr>
<tr>
<td>100</td>
<td>7.65 x 10$^{10}$</td>
<td>1.34 x 10$^{13}$</td>
<td>5.70</td>
<td>0.125</td>
<td>0.130</td>
</tr>
<tr>
<td>200</td>
<td>1.18 x 10$^{11}$</td>
<td>4.96 x 10$^{13}$</td>
<td>2.38</td>
<td>0.0568</td>
<td>0.103</td>
</tr>
<tr>
<td>300</td>
<td>1.56 x 10$^{11}$</td>
<td>1.16 x 10$^{14}$</td>
<td>1.34</td>
<td>0.0786</td>
<td>0.0844</td>
</tr>
<tr>
<td>400</td>
<td>1.88 x 10$^{11}$</td>
<td>2.12 x 10$^{14}$</td>
<td>0.867</td>
<td>0.0862</td>
<td>0.0703</td>
</tr>
<tr>
<td>500</td>
<td>2.14 x 10$^{11}$</td>
<td>3.30 x 10$^{14}$</td>
<td>0.648</td>
<td>0.0616</td>
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<tr>
<td>600</td>
<td>2.35 x 10$^{11}$</td>
<td>4.65 x 10$^{14}$</td>
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<tr>
<td>700</td>
<td>2.51 x 10$^{11}$</td>
<td>6.10 x 10$^{14}$</td>
<td>0.412</td>
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<td>7.61 x 10$^{14}$</td>
<td>0.347</td>
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<td>0.0522</td>
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<tr>
<td>900</td>
<td>2.73 x 10$^{11}$</td>
<td>9.14 x 10$^{14}$</td>
<td>0.299</td>
<td>0.0528</td>
<td>0.0531</td>
</tr>
<tr>
<td>1000</td>
<td>2.80 x 10$^{11}$</td>
<td>1.07 x 10$^{15}$</td>
<td>0.262</td>
<td>0.0526</td>
<td>—</td>
</tr>
</tbody>
</table>

Note: $N=6.55\times10^{20}$/m$^3$, $E_c=0.067$eV, $m^*=0.46\times m_0$, Mobility=40×$T^{-3/2}$ m$^2$/N·sec.

Fig. 7. Simulated temperature dependences of specific resistance with potential barrier heights that vary from 0.1 eV to 0.5 eV. Compared to the experimental results in Fig. 3.

the variation of the potential barrier height was simulated using a computer. The results are summarized as follows.

1. The height of the potential barrier could be controlled by varying the nitrogen pressure during sintering, at a constant temperature and the same holding time. As the nitrogen pressure increased, the height of the potential barrier became lower.

2. Using the WKB approximation, the number of carriers that passed through the potential barrier by the tunnel effect was calculated and the specific resistance of recrystallized SiC was formulated. The temperature dependence of the specific resistance was simulated using a computer. The simulated result agreed with the experimental result.

3. The simulated behavior of electrical properties when varying the height of the potential barrier corresponded fairly well to the experimental one. This simulation method will be useful in designing the electrical properties of recrystallized SiC.

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References