Supplemental Information

Effects of interface formation process on electronic properties of n-type $Ti_{0.3}Zn_{0.7}O_{1.3}$/ p-type Si stack structure

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[Band alignment]

Figure S1 shows the band alignment of $Ti_{0.6}Zn_{0.4}O_{1.6}$ /Si shown in the inset of Fig. 4 in the main text. The energy difference between the Fermi level (E_f) and the valence band maximum (E_v) shown in the figure were evaluated using the valence band spectra, and the band gaps were calculated using literature values[1,2], respectively. As shown in this figure, the $Ti_xZn_{1-x}O_{1+x}$ /Si used in this study has the type II heterostructure, but that the unintentionally formed SiO_2 layer exists at the interface.

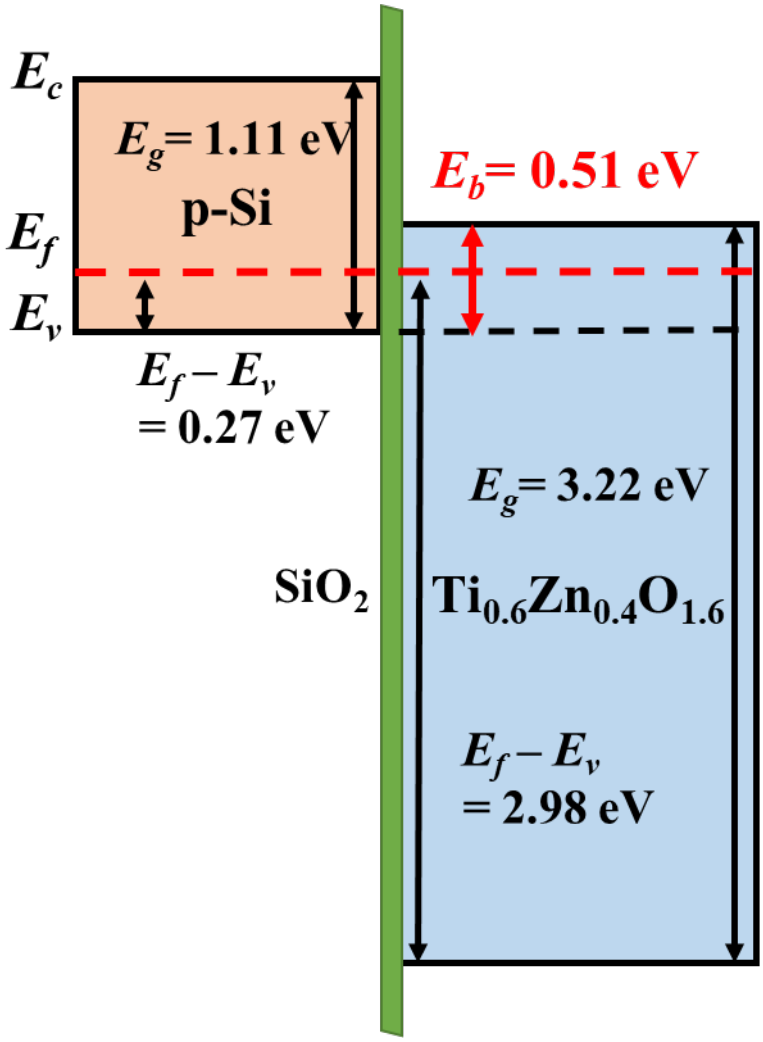
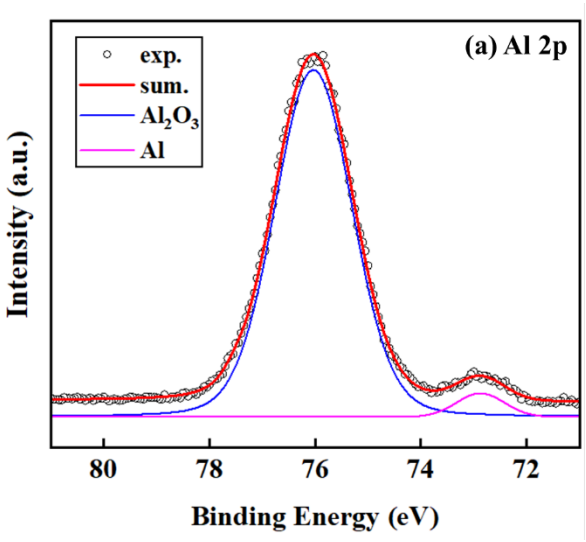


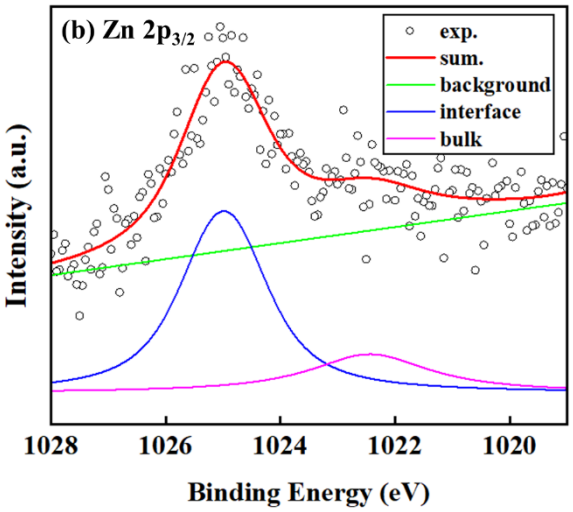
Figure S1 Band alignment of $Ti_{0.6}Zn_{0.4}O_{1.4}$ /SiO_2 /p-Si

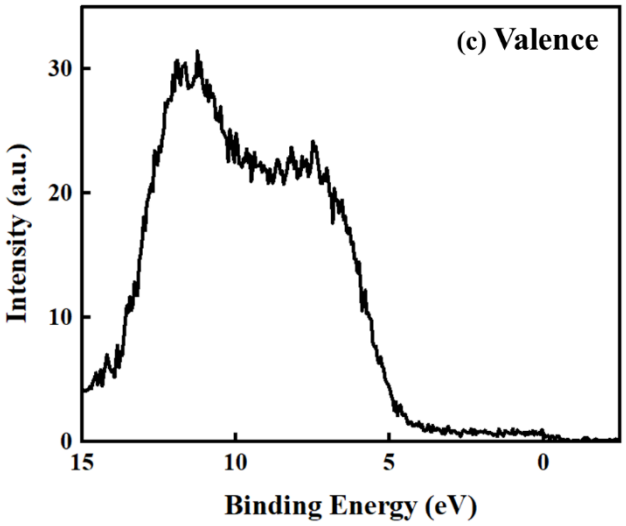
[The effects of Al electrode on I-V characteristics]

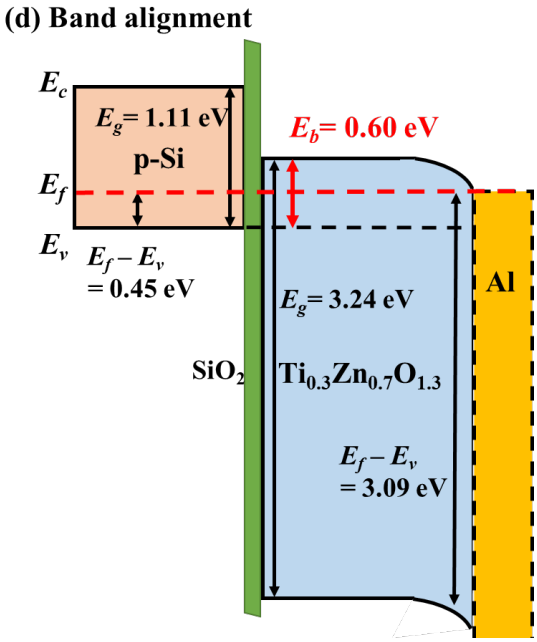
Figure S2 shows the (a) Al 2p, (b) Zn $2p_{3/2}$, (c) valence spectra, (d) band alignment from the aluminum electrodes on Single layer sample and (e) I-V characteristics of the Al/ $Ti_{0.3}Zn_{0.7}O_{1.3}$ junction formed on Al_2O_3 substrate. From the Al 2p spectra, it didn't observe only metal Al bonding sate around 73 eV, but also Al-O bonding state was observed around 76 eV. Aluminum thickness were almost 5 nm used this measurement. At the interface, there should be an unintentionally oxidized Al_2O_3 layer, which should not work as insulator. Because the valence band spectra shows electronic state at the Fermi level (0 eV), and the valence band maximum shift of ZnO near 5 eV. Furthermore, the Zn $2p_{3/2}$ spectra also showed broad two peaks around 1022 and 1025 eV. These valence band and Zn $2p_{3/2}$ energy shifts suggest the possibility that the interface is metallic and the formation of $Zn_xAl_yO_z$, considering the Fermi position of $Ti_{0.3}Zn_{0.7}O_{1.3}$. These results indicate that aluminum and $Ti_{0.3}Zn_{0.7}O_{1.3}$ form an ohmic junction, and band alignment should be as Fig. S2(d). Note, the measurement method of the band alignment except aluminum electrodes was same as Fig. S1. The evaluation of the electrical characteristics of the Al/ $Ti_{0.3}Zn_{0.7}O_{1.3}$ junction formed on Al_2O_3 substrate support these results, as shown in Fig. S2(e), and shows an ohmic property. The sheet resistance was 3.6×10^6 Ω/□ regarding the $Ti_{0.3}Zn_{0.7}O_{1.3}$ sample with thickness of 25 nm.

Based on these results, we think that the aluminum electrode forms an ohmic junction with $Ti_{0.3}Zn_{0.7}O_{1.3}$ and that the electrode does not affect the relative changes of the current mechanism described in the main text.


(a) Al 2p
exp.
sum.
Al2O3
Al
Intensity (a.u.)
80
78
76
74
72
Binding Energy (eV)


(b) Zn 2p3/2
exp.
sum.
background
interface
bulk
Intensity (a.u.)
1028
1026
1024
1022
1020
Binding Energy (eV)


(c) Valence
Intensity (a.u.)
30
20
10
0
15
10
5
0
Binding Energy (eV)


(d) Band alignment
Ec
Eg= 1.11 eV
p-Si
Eb= 0.60 eV
Ef
Ev
Ef – Ev
= 0.45 eV
Eg= 3.24 eV
Al
SiO2
Ti0.3Zn0.7O1.3
Ef – Ev
= 3.09 eV

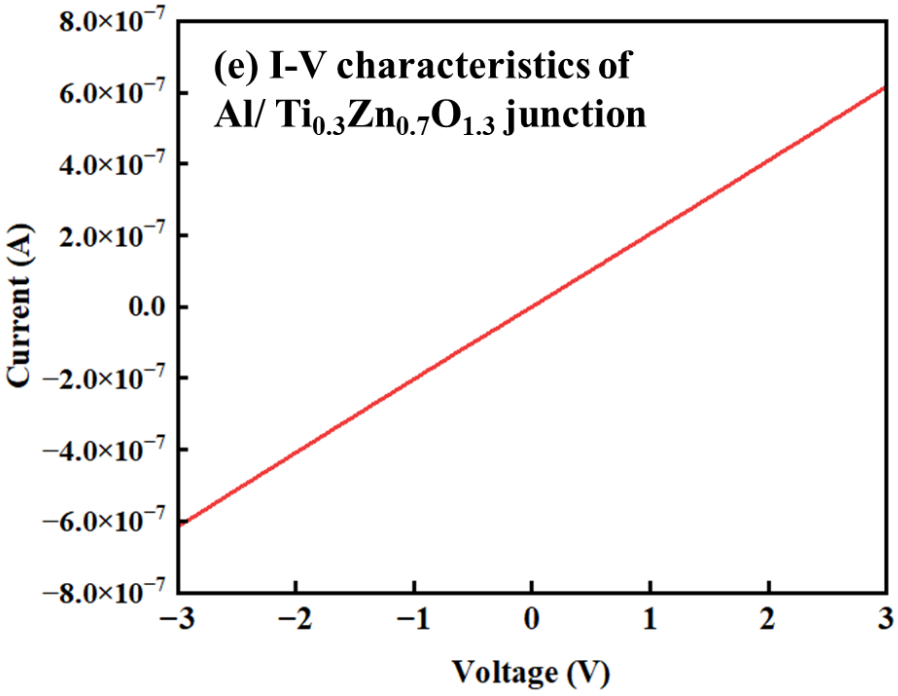


Figure S2 (a) Al 2p, (b) Zn $2p_{3/2}$, (c) Valence spectra, (d) band alignment from the aluminum electrodes on Single layer sample and (e) I-V characteristics of the Al/ $Ti_{0.3}Zn_{0.7}O_{1.3}$ junction formed on Al_2O_3.

[**Variations of area intensity of O 1s spectra of Single layer**]

Figure S3 shows the Zn $2p_{3/2}$, Ti $2p_{3/2}$, and O 1s spectra on three measurement points in Single layer. The spectra are labeled point_1, 2, and 3, and point_1 is the result shown in the main text. The film thickness of point_1 was 5 nm, that of point_2 was 3 nm, and that of point_3 was 2 nm. For using the same sample as the I-V measurement, we chose and described the point_1 in the main text. As shown in the figure, the area intensity of only O 1s spectra changes greatly at each measurement point, which is thought to be due to the variation in oxygen vacancies caused by the non-uniformity of Ti.

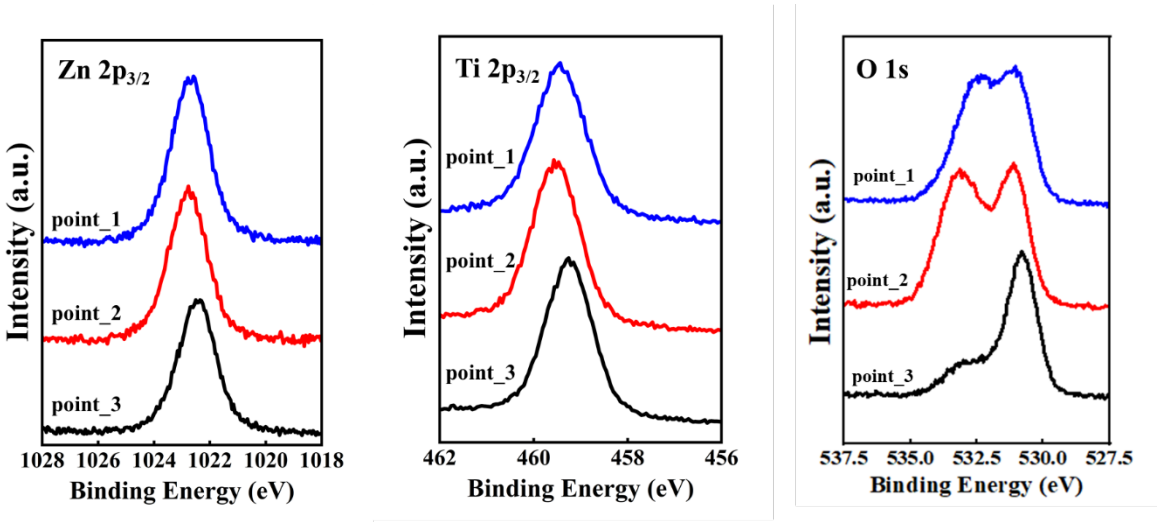


Figure S3 Zn $2p_{3/2}$, Ti $2p_{3/2}$, and O 1s spectra on three measurement points in Single layer.

[**Si 2p spectrum of ZnO first obtained by Al Kα-XPS**]

Figure S4 shows the Si 2p spectrum in ZnO first obtained by Al Kα-XPS. This result shows that the Zn 3p peak around 90 eV and its tail on the high binding energy side affect the Si 2p background. In addition, since Si 2p is affected by orbital splitting, when the signal at the stacking interface is weak, as shown in the figure, the difference between the three states seen in Si 1s becomes small, making the fit difficult. For these reasons, we have used Si 1s in our discussion of the interface.

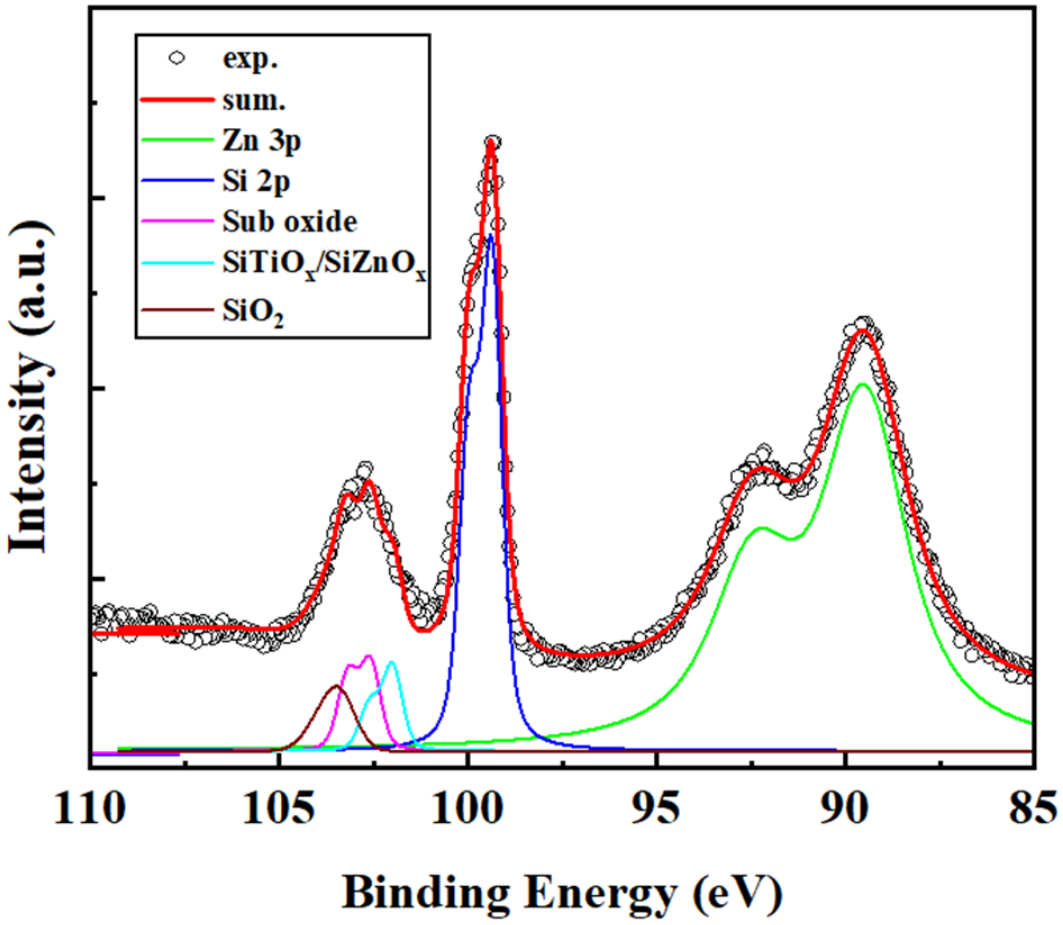


Fig. S4 Si 2p spectrum in ZnO first obtained by Al Kα-XPS

Reference

[1] A. Toghan, K. K. Taha, and A. Modwi, *J. Mater Sci: Mater Electron*, **32**, 2471 (2021).

[2] K. C. L. Khang, M. H. M. Hatta, S. L. Lee, and L. Yuliati, *J. Teknologi (Sciences & Engineering)* **80**, 153 (2018).