Josephson junctions of Weyl semimetal WTe$_2$ induced by spontaneous nucleation of PdTe superconductor

Manabu Ohtomo$^{1,*}$, Russell S. Deacon$^{2,3}$, Masayuki Hosoda$^{1,2}$, Naoki Fushimi$^{1}$, Hirokazu Hosoi$^{1}$, Michael D. Randle$^{2}$, Mari Ohluchi$^{1}$, Kenichi Kagawuchi$^{1}$, Koji Ishibashi$^{2,3}$, and Shintaro Sato$^{1}$

$^{1}$Fujitsu Research, Fujitsu Ltd, Atsugi, Kanagawa 243-0197, Japan
$^{2}$Advanced Device Laboratory, RIKEN, Wako, Saitama 351-0198, Japan
$^{3}$Center for Emergent Matter Science (CEMS), RIKEN, Wako, Saitama 351-0198, Japan

$^{*}$E-mail: ohtomo.manabu@fujitsu.com

Received April 18, 2022; revised May 19, 2022; accepted May 31, 2022; published online June 21, 2022

We report on the fabrication of Josephson junction devices with weak links utilizing the Weyl and higher-order topological semimetal WTe$_2$. We show that the WTe$_2$/Pd contact annealed at a low temperature of 80 °C did not exhibit superconducting properties because neither WTe$_2$ nor Pd are superconductors in the ground state. Upon 180 °C annealing, spontaneous formation of superconducting PdTe due to Pd diffusion enabled us to obtain the interface between WTe$_2$ and superconductor suitable for the Josephson junction. This result is a facile technique to make a Josephson junction and induce Cooper pairs into topological telluride semimetals. © 2022 The Japan Society of Applied Physics

Supplementary material for this article is available online

The Josephson junction (JJ) composed of a topological insulator (TI) is intensively studied as a platform to demonstrate topological superconductivity, which is one of the possible routes to realize Majorana particles$^{1-13}$ for future fault-tolerant Majorana qubits$^{4-7}$. As for the topological superconductors, while nanowire-based approaches with magnetic fields are advanced$^{8,9,10}$, another approach using one-dimensional conducting states protected by time-reversal symmetry in topological insulators (TI) or higher-order topological insulators (HOTI) is becoming an alternative option for hosting Majorana particles.$^{11}$ The advantage of the TI approach is that they are expected to host single-mode conduction and exhibit insensitivity to disorder, as well as no requirement for applied magnetic fields. Among various materials proposed for TI and HOTI, the transition metal dichalcogenide WTe$_2$ has the unique property that it behaves as a two-dimensional TI in its single-layer $I^T$ phase$^{12}$ and a type-II Weyl semimetal in its bulk $T_d$ phase.$^{13}$ The latter is also claimed to be a HOTI with characteristic hinge states.$^{13,14}$

The recipe for a topological superconductor is to induce superconductivity into a TI or HOTI using the proximity effect from an s-wave superconductor in contact with the TI or HOTI.$^{11,15}$ Making good contact with the edge state of the TI or hinge state of the HOTI using superconducting electrodes is particularly important because any interface barrier would hamper the proximity effect and make the induced superconducting gap “soft,”$^{16}$ which would invalidate topological protection.$^{17,18}$ This is problematic because the surfaces of s-wave superconducting materials are usually not stable in air. The surfaces of widely used Al or Nb, for example, are easily covered by a passive oxide film if a bottom contact geometry (electrodes are formed first before the lamination of WTe$_2$ on top) is employed. A top-contact geometry (electrodes are formed on top of WTe$_2$ crystals), on the other hand, is also challenging because of the surface oxidation of WTe$_2$. It is reported that the surface of WTe$_2$ is oxidized under ambient conditions, forming a surface oxide layer with a thickness of $\sim$2.5 nm.$^{19}$ During the fabrication process of the top-contact electrodes, any exposure of the WTe$_2$ surface to oxygen or water should be avoided, which is not easy to achieve in a conventional nano-patterning process. A JJ device is also an ideal platform to study the contact problem such as the interface oxide layer. The observation of JJ characteristics is clear evidence of the proximity effect.

In this letter, we report on the facile fabrication of a good WTe$_2$-superconductor junction suitable for a topological JJ using the spontaneous diffusion of Pd atoms at the WTe$_2$/Pd interface. A superconducting region is achieved at the WTe$_2$/Pd interface, even though neither WTe$_2$ nor Pd are superconducting in the ground state. From our Scanning Transmission Electron Microscope (STEM) and X-ray photoemission spectroscopy (XPS) analysis, we conclude that a PdTe superconducting layer is formed at the WTe$_2$/Pd interface due to Pd diffusion at annealing temperatures as low as 180 °C.

A $T_d$-WTe$_2$ single crystal (purchased from HQ graphene, see Fig. 1(a) for the crystal structure) was cleaved using the standard adhesive tape method.$^{20}$ The cleaved crystal was transferred using the so-called Polydimethylsiloxane (PDMS) stamp method [Fig. 1(b)].$^{21}$ A polycarbonate (PC) adhesion layer was placed onto a dome of PDMS [Fig. 1(b)(ii)] on a glass slide. This PC film is brought into contact with the target crystal and heated at 110 °C for pick-up [Fig. 1(b)(ii)]. The crystal was then transferred to the target position on the device substrate and annealed at 180 °C, releasing the PC from the PDMS. JJ devices were fabricated in the bottom contact geometry. WTe$_2$ was transferred onto pre-patterned Pd electrodes, fabricated using standard e-beam lithography (EBL) followed by electron beam deposition and lift-off. We took care not to contaminate the Pd electrode surface with resist, and the Pd electrode was formed as the last step of the substrate fabrication process. The melted PC polymer residue was intentionally left on the crystal as a passivation film in the bottom contact geometry [Fig. 1(b)(iii)]. The crystal cleavage and transfer processes were performed in a glove box filled with pure Ar (dew point less than $\sim$80 °C). Two devices (device I and II) were prepared with PC/PDMS domes using a maximum annealing temperature ($T_a$) of 180 °C. For device III, fabricated with low-temperature annealing ($T_a$ = 80 °C), the WTe$_2$ was directly exfoliated onto a PDMS stamp, which was then brought into contact with the pre-patterned Pd contacts. The sample was heated to...
80 °C for one minute before slow delamination of PDMS at 30 °C, leaving the flake in contact. Devices with the top-contact geometry were used to investigate the annealing temperature dependence of the resistance. Top electrodes were fabricated by EBL and lift-off after the PC film residue on WTe$_2$ was removed using chloroform. The details of the sample fabrication techniques can be found in the supplementary information (SI), available online at stacks.iop.org/APEX/15/075003/mmedia.

The optical microscope image of the bottom contact device (device I) fabricated using a PC stamp with 180 °C annealing is shown in Fig. 1(c). The channel length ($L$) and width ($W$) of the devices I and II are: $L = 1.47 \, \mu$m, $W = 1.65 \, \mu$m (device I), and $L = 1.50 \, \mu$m, $W = 2.29 \, \mu$m (device II). The other details of the device geometries are summarized in the SI. The temperature dependence of the device resistance [Fig. 1(d)] shows that the device with 180 °C annealing (device II fabricated by PC/PDMS transfer) works as a JJ with $T_C \approx 1.5 \, K$, which reproduces the results of previous reports. The $I$–$V$ relation [Fig. 1(e)(i)] extrapolates to zero, making it difficult to estimate the excess current. This is an unavoidable and well-established problem when using narrow electrodes ($\sim 300 \, \text{nm}$) to measure the Fraunhofer pattern without flux jumps. A Fraunhofer-like pattern is often controversial and beyond the scope of this study. These results are in clear contrast with the 80 °C-annealed device (device III; fabricated by PDMS transfer), which does not demonstrate any feature consistent with a superconducting transition [Fig. 1(d)]. After annealing device III at 200 °C in an Ar atmosphere, we confirmed a superconducting transition. This result indicates that 180 °C–200 °C annealing plays a key role in making the WTe$_2$/Pd contact superconducting.

Cross-sectional STEM images of WTe$_2$/Pd interfaces in device II, fabricated using a PC stamp with 180 °C annealing, are shown in Fig. 2. There are several notable changes in the STEM images such as swelling of the WTe$_2$ and roughening of the Pd electrode surfaces [Fig. 2(a)(ii-iii)]. While the typical surface roughness (arithmetical mean deviation $R_a$) of the Pd electrodes as deposited was small and in the order of $\sim 0.38 \, \text{nm}$, considerable roughening of the Pd surface was observed after contacting with WTe$_2$ and annealing. Similar swelling was observed in all the electrodes (denoted A–E) in this device [Fig. 2(a)]. The energy-dispersive X-ray spectroscopy (EDX) profile shown in Fig. 2(b) indicates that Pd diffusion triggered the WTe$_2$ swelling. While there are some WTe$_2$ layers without Pd diffusion, Pd diffusion was observed in the interface region of WTe$_2$ [see Fig. 2(b)(iii) for the magnified image] as well as in the swollen WTe$_2$. Line profiles from STEM-EDX are shown in Fig. 2(c). The crystals were separated into two layers, one assigned to WTe$_2$ as determined from the EDX profile. The atomic distribution of Pd shown in the scans indicates that the other layer mainly consists of Pd and Te, while a density gradient of W is also observed, which suggests sample nonuniformity in the direction parallel to the electron beam or W.
incorporation into PdTe crystals. It is noteworthy that the EDX signals of oxygen at the WTe2/PdTe interface were negligible, although the WTe2 surface is normally easily oxidized on its own. The Pd signal is also observed on the WTe2 surface, which is not in contact with Pd [Fig.2(b)(iii) and Fig. 2(c)], while the WTe2 bulk with layered structure mainly consists of W and Te. The origin of Pd on the WTe2 surface is probably side-wall diffusion of the WTe2 crystal. This result implies a high degree of Pd diffusion in WTe2 crystals.

Magnified STEM images of electrode C are shown in Figs. 2(a)(ii) and 2(d)(i–iii). The corresponding FFT analysis of the STEM images in Fig. 2d(i–iii) are shown in Fig. 2(d)(iv–vi), respectively. The initial stage of the Pd diffusion appears to be Pd intercalation because swelling starts in the middle of the WTe2 layers [Fig. 2(d)(i)]. While some of the swollen area consisting of Pd and Te were amorphous, the FFT analysis of the STEM images reveals the areas with a crystalline structure other than WTe2 or Pd in the middle of the interfaces [Fig. 2(d)(ii)]. From the FFT analysis [Fig. 2(d)(v)] and electron diffraction simulation [Fig. S8 in the SI], we determine that these polycrystals are either PdTe or PdTe2, which have hexagonal (space group P63/mmc) and trigonal (space group P3 m1) crystal structure, respectively, with almost identical lattice constants along the a and b axes [See Table S2 and Fig. S5 in the SI for the structures]. Both PdTe and PdTe2 are superconductors with $T_C$ of 2.3–4.5 K$^{25,26}$ and 2.0 K,$^{27}$ respectively. A similar structure was observed below WTe2 in electrode D [Fig. 2(e)], in which the FFT pattern is assigned to PdTe from systematic absences. Explicitly, the (0001) and (0002) diffractions are missing in Fig. 2(e)(ii) (indicated by broken line arrows), which is evidence for PdTe [See Fig. S8 in the SI for the simulation]. This is in contrast with another telluride-TI material, (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ (BST), where intermixing of Pd and Te results in the self-formation of superconducting PdTe$_2$.$^{23,28}$ In all electrodes, we confirmed that WTe2 without Pd diffusion maintained its $T_d$ structure as shown in Fig. 2(e)(iii).

The formation of PdTe is further confirmed by XPS [Fig. 3(a)]. The sample prepared for XPS analysis consists of cleaved WTe2 crystals on SiO2 with a thin Pd film ($\sim$5 nm) deposited on top (See SI for the other details). Pt

Fig. 2. (Color online) (a) (i) The cross-section STEM image of device II ($T_a = 180 \, ^\circ \text{C}$). Schematic diagram of the device is also shown. The magnified image of electrode C and D is shown in (ii) and (iii), respectively. The scale bars in (ii) and (iii) are 100 nm. (b) STEM-EDX mapping of electrode B for (i) Te, (ii), (iii) Pd and (iv) W. The area indicated by the white square is magnified in (iii). (c) EDX line-scan profile of the interface. The line scan is corrected from the area indicated by yellow lines in the STEM image (lower panel), which was taken at the position indicated by the white broken line in Fig. 2(b)(iii). (d) High-resolution HAADF-STEM (i) and BF-STEM (ii), (iii) images of electrode C. See Fig. 2(a)(ii) for the position. The FFT pattern obtained from the area indicated by a yellow circle in (i–iii) is shown in (iv)–(vi), respectively. (e) (i) High-resolution BF-STEM image of electrode D. See Fig. 2(a)(iii) for the position. The FFT pattern obtained from the area indicated by a yellow circle in (i) is shown in (ii), (iii). The missing diffraction is indicated by a broken line arrow in (ii).
3/2 peaks in the spectra were derived from the alignment markers on the sample. Three spectra are shown in Fig. 3(a), which were taken (i) as deposited, after (ii) 100 °C and (iii) 180 °C annealing, respectively. Sample annealing was performed ex situ in a glove box with Ar atmosphere. The position of Pd 3d3/2 and 3d5/2 peaks were observed to shift as the sample was annealed. Table I shows the binding energies (BE) observed experimentally, and BEs calculated by density functional theory (DFT) using the DFT package OpenMX with pseudoatomic orbital assuming core holes (see the SI for the details). For metals, the absolute binding energy (E_{b\text{metal}}) is estimated using the following formula:

\[ E_{b\text{metal}} = E_i^{(0)}(N) - E_j^{(0)}(N) \]  

where \( E_i^{(0)}(N) \) and \( E_j^{(0)}(N) \) are the intrinsic total energy of the ground state and the excited state with \( N \) electrons, respectively. The calculated BEs for PdTe and PdTe2 (Table I) reproduce the experimentally determined BEs reported from previous reports on Pd bulk and PdTe2 (see Fig. S5 in the SI for the models). After 180 °C annealing, the BEs of Pd 3d5/2 and 3d3/2 were shifted to the higher BE side (335.15 eV and 340.17 eV, respectively), close to the calculated BE of PdTe (335.56 eV and 341.17 eV for 3d5/2 and 3d3/2, respectively). These XPS results clearly indicate that the PdTe is formed at the WTe2/Pd interfaces during 180 °C annealing, and it is consistent with our STEM analysis.

The effect of Pd diffusion was also confirmed in the two-probe resistance measurement of the top-contact devices [Fig. 3(b)]. The top-contact devices were fabricated by depositing 50 nm thick Pd on the WTe2 crystals. The device was measured in vacuum (\( \sim 10^{-5} \) Pa) at 300 K and annealing was performed in situ. The dependence of the two-probe resistance (\( R_{2\text{probe}} \)) normalized by channel width \( W \) against annealing temperature (\( T_{\text{anneal}} \)) is plotted in Fig. 3(b) at various \( L \). Contact resistance (\( R_C \)) was evaluated by the transfer length method (TLM) and is also shown in Fig. 3(b). \( R_{2\text{probe}} \) and \( R_C \) monotonically decreased as annealing temperature increased, with a particularly large decrease after annealing at 100 °C. The decrease in both \( R_{2\text{probe}} \) and \( R_C \) was almost saturated at 150 °C, yielding \( R_C \cdot W \sim 18 \) Ωμm with a \( \sim 61.6 \) nm thick crystal. These results suggest that Pd diffusion and PdTe crystallization took place after annealing at 100 °C. The decrease in both \( R_{2\text{probe}} \) and \( R_C \) was almost saturated at 150 °C, yielding \( R_C \cdot W \sim 18 \) Ωμm with a \( \sim 61.6 \) nm thick crystal. These results suggest that Pd diffusion and PdTe crystallization took place after annealing at 100 °C. The decrease in both \( R_{2\text{probe}} \) and \( R_C \) was almost saturated at 150 °C, yielding \( R_C \cdot W \sim 18 \) Ωμm with a \( \sim 61.6 \) nm thick crystal. These results suggest that Pd diffusion and PdTe crystallization took place after annealing at 100 °C. The decrease in both \( R_{2\text{probe}} \) and \( R_C \) was almost saturated at 150 °C, yielding \( R_C \cdot W \sim 18 \) Ωμm with a \( \sim 61.6 \) nm thick crystal. These results suggest that Pd diffusion and PdTe crystallization took place after annealing at 100 °C.
was observed in the STEM image of two out of six electrodes (D and E) in the bottom contact device [See Fig. S9 and S13 in the SI]. The mechanism for amorphization and how to control it are not yet fully understood.

The experimental results presented above indicate the formation of a superconducting PdTe polycrystal layer at the WTe2/Pd interface upon 180 °C annealing in our samples. Let us briefly consider the charge transfer, which is one of the possible mechanisms for WTe2/Pd interfacial superconductivity suggested in the literature. Our DFT calculations reveal considerable charge transfer mainly due to Pd chemisorption on WTe2 (See Fig. S7 and Table S3 in the SI for the DFT results) when a clean and abrupt WTe2/Pd interface is assumed. The amount of charge transfer (Table S3 in the SI) is sufficient to induce superconductivity in monolayer 1T'-WTe2 but it is not evident that it is enough to induce superconductivity in the bulk material. This calls for a quantitative investigation into the phase diagram of these materials with respect to changes in charge doping, which is a subject of future work. From our experimental results, we conclude that the formation of PdTe is a plausible and straightforward origin of the observed superconductivity at WTe2/Pd interfaces.

In summary, we report on the spontaneous nucleation of superconducting PdTe at WTe2/Pd interfaces, which can be utilized to create Josephson junction devices of the Weyl semimetal WTe2. Pd diffusion during 180 °C annealing was confirmed by STEM and EDX analysis, while the formation of PdTe was evidenced by electron diffraction and XPS including first-principles estimation of binding energies. The STEM analysis revealed that the oxide layer at the WTe2/PdTe interface was negligible, which implies a clean interface between superconductors and HOTIs. This method is a novel technique to make good superconducting contacts to topological telluride materials for topological Josephson junction devices.

Acknowledgments A part of this work was conducted at NIMS Nanofabrication Platform, supported by “Nanotechnology Platform Program” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, Grant Number 21A019. This work was supported by JSPS Grant-in-Aid for Scientific Research (A) (No. 19H00687), Grant-in-Aid for Scientific Research (B) (No. 19H02548) and Grants-in-Aid for Scientific Research (S) (No. 19H05610). We thank Ms. Yumiko Shimizu (Toray Research Center, Inc.) for the STEM measurement.

ORCID IDs  Manabu Ohtomo https://orcid.org/0000-0001-8361-956X

1) Y. Li and Z.-A. Xu, Adv. Quantum Technol. 2, 1800112 (2019).
2) O. Breunig and Y. Ando, Nat. Rev. Phys. 4, 184 (2022).
3) E. Bocquillon, R. S. Deacon, J. Wiedenmann, P. Lebner, T. M. Klapwijk, C. Brüne, K. Ishibashi, H. Buhmann, and L. W. Molenkamp, Nat. Nanotech. 12, 137 (2017).
4) A. Y. Kitaev, Ann. Phys. 303, 2 (2003).
5) C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Rev. Mod. Phys. 80, 1083 (2008).
6) D. Asen et al., Phys. Rev. X 6, 031016 (2016).
7) A. D. Scheppe and M. V. Pak, Phys. Rev. A 105, 012415 (2022).
8) G. D’Olimpio, C. Guo, C.-N. Kuo, R. Edla, C. S. Lee, L. Ottaviano, P. Torelli, L. Wang, D. W. Boukhvalov, and A. Politano, Adv. Funct. Mater. 30, 1906556 (2020).
9) M. Valentin, F. Peñaranda, A. Hofmann, M. Brauns, R. Hauschild, P. Kroesstrup, P. San-Jose, E. Prada, R. Aguado, and G. Katsaras, Science 373, 82 (2021).
10) H. Pan and S. Das Sarma, Phys. Rev. B 104, 054510 (2021).
11) L. Fu and C. L. Kane, Phys. Rev. B 79, 161408 (2009).
12) Z. Fei, T. Palomaki, S. Wu, W. Zhao, X. Cai, B. Sun, P. Nguyen, J. Finney, X. Xu, and D. H. Cobden, Nat. Phys. 13, 677 (2017).
13) A. Kononov, G. Abulizi, K. Qu, J. Yan, D. Mandrus, K. Watanabe, T. Taniguchi, and C. Schönenberger, Nano Lett. 20, 4228 (2020).
14) Y.-B. Choi et al., Nat. Mater. 19, 974 (2020).
15) B. v Heck, T. Hyart, and C. W. J. Beenakker, Phys. Scr. T164, 014007 (2015).
16) C. R. Reeg and D. L. Maslov, Phys. Rev. B 94, 020501 (2016).
17) D. Rainis and D. Loss, Phys. Rev. B 85, 174513 (2012).
18) W. Chang, S. M. Albrecht, T. S. Jespersen, P. Kuemmeth, P. Kroesstrup, J. Nygård, and C. M. Marcus, Nat. Nanotech. 10, 232 (2015).
19) J. M. Woods, J. Shen, P. Komaravadivel, Y. Pang, X. Gie, A. A. Pan, M. Li, E. I. Altman, L. Lu, and I. I. Cha, ACS Appl. Mater. Interfaces 9, 23175 (2017).
20) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
21) D. G. Purdie, N. M. Pugno, T. Taniguchi, K. Watanabe, A. C. Ferrari, and A. Lombardo, Nat. Commun. 9, 5387 (2018).
22) A. Kononov, M. Endres, G. Abulizi, K. Qu, J. Yan, D. G. Mandrus, K. Watanabe, T. Taniguchi, and C. Schönenberger, J. Appl. Phys. 129, 113903 (2021).
23) M. Bai, F. Yang, M. Luysberg, J. Feng, A. Bliesener, G. Lippertz, A. A. Taskin, J. Mayer, and Y. Ando, Phys. Rev. Mater. 4, 094801 (2020).
24) S. Ghatak, O. Breunig, F. Yang, Z. Wang, A. A. Taskin, and Y. Ando, Nano Lett. 18, 5124 (2018).
25) B. T. Matthias, Phys. Rev. 92, 874 (1953).
26) B. Tiwari, R. Goyal, R. Jha, A. Dixit, and V. P. S. Awana, Supercond. Sci. Technol. 28, 055008 (2015).
27) J. Guggenheim, P. Hulliger, and J. Müller, Helv. Phys. Acta 34, 408 (1961).
28) I. L. Rosen, C. J. Trimble, M. P. Andersen, E. Mikheev, Y. Li, Y. Liu, L. Tai, P. Zhang, K. L. Wang, and Y. Cui, arXiv:2110.01309 (2021).
29) T. Ozaki and C.-C. Lee, Phys. Rev. Lett. 118, 026401 (2017).
30) OpenMX, http://openmx-square.org/ (accessed March 8, 2022).
31) E. Sajadi, T. Palomaki, Z. Fei, W. Zhao, P. Bement, C. Olsen, S. Luescher, X. Xu, J. A. Folk, and D. H. Cobden, Science 362, 922 (2018).