Supplementary Information

for

Controlled synthesis of (*hk*1) preferentially oriented Sb_2Se_3 rod arrays by co-evaporation for photovoltaic applications

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S1. Four steps of cluster growth by the diffusion of the adsorbed atoms

Firstly, the characteristics of the evaporated atom flux is affected by several factors, such as the source evaporation rate (source temperature), distance between the source and substrate, chamber pressure, and chamber gas composition [S1].

Secondly, the adsorption rate on the substrate surface is given by Eq. S1[S1]:

$$r_{ads} = \frac{(N_s - N_a)}{N_s} \alpha r_m \quad \text{(Eq. S1)}$$

where r_m is the mass transfer rate, α is the accommodation coefficient, and N_s and N_a are the numbers of surface sites per unit area and occupied area, respectively. In our case, r_m will be applied as a constant because the source temperature is kept constant.

Thirdly, the desorption rate from the substrate surface is given by Eq. S2[S1]:

$$r_{des} = v_o exp(-\frac{\Delta G_{des}}{k_b T_S}) N_a \quad \text{(Eq. S2)}$$

where v_o, k_B, T, ΔG_{des} are the bulk vibration frequency (10^{13} Hz), Boltzmann constant, substrate temperature (K), and Gibbs free energy for desorption, respectively. As the substrate temperature increases, the desorption rate increases.
Fourth, the surface diffusion coefficients of the adsorbed atoms during residency can be given by Eq. S3[S1]:

$$D_{surf} \propto v_o exp(\frac{-\Delta G_{surf.diff}}{k_B T_S}) \quad \text{(Eq. S3)}$$

where $\Delta G_{surf.diff}$ is the Gibbs free energy for the surface diffusion of an adsorbed atom. As the substrate temperature increases, the surface diffusion coefficient increases.

The density of stable nuclei can be given by Eq. S4[S2]:

$$N^* = n_s exp(\frac{-\Delta G^*}{k_B T_S}) \quad \text{(Eq. S4)}$$

where n_s is the total nucleation site density, and ΔG^* is the Gibbs free energy at the critical radius of the nuclei.

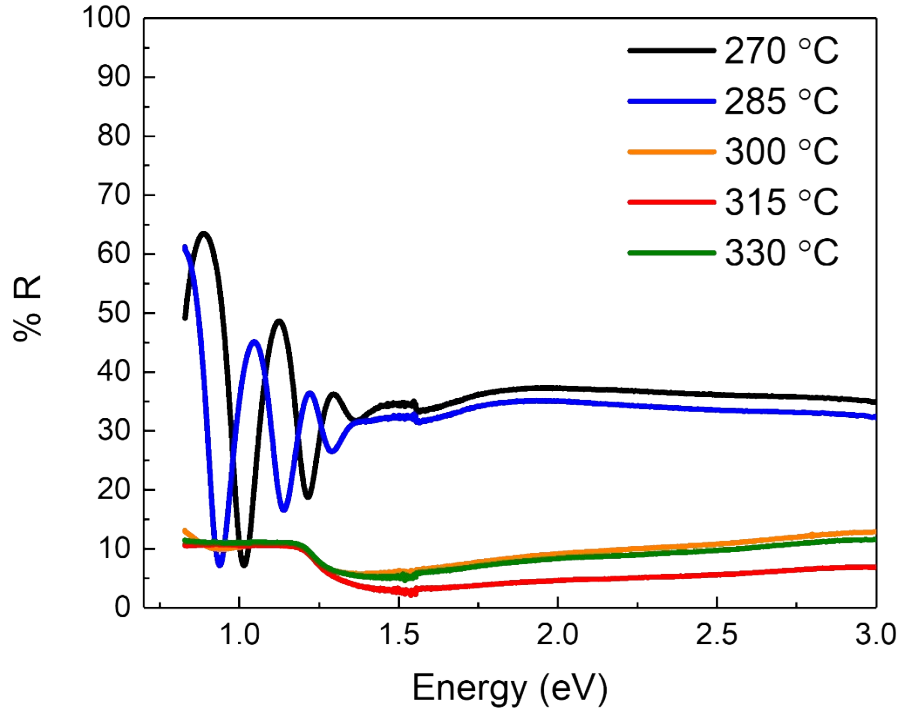

Figure S1. Reflectance of Sb_2Se_3 films grown at 270, 285, 300, 315, and 330 ℃ of substrate temperature.

We investigated the reflectance and photovoltaic properties, but it was difficult to distinguish the contribution of each factor. When comparing samples prepared at 270 ℃ and 315℃, it seems that the J_{SC} increase and the reflectance decrease are about 20%, respectively. As a result, it may be thought that J_{SC} is improved by a scattering effect. However, when comparing the 300 ℃ and the 315 ℃ samples, 25% of the J_{SC} difference exists while there is little reflectance difference. That is, in this case, the effect of scattering effect on the J_{SC} increase is negligible. As a result, in view of the J_{SC} increase and reflectance curves tendency of each sample, the three-dimensional p-n junction effect seems to contribute more to the J_{SC} improvement than the scattering effect.

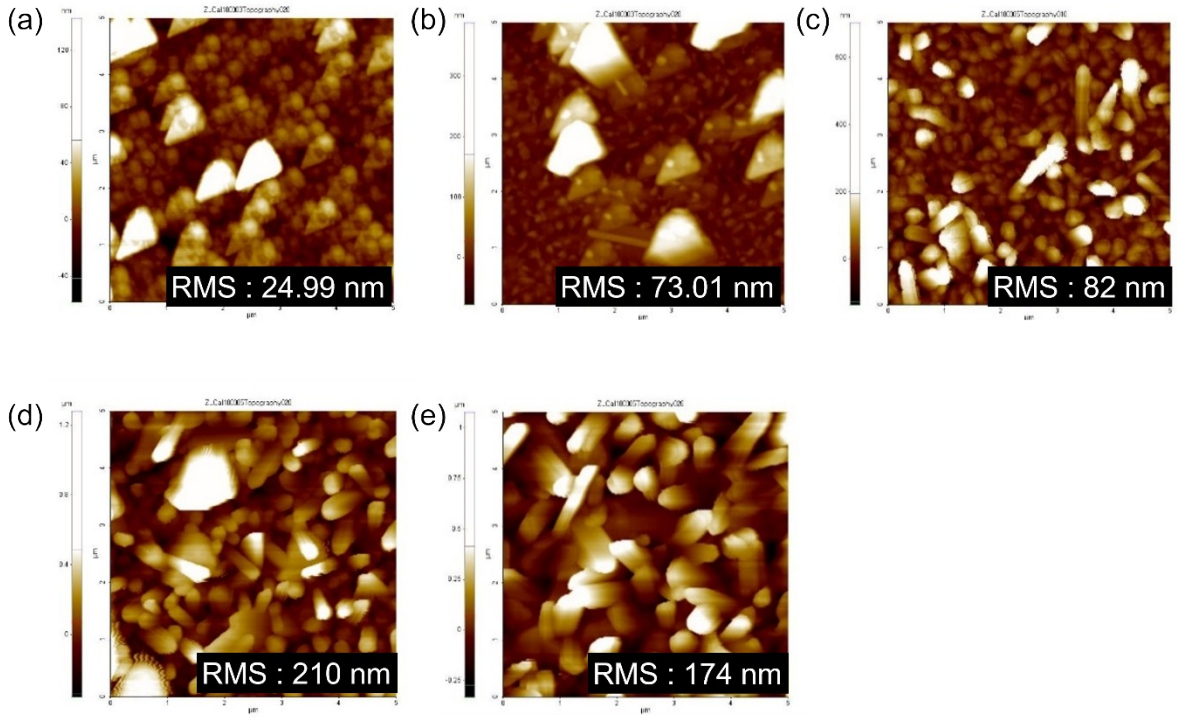

Figure S2. Film morphology (AFM measurement) of Sb_2Se_3 films grown at (a) 270, (b) 285, (c) 300, (d) 315, and (e) 330 ℃ of substrate temperature.

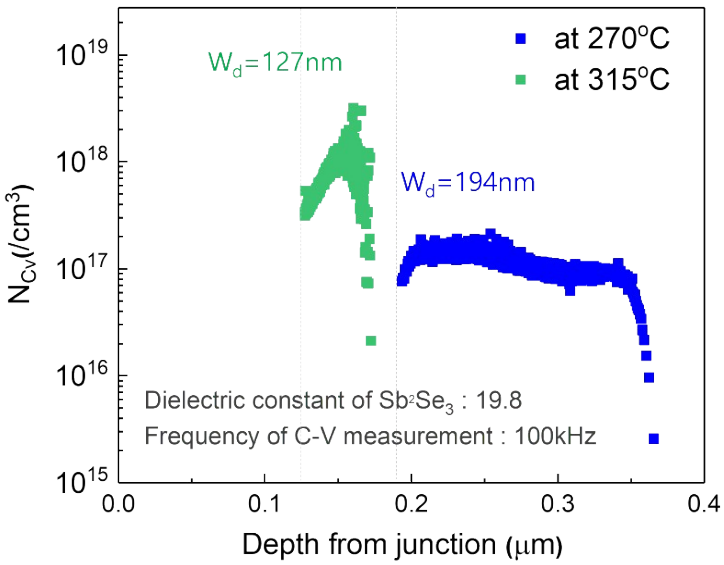

Figure S3: Capacitance–voltage measurements of the Sb_2Se_3 devices synthesized at 270 and 315 °C.

Depth profile of the charge density ($N_{C\text{-}V}$) as shown in Figure S4 can be obtained by measuring the capacitance–voltage (C-V) at RT following the expressions [S3]:

$$N_{C\text{-}V}(W) = 2/q\varepsilon_0\varepsilon_S\,[d/dV\,(1/C^2)^{-1}] \qquad \text{(Eq. S5)}$$

$$W(V) = \varepsilon_0\varepsilon_S/C(V) \qquad \text{(Eq. S6)}$$

where, W, q, ε_0, ε_S, and C denote the depletion width, elementary charge, di-electric constant, and unit area junction capacitance, respectively.

In our experiments, as a result of C-V measurement conducted at frequency of 100kHz condition, the depletion widths of flat and nano rod films were calculated to be about 193 and 127 nm, respectively, when dielectric constant of Sb_2Se_3 was adapted as 19.8 [S4,S5]; the dielectric constant of Sb_2Se_3 decease when frequency increase, and about 19.8 of dielectric constant was obtained at 100kHz frequency [S4]. Based on the result of C-V measurement, it was found that 193nm is the depletion width in the Sb_2Se_3 flat film having 550nm thickness, thus the remaining 257nm is the area where the photogenerated carrier collects by diffusion [S4]. On the other hand, since the depletion width is 127nm in the Sb_2Se_3 rod array device, it can be seen that most of the volume of the rod is included in the depletion width; the rod width is under about 200nm.

Reference

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