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Impact of hetero-interfaces in solar cells using ZnSnP_2 bulk crystals

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Keywords: Solar Cell, II-IV-V₂, chalcopyrite, ZnSnP_2 , back electrode, etching

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Abstract

We report on the optimization of interface structure in ZnSnP_2 solar cells. The effects of back electrode materials and related interface on photovoltaic performance were investigated. It was clarified that a conventional structure Mo/ZnSnP_2 showed a schottky-behaviour, while an ohmic-behaviour was observed in the Cu/ZnSnP_2 structure annealed at 300 °C. STEM-EDX analysis suggested that Cu-Sn-P ternary compound was formed at the interface. This compound is considered to play an important role to obtain the ohmic contact between ZnSnP_2 and Cu. In addition, it was clarified that the aqua regia etching of ZnSnP_2 bulk crystals before chemical bath deposition process for the preparation of buffer layer was effective to remove the layer including lattice defects introduced by mechanical-polishing, which was supported by TEM observations and photoluminescence measurements. This means that the carrier transport across the interface is improved due to the reduced defect at the interface. Consequently, the conversion efficiency of approximately 2 % was achieved with the structure of $\text{Al}/\text{ZnO};\text{Al}/\text{ZnO}/\text{CdS}/\text{ZnSnP}_2/\text{Cu}$, where the values of short circuit current density, J_{SC} , open circuit voltage, V_{OC} and fill factor, FF , were 8.2 mA cm^{-2} , 0.452 V and 0.533, respectively. However, the value of V_{OC} was largely low considering the bandgap value of ZnSnP_2 . In order to improve the high conversion efficiency, the optimization of buffer layer material is considered to be essential in the viewpoint of band alignment.

1. Introduction

Solar cells based on compound semiconductors have made large progress in late years. Particularly, chalcogenide compounds such as $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) and CdTe have recorded high conversion efficiencies of 22.6¹ and 22.1 %², respectively. However, these compounds contain rare or toxic elements, which disturbs widespread use of the solar cells based on these compound semiconductors. Because of this situation, light absorbing materials which consists of safe and earth-abundant elements have been investigated and $\text{Cu}_2\text{ZnSnS}_{4-x}\text{Se}_x$ recorded the conversion efficiency of 12.6 %.³ For other instances, Cu_2SnS_3 ,⁴ Cu_2O ,⁵ SnS ,⁶ FeS_2 ,⁷ and Zn_3P_2 ⁸ have been also investigated under the same concept.

In this work, ZnSnP_2 is focused on as a solar absorbing material consisting of safe and earth-abundant elements. In the previous works, it was reported that ZnSnP_2 showed a *p*-type conduction with the carrier concentration of $10^{16}\text{--}10^{18}\text{ cm}^{-3}$ and a direct bandgap of $\sim 1.6\text{ eV}$.^{9–17} Based on Shockley-Queisser limit,¹³ the theoretical conversion efficiency of about 30% is calculated in the single-junction solar cell using ZnSnP_2 under the condition of AM 1.5 G solar spectrum.¹⁴ The absorption coefficient of ZnSnP_2 was reported to be approximately 10^5 cm^{-1} in visible light range,^{14,15} which is comparable to that of CIGS.^{14,16} As mentioned above, ZnSnP_2 has a promising properties for a solar absorbing

material. However, in our previous works, ZnSnP_2 solar cells with the structure of $\text{Al}/\text{AZO}/\text{ZnO}/\text{CdS}/\text{ZnSnP}_2/\text{Mo}$ were realized using bulk crystals. However, the conversion efficiency of the solar cells was only 0.087 %.¹⁷ In particular, the series resistance, evaluated from the gradient of J - V characteristics in forward bias, was about $100 \Omega \text{ cm}^2$, which might lead to the low conversion efficiency. The resistance of ZnSnP_2 bulk crystals was evaluated to be $3.5 \Omega \text{ cm}^2$, which was based on the resistivity and the thickness.¹¹ Therefore, the large series resistance previously observed might be attributed to the resistance at the interface of $\text{CdS}/\text{ZnSnP}_2$ and/or ZnSnP_2/Mo . We thus investigated the structures of interfaces related to the absorbing material ZnSnP_2 to clarify the origin of high resistance and improve the photovoltaic performance in ZnSnP_2 solar cells.

2. Experimental method

2.1. ZnSnP_2 bulk crystal growth

ZnSnP_2 bulk crystals were grown by Sn flux method as reported in our previous work.¹¹ The raw materials, Zn shots (99.99%, Kojundo Chemical Laboratory), Sn shots (99.99%, Kojundo Chemical Laboratory) and red phosphorus flakes (99.9999%, Kojundo Chemical Laboratory) were sealed in evacuated quartz ampule with the inner diameter of 10 mm under the pressure of 10^{-2} Pa. The nominal composition was controlled to be 92 mol%Sn in Sn- ZnP_2 pseudo binary diagram.¹¹ The total weight of sample was set at

approximately 60 g. Then, the quartz ampoule was set in vertical furnace and heated up to 700 °C for homogenization. After that, the furnace moved upward by the rate of 0.2 mm/h and the sample was unidirectionally solidified from the bottom. The temperature of the bottom of the ampule was monitored by K-type thermocouple during crystal growth and the average cooling rate was approximately 0.7 °C/h. After the crystal growth, bulk crystals were cut into several wafers in perpendicular to the growth direction. The surface of each wafer was mechanically polished with a series of emery papers and finally with 1 µm diamond slurry on a buff sheet.

2.2. Preparation of electrode/ZnSnP₂ samples

In order to clarify the effects of back electrode and related interface in solar cells with the structure of Al/ZnO;Al(AZO)/ZnO/CdS/ZnSnP₂/Mo, electrode/ZnSnP₂ samples were prepared. In this study, some metals with various work functions,¹⁸ Cu (4.65 eV), Ag (4.26 eV) and Al (4.28 eV) were investigated as an electrode in addition to Mo (4.6 eV). Before preparation of the electrodes, ZnSnP₂ bulk crystals were etched by immersing in 0.02 M(= mol/L) Br₂ solution for 15 min to remove the surface oxides. The four electrodes with the diameter of 1 mm and the thickness of about 0.5 µm were deposited on the etched surface to be square corners. Cu and Mo electrodes were formed by direct current (DC) sputtering technique using Cu (99.99%, Furuuchi Chemical) and Mo (99.98%, Furuuchi

Chemical) target materials. Al and Ag electrodes were deposited by electron beam and resistive heating evaporation using Al shots (99.99%, Furuuchi Chemical) and Ag wire (99.99%, The Nilaco Corporation), respectively. After that, some samples were sealed in the evacuated quartz ampule below 10^{-2} Pa and annealed at 200 or 300 °C for 1 hour. Subsequently, current dependence of terminal resistance was measured using the resistivity/hall effect measurement system (ResiTest8300, Toyo Corporation). The cross-sectional observation was carried out using scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDX, JEM-2100F, JEOL) to observe interfacial structures. Samples for STEM were fabricated by focused ion beam process with Ga ion beam (FIB, SMI9200, SII).

2.3. Fabrication of solar cells using ZnSnP₂ bulk crystals

The solar cell structure of Al/AZO/ZnO/CdS/ZnSnP₂/Cu was adopted according to the experimental results in this work. The schematic illustration of the solar cells is shown in Figure 1. First of all, Cu back electrode with the thickness of approximately 0.5 μm was prepared by DC sputtering on the polished surface of ZnSnP₂ wafer with the diameter of about 6 mm and the thickness of about 200 μm . Before preparation of the electrodes, ZnSnP₂ bulk crystals were etched by immersing in 0.02 M Br₂ solution for 15 min. After the preparation of Cu back electrode, some samples were sealed in the evacuated quartz

ampoule below 10^{-2} Pa and annealed at 200 °C for 1 hour or 300 °C for 20 min. CdS with the thickness of about 50 nm was prepared on the opposite surface to back electrode by chemical bath deposition (CBD) method, where the chemical bath contains 11 mM of CdSO_4 (99 %, SIGMA-ALDRICH), 2.3 M of ammonia (28%, Nacalai Tesque) and 56 mM of thiourea (98 %, Nakalai Tesque). The temperature and the deposition time were 80 °C and 11 min, respectively. In our previous work, it was suggested that the conduction band offset of CdS/ ZnSnP_2 junction was about -1.2 eV,¹⁹ which is negatively large, “cliff”. In this study, CdS was used as a conventional and easily-obtained buffer material, although an appropriate material should be investigated to achieve higher conversion efficiency, which is a future work. Before preparation of CdS layer, the surface of ZnSnP_2 bulk crystals was etched by immersing in 1/2 or 1/4 diluted aqua regia solution for 1–30 min. The aqua regia solution was prepared using HCl (35%, Nacalai Tesque), HNO_3 (60%, Nacalai Tesque) and ultra-pure water. It was reported that aqua regia was necessary rather than conventional hydrochloric acid for etching of ZnSnP_2 in our previous study.²⁰ In order to investigate the effects of etching, photoluminescence (PL) spectra of ZnSnP_2 bulk crystals were measured at room temperature using the measurement system (Hamamatsu Photonics, C12132). The wavelength and the power of the excitation laser were 532 nm and 5.05 mW, respectively. The area of the excitation laser beam was set at

0.5 mm². Subsequently, ZnO and AZO films were formed on CdS layer by radio frequency (RF) magnetron sputtering at room temperature with the thickness of 50 and 300 nm, respectively. For the fabrication of ZnO and AZO films, ZnO (99.99 %, Furuuchi Chemical) and ZnO-2 wt. % Al₂O₃ (99.99 %, Furuuchi Chemical) were used as target materials. Finally, Al electrode with a grid pattern was fabricated by electron beam evaporation. The current density–voltage (J – V) characteristics and the external quantum efficiency (EQE) of solar cells were investigated under the illumination conditions of 100 mW cm^{−2} and AM 1.5 G using the measurement system with solar simulator (Bunkoukeiki, CEP-25RR). The cross-sectional observation was performed using STEM-EDX, where the samples were prepared by FIB.

3. Results and discussion

3.1. Effect of back electrode materials on photovoltaic performance

~~Generally, metals with larger work function than fermi level in p -type semiconductors are necessary for ohmic contact. Basically, it is necessary that work functions of metals are at deeper level than fermi level in p -type semiconductors for ohmic contacts at metal/ p -type semiconductor interfaces.~~ Hinuma *et al.* reported that the ionization potential of ZnSnP₂, corresponding to the energy between vacuum level and valence band

maximum, was calculated to be 5.53 eV based on first principles calculation.²¹ ~~And it is considered that ZnSnP₂, *p*-type semiconductor, has its fermi level near the valence band maximum. From above~~ Considering the fermi level in ZnSnP₂ near the valence band maximum because of *p*-type semiconductor, Cu (4.65 eV), Ag (4.26 eV) and Al (4.28 eV) and Mo (4.6 eV)¹⁸ seem to form schotkky contact with ZnSnP₂.

Figure 2 shows the current dependence of terminal resistance. In the case of Mo with relatively large work function, ~~4.6 eV~~,¹⁸ the terminal resistance decreases with increasing the current in both as-sputtered and annealed samples, which suggests the interface of Mo/ZnSnP₂ shows a Schottky behavior and leads to a high series resistance in solar cells. As shown in the supplemental materials, Al and Ag electrodes show the same tendency. The work functions of Al and Ag ~~is 4.28 and 4.26 eV, respectively,~~¹⁸ ~~which~~ are smaller compared with Mo. In the case of Cu shown in Figure 2b, the as-deposited sample also indicates a change of the terminal resistance, while the dependence of the resistance on current is smaller in the annealed samples. In particular, an ohmic behavior is observed in the sample annealed at 300 °C, despite the work function of Cu is similar to that of Mo.¹⁸ This indicates that the resistance was affected by annealing at 200 and 300 °C unlike in the case of Mo and the interface of Cu/ZnSnP₂ is a more promising structure in solar cells using ZnSnP₂ bulk crystals from the viewpoint of carrier transport.

Figure 3 shows the cross-sectional STEM images and corresponding line profiles obtained by EDX analysis. In Mo/ZnSnP₂ as shown in Figure 3a and b, the change of morphology and composition at the interface before and after annealing was not confirmed in 100 nm scale, which supports the results in the resistance measurements. On the other hand, in STEM images of Cu/ZnSnP₂, the measurable composition change due to interdiffusion at the interface was observed from the comparison between Figure 3c and d, where the range of composition change was wider after annealing. The interfacial morphology also changed by annealing and particles considered to be intermediate compounds or precipitates were observed at the interface. In detailed observations, the remarkable change region of Cu, Sn and P compositions in the composition profile coincides with the size of the particle in the STEM image. It is also understood that the particle does not contain Zn. This fact implies the particle at the interface consists of a Cu-Sn-P ternary compound. In this system, ternary compound Cu₄SnP₁₀ was actually reported by Bullet and Dawson²². It is thus concluded that the ternary compound formation at the interface impacts the contact behaviour between back electrode and ZnSnP₂. In the case of CIGS, it was also reported that the formation of MoSe₂ was important to obtain the ohmic contact between Mo back electrode and CIGS absorber.²³ However, as seen in Figure 3d, the region of the compound formation or the

interdiffusion is locally limited at the Cu/ZnSnP₂ interface. Consequently, it has room for establishing of appropriate interfacial structure and processing for such a structure.

Then, the solar cells using Cu as a back electrode material were fabricated in order to investigate the effect of back electrode materials on photovoltaic performance. Figure 4 shows the J - V characteristics of the solar cells with the structure of Al/AZO/ZnO/CdS/ZnSnP₂/Cu with and without annealing. The solar cell parameters are summarized in Table 1. The series resistances of the solar cells were roughly evaluated from the gradient of J - V curves in forward bias. The remarkable reduction of series resistance and the improvement of cell performance were achieved by using Cu back electrode, comparing to the case of Mo with the series resistance of $\sim 100 \Omega\text{cm}^2$ and the conversion efficiency of 0.09 %²². It is also observed that the series resistance depends on the annealing conditions, which are consistent with the current dependence of terminal resistance shown in Figure 2. Consequently, the conversion efficiency of 0.27 % was achieved.

3.2. Effects of aqua regia etching on CdS/ZnSnP₂ interface and photovoltaic performance

In this study, ZnSnP₂ crystals for solar cells were prepared by mechanical-polishing, which generally introduce some lattice defects such as vacancies and dislocation in crystals. An etching after polishing is carried out in conventional semiconductor processes for silicon. Before constructing solar cells, effects of etching on the crystal surface were investigated by PL measurements in this study. PL spectra before and after etching with 1/2 diluted aqua regia for various duration are shown in Figure 5. In each spectrum, the PL peak was observed at ~740 nm, corresponding to the bandgap of ZnSnP₂. The peak intensity increased by etching with any conditions. We considered the etching at least for 10-15 min was sufficient from the viewpoint of PL measurements since the peak intensity seemed to be same in any duration except for 10 min.

The cross-sectional STEM images of the solar cells with the structure of Al/AZO/ZnO/CdS/ZnSnP₂/Cu without and with etching by 1/2 diluted aqua regia for 15 min are shown in Figure 6. The etching of ZnSnP₂ crystals was carried out before the preparation of CdS. The Cu back electrode optimized in this study was used. A contrast due to lattice strain was actually observed in the ZnSnP₂ bulk crystal near the interface of CdS/ZnSnP₂ as shown in Figure 6a. As previously mentioned, when preparing ZnSnP₂

crystals for solar cells, the surface was mechanically polished, which might introduce some lattice defects. A region including defects generally makes higher the recombination rate of minority carriers and lower performance of solar cells. On the other hand, a strain contrast is not observed, and the smooth interface and the thin layer of CdS are clearly confirmed in the etched sample shown in Figure 6b. This image suggests that a region including defects was removed by etching under the above condition as expected.

The illuminated and dark J - V characteristics of the solar cells are shown in Figure 7a and b when etched under various conditions. The solar cell parameters are summarized in Table 2. The etching using aqua regia improved all cell parameters such as short circuit current density, J_{sc} , open circuit voltage, V_{oc} and fill factor, FF . J_{sc} is almost same value in any samples etched with 1/2 diluted aqua regia, while FF increases with increasing duration, which leads to an increase of V_{oc} . Consequently, the conversion efficiency of approximately 2 % was achieved in the cell etched for 15 min, where J_{sc} , V_{oc} and FF were 8.2 mA cm^{-2} , 0.452 V and 0.533, respectively. These results are considered to come from the removing of lattice defects by etching. However, the performance degraded in the sample with longer etching of 30 min, since the shunt resistance decreased as shown in Figure 7b. While, significant leakage was not observed in dark characteristics of other samples.

It is speculated that grain boundary in ZnSnP_2 crystal was preferentially etched and a part of the solar cells was short-circuit since ZnSnP_2 crystals composed of grains with the size of submillimeter. In the sample etched using 1/4 diluted aqua regia for 15 min, the significant improvement of photovoltaic performance was not observed compared with samples with 1/2 diluted aqua regia etching, which suggested that the etching condition was insufficient to remove the layer including defects.

Figure 8a and b show the EQE spectra of the solar cells without and with 1/2 diluted aqua regia etching for 15 min under various applied voltages of 0, -0.5 and -1 V, respectively. In conventional solar cells with high efficiency, EQE spectra are independent of applied reverse bias, while it is observed that EQE curves drastically change and the values increase with increasing the applied reverse bias in the sample without etching. One of the reasons for such a behavior in EQE spectra is a high recombination rate of light-induced minority carriers due to lattice defects near the interface of $\text{CdS}/\text{ZnSnP}_2$ as shown in Figure 6a. In the sample with etching, the voltage dependence of EQE spectra is smaller and EQE at 0 V is larger than that without etching. The above behavior in EQE spectra indicates the improvement of carrier transport at the interface between CdS and ZnSnP_2 due to removing regions including defects, which leads to higher efficiency. However, the maximum EQE under the voltage of -1.0 V was

about 0.6, which was lower compared with the sample without etching. The details of this decrease in the EQE spectra must be investigated in future works.

Here, the maximum V_{OC} in this study is 0.45 V, which is lower considering the bandgap of $ZnSnP_2$. In our previous work, it was suggested that the conduction band offset of $CdS/ZnSnP_2$ junction was about -1.2 eV, which is negatively large conduction band offset, “cliff” and limited the V_{OC} .¹⁹ Therefore, the optimization of buffer layer material is thus essential to achieve higher conversion efficiency in $ZnSnP_2$ solar cells from the viewpoint of band alignment.

4. Conclusions

In this study, we focused on the interfaces in ZnSnP_2 solar cells for high efficiency. The effects of back electrode materials, Mo, Cu, Ag and Al, and related interfaces on photovoltaic performance were investigated. It was clarified that Mo/ ZnSnP_2 showed a schottky behavior and Mo was unsuitable for back electrode material in ZnSnP_2 solar cells. This schottky-contact between Mo and ZnSnP_2 is one of the reasons that the high series resistance was observed in the solar cells with the structure of Al/AZO/ $\text{ZnO}/\text{CdS}/\text{ZnSnP}_2/\text{Mo}$. The junctions using Ag and Al also show Schottky behavior. On the other hand, the ohmic contact was obtained for the Cu/ ZnSnP_2 structure annealed at 300 °C. The cross-sectional STEM-EDX analyses suggested that Cu-Sn-P ternary compound was formed at the interface of the annealed Cu/ ZnSnP_2 structure. This compound might be important to obtain the ohmic contact between ZnSnP_2 and Cu.

For the interface between CdS and ZnSnP_2 , a strain contrast due to lattice defects introduced by mechanically-polishing was observed in the cross-sectional TEM image. In this study, it was revealed that the aqua regia etching of ZnSnP_2 bulk crystals before CBD process removed the layer including lattice defects, which improved FF and V_{oc} . Consequently, the conversion efficiency of approximately 2 % was achieved with the structure of Al/AZO/ $\text{ZnO}/\text{CdS}/\text{ZnSnP}_2/\text{Cu}$, where the values of J_{sc} , V_{oc} and FF were 8.2

mA cm⁻², 0.452 V and 0.533, respectively. However, longer etching reduced the cell performance because of shunting. The preferential dissolution of area around grain boundary in ZnSnP₂ crystals during etching is considered and further investigation is necessary to clarify the mechanism.

In addition, V_{OC} of the cells prepared in this study were quite low considering the bandgap of ZnSnP₂. For further improvement of the conversion efficiency, the optimization of band alignment is considered to be essential by developing appropriate buffer materials.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications web site at DOI:

Further information relating to the current dependence of terminal resistance in Al/ZnSnP₂ and Ag/ZnSnP₂ samples.

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Figure captions

Figure 1. Schematic illustration of ZnSnP_2 solar cells with the structure of Al/AZO/ZnO/CdS/ ZnSnP_2 /Cu.

Figure 2. Current dependence of terminal resistance in samples as-prepared and annealed at 200 and 300 °C for 1 hour. (a) Mo and (b) Cu electrodes.

Figure 3. Cross-sectional STEM-DF images and corresponding EDX profiles of Mo/ ZnSnP_2 (a) without annealing and (b) annealed at 300 °C for 1 hour, and Cu/ ZnSnP_2 (c) without annealing and (d) annealed at 300 °C for 1 hour. The gray frameworks in STEM-DF images show the area analysed by EDX.

Figure 4. J – V characteristics of the solar cells with the structure of Al/AZO/ZnO/CdS/ ZnSnP_2 /Cu with and without annealing at 200 or 300 °C. Annealing was performed after the Cu back electrode was formed.

Figure 5. Photoluminescence spectra of ZnSnP_2 bulk crystals before and after 1/2 diluted aqua regia etching for various duration.

Figure 6. Cross-sectional TEM images of ZnSnP_2 solar cells (a) without etching and (b) with aqua regia etching.

Figure 7. ~~(a)~~ J – V characteristics of ZnSnP_2 solar cells with and without aqua regia etching under (a) illuminated and (b) dark conditions. In these solar cells, Cu electrode annealed at 300 °C was used.

Figure 8. ~~(a)~~ EQE spectra of ZnSnP_2 solar cells (a) without etching and (b) with 1/2 diluted aqua regia etching for 15 min, under various applied voltages. In these solar cells, Cu electrode annealed at 300 °C was used.

■ Figures

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Figure 5. Photoluminescence spectra of ZnSnP₂ bulk crystals before and after 1/2 diluted aqua regia etching for various duration.

Figure 6. Cross-sectional TEM images of ZnSnP₂ solar cells (a) without etching and (b) with aqua regia etching.

Figure 7. (a) J - V characteristics of ZnSnP_2 solar cells with and without aqua regia etching under (a) illuminated and (b) dark conditions. In these solar cells, Cu electrode annealed at 300 °C was used.

Figure 8. ~~(a)~~ EQE spectra of ZnSnP₂ solar cells (a) without etching and (b) with 1/2 diluted aqua regia etching for 15 min, under various applied voltages. In these solar cells, Cu electrode annealed at 300 °C was used.

■ Tables

Table 1. Solar cell parameters of ZnSnP₂ solar cells with Cu back electrode.

	J_{SC} / mA cm ⁻²	V_{OC} / V	FF	Efficiency / %	R_s / Ω cm ²
Cu as deposited	3.3	0.261	0.27	0.23	~ 50
Cu 200 °C, 1hour, annealed	3.2	0.274	0.30	0.26	~ 25
Cu 300 °C, 1hour, annealed	4.1	0.217	0.30	0.27	~ 10

Table 2. Solar cell parameters of ZnSnP₂ solar cells with and without aqua regia etching.

	J_{SC} / mA cm ⁻²	V_{OC} / V	FF	Efficiency / %	R_s / Ω cm ²
1/2 diluted for 30 min	8.1	0.387	0.393	1.23	~ 8
1/2 diluted for 15 min	8.2	0.452	0.533	1.97	~ 11
1/2 diluted for 5 min	8.1	0.433	0.496	1.73	~ 11
1/2 diluted for 1 min	8.0	0.376	0.416	1.25	~ 8
1/4 diluted for 15 min	6.7	0.378	0.396	1.00	~ 6
w/o etching	4.1	0.217	0.308	0.27	~ 10

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