**Electric dipole effect in PdCoO₂/β-Ga₂O₃ Schottky diodes for high-temperature operation**

T. Harada¹*, S. Ito¹, A. Tsukazaki¹,²

High-temperature operation of semiconductor devices is widely demanded for switching/sensing purposes in automobiles, plants, and aerospace applications. As alternatives to conventional Si-based Schottky diodes usable only at 200°C or less, Schottky interfaces based on wide-bandgap semiconductors have been extensively studied to realize a large Schottky barrier height that makes high-temperature operation possible. Here, we report a unique crystalline Schottky interface composed of a wide-gap semiconductor β-Ga₂O₃ and a layered metal PdCoO₂. At the thermally stable oxide interface, the polar layered structure of PdCoO₂ generates electric dipoles, realizing a large Schottky barrier height of ~1.8 eV, well beyond the 0.7 eV expected from the basalt Schottky-Mott relation. Because of the naturally formed homogeneous electric dipoles, this junction achieved current rectification with a large on/off ratio approaching 10⁸ even at a high temperature of 350°C. The exceptional performance of the PdCoO₂/β-Ga₂O₃ Schottky diodes makes power/sensing devices possible for extreme environments.

**RESULTS**

We fabricated heterostructures of 20-nm-thick PdCoO₂/β-Ga₂O₃ (a commercial n-type substrate with a nominal donor density of 7.8 × 10¹⁷ cm⁻³) by pulsed-laser deposition. The c-axis–oriented growth was observed in typical x-ray diffraction patterns (fig. S1A). The

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¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.
²Center for Spintronics Research Network (CSRN), Tohoku University, Sendai 980-8577, Japan.
*Corresponding author. Email: t.harada@imr.tohoku.ac.jp
With a Schottky barrier of $1E_0$, indicating an epitaxial relationship of PdCoO$_2$ [0001]÷∥b-Ga$_2$O$_3$. The in-plane conductivity of the PdCoO$_2$/b-Ga$_2$O$_3$ was seen, and no threading dislocations were apparent (Fig. 1E), as shown in Fig. 1 (E and F). The layered crystal structure of PdCoO$_2$ was imaged with a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM), and the anisotropic in-plane conductivity is schematically shown (Fig. 1F). The alternating Pd$^+$ and [CoO$_2$]$^-$ charged layers are shown based on the nominal ionic charges in the bulk PdCoO$_2$. The actual charge state at the interface can be modified by electronic reconstruction with screening charges.

To investigate the Schottky characteristics of the PdCoO$_2$/b-Ga$_2$O$_3$ junctions, we patterned the PdCoO$_2$ thin films into circle-shaped devices using a water-soluble templating process (23). Typical $I$–$V$ characteristics (Fig. 2A) showed clear rectification with a resistance ratio of $>10^9$ and a reverse current density as low as the measurement limit of $10^{-9}$ A/cm$^2$ at 220°C (blue). Applying Eq. 1 to the forward-bias region made it possible to evaluate the Schottky barrier height $\phi_b$ (the symbol ** = 41.1 A/cm$^2$ (24).

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<th>Temperature (°C)</th>
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Saturation current density $J_s (A/cm^2)$

| $10^{-1}$ |
| $10^{-2}$ |
| $10^{-3}$ |
| $10^{-4}$ |
| $10^{-5}$ |
| $10^{-6}$ |
| $10^{-7}$ |
| $10^{-8}$ |
| $10^{-9}$ |

** = 41.1 A/cm$^2$
\(J_V\) is used to specify the measurement technique: \(J-V\) measurement and the ideality factor \(n\), which were approximately 1.85 eV and 1.04, respectively, at 220°C, using the \(A^*=41.1\,\text{A/cm}^2\) of \(\beta-\text{Ga}_2\text{O}_3\) (24). These values are close to the corresponding values of 1.78 eV and 1.06 characterized at room temperature. Such rectifying properties were maintained at 350°C (Fig. 2A, red) together with a large on/off ratio of approximately \(10^8\) and a reverse current density of \(10^{-6}\,\text{A/cm}^2\). Moreover, the weak temperature dependences of \(J_V\) (inset of Fig. 2A) and the ideality factor (fig. S3A) indicate the homogenous Schottky barrier height at the interface (see Materials and Methods for a detailed discussion). The value of \(\phi_0\) is mainly dominated by the activation process across the lowest-energy barrier region. The reverse current density (\(V=-20\,\text{V}\)) at high temperature (Fig. 2B) is compared with the ideal \(J_f\) lines (Fig. 1C) and data from previous studies (25-30). Owing to the large \(\phi_0\), the value of \(|J_{-20V}|\) at the \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) junction (Fig. 2B, red squares) is suppressed at the measured high temperatures. We compare our \(\phi_0\) values with metal/\(\beta-\text{Ga}_2\text{O}_3\) junctions of previous studies (table S1), where \(\phi_0\) is plotted as a function of the metal work function \(\phi_m\) (Fig. 2C). The large deviation of the reported \(\phi_0\) values for the specific metal/\(\beta-\text{Ga}_2\text{O}_3\) junctions probably arises because of the differences in interface quality, e.g., a partial Fermi-level pinning at the surface that can occur (31), even when the same metal contacts are used. As measured by ultraviolet photoelectron spectroscopy (fig. S4), the \(\text{PdCoO}_2\) film is plotted at a work function of 4.7 eV in Fig. 2C. The \(\phi_0\) value of 1.8 eV for \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) is located above the empirical trend of the reported values in the elemental metal/\(\beta-\text{Ga}_2\text{O}_3\) junctions (gray dotted line), whose barrier height lies in the range of 1.0 to 1.5 eV (table S1). Although partial oxidation of metals is known to increase \(\phi_0\) (11-13), the work function and crystal structures/orientations are unknown for the oxidized states of the polycrystalline film. The plot shown in Fig. 2C, which is based on the experimentally determined values of \(\phi_0\) and \(\phi_m\), indicates that \(\phi_0\) of \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) is strongly influenced by the interfacial effects existing at the abrupt interface with well-defined crystal orientation, as shown in Fig. 1 (E and F).

In addition to the \(J-V\) characteristics, we performed capacitance (C) measurements \(1/C^2-V\) (Fig. 3A) to determine the Schottky barrier height at the interface. The gradients of linear fits to the data in Fig. 3A for two device sizes (diameter \(D=100\) and 200 \(\mu\text{m}\)) indicate that the built-in potential at the \(\text{Ga}_2\text{O}_3\) \(qV_B\) and the donor density \(N_D\) are 2.0 eV and \(3 \times 10^{17}\,\text{cm}^{-3}\), respectively. This \(N_D\) value is comparable to the nominal donor concentration of a commercial substrate. The junction capacitance measured with \(V=0\,\text{V}\) is independent of the AC frequency (\(f\)) over a broad range from \(10^2\) to \(10^6\,\text{Hz}\), with a negligible deep trap-state capacitance \(C_{\text{trap}}(f)\) (inset of Fig. 3B), which suggests the potential application of this junction in high-frequency switching elements.

The band diagram for the \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) interface is depicted in Fig. 3C based on the experimental characteristics discussed above. First, the Schottky-Mott relation, \(\phi_0=\phi_m-\chi_e\) was adopted to estimate \(\phi_0\) to be approximately 0.7 eV, based on the work function \(\phi_m\) for \(\text{PdCoO}_2\) (4.7 eV; fig. S4) and the reported electron affinity \(\chi_e\) of \(\beta-\text{Ga}_2\text{O}_3\) (4.0 eV) (32). Although minor effects, such as energy lowering by an image force at the interface and the Fermi energy in \(\text{Ga}_2\text{O}_3\), might make an additional contribution to the estimated value of \(\phi_0\) (see Materials and Methods), it is difficult to explain the large mismatch between 0.7 eV and the experimentally evaluated result of 1.8 eV. As shown in Fig. 3C, the vacuum level shifted by \(\Delta \approx 1.1\,\text{eV}\), which contributed to the large \(\phi_0\). This shift is attributed to the polar nature of \(\text{PdCoO}_2\), which is composed of \(\text{Pd}^+\) and \([\text{CoO}_2]^-\). The formation of a polar interface \([\text{CoO}_2]^-/\text{Ga}_2\text{O}_3\) (STEM image in Fig. 1F) caused \(\phi_0\) to increase to 1.8 eV through electric dipole effects. The interface dipole caused by the \(\text{PdCoO}_2\) polar layered structure agrees well with the calculated surface potential at O- and

Fig. 2. High-temperature operation of the \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) Schottky junctions with a large barrier height. (A) Current-voltage characteristics of the \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\) junction with a diameter of 200 \(\mu\text{m}\) at 227°C (blue) and 356°C (red). The gray lines are the linear fitting for the forward-bias region. The temperature dependence of the Schottky barrier height is plotted in the inset. (B) Temperature-dependent reverse current density under the bias voltage of \(-20\,\text{V}\) \(|J_{-20V}|\) plotted together with the reported values (25-30). The ideal \(J_f\) in Fig. 1C is also shown for \(\phi_0=1.0\,\text{eV}\) (blue), 1.4 eV (green), and 1.8 eV (red). (C) Comparison of the Schottky barrier height with the reported values for elemental metal Schottky junctions (see the Supplementary Materials for the data and references used). Perpendicularly spread line data correspond to the range of the reported Schottky barrier height. The different colors correspond to the different surface orientations of the \(\beta-\text{Ga}_2\text{O}_3\) layers. The linear trend from the reported values is shown as a broken line. The large red square corresponds to the data obtained for \(\text{PdCoO}_2/\beta-\text{Ga}_2\text{O}_3\).
Pd-terminated PdO (111), which predicts an energy shift of 1.2 eV (33). The contributions of this interfacial dipole model to $\phi_b^{IV}$ are analogous to the barrier height control achieved in SrRuO$_3$/NbSrTiO$_3$ Schottky junctions by the insertion of [AlO$_2$]$^-$ or [LaO]$^+$, which increase and decrease, respectively, the Schottky barrier height from its original level at ~1.3 eV to 1.8 and 0.7 eV (34). In the PdCoO$_2$/β-Ga$_2$O$_3$ interfaces, the interface dipole is naturally activated owing to the unique polar layered structure and the [CoO$_2$]$^-$ initial layer favored by the crystal growth of PdCoO$_2$ electrodes (Fig. 1F).

We examined the uniformity and reproducibility of the junction properties by measuring arrays of PdCoO$_2$ circular devices on β-Ga$_2$O$_3$ with various junction areas (from 100 to 1000 μm$^2$), as shown in the sample picture (Fig. 4A). A large $\phi_b^{IV}$ of approximately 1.8 eV was obtained, irrespective of the diameter of the devices (Fig. 4B). This result contrasts with the expected inhomogeneous $\phi_b^{IV}$ in typical large Schottky junctions owing to the high probability of pinhole-generating regions. Moreover, 27 devices were characterized with $D = 100$ μm to confirm the uniformity of operation. The $J$-$V$ data were consistent, as shown in Fig. 4C. A histogram of $\phi_b^{IV}$ indicated a reproducible value of $\phi_b^{IV} = 1.76$ eV with a narrow distribution of approximately 0.045 eV. Unlike the broad distribution of $\phi_b^{IV}$ values for the polycrystalline metal/β-Ga$_2$O$_3$ junction, as summarized in Fig. 2C, the highly reproducible $\phi_b^{IV}$ could result from the layered structural features and the all-oxide high-quality interface with the homogeneous [CoO$_2$]$^2$/Ga$_2$O$_3$ polar stacks energetically favored during the thin-film growth (Fig. 1, E and F). Hexagonal interfaces of layered PdCoO$_2$ on other semiconductors, such as SiC and GaN, could also benefit from this interfacial electric dipole effect.
DISCUSSION
Superior Schottky junction properties were demonstrated with large on/off ratios, high-temperature operation at 350°C, no dependence of C-f characteristics, and considerable uniformity and reproducibility. This performance is attributed to the large \( \phi_b^{IV} \) induced by the naturally formed electric dipoles at the well-regulated polar oxide interface of PdCoO2 and \( \beta \)-Ga2O3. For applications under harsh conditions, PdCoO2 electrodes have considerable advantages owing to their exceptional stability to heat (~800°C), chemicals (acids/bases, pH 0 to 14), and mechanical stress (fig. S5), in addition to high optical transparency (35). The abrupt interface of the layered oxides PdCoO2 and \( \beta \)-Ga2O3 can extend applications of semiconductor devices to hot operating environments, such as those in automobile and aerospace applications.

MATERIALS AND METHODS
Substrate preparation
For the devices with acid-cleaned \( \beta \)-Ga2O3, commercially available unintentionally doped \( \beta \)-Ga2O3 (~200) substrates with the nominal \( N_D = 7.8 \times 10^{17} \) cm\(^{-3} \) (Novel Crystal Technology Inc.) were immersed in an acidic solution (water: 30 to 35.5%; H\(_2\)O: 95%; H\(_2\)SO\(_4\): 1:1:4) for 5 min, followed by rinsing in water for 15 min.

PdCoO2/\( \beta \)-Ga2O3 device fabrication
To pattern the PdCoO2 layer by soft lithography, we used the LaAlO3/ BaO template as a water-soluble sacrificial layer (23). First, an organic photoresist was patterned on the \( \beta \)-Ga2O3 substrates using a standard photolithography process. The LaAlO3 (~40 nm)/BaO (~100 nm) templates were then deposited by pulsed-laser deposition at room temperature under the base pressure of ~10\(^{-7}\) torr. Removing organic photoresist by hot acetone gave the patterned LaAlO3/BaO template on the \( \beta \)-Ga2O3 substrates. Just before the deposition of PdCoO2 thin films, the LaAlO3/BaO/\( \beta \)-Ga2O3 samples were put in O\(_2\) plasma for 50 s to remove the residual photoresist. The PdCoO2 thin films were grown by pulsed-laser deposition (35) at a growth temperature of 700°C and an oxygen partial pressure of 150 mtorr. A KrF excimer laser was used to alternately ablate the PdCoO2 stoichiometric target and Pd-PdO mixed phase target. After the thin-film growth, the LaAlO3/BaO templates were removed by sonication in water together with the unnecessary parts of the PdCoO2 to obtain the circular PdCoO2 electrodes with a diameter of 100 to 1000 \( \mu \)m.

Electrical transport measurement
Current-voltage characteristics of the Schottky junctions were measured via two-wire configuration using a Keithley 2450 source meter. Al wires were bonded to the top surface of the \( \beta \)-Ga2O3 substrates to form ohmic contacts to the \( \beta \)-Ga2O3 substrates. A needle prober was used to contact the PdCoO2 and Pt top electrodes for the room temperature measurement. The capacitance measurements were carried out using an Agilent E4980A precision LCR meter with an AC modulation voltage of 0.1 V. The resistivity of the PdCoO2 thin films was measured using a four-probe configuration.

Effect of image force lowering
For the interface of a metal and an n-type semiconductor with the relative permittivity of \( \varepsilon_r \), the image force lowering \( \Delta \phi \) under zero bias can be formulated as

\[
\Delta \phi = q/or e_0 [2 q V_{bi} N_D/e_r e_0]^{1/2} \]

Here, \( \epsilon_0 \) is the vacuum permittivity. Using the experimentally determined \( q V_{bi} \) and \( N_D \) for the PdCoO2/\( \beta \)-Ga2O3, \( q V_{bi} = 2.0 \) eV and \( N_D = 3 \times 10^{17} \) cm\(^{-3} \), and the reported \( \epsilon_r = 10 \) (36), \( \Delta \phi \) was estimated to be 0.08 eV.

Estimation of the spatial homogeneity of the Schottky barrier height
We analyzed the temperature-dependent Schottky barrier height and the ideality factor using the potential fluctuation model to estimate the homogeneity of the barrier height (37). We considered the spatial distribution of the Schottky barrier height (\( \phi_b \)) and the built-in potential (\( V_{bi} \)) by introducing the Gaussian distribution \( P(q V_{bi}) \) and \( P(\phi_b) \), with an SD \( \sigma_s \) around the mean values \( V_{bi} \) and \( \phi_b \).

\[
P(\phi_b) = \frac{1}{\sigma_s \sqrt{2 \pi}} e^{-v(\phi_b-\phi_f)^2/(2 \sigma_s^2)}
\]

\[
P(q V_{bi}) = \frac{1}{\sigma_f \sqrt{2 \pi}} e^{-(q V_{bi}-q V_{f})^2/(2 \sigma_f^2)}
\]

As discussed by Werner and Güttinger (37), the Schottky barrier height determined by the current-voltage characteristic, \( \phi_b^{IV} \), relates to the \( \phi_b \) and \( \sigma_s \) as

\[
\phi_b^{IV} = \phi_b - \frac{\sigma_s^2}{2k_B T}
\]

Capacitance-voltage (C-V) measurement probes the spatial average of the built-in potential, \( V_{bi}^{CV} = V_{bi} \) which relates to the Schottky barrier height \( \phi_b^{CV} \) to be

\[
\phi_b^{CV} = q V_{bi} + k_B T \ln (N_C/N_D) = \bar{\phi}_b
\]

where \( N_C \) and \( N_D \) denote the effective density of states in the conduction band and the doping concentration, respectively. Here, we neglected a possible contribution from the image force in the calculation of \( \phi_b^{CV} \), which did not change the estimation of \( \sigma_s \).

Comparing Eqs. 4 and 5, we found

\[
\phi_b^{CV} - \phi_b^{IV} = \frac{\sigma_s^2}{2k_B T}
\]

We fitted the experimental data by Eq. 6, as shown in fig. S3B, to obtain the SD \( \sigma_s = 54 \) meV, which is less than half of the reported value for Pt/\( \beta \)-Ga2O3 (\( \sigma_s = 130 \) meV) (38). The ideality factor \( n(V, T) \) reflects the voltage-dependent mean barrier \( \bar{\phi}_b(V) \) and the SD \( \sigma_s^2(V) \) as

\[
n^{-1}(V, T) = 1 = \frac{\bar{\phi}_b(V) - \phi_b(0)}{qV} + \frac{\sigma_s^2(V) - \sigma_s(0)^2}{2k_B T q V}
\]

Assuming that \( \bar{\phi}_b(V) \) and \( \sigma_s^2(V) \) vary linearly with the bias voltage \( V \), we can parameterize the voltage deformation of the barrier distribution.
using the coefficients $\rho_2$ and $\rho_3$.

\[
\begin{align*}
\bar{\phi}_b(V) - \bar{\phi}_b(0) &= \rho_2 q V \\
\sigma_2^2(V) - \sigma_2(0)^2 &= \rho_3 q V \\
n^{-1}(T) &= -\rho_1(T) = -\rho_2 + \frac{\rho_3}{2k_B T}
\end{align*}
\]

The experimental data for the PdCoO$_2$/β-Ga$_2$O$_3$ Schottky junction are fitted by Eq. 7, as shown in fig. S3C, to obtain the temperature-independent coefficients $\rho_2 = -0.073$ and $\rho_3 = -1.93$ meV.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/using the coefficients SCIENCE ADVANCES | RESEARCH ARTICLE Table S2. Summary of the partially oxidized metal/... challenges.

**REFERENCES AND NOTES**

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Foundation, and the Tanaka Foundation. **Author contributions:** T.H. and A.T. designed the experiments. T.H. prepared the samples, performed transport measurements, and analyzed the data. S.I. captured the HAADF-STEM image. T.H. and A.T. wrote the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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