Electrical properties of Si/diamond heterojunction diodes fabricated by using surface activated bonding

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We evaluated the current–voltage (I–V) and temperature-dependent I–V characteristics of n[+]-Si/p-diamond

heterojunction diodes (HDs) fabricated by using surface activated bonding and Ru/p-diamond Schottky barrier

diodes (SBDs). Both types of diodes were fabricated on diamond surface that was activated using a fast atom

beam of Ar. Their room-temperature reverse-bias characteristics were be explained using the trap-assisted

tunneling model, wherein the surface activation process affects the carrier transport across the Si/diamond and

1   Ru/diamond interfaces. In addition, we compared the electrical properties of n^+-Si/p-diamond HDs and Ru/p-

2   diamond SBDs with those of previously fabricated p^+-Si/p-diamond HDs and Al/p-diamond SBDs. A

3   correlation between the barrier heights and the work function of the contact materials (n^+-Si, p^+-Si, and Ru)

4   was observed.

5

1. Introduction

Diamond is the most promising material for fabricating high-power, high-temperature, and radiation-resistant semiconductor devices because of its outstanding electronic properties: a breakdown field of >10 MV cm^{-1}, high electron and hole mobilities >2000 cm^2 V^{-1}s^{-1}, saturated drift velocities as high as 2.5×10^7 cm s^{-1} for electrons and 1.4×10^7 cm s^{-1} for holes and high displacement energy (43 eV/atom) [1–5]. However, the energy levels of phosphorus (P) and nitrogen (N), typical n-type dopants for diamond, are too deep (~0.57 and 1.7 eV below the conduction band edge, respectively) for them to be efficiently activated at room temperature; this limits the applications of diamond to electronic devices [6,7]. Establishment of pn junctions is the key for producing diamond-based devices such as bipolar transistors and junction field effect transistors. A possible method of solving this problem is to use direct bonding technologies, such as surface activated bonding (SAB), in which samples are bonded to each other without heating after their bonding surfaces are activated by using a fast atom beam (FAB) [8–11]. Si/diamond [12,13], GaAs/diamond [14], and β-Ga$_2$O$_3$/diamond [15] heterojunction diodes (HDs) were previously fabricated by direct bonding. In particular, we previously fabricated p$^+$-Si/p-diamond HDs using SAB and investigated the band structure of Si/diamond bonding interfaces [12]. In addition, we demonstrated that p$^+$-Si/p-diamond HDs were more stable against thermal processing than Al/p-diamond and Cu/p-diamond Schottky barrier diodes (SBDs) [16,17]. However, there is not enough research on carrier transport at Si/diamond interfaces.

1   In this study, we evaluated the characteristics of n[+]-Si/p-diamond HDs and Ru/p-diamond SBDs and

2   compared their properties with those of previously fabricated p[+]-Si/p-diamond HDs [12] and Al/p-diamond

3   SBDs [16] to investigate the electrical properties of Si/diamond interfaces.

4

5   **2. Experimental methods**

6   A B-doped drift layer and 7-μm-thick metal-assisted termination (MAT) buffer layer [18,19] ([B] ~5×10^{20}

7   cm^{-3}, [W] ~1×10^{19} cm^{-3}) were epitaxially grown on a B-doped HPHT diamond (100) substrate ([B] ~1×10^{18}

8   cm^{-3}). The B concentration in the drift layer was estimated to be 1×10^{16} cm^{3} from cathodoluminescence spectra

9   [20,21]. The net concentration of ionized acceptors in the drift layer (N_a^-- N_d^+, where N_a^- and N_d^+ are the

10   concentrations of ionized acceptors and donors, respectively) was estimated to be 6.5×10^{13} cm^{-3} from

11   capacitance-voltage characteristics. We also prepared a silicon-on-insulator (SOI) substrate that was composed

12   of a 6.5-μm-thick heavily (~10^{19} cm^{-3}) Sb-doped device layer, a 1-μm-thick SiO$_2$ layer, and a Si (100) substrate.

13   The surface of the diamond drift layer was mechanically polished. The thickness of the drift layer (W_{drift}) was

14   estimated to be 20 μm after polishing. The average roughness (Ra) measured using an atomic force microscope

15   was 0.3 and 0.1 nm for the diamond and Si surfaces, respectively. The device layer of the SOI substrate was

16   bonded to the diamond drift layer by using SAB. Next, the Si substrate and SiO$_2$ layer were removed by

17   grinding and wet etching to fabricate an n[+]-Si/p-diamond heterojunction. We made n[+]-Si mesas by wet etching

18   and formed contacts on the back of the diamond substrate and the surface of the Si mesas by evaporating Ti/Au

1   multi layers. After forming the Si/diamond junctions, the uncovered diamond surface was terminated by

2   oxygen by irradiating it with ultraviolet light in an oxygen atmosphere [22,23]. The SBDs were fabricated by

3   evaporating Ru/Au multilayers as Schottky contacts on the diamond drift layer. A schematic cross section of

4   the fabricated diodes is shown in Fig. 1. Note that the HDs and SBDs were fabricated on the same diamond

5   substrate. We performed sequential post-process annealing on the fabricated diodes (703 K for 30 min and 873

6   K for 30 min). The current-voltage (I-V) characteristics at room temperature and I-V characteristics at ambient

7   temperatures between 293 K and 473 K (the temperature-dependent I-V characteristics) were measured for

8   respective diodes in a vacuum after each annealing step. A source measure unit (Agilent B2902A, B1505A)

9   was used for measurements of I-V characteristics.

10

11 **3. Results**

12   The I-V characteristics at room temperature for the n^+-Si/p-diamond HDs and Ru/p-diamond SBDs before

13 and after annealing at 703 K and 873 K are shown in Figs. 2(a)-2(c). The I-V characteristics of p^+-Si/p-diamond

14 HDs [12] are also shown for comparison. We computed the ideality factor from the steepest part of each I-V

15 curve between -1.7 and -0.7 V. We defined the reverse-bias current, turn-on voltage, and on/off ratio as the

16 magnitude of the current at 3 V, the forward-bias voltage for a current of 1 mA/cm^2, and the ratio of current at

17 -3 V to that at +3 V, respectively. The I-V characteristics of the n^+-Si/p-diamond HDs before annealing did not

18 show diode characteristics, which is assumed to be attributable to (I) that the properties of ohmic contacts

1 formed on back of the p$^+$-diamond substrate were poor and/or (II) that interface states were formed during the

2 surface activation process [24,25]. The turn-on voltage of the n$^+$-Si/p-diamond HDs was higher than that of

3 the p$^+$-Si/p-diamond HDs, which is due to the difference in band structure between these HDs. The parameter

4 values for the respective annealing conditions are summarized in Table 1. The parameters of the Al/p-diamond

5 SBDs [16] are also listed. The ideality factors of annealed HDs are close to that of annealed Ru/p-diamond

6 HDs. The ideality factor of Ru/p-diamond SBDs decreased by annealing, which was in good contrast to the

7 behavior of the ideality factor of Al/p-diamond SBD. The difference in the ideality factors between the two

8 SBDs might be attributed to the thermal stability of Ru/diamond interfaces superior to that of Al/diamond

9 interfaces [26,27]. In contrast to the Ru/p-diamond SBDs, the I-V characteristics of HDs annealed at 873 K

10 show a hump around -1.4 V, which might be attributable to defects formed at annealed interfaces. A possible

11 origin of such defects is (1) local strain and resultant deterioration in crystal quality at Si/diamond interfaces

12 because of large difference in the coefficients of thermal expansion between Si and diamond (1.8×10^{-6} °C^{-1})

13 [28] and (2) intermediate layers formed at Si/diamond interfaces during the annealing [29].

14 Figures 3(a) and 3(b) show the temperature-dependent I-V characteristics of the n$^+$-Si/p-diamond HDs after

15 annealing at 703 and 873 K while Figs. 3(c) and 3(d) show those of the Ru/p-diamond SBDs. The turn-on

16 voltage decreased as the ambient temperature was increased. In contrast, no marked increase was observed in

17 the reverse-bias current when the ambient temperature was changed.

18 The saturation current density J_s was obtained by extrapolating the forward-bias current density of each

1   curve to 0 V. Figure 4(a) shows the relationship between $\ln(J_s/T^2)$ and $1/k_BT$ (the Richardson plot) of the n^+-

2   Si/p-diamond HDs, Ru/p-diamond SBDs, p^+-Si/p-diamond HDs, [12] and Al/p-diamond SBDs [16] after

3   annealing at 703 K. The Richardson plots of these four diodes after annealing at 873 K are shown in Fig. 4 (b).

4   Here, k_B and T are the Boltzmann constant and ambient temperature, repectively. Using thermionic emission

5   (TE) model, J_s is expressed as

$$J_s = A^* T^2 \exp\left(-\frac{qV_b}{k_BT}\right), \tag{1}$$

7   where A^*, q, and qV_b are the Richardson constant, elementary charge, and barrier height, respectivley. On the

8   basis of the TE model, we fitted the relationship between $\ln(J_s/T^2)$ and $1/kT$ to a straight line and estimated the

9   barrier height. The barrier heights were found to be 1.65, 1.28, 0.85, and 0.78 eV for the n^+-Si/p-diamond HDs,

10   Ru/p-diamond SBDs, p^+-Si/p-diamond HDs, and Al/p-diamond SBDs after annealing at 703 K, respectively.

11   Moreover, the barrier heights for the diodes after annealing at 873 K were found to be 1.2, 1.0, 0.55, and 0.55

12   eV, for the n^+-Si/p-diamond HDs, Ru/p-diamond SBDs, p^+-Si/p-diamond HDs, and Al/p-diamond SBDs,

13   respectively.

14   Figures 5(a) and 5(b) show the reverse-bias characteristics of the n^+-Si/p-diamond HDs and Ru/p-diamond

15   SBDs after annealing at 703 K and 873 K. Breakdown occurred at 1080 V in the n^+-Si/p-diamond HDs and at

16   420 V in the Ru/p-diamond SBDs after annealing at 703 K. The breakdown voltages after annealing at 873 K

17   were 420 and 110 V for the n^+-Si/p-diamond HDs and Ru/p-diamond SBDs, respectively. The deterioration of

18   reverse-bias characteristics for n^+-Si/p-diamond HDs after annealing at 873 K may be due to the formation of

1 defects at annealed Si/diamond interfaces, as was suggested for the origin of the hump formed around -1.4 V.

2 A deeper understanding of the origin of the degradation in characteristics of annealed HDs might be obtained

3 by systematically investigating nanostructural properties of annealed Si/diamond interfaces using methods

4 such as transmission electron microscopy.

5 Using the trap-assisted tunneling (TAT) model [30–32], the reverse-bias current density is expressed as

6
$$J_{\text{TAT}} \propto \exp\left(-\frac{8\pi\sqrt{2qm^*}V_t^{3/2}}{3hE}\right)$$
(2).

7 Here, h, E, m^*, and qV_t are the Planck constant, electric field at the interface, effective mass of the carrier, and

8 trap energy level. We assumed that m^* was 0.908 m_0 [33], where m_0 is the electron rest mass. The depletion

9 region thickness ($W_{\text{depletion}}$) is given by

10
$$W_{\text{depletion}} = \sqrt{\frac{2\varepsilon_{\text{dia}}\varepsilon_0}{qN_A}\left(V_{\text{bi}} + V - \frac{k_BT}{q}\right)}$$
(3)

11 where ε_0, ε_{dia}, V_{bi}, and V are the permittivity of the vacuum, dielectric constant of diamond, built-in potential,

12 and applied reverse-bias voltage, respectively. We set ε_{dia} at 5.7 [33]. V_{bi} of the n+-Si/p-diamond HDs and

13 Ru/p-diamond SBDs after annealing at 703 K was estimated to be 1.27 and 0.87 V, respectively, from the

14 Richardson plots. Using Eq. (3), thickness of the depletion region was found to be larger than that of the drift

15 layer at a reverse-bias voltage of 1080 V, which implied that the drift layer was completely depleted. Thus, E

16 was given by

17
$$E = \frac{V + V_{\text{bi}}}{W_{\text{drift}}}.$$
(4)

18 Figures 5(c) and 5(d) shows the relationship between ln(J) and 1/E (TAT plot) [31,32], where J is the current

1   density, of the n^+-Si/p-diamond HDs and Ru/p-diamond SBDs after annealing at 703 K and 873 K. qV_t was

2   estimated to be 0.13, 0.08, and 0.03 eV for n^+-Si/p-diamond HDs and Ru/p-diamond SBDs after annealing at

3   703 K, and n^+-Si/p-diamond HDs after annealing at 873 K, respectively, by fitting the measured reverse-bias

4   characteristics using eq. (2). These qV_t values are slightly smaller than the reported depths of defects in CVD-

5   grown diamond (0.2-1.7 eV) [34–39]. The reverse-bias characteristics of the Ru/p-diamond SBDs after

6   annealing at 873 K were not explained using TAT model. The breakdown field for HDs and SBDs, which was

7   estimated to be 0.5 and 0.2 MV/cm, respectively, was lower than the ideal breakdown field of diamond(7.7-20

8   MV/cm) [40]. Noting that the breakdown field of SBDs with field plate (1.8 MV/cm) was reportedly higher

9   than that of SBDs without field plate (0.8 MV/cm) [41], the breakdown field of HDs and SBDs may be

10   increased by incorporating edge-termination techniques.

11   We also examined possibility of other models such as the thermionic emission (TE) model [42], TE model

12   with barrier lowering effects considered (TE + BL model) [43], thermionic field emission (TFE) model [25],

13   TFE model with barrier lowering effects considered (TFE + BL model) [44–47], and Poole-Frenkel emittion

14   (PFE) model [48,49] for explaining the reverse-bias characteristics of HDs and SBDs. No good fits were

15   obtained using models other than TAT model.

16

17   **4. Discussion**

18   Figure 6 shows the energy-band diagram of n^+-Si/p-diamond HDs at reverse-bias voltage estimated by

9

assuming that no offset is formed in the vacuum level across n$^+$-Si/p-diamond bonding interface. On this assumption, the band offset for n$^+$-Si/p-diamond HDs ΔE_c and ΔE_v is expressed as

$$\Delta E_c = E_{g,dia} - qV_b - \delta_{n,Si}, \tag{5}$$

$$\Delta E_v = E_{g,dia} - \Delta E_C - E_{g,Si}. \tag{6}$$

where $E_{g,dia}$ ($E_{g,Si}$) and $\delta_{n,Si}$ are the bandgap energy of diamond (Si) and the difference between the Fermi level and the conduction band minimum in n$^+$-Si, respectively. We use $E_{g,Si}$ =1.12 eV and $E_{g,dia}$=5.47 eV in the literature [42]. We estimate $\delta_{n,Si}$ =0.03 eV from the ionized acceptor concentration in the drift layer and effective density of states in conduction band of Si. We assume that qV_b is 1.60 eV based on the analysis of the Richardson plot. We find that ΔE_C=3.84 eV and ΔE_v=0.51 eV.

We previously reported that Ar FAB irradiation of surfaces led to the formation of amorphous-like layers at the bonding interfaces of diamond/Si heterojunctions [50,51]. Given that the reverse-bias characteristics of the n$^+$-Si/p-diamond HDs and Ru/p-diamond SBDs were explained by TAT model, the current is assumed to be due to the following two-step process (Fig. 6). First, holes are thermally excited to the trap states. Second, the holes tunnel to the valence band of the p-diamond. Noting that a larger breakdown voltage was observed for SBDs with higher Schottky barriers [52], the larger breakdown voltage of the n$^+$-Si/p-diamond HDs than that of the Ru/p-diamond SBDs is likely to be due to the higher barrier of the n$^+$-Si/p-diamond interfaces. The reverse-bias characteristics of typical SBDs fabricated using the conventional process were explained by the TE and TFE+BL models [43–47], which is in good contrast to the present work. The difference in the features

1   of the reverse-bias characteristics suggests that the traps were also formed during the surface activation process

2   of diamond and/or the Si surface, as was reported for p-Si/n-Si bonding interfaces [30]. Advanced

3   characterization of bonding interfaces such as transient photo-response spectroscopy is expected to play an

4   important role for clarifying their electrical properties [53–55].

5   Figure 7 shows the correlation between the barrier height estimated by the Richardson plot and the work

6   functions of the contact materials (n$^+$-Si, p$^+$-Si, Ru, and Al). The S factors (S=$\partial qV_\mathrm{b}/\partial \chi_\mathrm{m}$, where χ_m is the

7   work function) of the Si/p-diamond HDs and Ru/p-diamond SBDs after annealing at 703 K and 873 K are

8   close to 0.7 and 0.6, respectively. The measured barrier heights of the Al/p-diamond SBDs after annealing at

9   703 K and 873 K are placed below lines for S=0.7 and 0.6, which is due to the thermal stability of Al/diamond

10   interfaces inferior to those of Si/diamond and Ru/diamond interfaces [16,17,26,27]. The observed S factor

11   close to 1, which is significantly larger than that reported for p-diamond SBDs fabricated on oxygen-terminated

12   surfaces (0.47) [56], suggests formation of partially "pinning-free" interfaces in the present work. A possible

13   explanation is that the Ar FAB irradiation partially removed the high-density oxygen-related surface states [57],

14   which were assumed to pin the Fermi level at the diamond surface. The surface activation process of diamond

15   by Ar FAB irradiation is assumed to play an important role of realizing its pinning-free surface. The

16   controllability of performances of diamond-based devices such as turn-on voltage and breakdown

17   characteristics might be enhanced by bonding diamond to materials with different work functions (such as

18   semiconductors with different polarities) and fabricating pinning-free interfaces.

1

2

5. Conclusion

We fabricated n^+-Si/p-diamond HDs and Ru/p-diamond SBDs on diamond surfaces activated using Ar FAB. Their reverse-bias characteristics were explained by the TAT model, which suggested that traps were formed during the surface activation process. The S factors of Si/diamond HDs and Ru/p-diamond SBDs after annealing at 703 K and 873 K were close to 0.7 and 0.6, respectively. The correlation between the barrier height and the work function of the contact materials (n^+-Si, p^+-Si, and Ru) suggested formation of partially ''pinning-free'' interfaces in HDs and SBDs wherein the Ar FAB irradiation partially removed the high-density oxygen-related surface states. These results imply that fabrication of diamond/semiconductor HDs by using surface activated bonding is assumed to play an important role in promoting the development of diamond devices.

16

1 **Table I.** Ideality factor, reverse-bias current, turn-on voltage, rectification

2 factor of n^+-Si/p-diamond HDs, Ru/p-diamond SBDs, previously fabricated p^+-Si/p-diamond HDs

3 [12], and Al/p-diamond SBDs [16].

	Annealing temperature	Ideality factor	Reverse-bias Current (mA/cm^2)	Turn-on voltage (V)	Rectification factor
n^+-Si/p-diamond HDs	Before annealing	-	2.74	1.00	10^0
	703 K	1.20	1×10^{-3}-1×10^{-2}	1.56	10^4
	873 K	1.30	1×10^{-3}-1×10^{-2}	1.15	10^5
Ru/p-diamond SBDs	Before annealing	2.76	1×10^{-3}-1×10^{-2}	1.77	10^4
	703 K	1.38	1×10^{-3}-1×10^{-2}	1.56	10^4
	873 K	1.22	1×10^{-3}-1×10^{-2}	1.32	10^5
p^+-Si/p-diamond HDs [12]	Before annealing	2.62	1.12	1.27	10^7
	703 K	1.85	1×10^{-3}-1×10^{-2}	1.38	10^7
	873 K	1.25	1×10^{-3}-1×10^{-2}	0.83	10^7
Al/p-diamond SBDs [16]	Before annealing	1.38	1×10^{-3}-1×10^{-2}	0.97	10^7
	703 K	1.37	1×10^{-3}-1×10^{-2}	0.96	10^7
	873 K	1.57	1×10^{-3}-1×10^{-2}	0.90	10^7

4

1   **Figure Captions**

2   **Fig. 1.** Schematic cross section of fabricated n^+-Si/p-diamond HDs and Ru/p-diamond SBDs.

3

4   **Fig. 2.** *I-V* characteristics at room temperature for n^+-Si/p-diamond HDs, Ru/p-diamond SBDs, and

5   p^+-Si/p-diamond HDs [12] before annealing (a) and after annealing at 703 K (b) and 873 K (c).

6

7   **Fig. 3.** Temperature-dependent *I-V* characteristics of n^+-Si/p-diamond HDs after annealing at 703 K

8   (a) and 873 K (b). Temperature-dependent *I-V* characteristics of Ru/p-diamond SBDs after

9   annealing at 703 K (c) and 873 K (d).

10

11   **Fig. 4.** Relationship between J_s and $1/k_B T$ (Richardson plot) of n^+-Si/p-diamond HDs, Ru/p-diamond

12   SBDs, p^+-Si/p-diamond HDs [12], and Al/p-diamond SBDs [16] after annealing at 703 K (a) and 873

13   K (b).

14

15   **Fig. 5.** Reverse-bias characteristics of n^+-Si/p-diamond HDs and Ru/p-diamond SBDs after annealing

16   at 703 K (a) and 873 K (b). TAT plots of n^+-Si/p-diamond HDs and Ru/p-diamond SBDs after
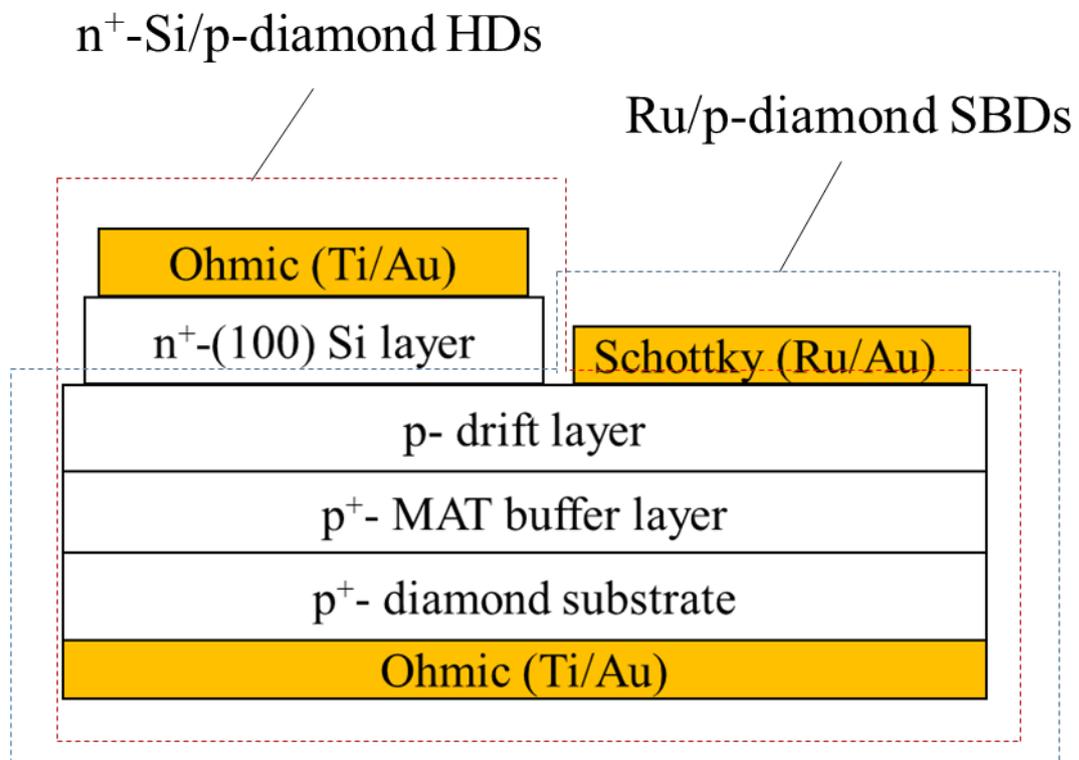
17   annealing at 703 K (c) and 873 K (d).

18

1   **Fig. 6.** Carrier transport of n^+-Si/p-diamond interfaces under reverse bias.

2

3   **Fig. 7.** Correlation between barrier height estimated by Richardson plot and work function of contact

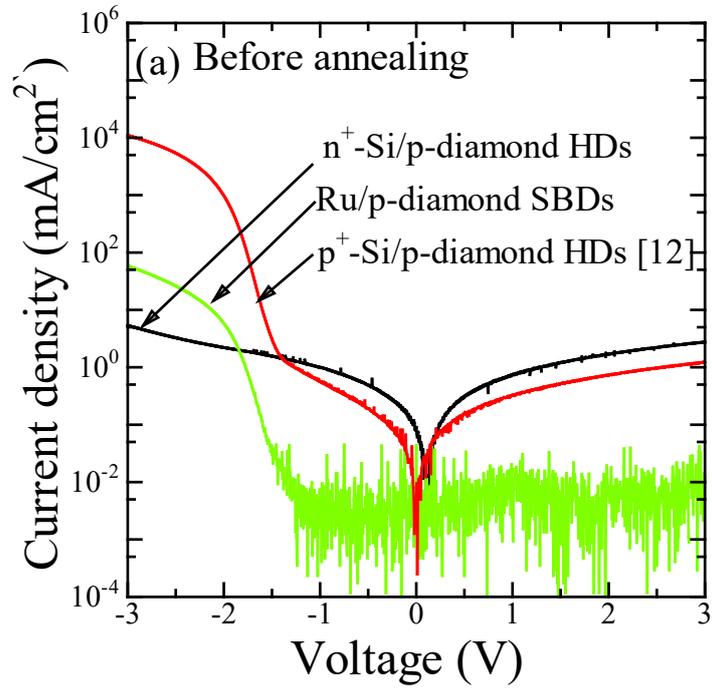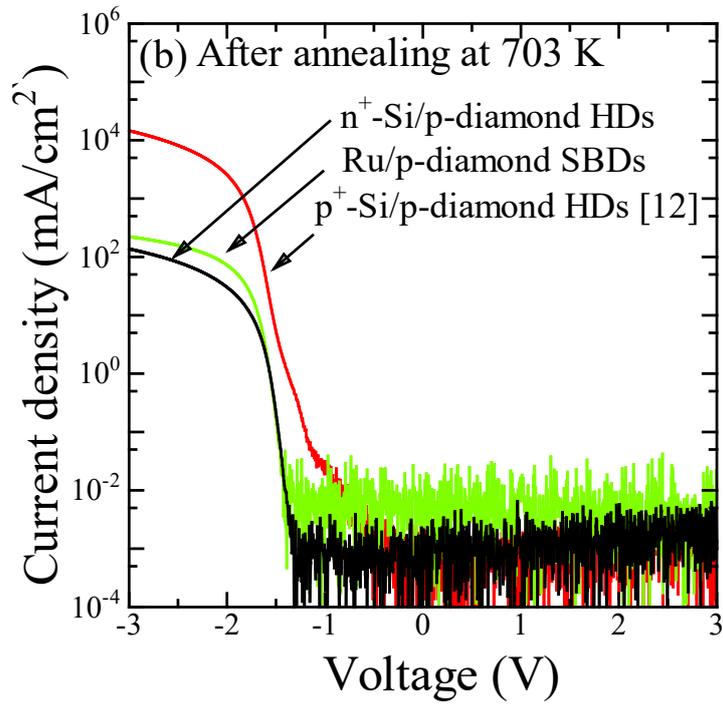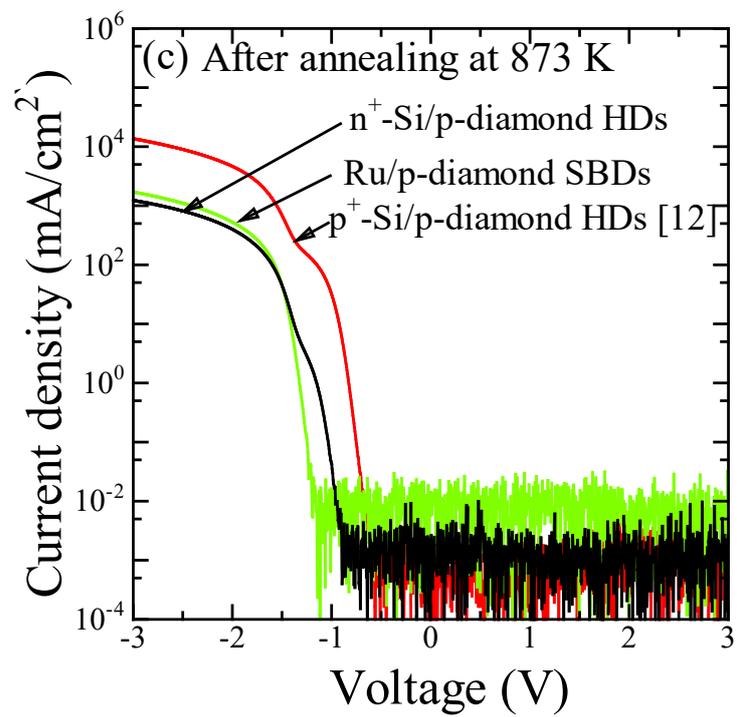4   materials (n^+-Si, p^+-Si, Ru, and Al).

1 **Fig. 1.**

n$^+$-Si/p-diamond HDs

Ru/p-diamond SBDs

Ohmic (Ti/Au)	
n$^+$-(100) Si layer	Schottky (Ru/Au)
p- drift layer	
p$^+$- MAT buffer layer	
p$^+$- diamond substrate	
Ohmic (Ti/Au)	

2
3

1   **Fig. 2.**

(a) Before annealing

n⁺-Si/p-diamond HDs
Ru/p-diamond SBDs
p⁺-Si/p-diamond HDs [12]

(b) After annealing at 703 K

n⁺-Si/p-diamond HDs
Ru/p-diamond SBDs
p⁺-Si/p-diamond HDs [12]

2

3

(c) After annealing at 873 K

n$^+$-Si/p-diamond HDs
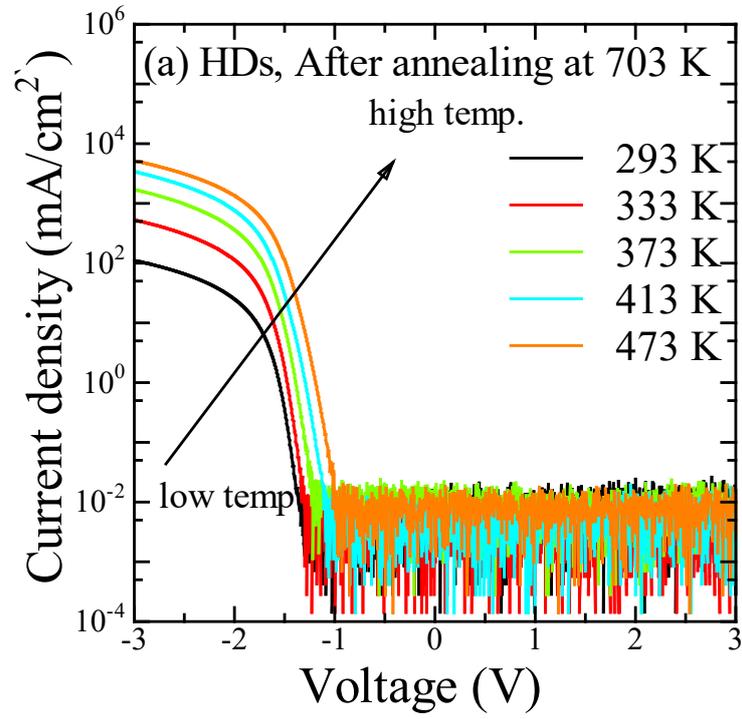
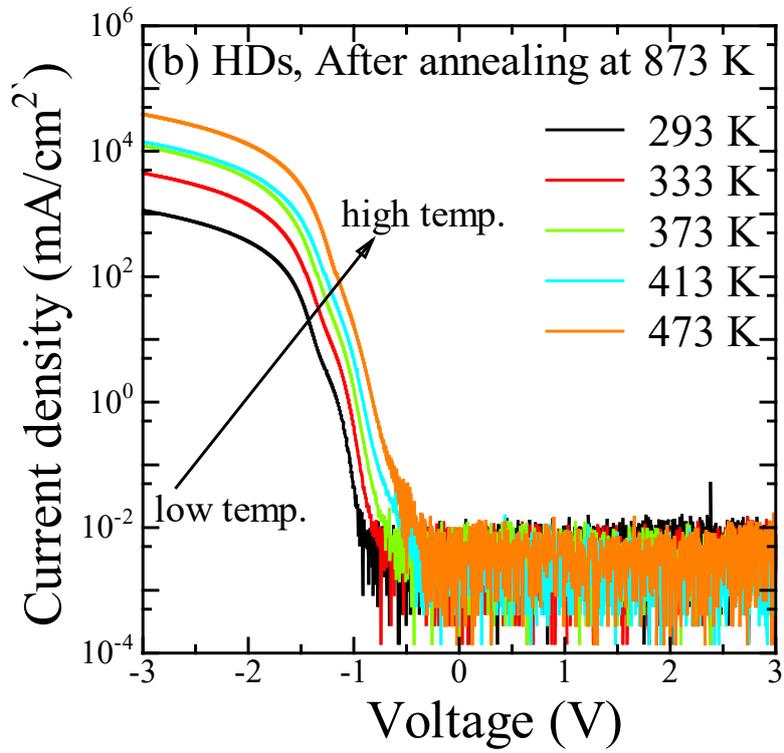Ru/p-diamond SBDs

p$^+$-Si/p-diamond HDs [12]

Current density (mA/cm^2)

Voltage (V)

1

2

3

1   **Fig. 3.**

2

3
4

(c) SBDs, After annealing at 703 K

high temp.

	293 K
	333 K
	373 K
	413 K
	473 K

low temp.

(d) SBDs, After annealing at 873 K

high temp.

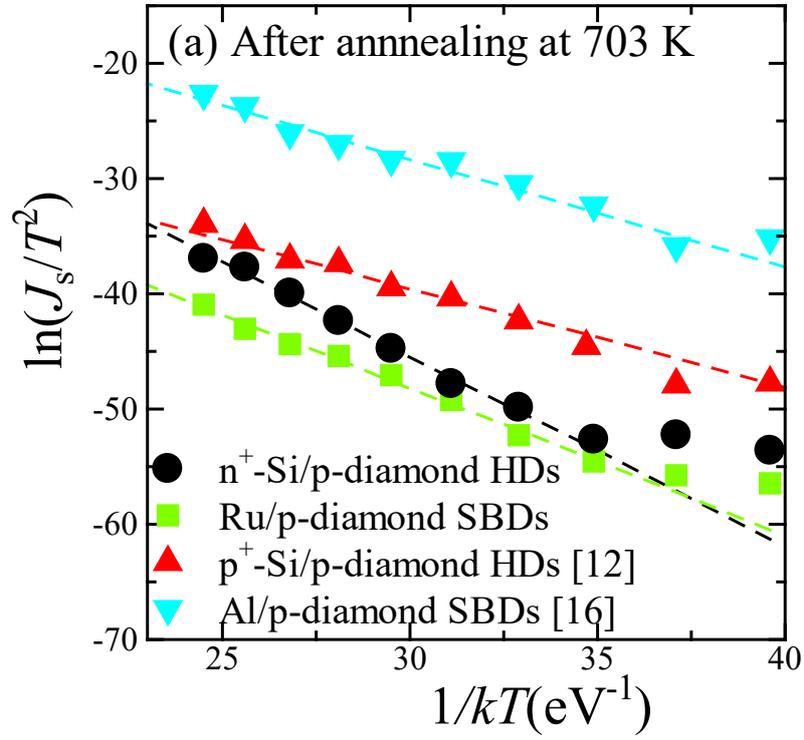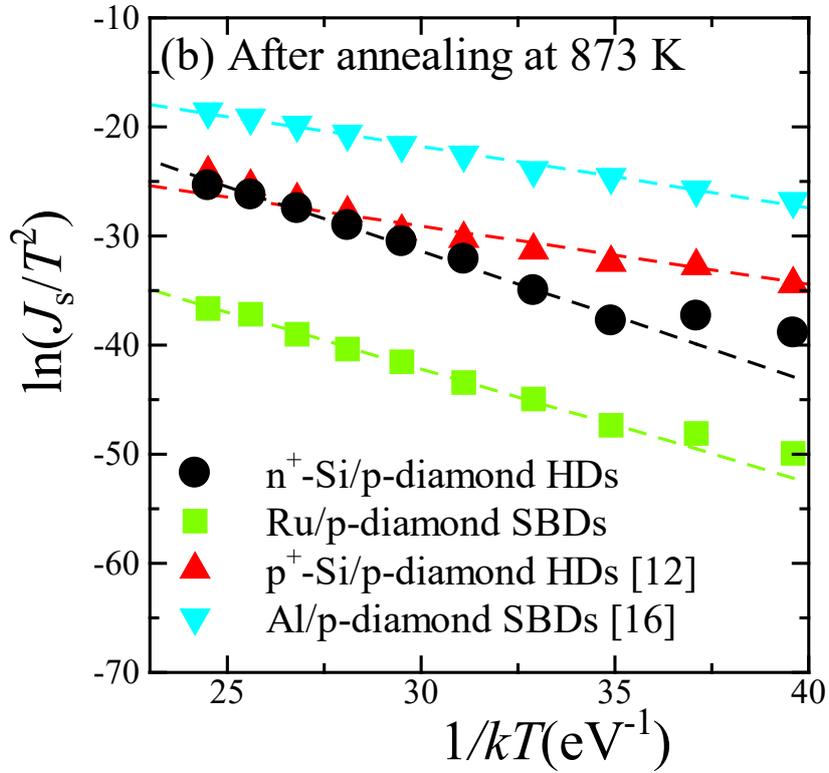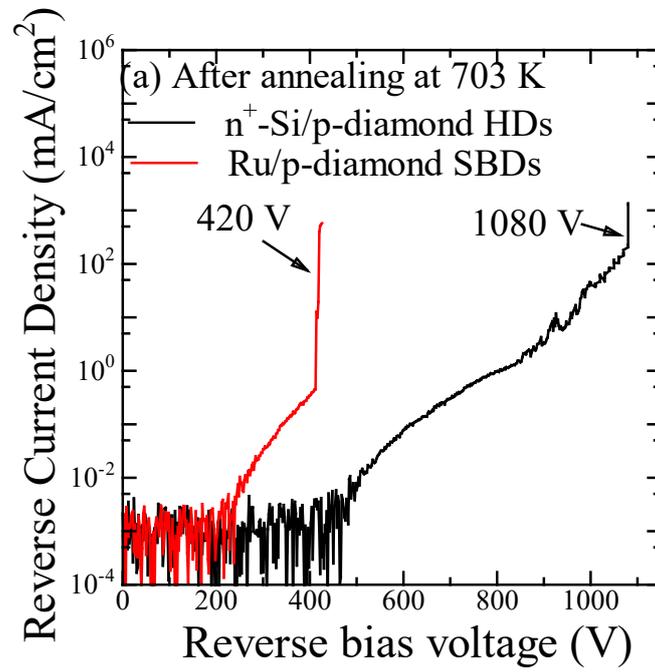|	293 K
	333 K
	373 K
	413 K
	473 K

low temp.

1

2

3

1 **Fig. 4.**

2

3

4

1   **Fig. 5.**

2

3

4

(c) After annealing at 703 K

— n⁺-Si/p-diamond HDs
— Ru/p-diamond SBDs

qV_t=0.13 eV

qV_t=0.08 eV

$\ln(J)$ (mA/cm²)

$1/E$ (cm/V)　(×10⁻⁵)

(d)　After annealing at 873 K

— n⁺-Si/p-diamond HDs
— Ru/p-diamond SBDs

qV_t=0.03 eV

$\ln(J)$ (mA/cm²)

$1/E$ (cm/V)　(×10⁻⁵)

1

2

3

23

1   **Fig. 6.**

E_C

$E_{g,dia}$=5.47 eV

ΔE_c=3.84 eV

E_f
E_v

$\delta_{n,Si}$=0.03 eV

$E_{g,Si}$=1.12 eV

qV_b=1.60 eV ΔE_v=0.51 eV

n$^+$-Si   p-diamond

qV_t=0.13 eV

① ②

n$^+$-Si   p-diamond

2
3

1 **Fig. 7.**

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Fig. 7 plot of Barrier height (eV) versus Work function (eV). Labeled data points: n⁺-Si #1, n⁺-Si #2; Ru #1, Ru #2; Al #1, Al #2; p⁺-Si #1, p⁺-Si #2; dashed lines S=0.7 and S=0.6. Legend: ○ n⁺-Si/p-diamond HDs; ◇ Ru/p-diamond SBDs; △ p⁺-Si/p-diamond HDs [12]; ▽ Al/p-diamond SBDs [16]. #1: Annealed at 703 K; #2: Annealed at 873 K.
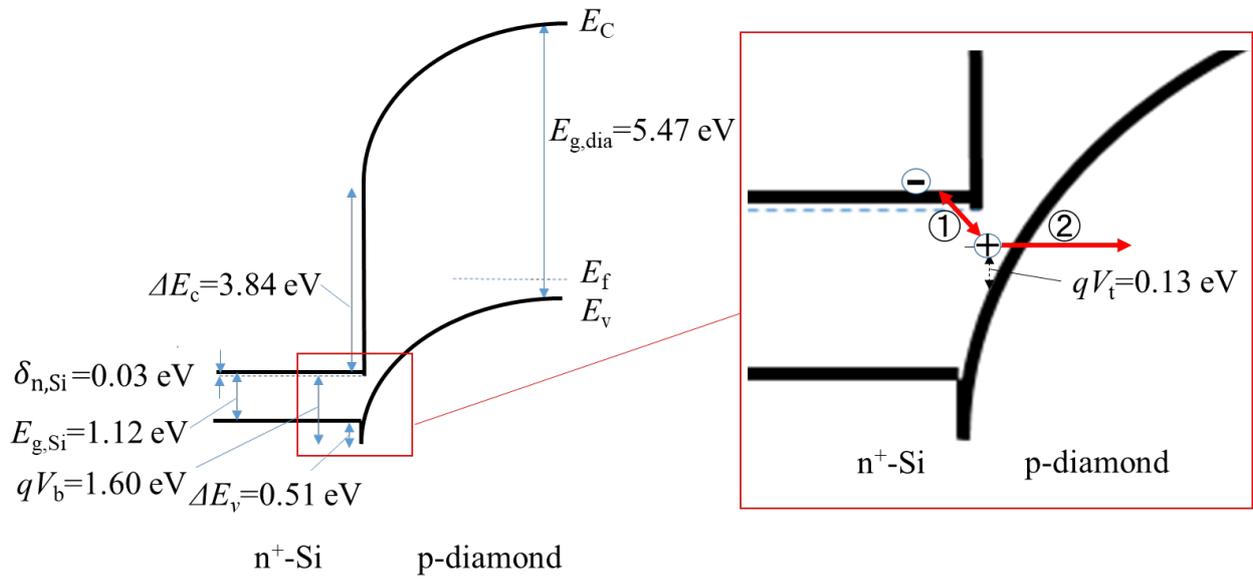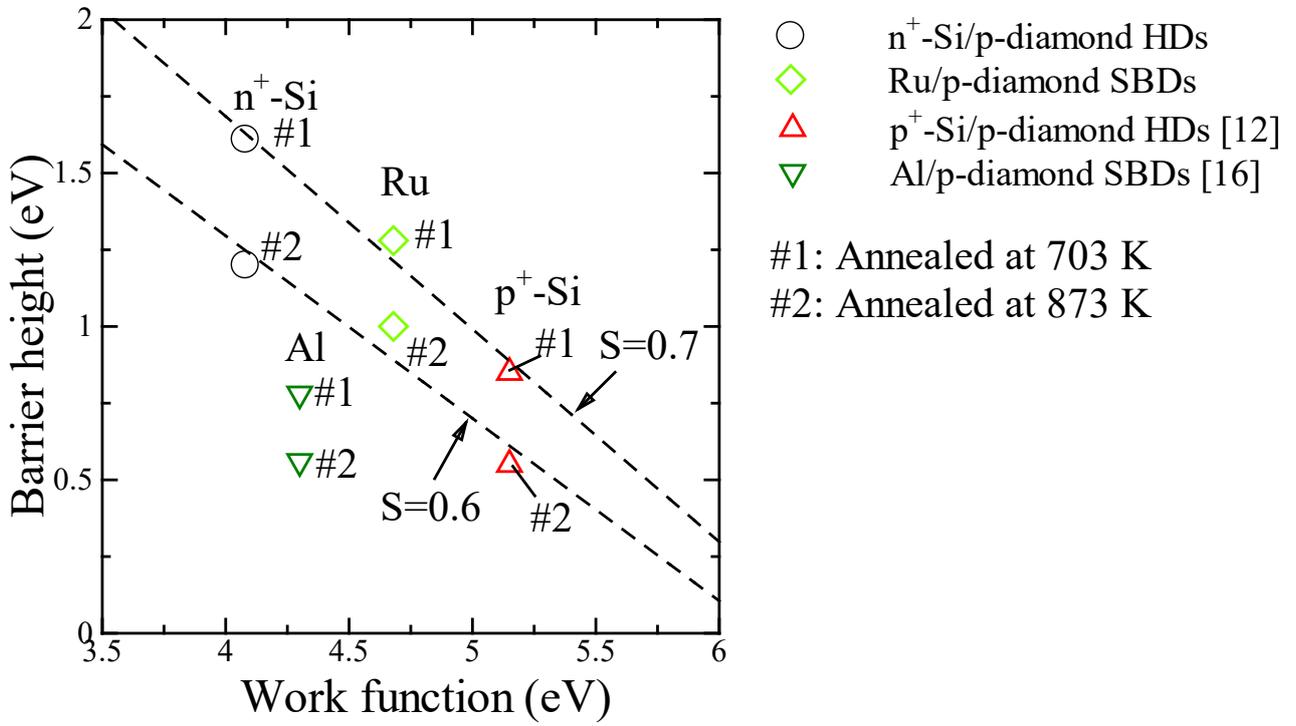
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