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Performance improvement of $(NH_4)_2S_x$-treated III–V compounds multi-junction solar cell using surface treatment

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Recently, III-V compound solar cells have been studied extensively. Owing to their high conversion efficiency and high radiation hardness, tandem-type III–V compound multi-junction solar cells are widely being used in space and applied in the terrestrial concentrator photovoltaic system. However, high surface state density and high surface recombination velocity deteriorated the performances of the III–V solar cells. In this study, $(NH_4)_2S_x$-treatment was used to improve conversion performances. An X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of $(NH_4)_2S_x$-treated window layer (n-AlInP) of solar cells. To identify the function and mechanism of the reduction of surface states, the current-voltage characteristics of associated Schottky diodes were measured.

Figure 1 shows the InGaP / InGaAs / Ge triple-junction solar cell structures grown on p-type Ge substrates by metal organic chemical vapor deposition (MOCVD) system. The samples were first cleaned with chemical solutions of trichlorethylene, acetone and methanol, and then the InGaAs contact layer was etched to AlInP window layer using selective etching solution of NH_4OH / H_2O_2 / H_2O (1/1/50). The as-etched sample was dipped into an $(NH_4)_2S_x$ solution (with 6% of S) at 60°C for 30 min, rinsed with deionized water and blown dry with N_2. The $(NH_4)_2S_x$-treated area on AlInP surface is 92.5% in each defined pattern. To further investigate the mechanism of $(NH_4)_2S_x$-treatment, both as-etched and $(NH_4)_2S_x$-treated specimens were immediately loaded into ESCA vacuum chamber for XPS examination. The current-voltage characteristics of the solar cells are measured using a continuous solar simulator system (AM 1.5G and 100 mW/cm^2 at 25 °C).

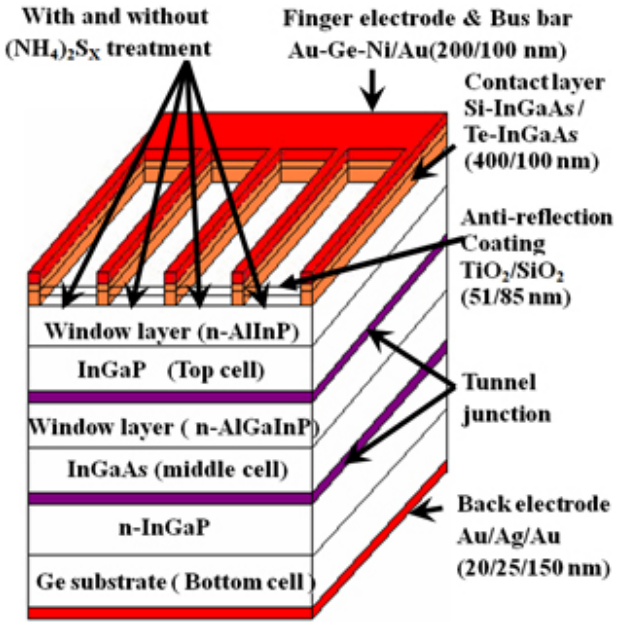

Fig. 1 The structure of InGaP/InGaAs/Ge triple-junction solar cell.

Figure 2 shows the current-voltage characteristics of the III–V compound solar cells with and without $(NH_4)_2S_x$-

treatment. The short-circuit current density (J_{sc}) of 16.69 mA/cm^2 and 14.73 mA/cm^2 was obtained for the solar cells with and without $(NH_4)_2S_x$-treatment, respectively. The associated open-circuit voltage (V_{oc}) is 2.07V and 2.05V, respectively. Furthermore, after the $(NH_4)_2S_x$ surface treatment, the conversion efficiency was improved from 23.2% to 27.3%. To investigate the mechanisms of the conversion efficiency improvement of the $(NH_4)_2S_x$-treated solar cell, the surfaces of the AlInP layer with and without $(NH_4)_2S_x$-treatment were examined using X-ray photoelectron spectroscopy (XPS, VG ESCA-210D) with Al Kα radiation (1486.6 eV). Figure 3 shows the XPS spectra of In $3d_{5/2}$ core levels of the as-etched and $(NH_4)_2S_x$-treated samples. By using an interative least-square computer program, the XPS spectra of In $3d_{5/2}$ were deconvolved into three components associated 444.5, 444.9 and 445.1 eV, which corresponded to In-P, In-S and In-O bonds, respectively. Although it is difficult to measure the distinction between S and O bonding to In, it still can be seen that the higher binding energy shoulder was broadened for the as-etched sample than that of the $(NH_4)_2S_x$-treated sample. Therefore, we can deduce that the InO_x composition was removed and the InS_x was formed by the $(NH_4)_2S_x$-treatment

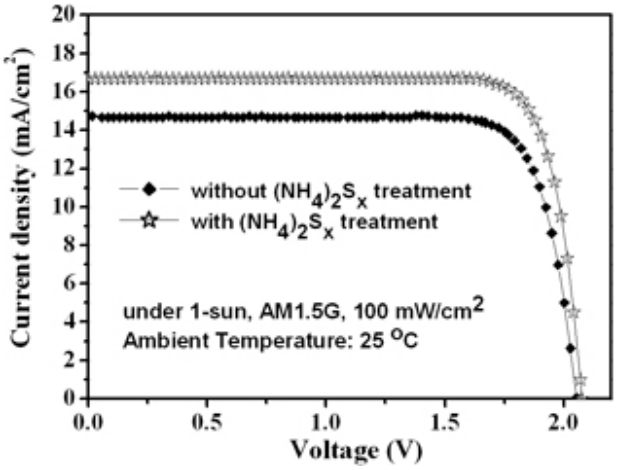

Fig. 2 Illuminated J–V curves under AM1.5G spectra for InGaP/InGaAs/Ge triple- junction solar cells fabricated with and without $(NH_4)_2S_x$ treatment.

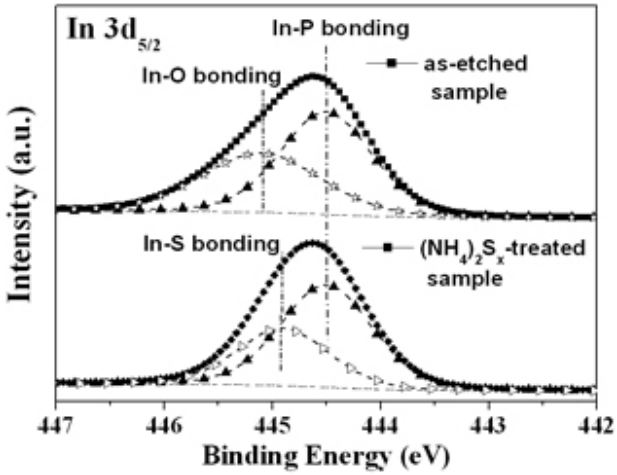

Fig. 3 The XPS spectra of In $3d_{5/2}$ core level for AlInP surfaces with and without $(NH_4)_2S_x$ treatment.

To identify the Al-P binding energy, the depth profile of XPS spectra around 74 eV of the AlInP was performed. In the depth of 6nm of the AlInP layer, the XPS spectra around 74 eV would be the Al-P bonds. According to the XPS spectrum, the XPS spectra of 73.9 eV for Al-P bonds can be deduced. The binding energy of Al 2p core level of the AlInP surfaces with and without $(NH_4)_2S_x$-treatment was shown in Fig. 4. Similar to the analysis of In $3d_{5/2}$ binding configuration, the XPS spectra of Al 2p were deconvolved into components associated Al-P bond (73.9 eV), Al-S bond (74.4 eV) and Al-O bond (74.7 eV). According to the experimental results shown in Fig.4, the AlO_x can be completely removed and AlSx can be formed using $(NH_4)_2S_x$-treatment. Furthermore, according the XPS spectra shown in Fig.3 and 4, we can deduce that the $(NH_4)_2S_x$ surface treatment can effectively passivate the In and Al dangling bonds to replace weak metal oxide (InO_x or AlO_x) formation.

To investigate the function of the sulfur on the $(NH_4)_2S_x$-treated AlInP, the XPS spectra of S 2p core levels are shown in Fig.5. The XPS spectra of S 2p core level were deconvolved into three components associated S2p $_{3/2}$ at 162.7 eV (monosulfide), 163.5 eV(disulfide) and 164.4 eV(elemental sulfur). The high-energy at 164.4 eV of S2p core level presumably originated from the sulfur atoms bonded to form elemental sulfur during the $(NH_4)_2S_x$ treatment. It has

been reported that metal and sulfur bondings can be identified the monosulfide (M-S-M) and disulfide (M-S-S-M) where the M is metal In or Al atoms in this experiment. According to the experimental results, not only does the sulfur react with In and Al, but elemental sulfur exisits on the AlInP surface to avoid the formation of native oxide before the samples are loaded into chamber for next process.

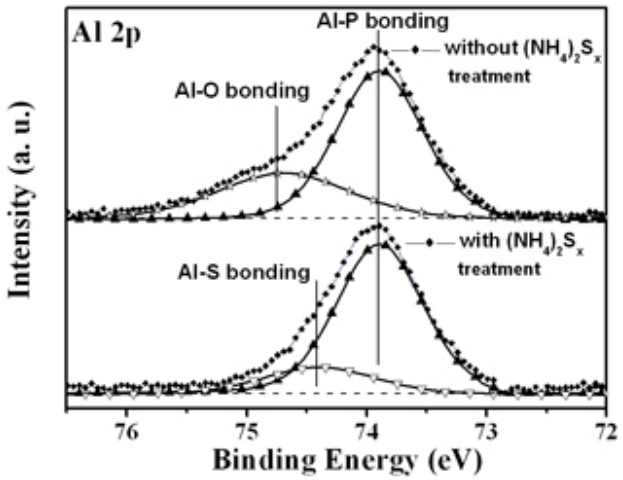

Fig. 4 The XPS spectra of Al 2p core level for AlInP surfaces with and without $(NH_4)_2S_x$ treatment.

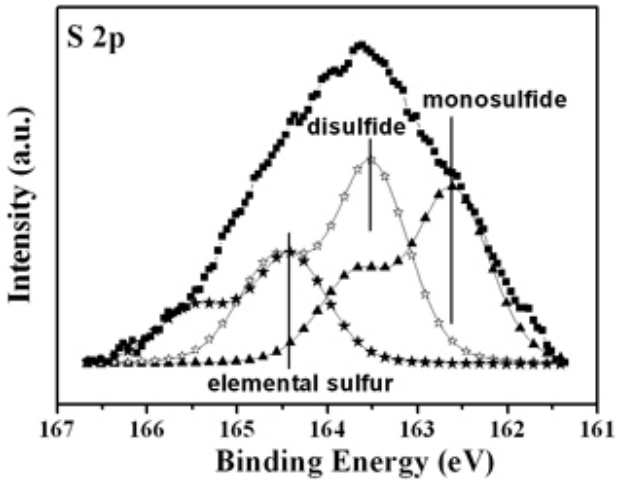

Fig. 5 The XPS spectra of S 2p core level for AlInP surfaces with and without $(NH_4)_2S_x$ treatment.

To investigate the dependence of $(NH_4)_2S_x$ treatment on the surface state density, Schottky diodes of indium tin oxide (ITO) contacted to AlInP with and without $(NH_4)_2S_x$ treatment were fabricated. Using an HP4145B semiconductor parameter analyzer, the current-voltage characteristics as a function of temperature of the Schottky diodes were measured. The current (I) transport over the Schottky barrier height Φ_B as a function of various temperatures (T) can be expressed as

$$I=A^{*}ST^{2}\exp(-q\Phi_B/KT) \quad (1)$$

where A^{*} is the effective Richardson constant of AlInP, S is the Schottky contact area, T is the absolute temperature and q is the electronic charge. From the Napierian logarithm plot of $[\ln(J/T^2)]$ as a function of various temperatures shown in Fig. 6, the associated Schottky barrier height Φ_B of 0.766 eV and 0.569 eV and ideality factor n of 1.44 and 1.19 were obtained for the Schottky diodes of ITO contacts with AlInP with and without $(NH_4)_2S_x$ treatment, respectively. In general, the Schottky barrier height is decreased due to the presence of dangling bonds and oxide formation which are considered as surface states. The reduction of the surface states for the $(NH_4)_2S_x$ –treated III-V solar cell is attributed to the complete removal of native oxide and the passivation of dangling bond and occupation of phosphorous related vacancies due to the formation of In-S and Al-S bonds.

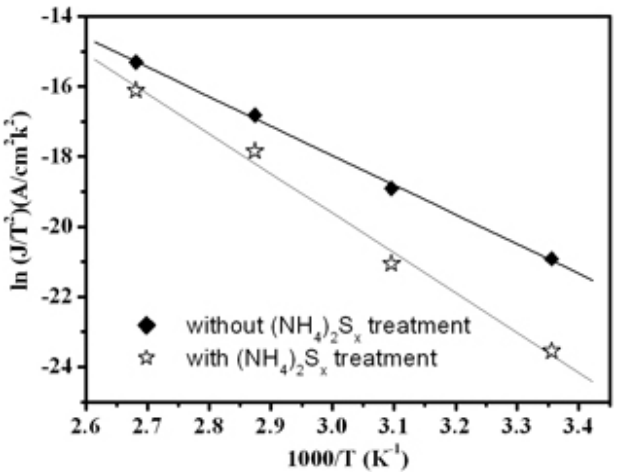

Fig. 6 Dependence of current - voltage characteristics on temperature of the Schottky junction of ITO/as-etched or ITO/$(NH_4)_2S_x$ treated AlInP.

In summary, the passivation mechanism for $(NH_4)_2S_x$-treated III–V compounds multi-junction solar cell was

investigated. The $(NH_4)_2S_x$ surface treatment can improve the conversion efficiency of III-V compound solar cells due to the reduction of the surface states and promote Schottky barrier height by using the $(NH_4)_2S_x$ treatment. Therefore, the higher photovoltaic electricity performances of the III–V compounds multi-junction solar cell can be obtained.