

## Investigation An Universal Way To Fabricate Nanotip Structure On Chalcopyrite-Series Materials

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Nanostructure has promoted efficiency of Si based photovoltaic (PV) devices in the past decade. The unique characteristic such as intrinsic anti-reflectance, self-clean, and enhanced carrier concentration attracts tremendous attention from both academic and industry fields.<sup>1-4</sup> Recently, such concepts are focused on thin film PV devices. Especially  $\text{Cu}(\text{In}_x\text{Ga}_{1-x})(\text{S}_y\text{Se}_{1-y})_2$  (CIGSSe) and its related chalcopyrite series material owing to the highest efficiency beyond 20 % has been achieved<sup>5</sup>, researchers are eager to reveal how the nanostructure can promote the CIGSSe PV performance as it was applied in Si PV.<sup>4</sup>

Due to the multi-elements stoichiometry of CIGSSe and its related chalcopyrite series material, conventional processes on fabrication nanostructure on Si substrate such as photolithography and anisotropic chemical etching are unable to reproduce on CIGSSe. Despite some researchers devote on synthesis nano scale CIGSSe by “bottom up” process as nanocrystal<sup>6</sup> or nanowire<sup>7</sup>. It is still crucial to develop the process for readily aligned nanostructure arrays for practical PV device.

In this work, we demonstrate a template-free and facile way to create large area nanotip arrays on CIGSSe, its related chalcopyrite series material, and even  $\text{Cu}_2(\text{Zn}_z\text{Sn}_{1-z})\text{S}_4$ . Five kinds of promising thin film PV materials, including  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ ,  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ ,  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ , and  $\text{Cu}_2\text{Zn}_z\text{Sn}_{1-z}\text{S}_4$  were investigated, respectively. By simply utilizing one-step  $\text{Ar}^+$  bombardment process, nanotip arrays can be formed with controllable lengths and tilting orientations by adjusting sputter energy and  $\text{Ar}^+$  incident angles. Spectrometer reveals the nanotips arrays show a significant decrease in reflectance compared with the pristine thin film samples. XRD and Raman analysis were used to further confirm the phase of investigated materials. Detail mechanisms were proposed with help of TEM and affiliated EDX analysis in this study.

In conclusion, by applying a single manner, nanotip arrays can be formed at five kinds of materials. The length and orientation can be precisely controlled. Furthermore, mechanism has been proposed for widely application on fabrication of nanostructure arrays among other chalcopyrite series materials. We believe that our unique approach of creating nanotip arrays, including one-step fast process with free of template, can stimulate great attention not only from academic investigations but also industrial side for practical applications.

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