Large Scale Single-Crystal Cu(In,Ga)Se₂ Nanotip Arrays For High Efficiency Solar Cell

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Supporting Information

ABSTRACT: In this paper, we demonstrated direct formation of large area Cu(In,Ga)Se₂ nanotip arrays (CIGS NTRs) by using one step Ar⁺ milling process without template. By controlling milling time and incident angles, the length of CIGS NTRs with adjustable tilting orientations can be precisely controlled. Formation criteria of these CIGS NTRs have been discussed in terms of surface curvature, multiple components, and crystal quality, resulting in a highly anisotropic milling effect. The CIGS NTRs have very low reflectance <0.1% at incident wavelengths between 300 to 1200 nm. Open circuit voltage and short circuit current of CIGS NTRs solar cell were measured to be ∼390 mV and ∼22.56 mA/cm², yielding the filling factor and the efficiency of 59 and 5.2%, respectively. In contrast to CIGS thin film solar cell with efficiency of 3.2%, the nanostructured CIGS NTRs can have efficiency enhancement of ∼160% due to the higher light absorption ability because of the nanostructure. The merits of current approach include the latest way via template-free direct creating process of nanostructured CIGS NTRs with controllable dimensionality and large scale production without post-selenization process.

KEYWORDS: Cu(In,Ga)Se₂ nanotip arrays, milling process, post-selenization, solar cell

Solar cells have drawn much attention as one of the most promising candidates for renewable clean energy. Solar cells can be roughly divided into bulk and thin film devices in terms of their structures.⁵ For bulk devices, silicon-based materials, including single and polycrystalline structures, which are the leading materials, have been extensively studied. However, drawbacks such as indirect bandgap and poor light absorption could result in poor efficiency for Si-based solar cells. Among all solar materials, Cu(In,Ga)Se₂ (CIGS) is the most promising material owing to its excellent light trapping ability, broadband light absorption, and environment-friendly manufacturing processes.³⁻⁵ Up to the present time, several approaches have been demonstrated to boost light-to-electricity efficiency of CIGS thin film solar cell, including double bandgap grading engineering,⁶ control of CIGS orientations from (112) to (220)/(204),⁷ and precisely compositional control of CIGS with different bandgaps.⁷ An alternative to further improve solar efficiency will highly rely on creation of nanostructure in CIGS thin film because of the broadband and omnidirectional light-harvesting characteristics, which can particularly enable higher electron–hole pairs (EPHs), shorter carrier diffusion length, and lower reflectance of device surface, thereby achieving the highest device efficiency.⁸

In the past decade, many techniques have been developed to create different nanostructured arrays for solar cell devices, including growth of II–VI semiconductor nanopillar arrays from highly periodic anodic alumina membranes (AAMs),⁹ epitaxial growth of nanowire arrays from lattice matched substrate,⁹ and chemical/physical etching or deposition on patterned substrate.¹⁰ However, they are limited by the impracticality for mass production in large area. In this paper, we demonstrate a low-cost, template-free and nontoxic in mass production to fabricate large area and uniform CIGS nanostructures, especially CIGS nanotip arrays (NTRs), from CIGS thin films (TF) via direct sputtering of CIGS target without post-selenization process, which enables the exploration of a new field on the nanostructured CIGS solar cell. Conventionally, the CIGS TF solar cells have been fabricated via a number of vacuum and nonvacuum processes, including coevaporation,⁶ sputtering with post-selenization,¹¹ and electrochemical deposition with post selenization.¹² However, they are suffering from several critical obstacles to meet the commercial demands for larger area and higher throughput. To achieve these goals, our CIGS TF was prepared by direct sputtering of a quaternary CIGS target, providing advantages of mass production, large area process, low cost, and high production yield (see Methods in Supporting Information).¹³

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The schematic for the process to create directly CIGS NTRs is shown in Figures 1a and 1b. Ion milling system with 4-in. working area was used for creating CIGS NTRs with adjustable incident angles from 90° to 15° under an accelerated voltage of 0.3 kV in a vacuum pressure of 1.2 × 10⁻⁴ Torr (see Methods Summary in Supporting Information). By applying this milling approach, we can fabricate CIGS nanostructure in large area with high throughput, depending on milling size (4 in. substrate size for our ion miller). Figure 1c shows an optical image of as-grown CIGS TF sample with 2 × 2 cm² before and after milling, demonstrating the capability of larger area and high throughout production. Figure 1d,e shows the scanning electron microscopy (SEM) images of a uniform CIGS/Mo layer deposited by sputtering (see Methods Summary in Supporting Information). The SEM images of the sample milled for 30 min at a normal incident angle to CIGS TF are shown in Figure 1f,g, for which uniform CIGS NTRs were formed on top of CIGS TF. Interestingly, apex angles of CIGS NTRs are controllable, depending on milling angle as shown in Figure 1h,i, providing an excellent controllability of nanostructure. In addition, the length of CIGS NTRs increases as milling time increases while a maximum length of CIGS NTRs was achieved after milling time of 30 min (see Supporting Information, Figure S1a). All samples are still of CIGS phase while obvious Cu segregation from CIGS NTRs can be observed once milling time exceeds 30 min at all milling angles (Supporting Information Figure S1b,c).

To shed light on crystalline quality of the CIGS NTRs, transmission electron microscope (TEM) observations are imperative. Figure 2a,b shows the cross-section TEM images of CIGS TF before and after Ar⁺ milling process with an incident angle of 90° for 10 min. The CIGS TF with columnar structure induced

Figure 1. (a,b) Schematic of fabricating CIGS NTRs under ion milling process. (c) The corresponding optical images of CIGS samples before and after ion milling processes. Sample size was set at 2 × 2 cm² while the milling area can be as large as 4 in. in size. The milling angle is set at 90° with milling time of 30 min. (d,e) The cross-section and planar SEM images of as-sputtered CIGS thin film. (f,g) The cross-section and planar SEM images of the CIGS thin film after ion milling at 90° for 30 min. By tilting of milling angles at (h) 45° and (i) 15°, CIGS NTRs exhibited different orientations. Insets in (h) and (i) show the cross-section SEM images of milled CIGS samples. The milling time was set at 30 min.

Figure 2. (a–d) Transmission electron microscopy (TEM) images of CIGS TF, CIGS NTRs obtained with milling angles of 90° and 45° at milling time from 10 to 60 min, respectively. Insets in (a–c) show the corresponding high-resolution TEM images and selected area diffraction patterns, indicating the single crystalline nature. The zone axis was indexed to be [201] for all CIGS thin film and CIGS NTRs. The compositional information was analyzed by energy dispersive spectroscopy in TEM for CIGS TF samples (a) with milling and after milling at (b) 10°, (c) 30°, and (d) 60° at different angles. Compositions at each point from a–o are listed in Table 1.
by the sputtering process can be confirmed while vertical CIGS NTRs can be clearly observed after Ar⁺ milling process. Insets in Figure 2a,b shows the corresponding high-resolution TEM images and selected area diffraction (SAD) patterns, indicating the single-crystalline feature after milling process. The examinations on compositional distribution of CIGS TF samples before and after ion milling at different milling angles with different milling times of 10 to 60 min are illustrated in Figure 2a–d and the corresponding quantitatively compositional results at points a–o were collected in Table 1. For CIGS thin film, the atomic concentrations of Cu, (In, Ga), and Se are in average to be ~25, ~31, and ~44 at %, respectively, which match well with desired phase of CIGS.14 However, the high concentration Cu (~50 at %) owing to Cu segregation, secondary phase, or formation of Cu-rich CIGS phase can be found around the tip region, which is consistent with XRD results with milling time over 30 min, even at different milling angles. (See Supporting Information, Figure S1b,c).

To unveil the detailed growth mechanism of CIGS NTRs via ion milling process, samples were milled for different periods of time. Examples are shown in Figure 3a–c. The CIGS nanoparticles are initially formed after 2 min milling while the CIGS NTRs are formed after milling time extended to 10 min. In a previous study, the self-formation of ordered nanoparticles can be achieved via ion milling process, which is explained by the Bradley-Harper (BH) model in terms of a compensation between surface curvature and sputtering yield.15 The surface curvature mainly depend on the intrinsic surface roughness determined by crystalline quality and grain orientation while the surface diffusion smoothen the surface.16 Once Ar⁺ ions with high energy milling the surface of CIGS TF, Cu, In, Ga, and Se atoms will be sputtered away from the surface of the CIGS TF with different sputtering yields, which can be roughly estimated to be in the order of Ga > Se > In > Cu by taking the case of multicompositional elements inside CIGS into consideration.16 Therefore, a possible growth model of CIGS NTRs is schematically illustrated in Figure 3d. The rough surface of CIGS TF with different surface curvature and different sputtering yield of multicomponent induce nucleation sites for the formation of CIGS NTRs at initial milling stage, resulting in the highly Cu-rich CIGS region around the tip as shown in Figure 3b,d. The highly Cu-rich CIGS regions around the tip were also confirmed by Auger mapping via Auger electron spectroscopy (Supporting Information Figure S2). These highly Cu-rich CIGS nucleation sites, which are more resistant to ion milling than other regions, become a self-mask and lead to unequal milling rate around CIGS tip region, namely, anisotropic milling effect (inset in Figure 3d). Accordingly, sharp CIGS cones can be formed as shown in Figure 3c,d. In addition, the morphology of CIGS NTRs is also another factor to alter sputtering yield. The higher the curvature region (sharp cone region) is, the lower the sputtering yield of surface is, which explains the increasing length of CIGS NTRs with the milling time.17 However, the length of CIGS NTRs decreases for milling more than 30 min. The reason is due to the continuous removal of high Cu-rich CIGS NTRs surface by high energy Ar⁺ with prolonged milling time (see Supporting Information Figure S1a). In addition to surface curvature and different sputtering yield, the crystal quality of CIGS film was also found to significantly influence the formation of CIGS NTRs. No CIGS NTRs can be formed from amorphous CIGS films while these CIGS NTRs can be achieved again once the crystal characteristics of CIGS films were changed from amorphous to polycrystalline with postannealing treatment as shown in Figure 3e,f (see the Supporting Information, Figure S3). Therefore, we can conclude the criteria for formation of CIGS NTRs by ion milling process, arising from (i) different surface curvature due to surface roughness, (ii) multiple

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<td>d</td>
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* Points a to o correspond to positions in Figure 2; at % means atomic percentage.
components, and (iii) good crystal quality, thereby enabling highly anisotropic milling effect.

Reflectance measurements were performed to characterize the optical properties of CIGS NTRs at different milling angles from 90 to 15° at a fixed milling time of 30 min, as shown in Figure 4a. The corresponding optical images are shown in the inset of Figure 4a. The minimum reflectance <0.1% for CIGS NTRs can be found at the normal milling angle with a black visual appearance while shining gray color was observed for CIGS films with reflectance of ~10%.18,19 Figure 4b shows the CIGS samples with different milling time from 10 to 60 min at the milling angle of 90°. The reflectance decreases first with the increase of milling time and increases as the milling time over 30 min. The increase can be attributed to the decreasing length of CIGS NTRs for prolonged milling time. Thus, the minimum reflectance <0.1% for CISG TF sample can be achieved after milling for 30 min. Optical image as shown in the inset of Figure 4b reveals the darkest color for CIGS TF sample after ion milling for 30 min. This remarkably low reflectance of CIGS NTRs can be attributed to cone-shaped feature of the structures and vertical orientation arising from their high surface density. To further characterize the antireflection properties, angular dependent reflectance mapping were performed on the CIGS NTRs at wavelengths from 400 to 1000 nm with different milling angles and milling time as shown in Figures 4c–f. The reflectance spectra were recorded with incident angle varied from −60° to 60° as illustrated in the inset of Figure 4c. These angular dependent mappings clearly indicate uniformly minimal reflectance of CIGS NTRs at milling angle of 90° for 30 min (Supporting Information Figure S4a–c) while reflectance increases again with more than 30 min milling time (Supporting Information Figure S4d–f).

The observed reflectance behavior is attributed to a concept of gradual refractive index that has been theoretically and experimentally demonstrated by several research groups with tapered or conical-shaped vertical structures.20,21 Therefore, the large Fresnel reflection observed on planar CIGS surface due to the different refractive index mismatch between the air (n = 1) and CIGS (n = 2.8 at 620 nm) can be significantly reduced through smooth transition of refractive index from the tip to the base of the vertical CIGS NTRs.

To illuminate how the efficiency of device can be improved by CIGS NTRs, we fabricate the CIGS NTRs solar cell with
structural configuration of Al/TCO/CIGS NTRs/Mo/glass as shown in Figure 5a (see methods in Supporting Information). In brief, the KCN solution was used to effectively remove the segregated Cu, Cu-rich CIGS, and secondary phase out of CIGS NTRs. Note that the CIGS NTRs become much sharper with longer KCN wash (Supporting Information Figure S5). Subsequently, the n-type CdS buffer layer was uniformly coated by chemical bath deposition (CBD) (Supporting Information Figure S6). Obviously, very low reflectance remains after deposition of n-type CdS buffer layer (Supporting Information Figure S7). ZnO doped with Al layer, a transparent conducting oxide layer (TCO), and Al electrode were used as the transparent conductive layer and contact electrode deposited by rf sputtering and e-beam evaporation, respectively. The devices were then annealed at 250 °C for 10 min to reduce the contact problem and improve the interface qualities between CIGS NTRs and CdS buffer layer. The solar efficiency and external quantum efficiency (EQE) was measured using Keitheley 4200 under the solar simulator of AM 1.5 (100 mW/cm²) at room temperature. To optimize the efficiency of CIGS NTRs device, different KCN washing time and different thickness of n-type CdS buffer layers were investigated (Supporting Information Figures S8 and S9). As the longer time KCN washing was applied, the higher efficiency of device can be obtained while the efficiency degrades as the thickness of n-type CdS buffer layer is increased over 100 nm. The decrease of efficiency is contributed to the thicker CdS layer, resulting in higher series resistance and thus lower efficiency. Advantageously, after KCN washing for 20 min with n-type CdS buffer layer of 100 nm, the best CIGS NTRs solar cell can be achieved with an open circuit voltage ($V_{oc}$) of ~390 mV and a short circuit current ($J_{sc}$) of 22.6 mA/cm², yielding an efficiency of 5.2% with a filling factor (FF) of 59% as shown in Figure 5c. For comparison, CIGS thin film device with identical device configuration was prepared. The open circuit voltage and short circuit were measured to be 360 mV and 17.98 mA/cm² with the highest efficiency and the filling factor of 3.1 and 48%, respectively (Figure 5c). Remarkably, an enhancement of efficiency ~160% can be achieved for CIGS NTRs solar cell. To further analyze the increase of efficiency for CIGS NTRs, we measured the external quantum efficiency from 400 to 1300 nm, which provides the information on the variation of conversion efficiency for photon to electron–hole pairs (EHPs) when illuminated by a particular wavelength as shown in Figure 5d. The increased EQE response from wavelengths of 500 to 1000 nm can be attributed to the increase of effective light absorption ability to increase EHPs concentration, thereby enhancing $J_{sc}$ and FF. The improved $V_{oc}$ can be explained by the decrease of contact resistance due to the improvement of interfaces between CIGS NTRs/CdS because of the formation of interior diffusion layers, such as CdSSe layer between CdS and CIGS NTRs owing to the similar ionic radii of Cd²⁺ (0.097 nm) and Cu⁺ (0.096 nm) after annealing treatment. As a result, the significantly enhanced efficiency is attributed to vertically aligned conical structure, which has been known to have advantages over multilayer antireflector in terms of broad ranges of spectrally absorbed bandwidths at various incident angles, leading to a broadband and omnidirectional light harvesting behavior that makes CIGS NTRs as an excellent absorber layer with much thinner thickness than that of films (5.2 and 3.1% for CIGS NTRs and thin film with thickness of 1.7 and 2.7 μm, respectively).

In the future, a great deal of works are needed to further improve the quality of CIGS film from the present one-step sputtering of quaternary CIGS target without postselenization process, such as control of (220)/(204) preferred orientation with desired compositions, reduction of secondary phase, control of Na concentration, and modification of bandgap gradient to better benchmark efficiency than that of coevaporation process. In addition, materials and device optimization is imperative to further enhance the efficiency. Specifically, quality of CIGS thin film, thickness of CdS layer, i-ZnO layer, and interface of CIGS NTRs require additional explorations. Although the efficiency of CIGS NTRs achieved in the present study does not match the highest
record in the world since the sputtered CIGS film was not opti-
mized, the results shown here are quite promising with sig-
nificant efficiency enhancement $\sim 160\%$ after formation of CIGS NTRs. With optimized postannealing processes, such as anneal-
ing the as-milled CIGS NTRs before CdS deposition or deposit
insulating layer onto as-milled CIGS NTRs for minimizing
current leakage path. The merits of current approach include
the latest developments via template-free direct fabrication
process of nanostructured CIGS NTRs with controllable di-
menionality and large scale production without postseleniza-
tion process.

In summary, a direct formation of large area Cu(In,Ga)Se$_2$

 nanotip arrays (CIGS NTRs) by using one step Ar$^+$ milling

 process without template was demonstrated. The length of CIGS

 NTRs with adjustable tilting orientations can be precisely con-
trolled by controlling milling time and incident angles. Forma-
tion criteria of these CIGS NTRs have been discussed in terms of

surface curvature, multiple components, and crystal quality,

resulting in a highly anisotropic milling effect. The CIGS NTRs

have very low reflectance $<0.1\%$ at incident wavelengths between

300 to 1200 nm. Open circuit voltage and short circuit current of

CIGS NTRs solar cell were measured to be $\sim 390$ mV and

$\sim 22.56$ mA/cm$^2$, yielding the filling factor and the efficiency

of 59 and 5.2%, respectively. In contrast to CIGS thin film solar

cell with efficiency of 3.2%, the nanostructured CIGS NTRs can

have efficiency enhancement of $\sim 160\%$ due to the higher light

absorption ability because of the nanostructure. The significantly

enhanced efficiency is attributed to vertically aligned conical struc-
ture, leading to a broadband and omnidirectional light harvesting

behavior that makes CIGS NTRs as an excellent absorber layer

with much thinner thickness than that of films. We believe that

our unique approach of creating CIGS NTRs, including (i) one-

step fast process free of template, (ii) easy integration with in-line

sputtering process, and (iii) no postselenezation process can

lead to further significant progress in fundamental research as

well as practical applications.

**REFERENCES**

(1) Fu, Y. P.; You, R. W.; Lew, K. K. J. Electrochem. Soc. 2009, 156,

D553–D557.

(2) Dobson, K. D.; Visoly-Fisher, I.; Hodes, G.; Cahen, D. Sol. Energy


(4) Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf, J.;


(5) Nelson, J. The physics of solar cells, Imperial College Press,


(6) Hanket, G. M.; Shafarman, W. N.; McCandless, B. E.; Birkmire,


41, 507–513.

(8) Fan, Z.; Razavi, H.; Doj; Moriwaki, A.; Ergen, O.; Chueh, Y. L.;


(10) Rayes, B. M.; Filler, M. A.; Putnam, M. C.; Kelzenberg, M. D.;


451—452, 207–211.


Volobujeva, O.; Stratieva, N.; Tiwari, A. Thin Solid Films 2006,

511, 325–327.


Procceeding of the 37th IEEE Photovoltaic Specialists Conference 2011,


(14) Chang, C. H.; Davydov, A.; Stanberry, B. J.; Anderson, T. J.

Procceeding of the 25th IEEE Photovoltaic Specialists Conference 1996,


6, 2390–2395.


(18) Jia Zhu, Z. Y.; Burkhard, G. F.; Hsu, C.-M.; Connor, S. T.; Xu,

Y.; Wang, Qi; McGehee, M.; Shanhu, F.; Cui, Y. Nano Lett. 2010,

9, 279–282.

(19) Zhu, J.; Hsu, C.-M.; Yu, Z.; Shanhu, F.; Cui, Y. Nano Lett. 2010,


(20) Xi, J. Q.; Schubert, M. F.; Kim, J. K.; Schubert, E. F.; Chen, M.;


(21) Huang, Y. F.; Chattopadhyay, S.; Jen, Y. J.; Peng, C. Y.; Liu,

T. A.; Hsu, Y. K.; Fan, C. L.; Lo, H. C.; Hsu, C. H.; Chang, T. H.; Lee,


(22) Repins, I.; Glynn, S.; Duenow, J.; Coutts, T. J.; Metzger, W. K.;
