Stability enhancement of flexible CZTSSe solar cells by using nanopore array substrate

Jinze Li, Wenbin Hao, Jingjing Duan and Jie Xu

College of Electronic and Optical Engineering & College of Microelectronics, Nanjing University of Posts and Telecommunications, 9 Wenyuan Road, Nanjing 210023, People’s Republic of China

Abstract. Flexible CZTSSe solar cells were prepared on both thinned silicon substrate with and without nanopore array surface. The nanopore array structure could release thermal stress during the CZTSSe thin film preparation process, which improved the crystallization of CZTSSe thin film. The array structure could also absorb some bending stress during the bending test of CZTSSe solar cell, leading to obtaining a more reliable device. A flexible CZTSSe solar cell with only 14% efficiency loss after 3 times bending at 50mm radius was prepared by using nanopore array substrate.

1. Introduction

In recent years, Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) thin film proved to be a promising absorber material for next generation solar cell and gained more and more attention from researchers all over the world [1]. As its high light absorption coefficient, CZTSSe thin film could be applied in flexible occasions. Thus, the manufacture cost could be further reduced due to the compatibility with high throughput roll-to-roll industrial processes [2].

However, most flexible solar cells would suffer efficiency loss after bending [3]. Peng C found that the efficiency of CZTSSe solar cell on flexible glass substrate decreased nearly 20% after the cell was bent to a 50mm radius [4]. They observed that cracks appeared in CZTSSe thin film and ITO window layer due to the bending stress. Some efforts have been done to suppress this problem. E. Lee used silver nanowires to replace traditional ITO layer in perovskite solar cells [5]. The cell maintained most of its performance after bending test as the nanowire could release some stress during this process. AZO nanorod structure was also be used as electrode in solar cells and showed a good reliability [6].

In this paper, we used flexible silicon wafer with nanopore array structure on its surface as the substrate of CZTSSe solar cells. It is expected that these nanopore array structure could help release bending stress and improve the solar cell’s stability.

2. Experimental details

P-type (111) monocrystalline silicon wafers were first immersed in 30% (volume fraction) NaOH solution at 85°C to reduce their thickness to 70µm, which made them suitable as bendable substrates for flexible CZTSSe solar cells in this work. The nanopore array structure was prepared by one-step metal assisted chemical etching method. The thinned wafer was immersed in a mixed solution of 4M HF, 0.6M H$_2$O$_2$ and 0.025mM AgNO$_3$ for 10min to form nanopore array structure on its surface. Then the as-etched wafer was immersed into a solution containing ammonia and H$_2$O$_2$ for 90s to remove the remaining silver particles in the nanostructure. The CZTSSe solar cells were fabricated on both silicon wafers with or without nanostructure. The preparation process of CZTSSe thin films and solar cells was...
the same as what our previous work described\cite{7}. The pictures of silicon wafers with nanopore array structure and coated with CZTSSe thin film were shown in Figure. 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{The pictures of silicon wafers: (a) etched with nanopore array structure; (b) coated by CZTSSe thin film.}
\end{figure}

The cross-section morphology of CZTSSe thin films was observed by scanning electron microscopy (SEM, Hitachi S4800). X-ray diffraction (XRD, Rigaku Ultima-IV diffraction-meter with Cu–Kα radiation source) test was used to analyze the phases and crystallization of the samples. The performance of CZTSSe solar cells was measured with a Keithley 2400 source meter under AM1.5G spectrum (Oriel Solar simulator, 91192-1000W).

3. Results and discussions

Figure 2 showed the XRD diffraction peaks of CZTSSe thin films on silicon wafer with or without nanostructure. Besides the peaks from Si, the two patterns both showed diffraction peaks from (112), (200), (220), (312) and (316) planes of CZTSSe phase (JCPDS 26-0575 and JCPDS 52-0868) \cite{8}. The sample on silicon wafer with nanoarray structure showed a decreased ratio of peak intensity of (112) to that of (220), indicating the nanoarray structure affected the preference orientation of CZTSSe grain growth. However, the full width at half maximum (FWHM) of (112) peak of CZTSSe thin film with nanoarray was smaller than that of sample directly on silicon wafer. This array structure may help release the thermal stress during CZTSSe preparation process, leading to form a CZTSSe thin film with better crystallization \cite{9}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{XRD patterns of CZTSSe thin films on silicon wafers with or without nanopore array structure.}
\end{figure}
The cross-section SEM images of CZTSSe thin films on silicon wafers with or without nanopore array structure were presented in Figure 3. The length of nanopores was around 2µm and they formed a compact morphology. The surface of Mo layer in CZTSSe thin film on nanoarray structure was rougher than that in sample without nanopores. It could be seen that some points of nanopores were coated with Mo. This enlarged surface roughness of Mo layer may be the reason of that CZTSSe thin film on nanopores had a weaker preference orientation, which was checked out by XRD test. Despite this, both CZTSSe thin film presented a monograin layer structure.

![Figure 3. Cross-section SEM images of CZTSSe thin films: (a) without nanopore structure; (b) with nanopore structure.](image)

Current density–voltage (J–V) curves of these two kinds of CZTSSe solar cells were shown in Figure 4 and their photovoltaic performance parameters were summarized in Table 1. Due to the better crystallization of the absorber layer, CZTSSe solar cell with nanopore array structure had an improved performance with an open-circuit voltage of 233 mV, a short-circuit current density of 18.06 mA/cm², a fill factor of 28.52% and a conversion efficiency of 1.20%. We made a bending test to check the stability of these flexible CZTSSe solar cells. These solar cells were bent to a 50 mm radius for 3 times and their conversion efficiency after bending was also recorded in Table 1. The value and the percentage of efficiency loss of CZTSSe solar cell with nanopore array structure was smaller than that of sample without nanostructure, which proved that this array structure may help absorb some stress during sample bending process.

![Figure 4. Current density–voltage curves of prepared flexible CZTSSe solar cells.](image)
Table 1. Photovoltaic performance parameters of prepared CZTSSe solar cells.

| Sample   | $V_{OC}$ (mV) | $J_{SC}$ (mA·cm$^{-2}$) | $FF$ (%) | Eff (%) | Eff (%) after bending |
|----------|---------------|--------------------------|----------|---------|----------------------|
| Silicon  | 213           | 16.83                    | 27.34    | 0.98    | 0.77                 |
| Nanopore | 233           | 18.06                    | 28.52    | 1.20    | 1.03                 |

4. Conclusion
Nanopore array structure on the surface of substrate could help release thermal and bending stress during flexible CZTSSe solar cell’s preparation and working process, respectively. Compared with CZTSSe solar cell on flat substrate, a CZTSSe solar cell with better and more stable performance was obtained by using nanopore array substrate. However, nanopore array substrate would cause rougher surface of Mo layer. The efficiency of flexible CZTSSe solar cell could be further improved when this problem got solved.

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