Donor Densities and Donor Levels in SiC Uniquely Determined by a New Method Based on Hall-Effect Measurements

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Background

Silicon carbide (SiC) has been regarded as a promising semiconductor for power electronic applications.

In order to use SiC wafers or epilayers to electronic devices, **an accurate evaluation of densities and energy levels of dopants and defects in SiC** is essential.

Aim

1. To determine **how many types** of impurities and defects are included in SiC
2. To determine **the densities and energy levels** of impurities and defects
3. To **verify** the obtained results

Experimental method

Hall-effect measurement

New evaluation method

Propose a function to be evaluated

$$H(T, E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right)$$

Proposed function to be evaluated

$$H(T,E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}}\exp\left(\frac{E_{\mathrm{ref}}}{kT}\right)$$

$n(T)$: temperature dependence of majority carrier concentration

k : Boltzmann constant T : absolute temperature

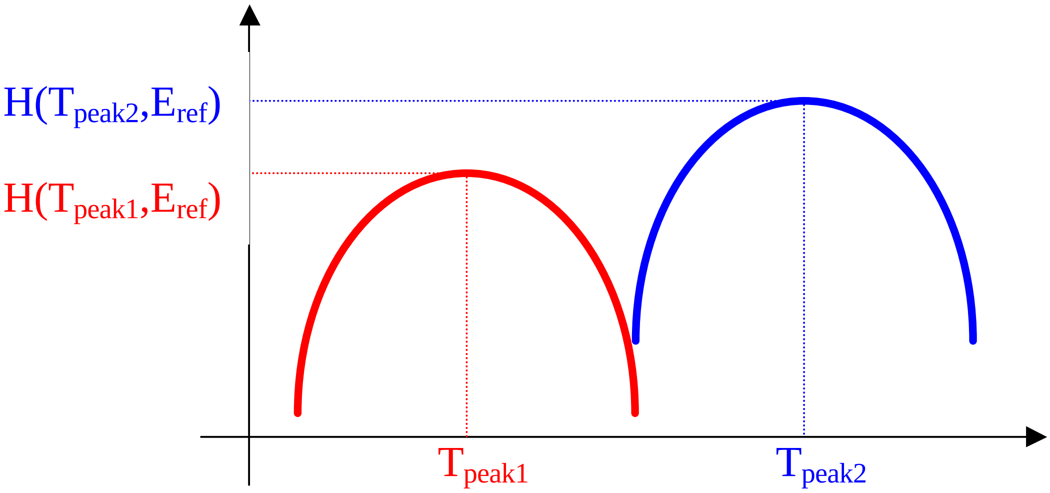
E_{ref} : parameter that can shift the peak temperature of $H(T,E_{\mathrm{ref}})$

Good points of this function

1. $H(T,E_{\mathrm{ref}})$ has **a peak corresponding to each energy level** of impurity or defect.

i-th peak temperature → energy level of i-th impurity or defect

i-th peak value → density of i-th impurity or defect



2. **Compensated density can be determined.**

Theoretical consideration

$$H(T, E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right)$$

Consider n-type semiconductor

Substitute two different $n(T)$ expressed as follows

for each $n(T)$ in definition.

1. $n(T)$ from charge neutrality condition

$$n(T) = \sum_{i=1}^{n} N_{\mathrm{D}i}[1 - f(E_{\mathrm{D}i})] \qquad \text{n types of donors}$$

$$- \sum_{i=1}^{m} N_{\mathrm{TE}\,i}\, f(E_{\mathrm{TE}i}) \qquad \text{m types of electron traps}$$

$$- N_{\mathrm{A}} \qquad \text{acceptor}$$

2. $n(T)$ from effective density of states

$$n(T) = N_{\mathrm{C}}(T) \exp\left(-\frac{E_{\mathrm{C}} - E_{\mathrm{F}}}{kT}\right)$$

E_{C}: energy level at the bottom of the conduction band

E_{F}: Fermi level

$f(E)$: Fermi-Dirac distribution function

$E_{\mathrm{D}i}$: i-th donor level

$N_{\mathrm{D}i}$: i-th donor density

$E_{\mathrm{TE}i}$: i-th electron trap level

$N_{\mathrm{TE}i}$: i-th electron trap density

N_{A}: acceptor density

$N_{\mathrm{C}}(T)$: effective density of states in the conduction band

$$\begin{aligned} H(T, E_{\mathrm{ref}}) = {} & \sum_{i=1}^{n} \underline{\frac{N_{\mathrm{D}i}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D}i}) - E_{\mathrm{ref}}}{kT}\right]} I(E_{\mathrm{D}i}) \\ & + \sum_{i=1}^{m} \underline{\frac{N_{\mathrm{TE}i}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{TE}i}) - E_{\mathrm{ref}}}{kT}\right]} I(E_{\mathrm{TE}i}) \\ & - \left(N_{\mathrm{A}} + \sum_{i=1}^{m} N_{\mathrm{TE}i}\right) \frac{N_{\mathrm{C0}}}{kT} \exp\left[\frac{E_{\mathrm{ref}} - (E_{\mathrm{C}} - E_{\mathrm{F}})}{kT}\right] \end{aligned}$$

where

$$I(E) = \frac{N_{\mathrm{C0}}}{2 + \exp\left(\frac{E - E_{\mathrm{F}}}{kT}\right)}$$

and

$$N_{\mathrm{C}}(T) = (kT)^{1.5} N_{\mathrm{C0}}$$

Pay attention to the function

$$\frac{N_i}{kT} \exp\left(-\frac{(E_{\mathrm{C}} - E_i) - E_{\mathrm{ref}}}{kT}\right)$$

in the above equation.

Peculiar feature of

$$F(T, E_{\mathrm{ref}}) \equiv \frac{N_i}{kT} \exp\left(- \frac{(E_{\mathrm{C}} - E_i) - E_{\mathrm{ref}}}{kT} \right)$$

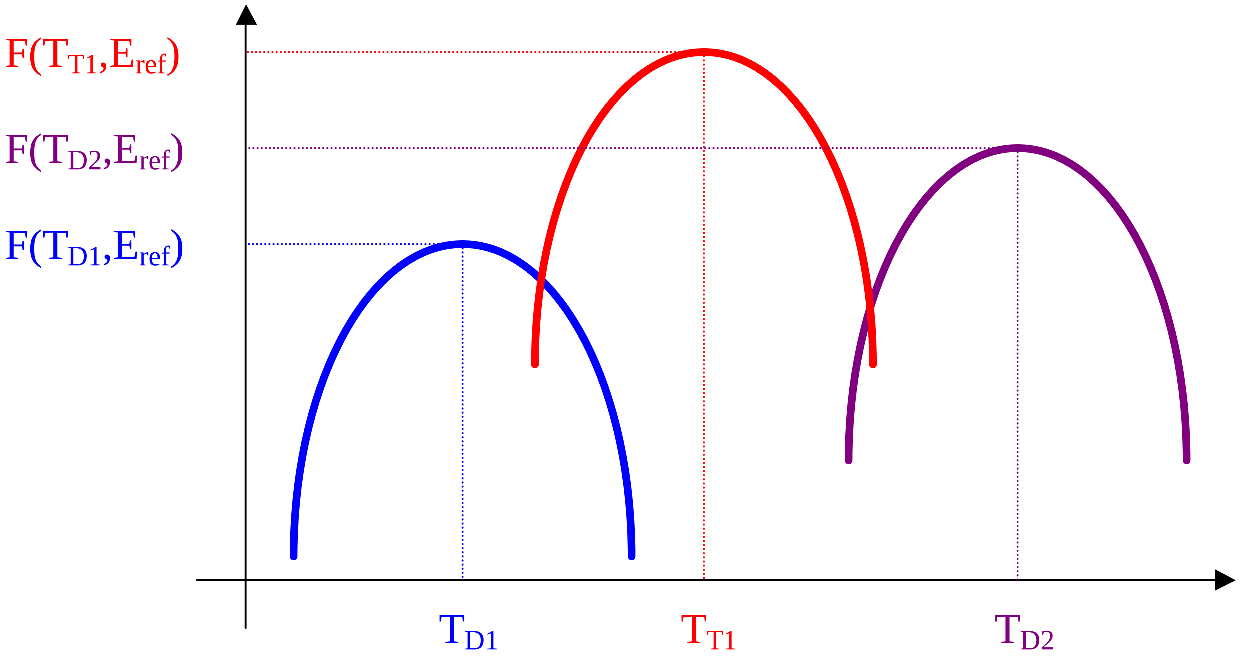
$F(T, E_{\mathrm{ref}})$ has **a peak value** of

$$\frac{N_i}{kT_{\mathrm{peak}i}} \exp(-1)$$

at **a peak temperature**

$$T_{\mathrm{peak}i} = \frac{(E_{\mathrm{C}} - E_i) - E_{\mathrm{ref}}}{k} .$$

For example



$$E_{\mathrm{C}} - E_{\mathrm{D1}} = kT_{\mathrm{D1}} + E_{\mathrm{ref}} \quad N_{\mathrm{D1}} = F(T_{\mathrm{D1}}, E_{\mathrm{ref}}) kT_{\mathrm{D1}} / \exp(-1)$$

$$E_{\mathrm{C}} - E_{\mathrm{T1}} = kT_{\mathrm{T1}} + E_{\mathrm{ref}} \quad N_{\mathrm{T1}} = F(T_{\mathrm{T1}}, E_{\mathrm{ref}}) kT_{\mathrm{T1}} / \exp(-1)$$

$$E_{\mathrm{C}} - E_{\mathrm{D2}} = kT_{\mathrm{D2}} + E_{\mathrm{ref}} \quad N_{\mathrm{D2}} = F(T_{\mathrm{D2}}, E_{\mathrm{ref}}) kT_{\mathrm{D2}} / \exp(-1)$$

Good points of our analysis

1. Using $H(T,E_{\mathrm{ref}}) \equiv \dfrac{n(T)^2}{(kT)^{2.5}} \exp\left(\dfrac{E_{\mathrm{ref}}}{kT}\right)$,

   we can determine the density and energy level of the impurity or defect corresponding to each peak.

2. As is clear from $T_{\mathrm{peak}i} = \dfrac{(E_{\mathrm{C}} - E_i) - E_{\mathrm{ref}}}{k}$,

   a parameter E_{ref} can shift **the peak of $H(T,E_{\mathrm{ref}})$ to the measurement temperature range** even when none of the peaks of $H(T,0)$ appear within the measurement temperature range.

3. Although $T_{\mathrm{peak}i}$ is a little different from

   $\dfrac{(E_{\mathrm{C}} - E_i) - E_{\mathrm{ref}}}{k}$ due to the temperature dependence of

   $I(E_i)$,

   we can easily determine **the accurate N_i and E_i from each peak temperature and peak value** using a personal computer.

4. We can determine **how many types of impurities and defects are included in the semiconductor** from the number of peaks in $H(T,E_{\mathrm{ref}})$.

Undoped 3C-SiC

Growth conditions

(Atmospheric pressure chemical vapor deposition)

1. (100) n-type Si substrate
2. Etching of Si substrate surface

   1175 ^{o}C, 11 min., HCl: 63 sccm, H_2: 1.5 slm
3. Formation of buffer layer

   (Carbonization of Si substrate surface)

   1350 ^{o}C, 3 min., C_3H_8: 1 sccm, H_2: 1 slm
4. Growth of **undoped 3C-SiC**

   1350 ^{o}C, **$Si_2(CH_3)_6$**: 0.5 sccm, H_2: 2.5 slm

   growth rate: 4.3 μm/h

Conditions of Hall-effect measurement

Removal of Si substrate (chemical etching)

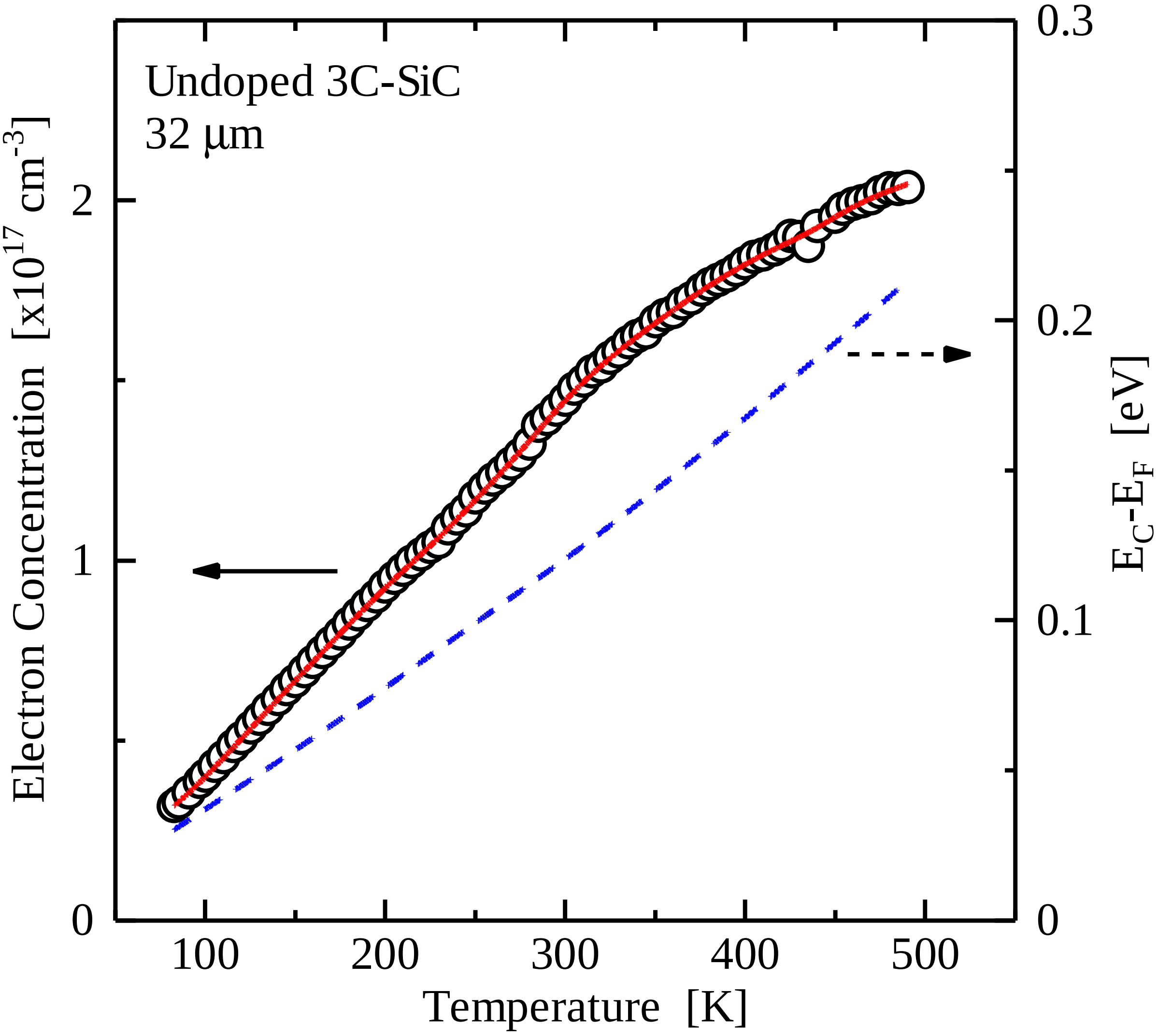
Thickness: 32 μm

Size: 5x5 mm^2

Magnetic field: 5 kG

Temperature range: 85 K ~ 500 K

Electron concentration and Fermi level



○ : experimental $n(T)$

— : $n(T)$ interpolated by the cubic smoothing natural spline function

- - - : Fermi level

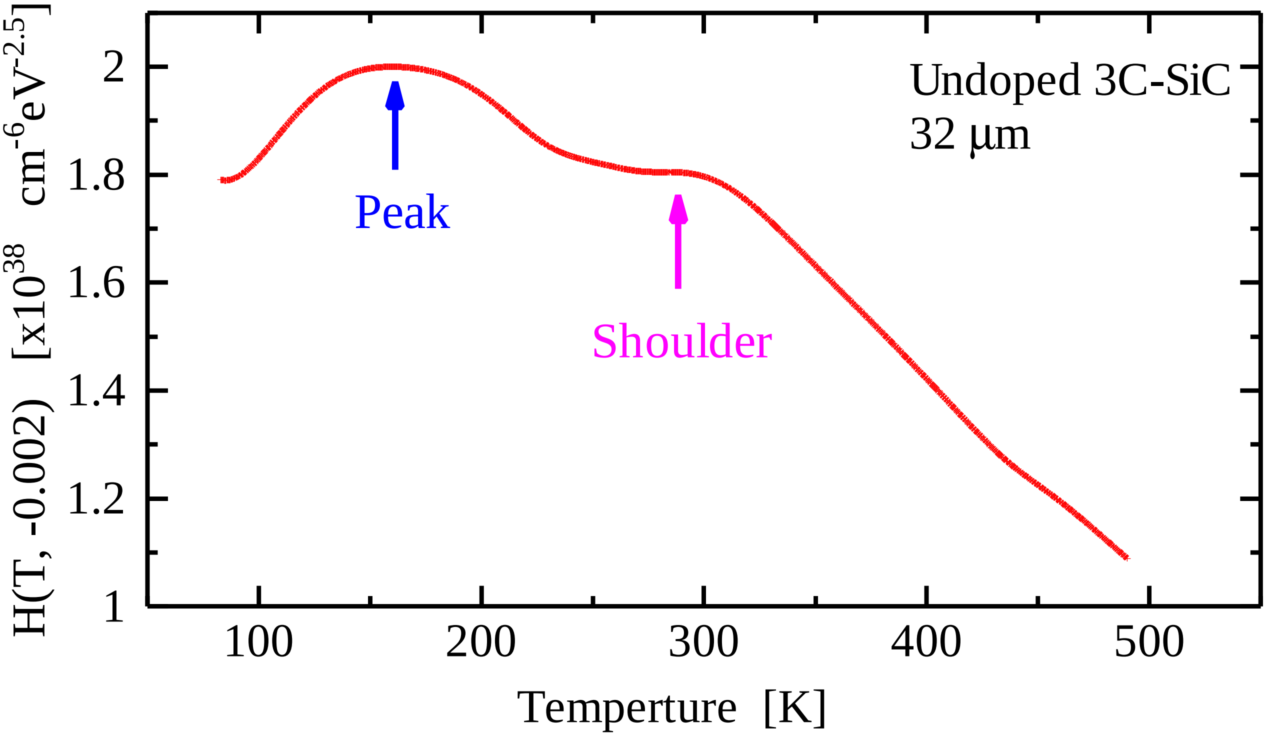
$$E_C - E_F = kT \ln\left[\frac{N_C(T)}{n(T)}\right]$$

where

$$N_C(T) = 3.0\times10^{15} T^{3/2} \text{ cm}^{-3}$$

Function to be evaluated

$$H(T, E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT} \right)$$



One peak and one shoulder appear.

↓

At least **two kinds of energy levels are included.**

Determination of the density N_{D2} and energy levels E_{D2}

of the donor corresponding to the lower peak

$$T_{\mathrm{peak}} = 160 \text{ K}$$

$$H(T_{\mathrm{peak}}, -0.002) = 2.0 \times 10^{38} \text{ cm}^{-6}\text{eV}^{-2.5}$$

Around 160 K, $n(T)$ is approximately expressed as

$$n(T) \cong (N_{D1} - N_A) + N_{D2}[1 - f(E_{D2})],$$

N_{D1}: density of the donor shallower than donor corresponding to 160 K when a shallower donor is included.

Therefore, $H(T, E_{ref})$ is approximately described as

$$H(T, E_{ref}) \cong \frac{N_{D2}}{kT} \exp\left[-\frac{(E_C - E_{D2}) - E_{ref}}{kT} \right] I(E_{D2}) + (N_{D1} - N_A) \frac{N_{C0}}{kT} \exp\left[\frac{E_{ref} - (E_C - E_F)}{kT} \right]$$

$T_{peak} = 160$ K

$H(T_{peak}, -0.002) = 2.0\times10^{38}$ cm^{-6}eV$^{-2.5}$

$\downarrow$

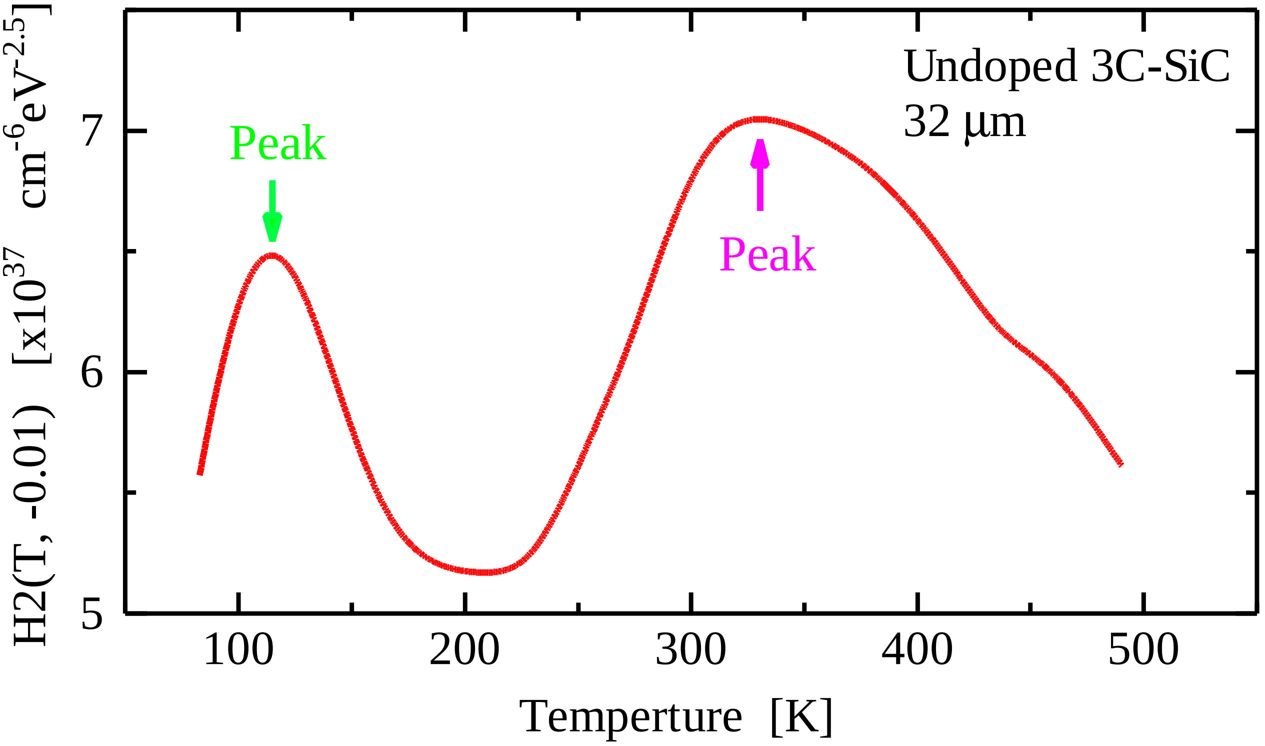
$$\boxed{\begin{aligned} E_C - E_{D2} &= 54 \text{ meV} \\ N_{D2} &= 8.1\times10^{16} \text{ cm}^{-3} \end{aligned}}$$

Function $H2(T, E_{\mathrm{ref}})$ that is not influenced by the second donor

$$H2(T, E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) - \frac{N_{\mathrm{D2}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D2}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D2}})$$

with

$$N_{\mathrm{D2}} = 8.1 \times 10^{16} \ \mathrm{cm}^{-3} \text{ and } E_{\mathrm{C}} - E_{\mathrm{D2}} = 54 \ \mathrm{meV}$$



Determination of the density N_{D1} and energy levels E_{D1} of the donor corresponding to the lower peak

$$T_{\mathrm{peak}} = 115 \ \mathrm{K}$$

$$H2(T_{\mathrm{peak}}, -0.01) = 6.5 \times 10^{37} \ \mathrm{cm}^{-6}\mathrm{eV}^{-2.5}$$

Around 115 K, $n(T)$ is approximately expressed as

$$n(T) \cong N_{\mathrm{D1}}\left[1 - f(E_{\mathrm{D1}})\right] - N_{\mathrm{A}},$$

Therefore, $H2(T, E_{\mathrm{ref}})$ is approximately described as

$$H2(T, E_{\mathrm{ref}}) \cong \frac{N_{\mathrm{D1}}}{kT}\exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D1}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D1}}) \\ - N_{\mathrm{A}}\frac{N_{\mathrm{C0}}}{kT}\exp\left[\frac{E_{\mathrm{ref}} - (E_{\mathrm{C}} - E_{\mathrm{F}})}{kT}\right]$$

$$T_{\mathrm{peak}} = 115 \text{ K}$$

$$H2(T_{\mathrm{peak}}, -0.01) = 6.5\times10^{37} \text{ cm}^{-6}\text{eV}^{-2.5}$$

$$\downarrow$$

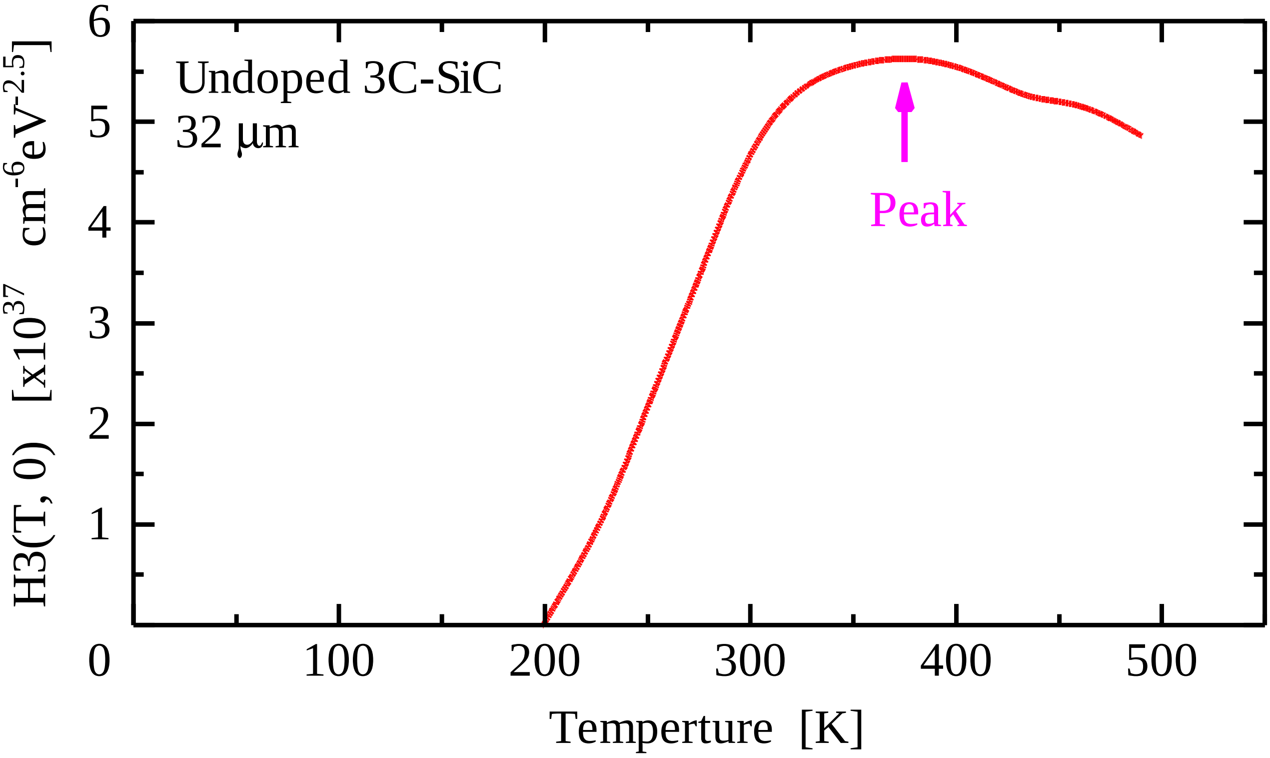
$$E_{\mathrm{C}} - E_{\mathrm{D1}} = 14 \text{ meV}$$

$$N_{\mathrm{D1}} = 4.7\times10^{16} \text{ cm}^{-3}$$

$$N_{\mathrm{A}} = 5.7\times10^{15} \text{ cm}^{-3}$$

Function $H3(T, E_{\mathrm{ref}})$ that is not influenced by the first and second donors, and the acceptor

$$
\begin{aligned}
H3(T, E_{\mathrm{ref}}) \equiv{} & \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \\
& - \frac{N_{\mathrm{D1}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D1}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D1}}) \\
& - \frac{N_{\mathrm{D2}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D2}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D2}}) \\
& + N_{\mathrm{A}} \frac{N_{\mathrm{C0}}}{kT} \exp\left[\frac{E_{\mathrm{ref}} - (E_{\mathrm{C}} - E_{\mathrm{F}})}{kT}\right]
\end{aligned}
$$



$T_{\mathrm{peak}} = 375$ K

$H3(T_{\mathrm{peak}}, 0) = 5.6 \times 10^{37}$ $\mathrm{cm^{-6}eV^{-2.5}}$

Around 375 K, $H3(T, E_{\mathrm{ref}})$ is approximately described as

$$H3(T, E_{\mathrm{ref}}) \cong \frac{N_{\mathrm{D3}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D3}}) - E_{\mathrm{ref}}}{kT} \right] I(E_{\mathrm{D3}})$$

$$T_{\mathrm{peak}} = 375 \ \ \mathrm{K}$$

$$H3(T_{\mathrm{peak}}, 0) = 5.6 \times 10^{37} \ \ \mathrm{cm}^{-6}\mathrm{eV}^{-2.5}$$

$$\Big\downarrow$$

$$\boxed{\begin{array}{l} E_{\mathrm{C}} - E_{\mathrm{D3}} = 120 \ \ \mathrm{meV} \\ N_{\mathrm{D3}} = 1.0 \times 10^{17} \ \ \mathrm{cm}^{-3} \end{array}}$$

Origin of donors

14 meV donor

defect-impurity complex or nonstoichiometric defect

(this donor reported in undoped 3C-SiC grown by a mixture of SiH_4 and C_3H_8)

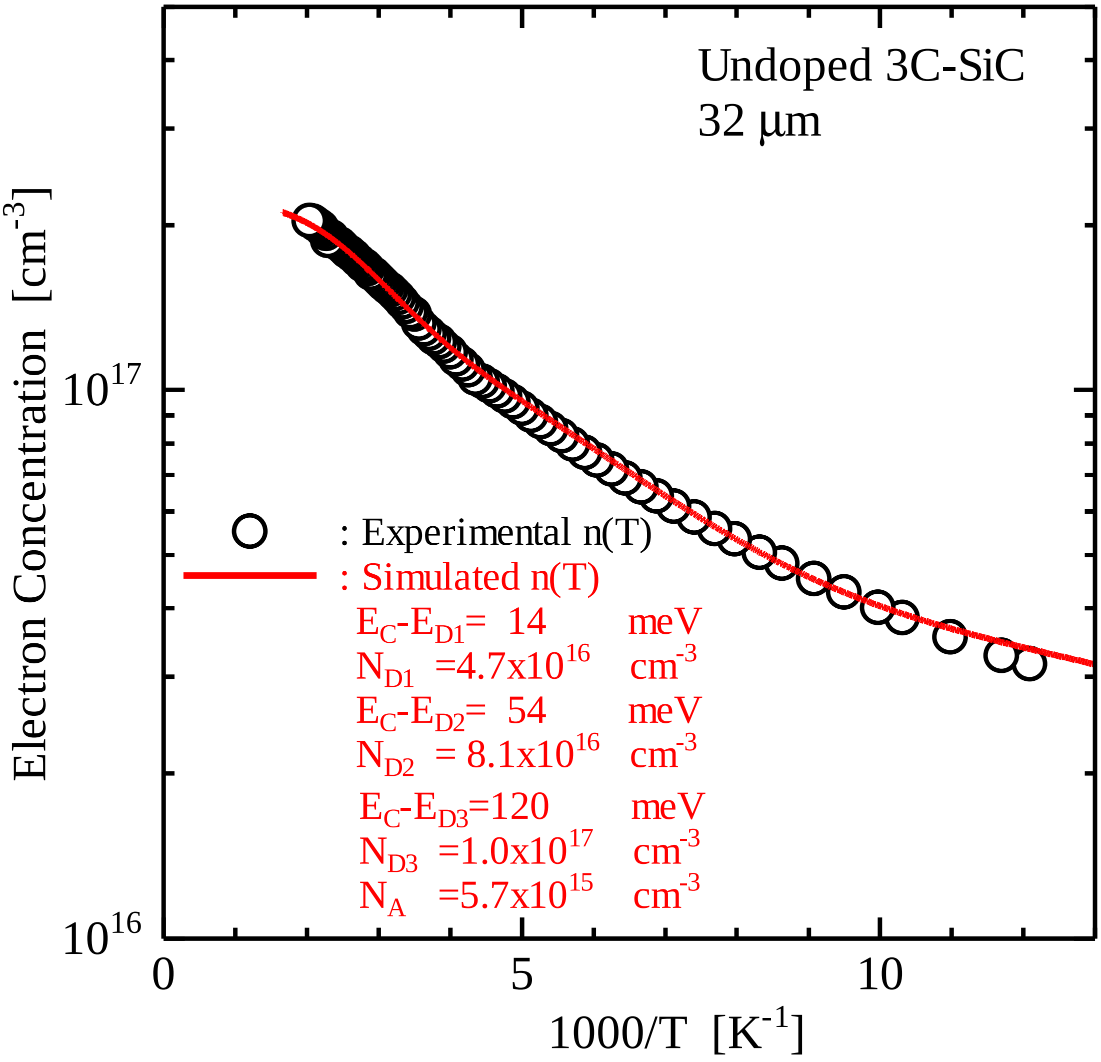
54 meV donor

substitutional nitrogen atom

120 meV donor

this donor not reported yet

Comparison of experimental $n(T)$ with simulated $n(T)$



The $n(T)$, which is simulated using the results determined by $H(T, E_{\mathrm{ref}})$, is **qualitatively in agreement with** the experimental $n(T)$.

↓

The obtained results are reasonable.

N-doped 4H-SiC

Growth condition (chemical vapor deposition)

Gases: 1% SiH_4 with H_2

1% C_3H_8 with H_2

Pressure: 760 Torr

Temperature: 1560 °C

1. Preparation of 4H-SiC with off-orientation of about 5° from {0001} toward <1120> by a sublimation method
2. Growth of 2 μm thick p-type 4H-SiC on 4H-SiC substrate
3. Growth of **5 μm thick N-doped (n-type) 4H-SiC** on p-type 4H-SiC

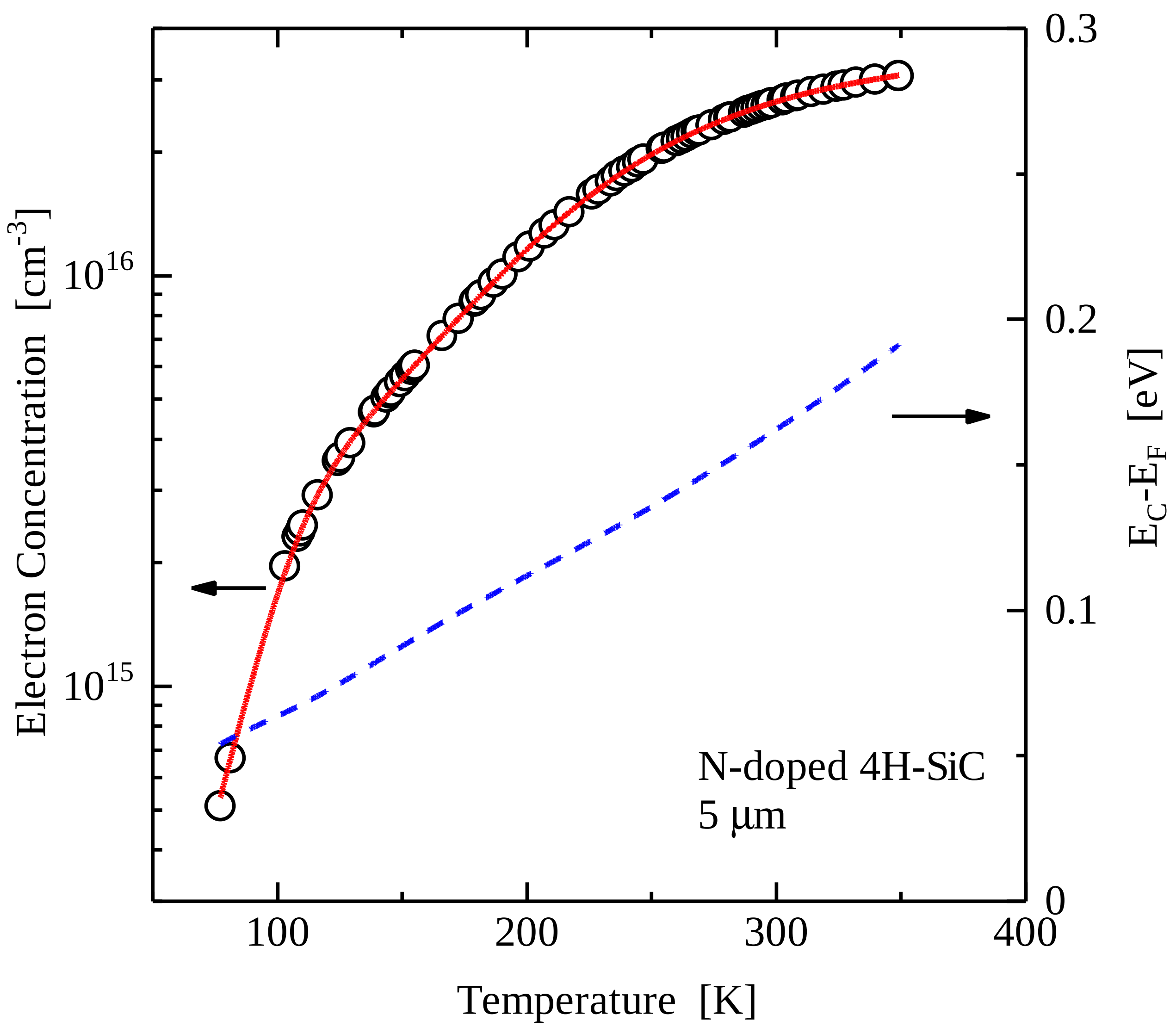
   SiH_4: 0.30 sccm

   C_3H_8: 0.20 sccm

   H_2: 3.0 slm

   N_2: 2.5x10^{-2} sccm

Electron concentration and Fermi level



○ : experimental $n(T)$

— : $n(T)$ interpolated by the cubic smoothing natural spline function

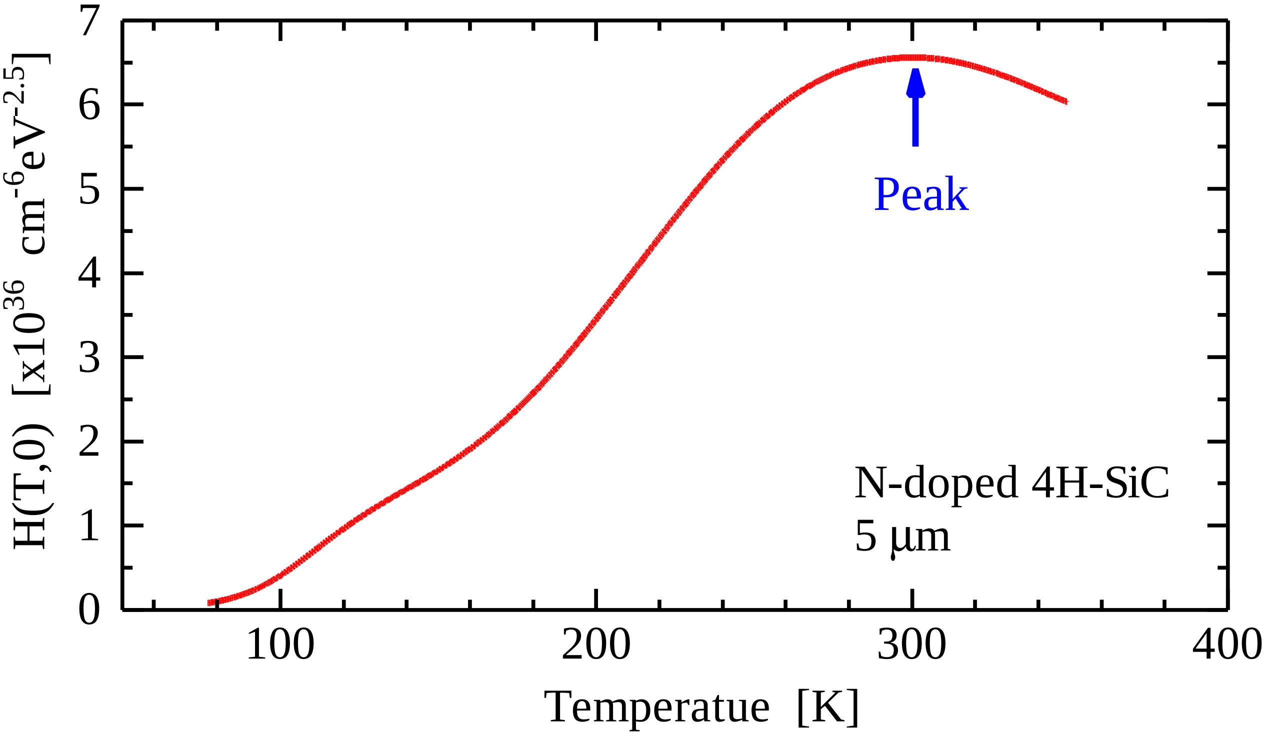
- - - : Fermi level

$$E_C - E_F = kT \ln\left[\frac{N_C(T)}{n(T)}\right]$$

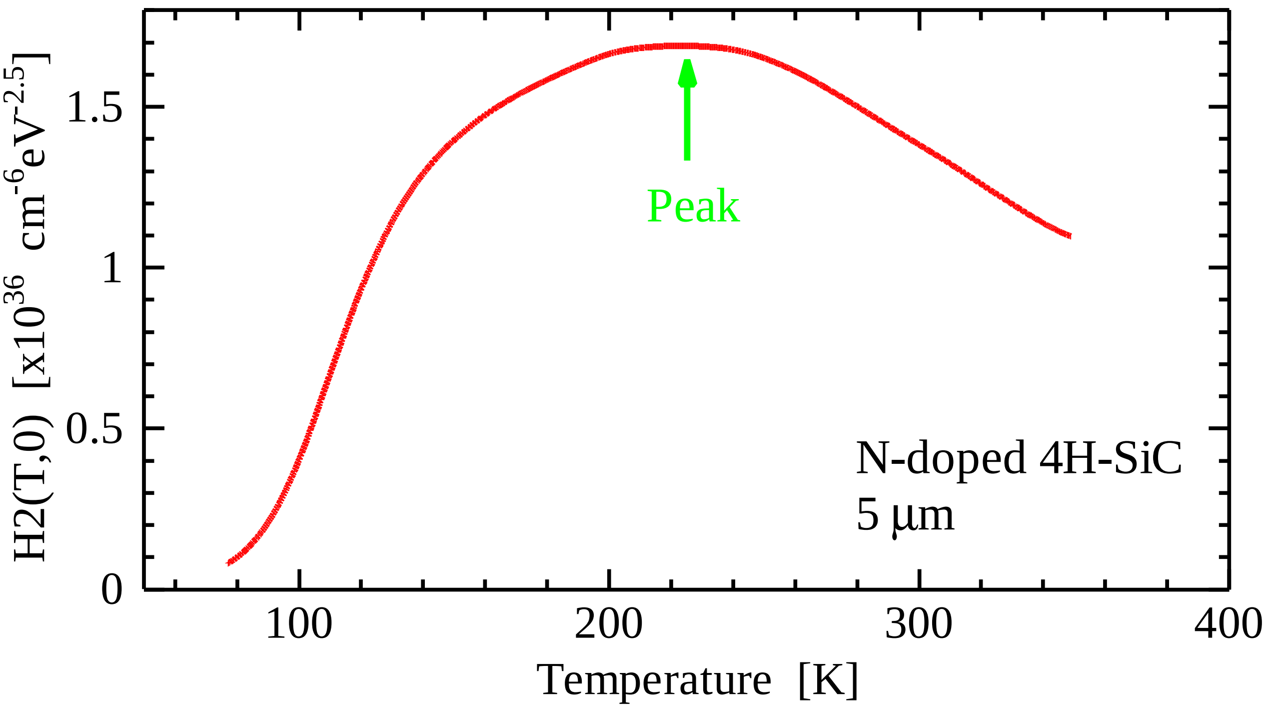
where

$$N_C(T) = 2.7\times10^{15} T^{3/2} \text{ cm}^{-3}$$

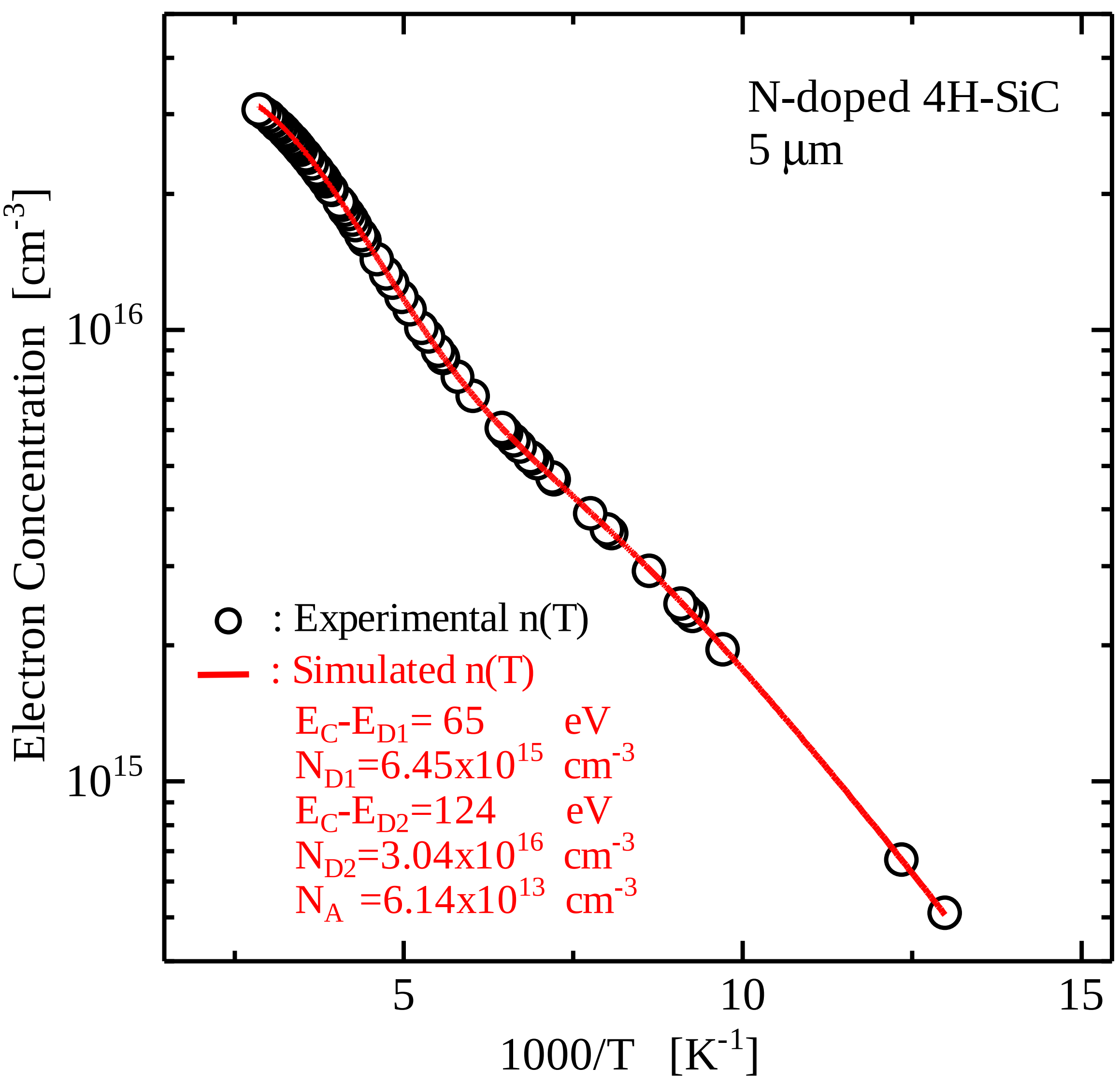
$$H(T,E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right)$$



$$H2(T,E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) - \frac{N_{\mathrm{D2}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D2}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D2}})$$



Comparison of experimental $n(T)$ with simulated $n(T)$



The $n(T)$, which is simulated using the results determined by $H(T, E_{\mathrm{ref}})$, is **qualitatively in agreement with** the experimental $n(T)$.

↓

The obtained results are reasonable.

65 meV donor → N donor at the hexagonal site

124 meV donor → N donor at the cubic site

Undoped 6H-SiC

Growth condition (chemical vapor deposition)

Gases: 1% SiH_4 with H_2

1% C_3H_8 with H_2

Pressure: 760 Torr

Temperature: 1500 °C

1. Preparation of 6H-SiC substrate by a sublimation method
2. Growth of thick p-type 6H-SiC on 6H-SiC substrate
3. Growth of **10 µm thick undoped (n-type) 6H-SiC** on p-type 6H-SiC

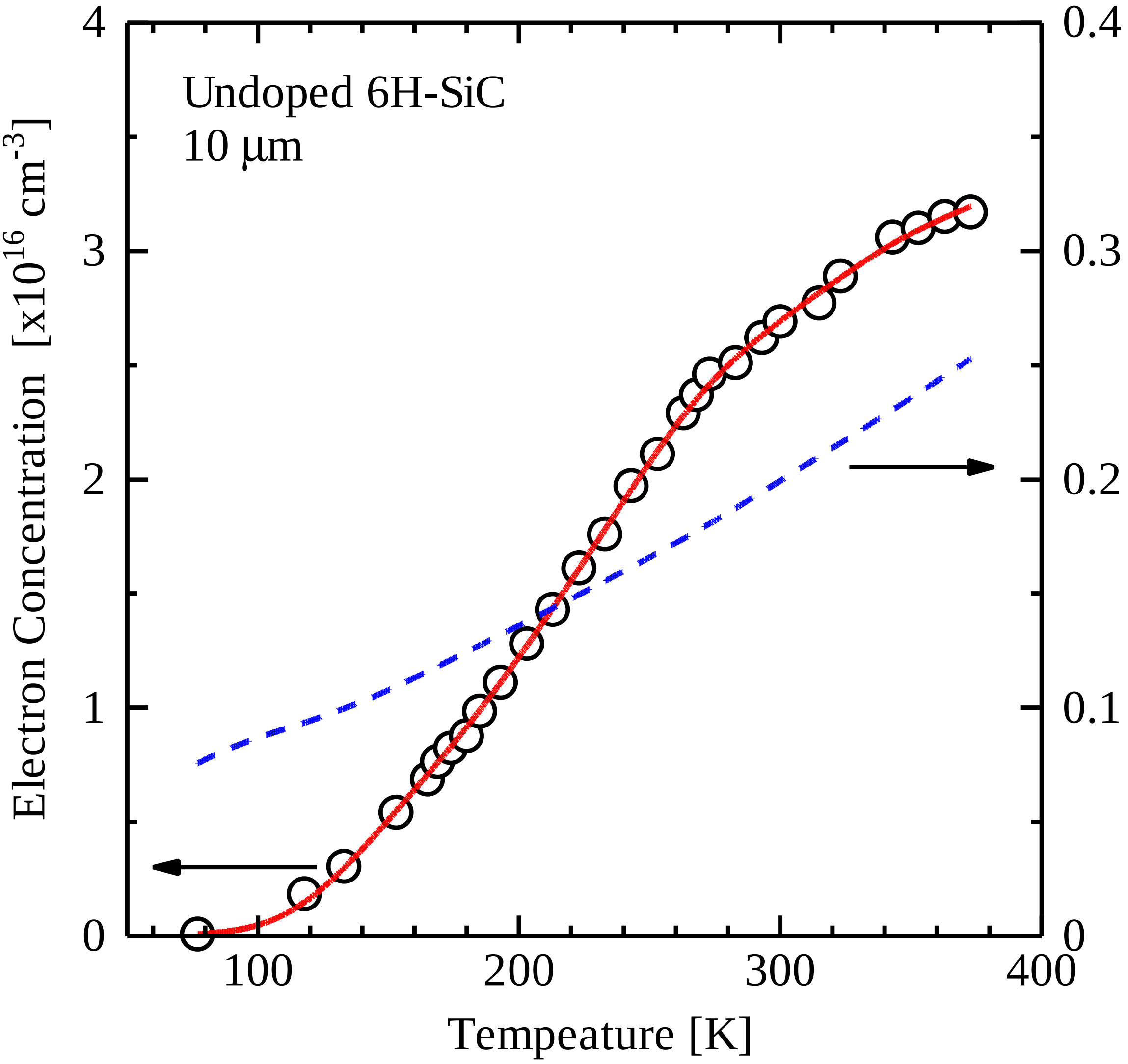
SiH_4: 0.30 sccm

C_3H_8: 0.20 sccm

H_2: 3.0 slm

C/Si ratio in source gases: 2

Electron concentration and Fermi level



○ : experimental $n(T)$

— : $n(T)$ interpolated by the cubic smoothing natural spline function

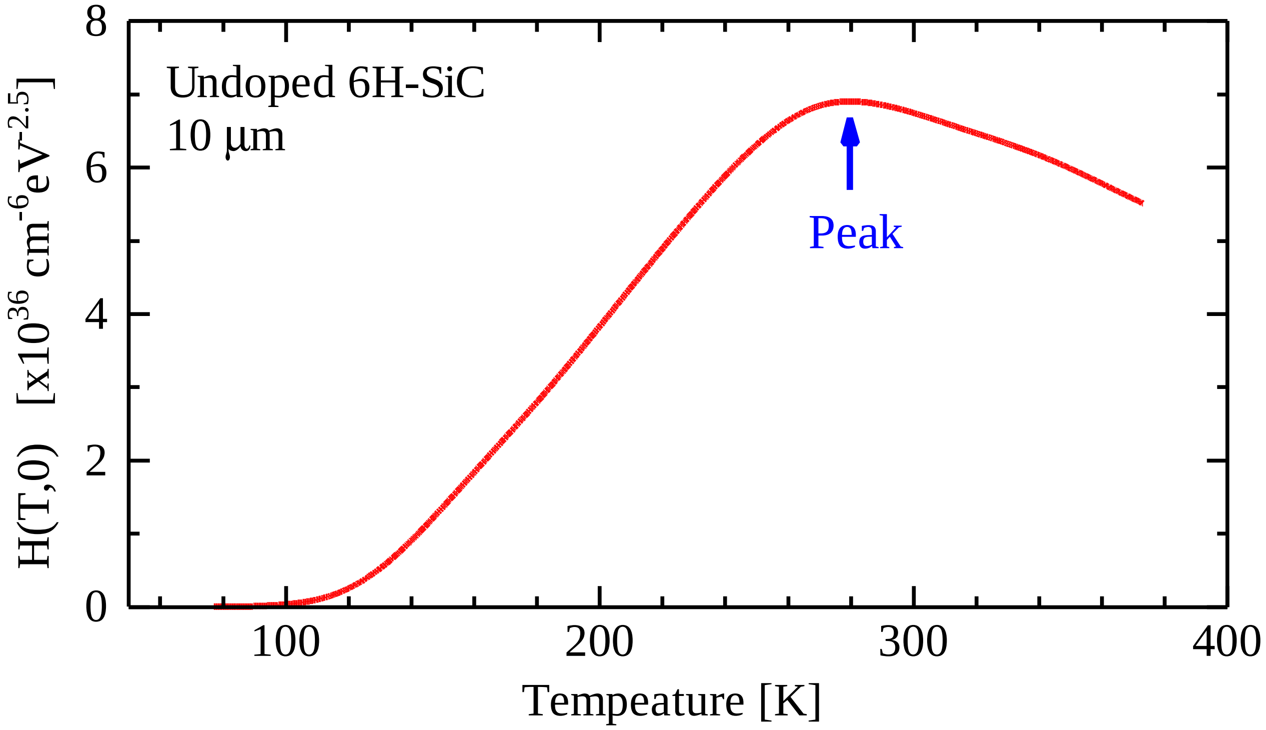
- - - : Fermi level

$$E_C - E_F = kT \ln\left[\frac{N_C(T)}{n(T)}\right]$$

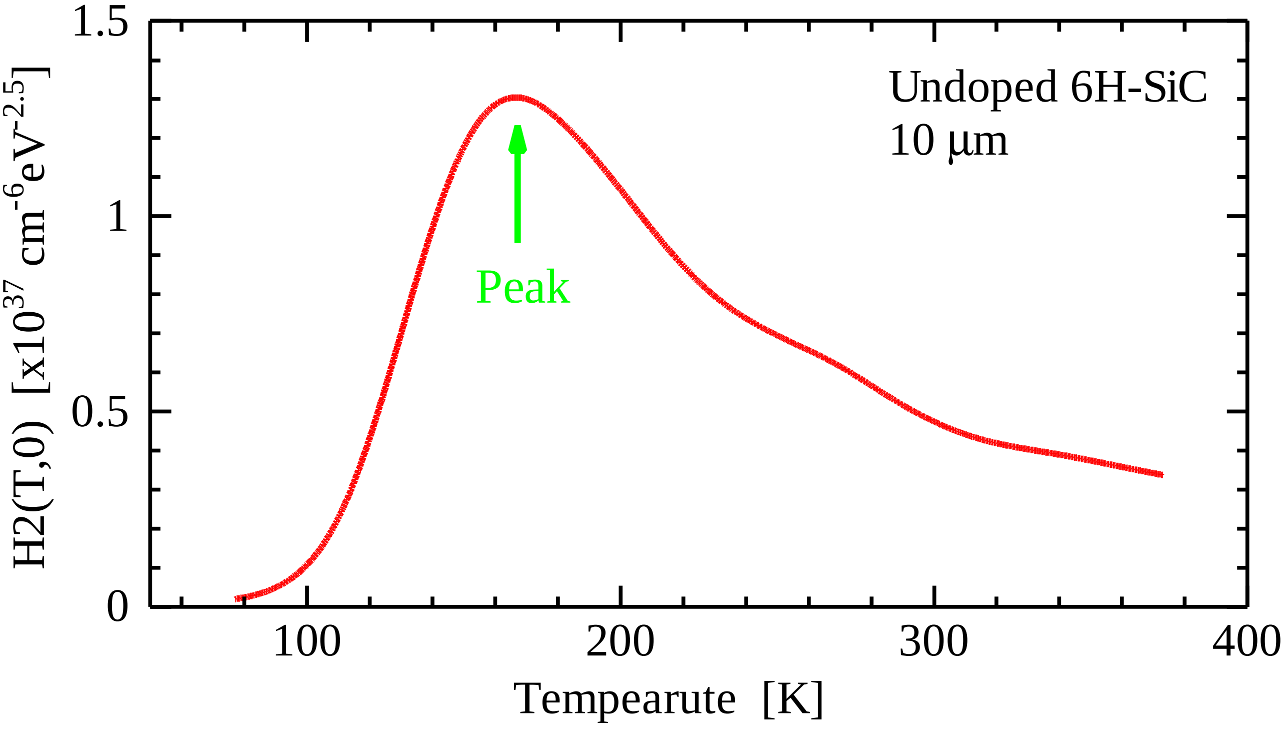
where

$$N_C(T) = 1.2\times10^{16} T^{3/2} \text{ cm}^{-3}$$

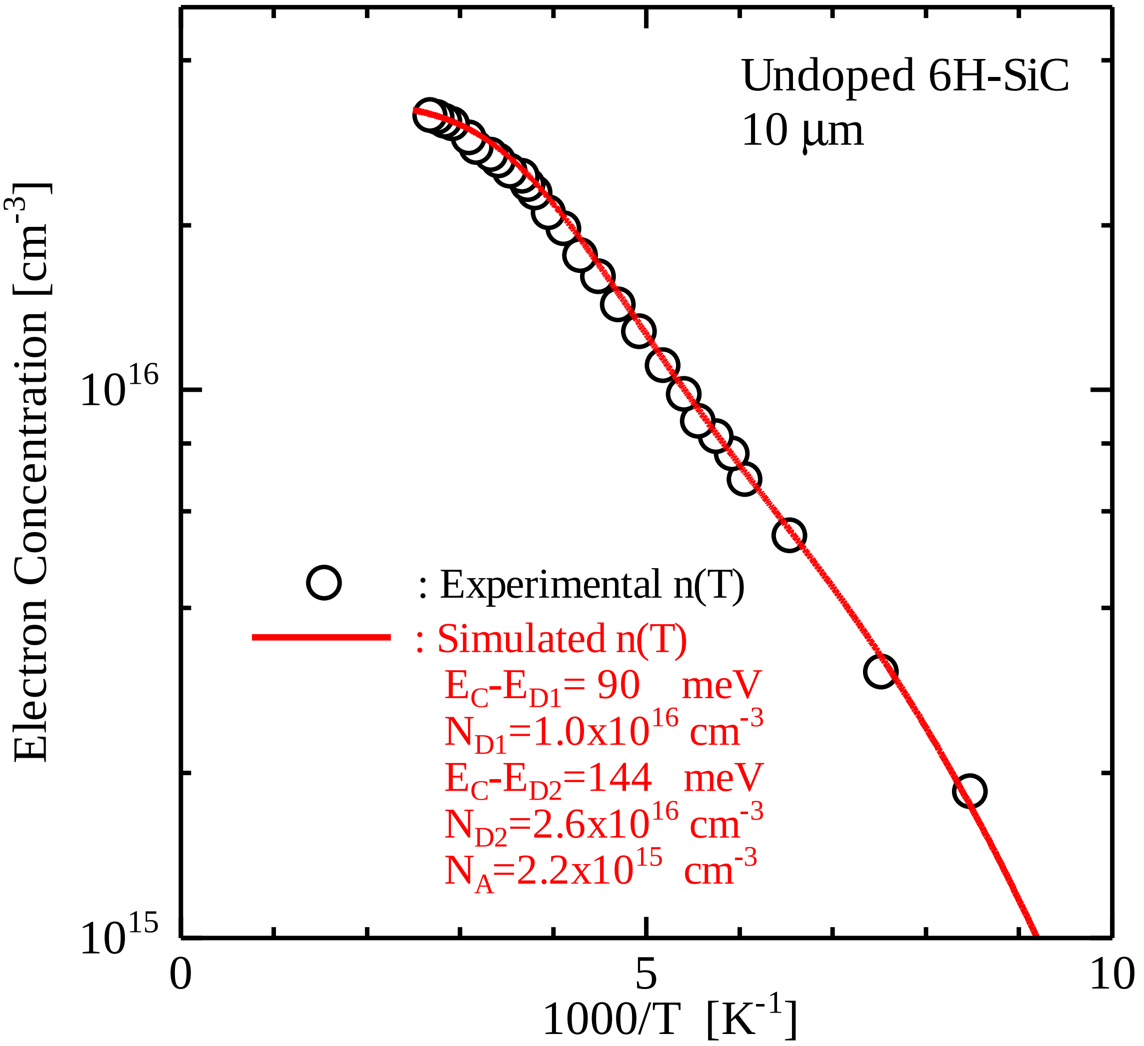
$$H(T,E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right)$$



$$H2(T,E_{\mathrm{ref}}) \equiv \frac{n(T)^2}{(kT)^{2.5}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) - \frac{N_{\mathrm{D2}}}{kT} \exp\left[-\frac{(E_{\mathrm{C}} - E_{\mathrm{D2}}) - E_{\mathrm{ref}}}{kT}\right] I(E_{\mathrm{D2}})$$



Comparison of experimental $n(T)$ with simulated $n(T)$



The $n(T)$, which is simulated using the results determined by $H(T, E_{\text{ref}})$, is **qualitatively in agreement with** the experimental $n(T)$.

↓

The obtained results are reasonable.

90 meV donor → N donor at the hexagonal site

144 meV donor → N donor at the cubic site

Conclusions

The temperature dependence of the majority-carrier concentration $n(T)$ is obtained by Hall-effect measurements.

Using $H(T, E_{\mathrm{ref}}) \equiv \dfrac{n(T)^2}{(kT)^{2.5}} \exp\left(\dfrac{E_{\mathrm{ref}}}{kT}\right)$ that we proposed,

1. we can **determine how many types of donors are included in SiC**,
2. we can **determine the density and energy levels of each donor accurately**,
3. we can **verify the obtained results easily**.

References

1) H. Matsuura and K. Sonoi: Jpn. J. Appl. Phys. **35** (1996) L555.
2) H. Matsuura: Jpn. J. Appl. Phys. **36** (1997) 3541.
3) H. Matsuura, Y. Uchida, T. Hisamatsu and S. Matsuda: Jpn. J. Appl. Phys. **37** (1998) 6034.
4) H. Matsuura, T. Kimoto and H. Matsunami: Jpn. J. Appl. Phys. **38** (1999) 4013.
5) H. Matsuura: Jpn. J. Appl. Phys. **38** (1999) 5176.
6) H. Matsuura, Y. Uchida, N. Nagai, T. Hisamatsu, T. Aburaya and S. Matsuda: Appl. Phys. Lett. **76** (2000) 2092.

More information is in the web site (http://www.osakac.ac.jp/labs/matsuura).