

PEDOT:PSS-mediated semiconductor wafer bonding for built-in middle subcells in multijunction solar cells

Author names:

Kazuya Okamoto, Kodai Kishibe, Naoki Sano, and Katsuaki Tanabe*

Affiliation:

Department of Chemical Engineering, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

Corresponding author:

*Email: tanabe@cheme.kyoto-u.ac.jp

Keywords:

Silicon; InP; Interface; Heterostructure; Device; Optoelectronics; Photovoltaics

Abstract

We propose and experimentally demonstrate a novel concept of semiconductor wafer bonding that simultaneously realizes bond formation and solar cell implementation. Firstly, a semiconductor bonding technique mediated by poly(3,4-ethylenedioxythiophene) - poly(styrenesulfonate) (PEDOT:PSS) is developed. By utilizing the PEDOT:PSS-mediated bonding, we subsequently fabricate an InP/Si heterostructure. The PEDOT:PSS/Si heterojunction derivatively formed at the bonded interface is then demonstrated to operate as a photovoltaic device. The prepared InP/PEDOT:PSS/Si heterostructure can thus be regarded as a prototype architecture representing an intermediate section of a multijunction solar cell with a built-in subcell. Our facile semiconductor bonding scheme mediated by functional agents could lead to low-cost, high-throughput production of high-efficiency multijunction solar cells.

Main text

Wafer bonding is a versatile semiconductor fabrication process technology that allows for the stacking and integration of dissimilar, lattice-mismatched materials, and is utilized for the realization of various heterostructured optoelectronic devices.¹⁻⁶ Conventionally, the interfacial bonding agents, such as oxides, metals, and polymers, have played fundamental roles of mechanical adhesion and/or electrical conductance. We propose the functional bonding concept for the simultaneous realization of bonding formation and optoelectronic function implementation, by employing proper functional materials as the bonding agent, to provide a manufacturing efficacy.⁷⁻¹⁰ In the present study, we develop PEDOT:PSS-mediated semiconductor wafer bonding, where PEDOT:PSS is poly(3,4-ethylenedioxythiophene) - poly(styrenesulfonate), and subsequently fabricate an InP/Si heterostructure, mediated by a PEDOT:PSS interlayer. By the bonded InP/PEDOT:PSS/Si heterostack as an example, we demonstrate a derivative photovoltaic functionality generation at the bonded InP/Si interface owing to the PEDOT:PSS/Si heterojunction, potentially applicable for multijunction solar cell fabrication.

In the first phase of this study, we conducted a fundamental investigation of PEDOT:PSS-mediated semiconductor wafer bonding. Single-side-polished *n*-type Si wafers (thickness: 625 μm , crystalline plane orientation: $\langle 100 \rangle$, dopant: phosphorus, doping concentration: $8 \times 10^{17} \text{ cm}^{-3}$) were used. The Si wafer was diced into $(1 \text{ cm})^2$ square pieces. The Si pieces were then subject to a wet hydrofluoric acid (HF) treatment (10 wt% aq, 1 min) to remove the native oxide layer on the Si surface. Subsequently, the Si pieces were submerged in deionized water for 1 min, which is not essential for basic wafer bonding, but was carried out for consistency with the following solar cell fabrication process. As the

bonding agent, we employed poly(3,4-ethylenedioxythiophene) - poly(styrenesulfonate) (PEDOT:PSS), a transparent conductive polymer, intensively used in various organic optoelectronic devices.^{11–16} Dimethyl sulfoxide was mixed into a PEDOT:PSS aqueous solution (3.0 – 4.0 w/v%) to a concentration of 5 v/v%, to enhance the electrical conductivity of PEDOT:PSS.¹⁷ This PEDOT:PSS solution was then spin-coated onto the surface of the polished side of a Si piece with a rotation velocity of 1500 rpm for 1 min. The PEDOT:PSS-coated Si piece was subsequently bonded to the surface of the polished side of a bare Si piece under a uniaxial pressure of 0.1 MPa in ambient air at various temperatures for various durations. After the wafer bonding process, the detachment normal stress of the bonded sample was measured as the interfacial mechanical bonding strength. For electrical measurements, Ag paste was applied on both of the outer surfaces of the bonded Si piece as electrodes. The current–voltage characteristics were then measured across the bonded interface.

We secondly demonstrate the built-in solar cell functionality at the wafer-bonded heterointerface. The Si wafer was diced, submerged in the HF aqueous solution and then deionized water, spin-coated with the PEDOT:PSS solution in the same manner as above. The water submergence process is essential to secure the photovoltaic characteristics in the PEDOT:PSS/Si heterojunction. The resulting implementation of an oxide layer at the PEDOT:PSS/Si interface plays a role of a certain degree of potential barrier, to suppress the undesirable tunneling leakage current.¹⁸ A double-side-polished *n*-type InP wafer (thickness: 365 μm , crystalline plane orientation: $\langle 100 \rangle$, dopant: sulfur, doping concentration: $7 \times 10^{18} \text{ cm}^{-3}$) was similarly diced into a $(1 \text{ cm})^2$ square piece. The InP piece was then subject to a wet HF treatment (10 wt% aq, 1 min) to remove the native oxide layer on the InP surface, followed by a rinse with deionized water. The PEDOT:PSS-coated Si piece was subsequently bonded to the surface of the polished side of the InP piece under a uniaxial pressure of 0.1

MPa in ambient air at various temperatures for 1 hour. After bonding, Ag paste was applied on the top and bottom surfaces of the bonded InP/Si piece as electrodes of a solar cell device. No anti-reflective coating was applied on the top surface. Importantly, note that such a simple procedure forms heterostructure bonding and solar cell functionality.

Firstly, we carry out a series of fundamental investigation of PEDOT:PSS-mediated semiconductor wafer bonding by using Si wafers. Figure 1 presents the current–voltage characteristics of the Si/Si samples bonded via PEDOT:PSS for 1 hour at various temperatures. Most current–voltage curves exhibit straight, Ohmic characteristics, which is preferable for many optoelectronic applications. Figure 2 plots the dependence of the electrical resistivity at the bonded Si/Si interface mediated by PEDOT:PSS on the bonding temperature for the bonding duration of 1 hour. The interfacial electrical resistivity was determined from the total series resistivity through the sample, represented by the inverse slope at the origin of the current–voltage curve plotted in Fig. 1, subtracted by the Ag/Si contact resistivities determined by the transmission line method for each bonding condition. It should be noted that the apparent turnover of the resistivities between those for the bonding temperatures of 100 and 200 °C between Figs. 1 and 2 is because of the higher Ag/Si contact resistivities for the case of 200 °C. The relatively high interfacial resistivities in the field of semiconductor optoelectronics observed in Fig. 2 can be attributed to the water submergence of the Si wafer for 1 min, which causes the formation of the insulating surface oxide, after the HF treatment. To improve the electrical conductivity, the water submergence process can be simply omitted. As observed in Figs. 1 and 2, bonding at 200 °C is found to provide the lowest interfacial resistivity or highest electrical conductivity. This trend indicates the existence of the optimal bonding temperature, resulting from the trade-off between the bond establishment and the interfacial oxidation due to the ambient air of our bonding atmosphere. In other words, the chemical bonds insufficiently form at too low temperatures, while the

bonded interface tends to electrically suffer from severe oxidation at too high temperatures. Next, we investigate the influence of the length of the bonding duration. Figure 3 presents the dependence of the bonding interfacial electrical resistivity on the bonding duration, for the bonding temperature of 200 °C. As observed, it is indicated that there is an optimum bonding duration in terms of the interfacial electrical conductivity. In a similar logic as that for the influence of the bonding temperature, both insufficient bond formation in the shorter bonding process and intense interfacial oxidation by longer bonding are considered to provide us with undesirable outcomes. So far, we have investigated the electrical property of the bonded interface. Let us move on to the mechanical property, another important characteristic parameter for wafer-bonded semiconductor interfaces. Figure 4 plots the dependence of the mechanical strength of the bonded Si/Si interface mediated by PEDOT:PSS on the bonding temperature for the bonding duration of 1 hour. Figure 5 plots the dependence of the mechanical strength of the bonded Si/Si interface mediated by PEDOT:PSS on the bonding duration for the bonding temperature of 200 °C. Interestingly, as observed in these graphs, the optimal bonding condition for the interfacial mechanical bonding strength happened to coincide with that for the interfacial electrical conductance, as 200 °C, 1 hour. It should be noted that although we added dimethyl sulfoxide to enhance the electrical conductivity of the PEDOT:PSS interlayer for the performance improvement of the PEDOT:PSS/Si heterojunction solar cell, an interfacial bonding strength of 1.1 MPa was observed for 25 °C, 3 hours in the case without dimethyl sulfoxide in our preliminary bonding test. The series of results in the fundamental bonding experiments presented above has thus brought us to an interim conclusion: the optimal bonding condition is a bonding temperature of 200 °C and a bonding duration of 1 hour, accounting for optoelectronic device applications.

In the second phase of this study, we experimentally demonstrate that the PEDOT:PSS-mediated semiconductor wafer bonding is able to simultaneously form a solar

cell at the bonded interface. As our experimental example, we employ an InP/PEDOT:PSS/Si layered heterostructure formed by InP/Si wafer bonding mediated by PEDOT:PSS, where PEDOT:PSS acts as a hole transport layer to activate a PEDOT:PSS/Si heterojunction solar cell.^{19–23} Figure 6 presents a cross-sectional scanning electron microscope image of the bonded InP/PEDOT:PSS/Si heterostructure. This bonded heterostructure is positioned as a prototype of our photovoltaic functional bonding concept, mimicking an intermediate subcell section in a multijunction solar cell architecture. Assuming the InP layer as an upper subcell of a multijunction cell, the PEDOT:PSS/Si heterojunction solar cell part simultaneously formed in the bonding process can be regarded as a lower subcell. Figure 7 presents the light current–voltage characteristics under AM1.5G, 1-sun illumination (100 mW/cm^2) of the InP/PEDOT:PSS/Si heterostructure bonded at 25 and 200 °C for 1 hour. The bias direction of the output photovoltage coincided with that of (*p*-)PEDOT:PSS/*n*-Si, but not *n*-InP/(*p*-)PEDOT:PSS. The device performance was: the open-circuit voltage of 0.396 and 0.392 V, the short-circuit current density of 3.26 and 4.86 mA/cm^2 , the energy conversion efficiency of 0.376 and 0.521%, and the fill factor of 0.291 and 0.274, for the samples bonded at 25 and 200 °C, respectively. The short-circuit current density and thus the conversion efficiency are observed to be higher for the sample bonded at 200 °C than that for 25 °C presumably owing to the lower electrical resistivity at the bonded interface, as presented in the first phase of this study (Fig. 2). Nevertheless, the fact that such a semiconductor heterostructure is realized by room-temperature bonding process can be also thought to be fascinating. The thickness of the PEDOT:PSS layer was observed to be around 430 nm in scanning electron microscopy. Accounting for the reported trend that the PEDOT:PSS thickness typically ranges in 100 – 250 nm for high-efficiency PEDOT:PSS/Si heterojunction solar cells,^{17,20,21} ours could be too thick to obtain high cell performance. The apparently low energy conversion efficiency of the samples is attributed to the fact that the 365- μm -thick InP wafer on the top of the PEDOT:PSS/Si solar cell structure completely absorbs the incident

solar-simulator spectrum for the region above the InP bandgap energy of 1.34 eV, or 925 nm, and also, the spectral window between the bandgap energies of InP and Si (1.12 eV, 1110 nm) is very narrow (< 200 nm) and covers only a small energy fraction in the whole AM1.5G spectrum. The conversion efficiency of the InP/PEDOT:PSS/Si sample bonded at 200 °C essentially corresponds to 4.82% based on the illumination intensity of 10.8 mW/cm² in the spectral region between the bandgap energies of InP and Si in the AM1.5G, 1-sun spectrum. Furthermore, an additional loss of the incident light by free-carrier absorption of the photons even below the bandgap energy of InP in the thick, heavily doped InP wafer should also be accounted for. The major cause of the low fill factors can be attributed to the relatively large series resistance across the whole device due to the unoptimized fabrication process conditions, but electrical shunting at the photovoltaic junction (i.e., the PEDOT:PSS/Si interface) by insufficient interfacial oxidation might also matter.¹⁸ Although we cannot exclude the possibility that the *n*-InP/PEDOT:PSS heterointerface also acts as a solar cell, our demonstration has anyway verified the formation of built-in subcell at the InP/Si interface. The potential, undesirable counter photovoltaic competition effect, such as that between the *n*-InP/PEDOT:PSS and PEDOT:PSS/*n*-Si interfaces, could be circumvented by adopting proper doping polarities and concentrations in the upper and lower semiconductor materials. In this context, it should be noted for our present experiments that we intentionally omitted the water submergence process for InP, in contrast to Si. As a reference test, we fabricated spin-coated PEDOT:PSS/*n*-InP solar cell structures with deionized water submergence for 0, 1, and 10 min, all resulting in energy conversion efficiencies below 0.01%. Therefore, the photovoltaic effect at the *n*-InP/PEDOT:PSS interface is considered to be negligibly small, at least for our condition. Accounting for the status that various kinds of multijunction solar cells utilizing semiconductor wafer bonding have been intensively fabricated for more than a decade,^{24–29} our scheme of photovoltaic functional bonding could be useful in the field. Our proposed and demonstrated scheme of built-in subcells induced by semiconductor wafer

bonding mediated by functional agents could lead to low-cost, high-throughput production of high-efficiency multijunction solar cells.

In this study, we proposed and experimentally demonstrated a new concept of semiconductor wafer bonding that simultaneously realizes bond formation and solar cell implementation. Firstly, a semiconductor bonding technique mediated by poly(3,4-ethylenedioxythiophene) - poly(styrenesulfonate) (PEDOT:PSS) was developed. By using the PEDOT:PSS-mediated bonding method, we subsequently fabricated an InP/Si heterostructure with a PEDOT:PSS interlayer. It was then demonstrated that the PEDOT:PSS/Si heterojunction spontaneously formed at the bonded InP/Si interface operates as a photovoltaic device. The prepared InP/PEDOT:PSS/Si heterostructure can thus be regarded as a prototype architecture of an intermediate part in a multijunction solar cell with a built-in subcell. Our simple semiconductor bonding scheme mediated by functional agents could lead to the efficient production of high-efficiency multijunction solar cells.

Acknowledgments

This study was financially supported, in part, by the Masuya Memorial Basic Research Foundation.

ORCID iDs

Katsuaki Tanabe: <https://orcid.org/0000-0002-0179-4872>

References

[1] R. Takigawa, E. Higurashi, T. Suga, and R. Sawada, Appl. Phys. Express **1**, 112201 (2008).

<https://doi.org/10.1143/APEX.1.112201>

[2] M. Takenaka, M. Yokoyama, M. Sugiyama, Y. Nakano, and S. Takagi, Appl. Phys. Express **6**, 042501 (2013).

<https://doi.org/10.7567/APEX.6.042501>

[3] K. Tanabe, T. Rae, K. Watanabe, and Y. Arakawa, Appl. Phys. Express **6**, 082703 (2013).

<https://doi.org/10.7567/APEX.6.082703>

[4] B. Jang, K. Tanabe, S. Kako, S. Iwamoto, T. Tsuchizawa, H. Nishi, N. Hatori, M. Noguchi, T. Nakamura, K. Takemasa, M. Sugawara, and Y. Arakawa, Appl. Phys. Express **9**, 092102 (2016).

<https://doi.org/10.7567/APEX.9.092102>

[5] Z. Gu, D. Inoue, T. Amemiya, N. Nishiyama, and S. Arai, Appl. Phys. Express **11**, 022102 (2018).

<https://doi.org/10.7567/APEX.11.022102>

[6] J. Liang, S. Masuya, S. Kim, T. Oishi, M. Kasu, and N. Shigekawa, Appl. Phys. Express **12**, 016501 (2019).

<https://doi.org/10.7567/1882-0786/aaeedd>

[7] T. Naito and K. Tanabe, *Nanomaterials* **8**, 1048 (2018).

<https://doi.org/10.3390/nano8121048>

[8] K. Kishibe, S. Hirata, R. Inoue, T. Yamashita, and K. Tanabe, *Nanomaterials* **9**, 1742 (2019).

<https://doi.org/10.3390/nano9121742>

[9] K. Nishigaya, K. Kishibe, and K. Tanabe, *C – J. Carbon Res.* **6**, 28 (2020).

<https://doi.org/10.3390/c6020028>

[10] N. Sano, K. Nishigaya, and K. Tanabe, *Appl. Phys. Lett.* **121**, 011601 (2022).

<https://doi.org/10.1063/5.0097427>

[11] Y. Kim, A. M. Ballantyne, J. Nelson, and D. D. C. Bradley, *Org. Electron.* **10**, 205 (2009).

<https://doi.org/10.1016/j.orgel.2008.10.003>

[12] B. Friedel, P. E. Keivanidis, T. J. K. Brenner, A. Abrusci, C. R. McNeill, R. H. Friend, and N. C. Greenham, *Macromolecules* **42**, 6741 (2009).

<https://doi.org/10.1021/ma901182u>

[13] D. Antiohos, G. Folkes, P. Sherrell, S. Ashraf, G. G. Wallace, P. Aitchison, A. T. Harris, J. Chen, and A. I. Minett, *J. Mater. Chem.* **21**, 15987 (2011).

<https://doi.org/10.1039/C1JM12986D>

[14] J. Ouyang, *Displays* **34**, 423 (2013).

<https://doi.org/10.1016/j.displa.2013.08.007>

[15] P. Gkoupidenis, N. Schaefer, B. Garlan, and G. G. Malliaras, *Adv. Mater.* **27**, 7176 (2015).

<https://doi.org/10.1002/adma.201503674>

[16] I. Uguz, M. Ganji, A. Hama, A. Tanaka, S. Inal, A. Youssef, R. M. Owens, P. P. Quilichini, A. Ghestem, C. Bernard, S. A. Dayeh, and G. G. Malliaras, *Adv. Healthcare Mater.* **5**, 3094 (2016).

<https://doi.org/10.1002/adhm.201600870>

[17] S. Mahato, J. Puigdollers, C. Voz, M. Mukhopadhyay, M. Mukherjee, and S. Hazra, *Appl. Surf. Sci.* **499**, 143967 (2020).

<https://doi.org/10.1016/j.apsusc.2019.143967>

[18] L. He, C. Jiang, H. Wang, D. Lai, and E. Rusli, *Appl. Phys. Lett.* **100**, 073503 (2012).

<https://doi.org/10.1063/1.3684872>

[19] J. P. Thomas and K. T. Leung, *Adv. Funct. Mater.* **24**, 4978 (2014).

<https://doi.org/10.1002/adfm.201400380>

[20] S. Jäckle, M. Mattiza, M. Liebhaber, G. Brönstrup, M. Romme, K. Lips, and S. Christiansen, *Sci. Rep.* **5**, 13008 (2015).

<https://doi.org/10.1038/srep13008>

[21] S.-S. Yoon and D.-Y. Khang, *Adv. Energy Mater.* **8**, 1702655 (2018).

<https://doi.org/10.1002/aenm.201702655>

[22] V. H. Nguyen, S. Kato, K. Gotoh, Y. Kurokawa, and N. Usami, *Sustainable Energy Fuels* **3**, 1448 (2019).

<https://doi.org/10.1039/c9se00093c>

[23] K. Okamoto, Y. Fujita, K. Nishigaya, and K. Tanabe, submitted.

[24] K. Tanabe, A. Fontcuberta i Morral, H. A. Atwater, D. J. Aiken, and M. W. Wanlass, *Appl. Phys. Lett.* **89**, 102106 (2006).

<https://doi.org/10.1063/1.2347280>

[25] K. Tanabe, K. Watanabe, and Y. Arakawa, *Sci. Rep.* **2**, 349 (2012).

<https://doi.org/10.1038/srep00349>

[26] P. T. Chiu, D. C. Law, R. L. Woo, S. B. Singer, D. Bhusari, W. D. Hong, A. Zakaria, J. Boisvert, S. Mesropian, R. R. King, and N. H. Karam, *IEEE J. Photovolt.* **4**, 493 (2014).

<https://doi.org/10.1109/JPHOTOV.2013.2279336>

[27] F. Dimroth, T. N. D. Tibbits, M. Niemeyer, F. Predan, P. Beutel, C. Karcher, E. Oliva, G. Siefert, D. Lackner, P. Fuß-Kailuweit, A. W. Bett, R. Krause, C. Drazek, E. Guiot, J. Wasselin, A. Tauzin, and T. Signamarcheix, *IEEE J. Photovolt.* **6**, 343 (2016).

<https://doi.org/10.1109/JPHOTOV.2015.2501729>

[28] S. Essig, C. Allebé, T. Remo, J. F. Geisz, M. A. Steiner, K. Horowitz, L. Barraud, J. Scott

Ward, M. Schnabel, A. Descoeudres, D. L. Young, M. Woodhouse, M. Despeisse, C. Ballif, and A. Tamboli, *Nat. Energy* **2**, 17144 (2017).

<https://doi.org/10.1038/nenergy.2017.144>

[29] K. Makita, H. Mizuno, T. Tayagaki, T. Aihara, R. Oshima, Y. Shoji, H. Sai, H. Takato, R. Muller, P. Beutel, D. Lackner, J. Benick, M. Hermle, F. Dimroth, and T. Sugaya, *Prog. Photovolt.* **28**, 16 (2020).

<https://doi.org/10.1002/pip.3200>

Figure Captions

Fig. 1. Current–voltage characteristics of the Si/Si samples bonded via PEDOT:PSS for 1 hour at various temperatures.

Fig. 2. Dependence of the electrical resistivity at the bonded Si/Si interface mediated by PEDOT:PSS on the bonding temperature for the bonding duration of 1 hour.

Fig. 3. Dependence of the electrical resistivity at the bonded Si/Si interface mediated by PEDOT:PSS on the bonding duration for the bonding temperature of 200 °C.

Fig. 4. Dependence of the mechanical strength of the bonded Si/Si interface mediated by PEDOT:PSS on the bonding temperature for the bonding duration of 1 hour.

Fig. 5. Dependence of the mechanical strength of the bonded Si/Si interface mediated by PEDOT:PSS on the bonding duration for the bonding temperature of 200 °C.

Fig. 6. Cross-sectional scanning electron microscope image of the bonded InP/PEDOT:PSS/Si heterostructure.

Fig. 7. Light current–voltage characteristics under AM1.5G, 1-sun illumination (100 mW/cm²) of the InP/PEDOT:PSS/Si heterostructure bonded at 25 and 200 °C for 1 hour.

Figures

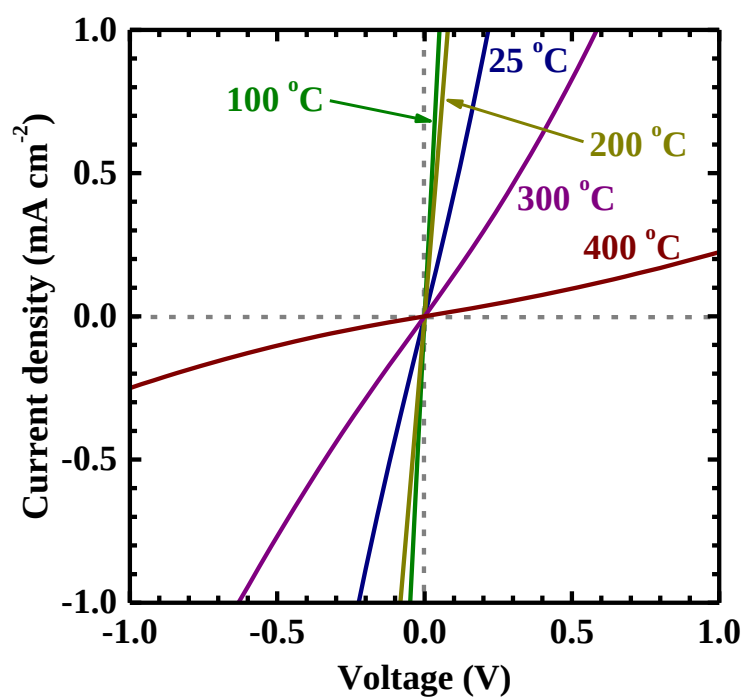


Fig. 1

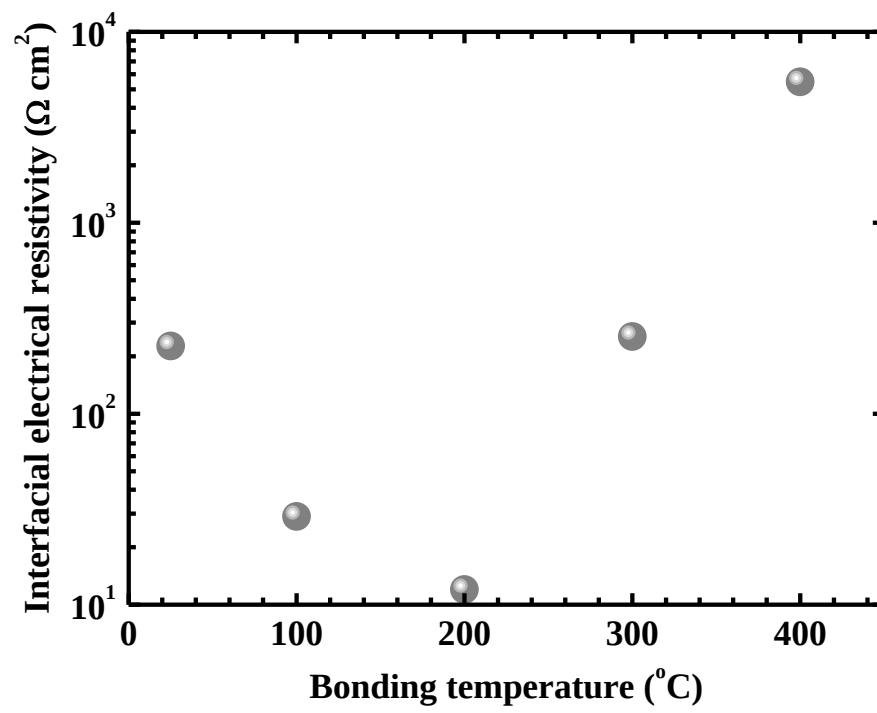


Fig. 2

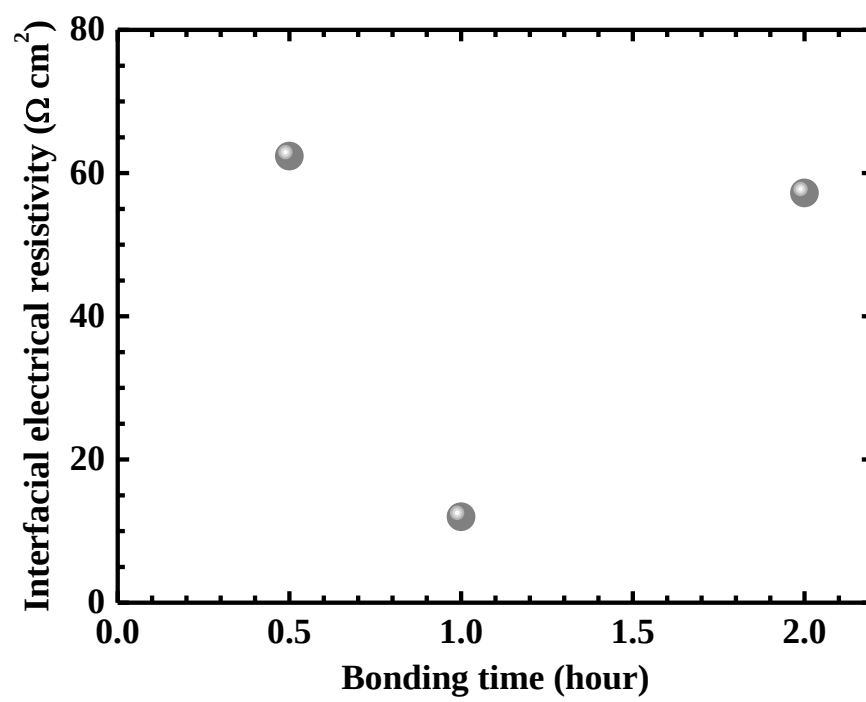


Fig. 3

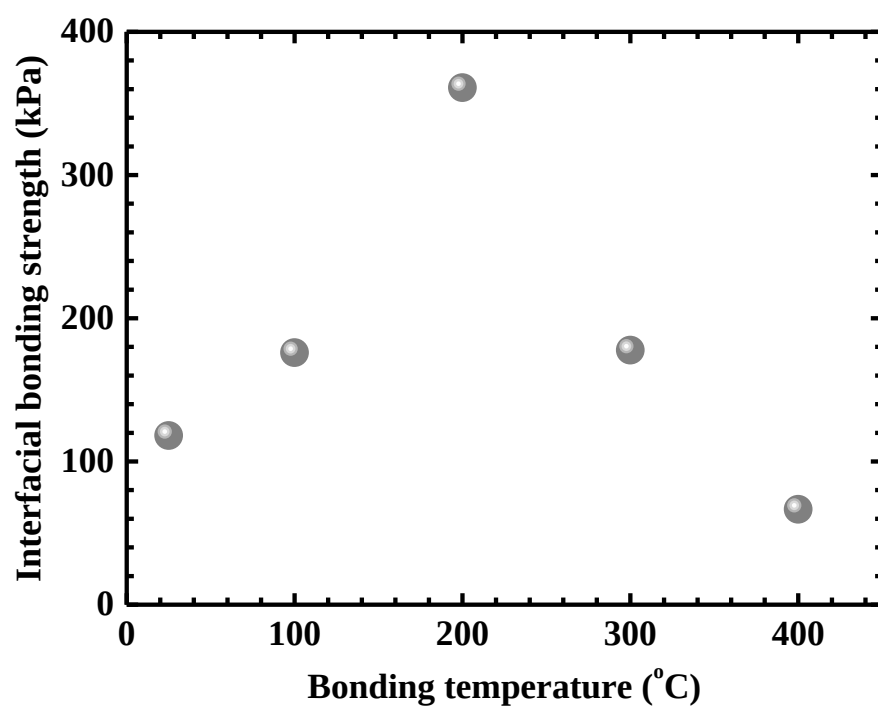


Fig. 4

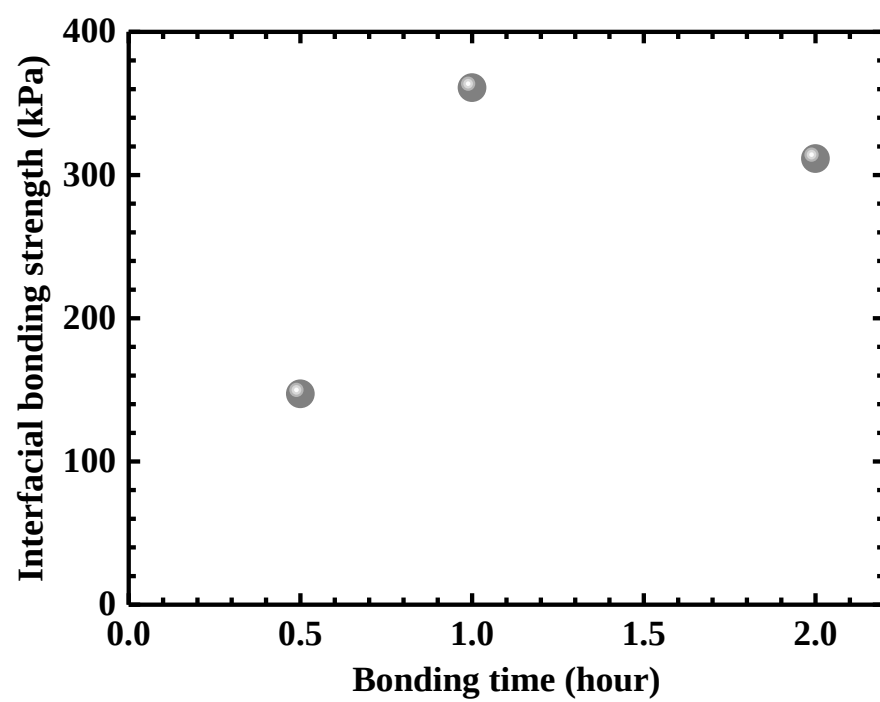


Fig. 5

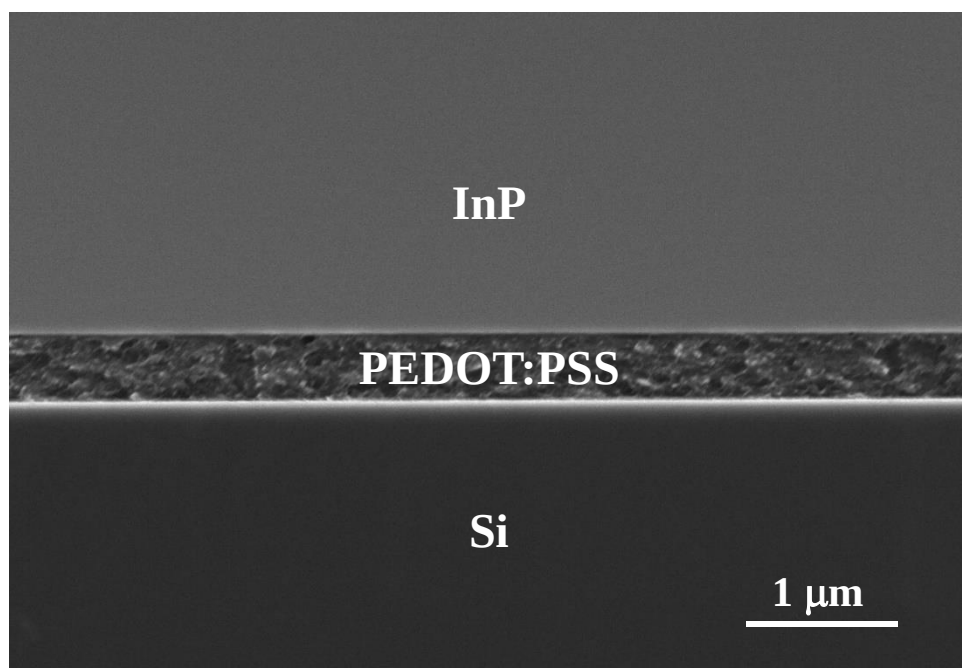


Fig. 6

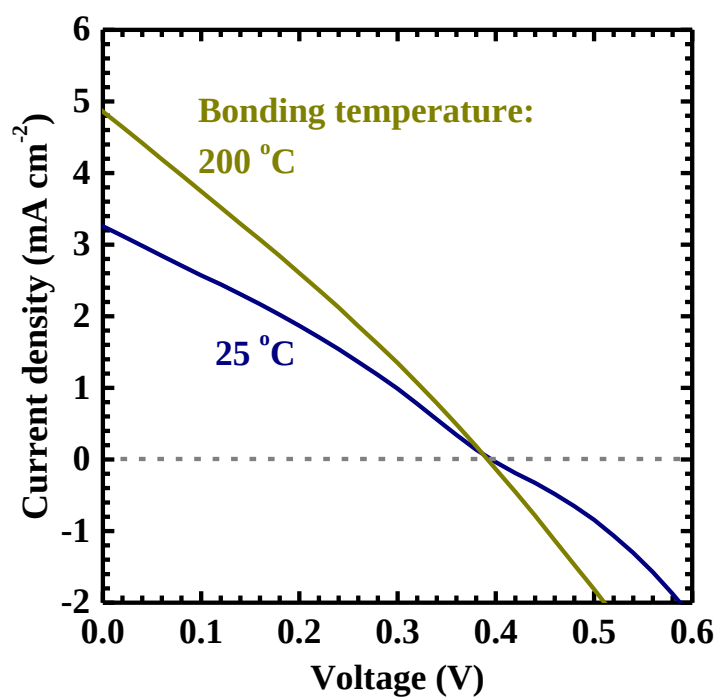


Fig. 7