

## Influence of Nano-particles on Multi-hollow Discharge Plasmas for Microcrystalline Silicon Thin Film Deposition

微結晶シリコン薄膜作製用マルチホロー放電プラズマに対する  
ナノ粒子の影響

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Effects of nano-particles on formation kinetics of microcrystalline silicon films were studied by X-ray diffraction spectroscopy (XRD) and optical emission spectroscopy (OES). Volume fraction of (220) orientation crystals of films without incorporating nano-particles is higher than that of those with nano-particles. The  $I_{\text{H}\alpha}/I_{\text{Si}^*}$  value in the region with nano-particles is slightly higher than that in the region without nano-particles. The  $I_{\text{Si}^*}/I_{\text{SiH}^*}$  value is almost the same as that in the region with and without nano-particles. These results suggest that (220) orientation crystal growth is suppressed by incorporation of nano-particles.

### 1. Introduction

Hydrogenated microcrystalline silicon ( $\mu\text{c-Si:H}$ ) films are key materials for development of Si thin film tandem solar cells. High-pressure depletion method has been proposed to overcome the trade-off between deposition rate and film qualities [1,2]. A good correlation of (220) preferential orientation in  $\mu\text{c-Si:H}$  films with cell efficiencies was reported [3]. However the mechanism to determine the crystalline orientation has not been clarified yet.

We have developed a multi-hollow discharge plasma CVD method by which incorporation of nano-particles formed in discharges is considerably reduced in the upstream region using gas flow that drives nano-particles toward the downstream region of the reactor [4]. To reveal effects of incorporation of nano-particles on the formation kinetics of the  $\mu\text{c-Si:H}$  films, we have deposited  $\mu\text{c-Si:H}$  films with and without nano-particles using the multi-hollow discharge plasma CVD method, and then we have measured the volume fraction of (220) crystalline orientation of films and plasma emissions. Here we report these experimental results.

### 2. Experimental setup

Combinatorial deposition of  $\mu\text{c-Si:H}$  films was carried out with a multi-hollow discharge plasma CVD reactor as shown Fig. 1.  $\text{H}_2$  dilution ratio  $R = ([\text{SiH}_4] + [\text{H}_2])/[\text{SiH}_4]$  was set to be 15, 30, 50, 100 and 300. The total pressures were 2 or 4 Torr. The peak-to-peak discharge voltage was 80 V and the discharge frequency was 60 MHz. The reactor temperature and the quartz glass substrate temperature were set to be 250°C.

Plasma emissions were measured with a spectroscop (ACTON SP2300i).

Crystallinity,  $X_C$ , and crystalline orientation were determined with a Raman spectroscop (Jasco,

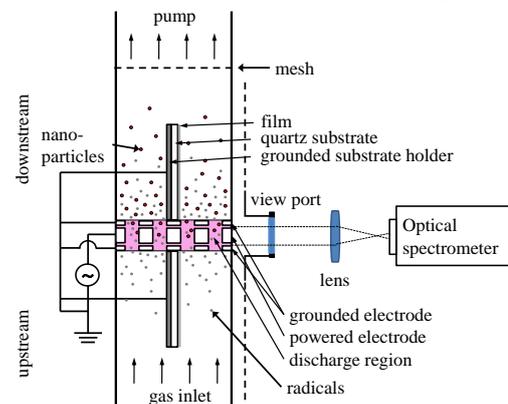


Fig. 1. Schematic of experimental setup.

NRS-3100) and an X-ray diffraction (XRD) spectrometer (Bruker, EMX), respectively. Nano-particles were trapped on a stainless mesh which is placed in the downstream region and their size and crystallinity were evaluated with a transmission electron microscope (TEM).

### 3. Results and Discussion

TEM observation of nano-particles show that their mean size is 1.2 nm and 7 nm for  $P=2$ Torr and 4Torr, respectively. They are crystalline.

Figure 2 shows dependence of the volume fraction of (220) crystalline orientation crystals of the films with and without nano-particles on the distance from the electrode. For 4Torr, the volume fraction of (220) crystalline orientation crystals of the films without nano-particles is higher than that with nano-particles. The same tendency was seen in the pressure of 2Torr. These results suggest that crystalline growth of (220) orientation is interfered by incorporating of crystalline silicon nano-particles.

Figure 3 shows dependence of emission intensity ratio from  $H_{\alpha}$  (656.3nm) and  $Si^*$ (288.1nm)  $I_{H\alpha}/I_{Si^*}$  on  $H_2$  dilution ratio  $R$ . The  $I_{H\alpha}/I_{Si^*}$  increases with increasing  $R$  and the value in the downstream

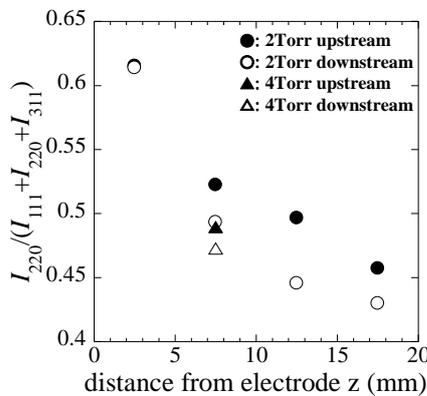


Fig. 2. Dependence of volume fraction of (220) crystalline orientation  $\mu c$ -Si:H films on the distance from electrode. Condition:  $H_2$  dilution ratio  $R=300$ .

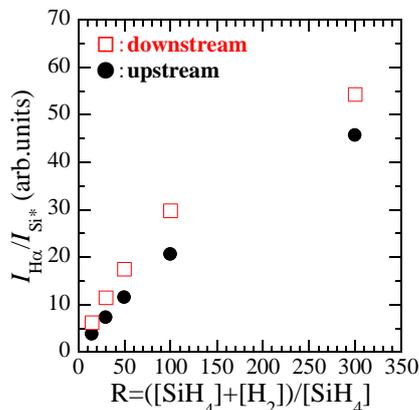


Fig. 3. Dependence of  $I_{H\alpha}/I_{Si^*}$  on the  $H_2$  dilution ratio  $R$ .

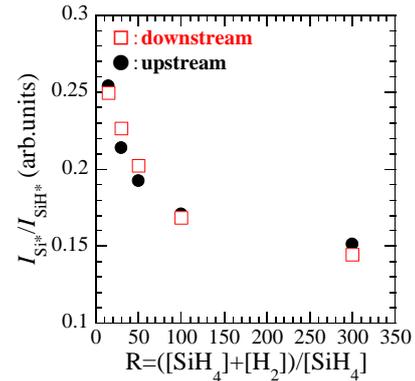


Fig. 4. Dependence of  $I_{Si^*}/I_{SiH^*}$  on the  $H_2$  dilution ratio  $R$ .

region is higher than that in the upstream region. The  $I_{H\alpha}/I_{Si^*}$  shows the generation rate ratio of the H and  $SiH_x$  radicals. The higher density ratio of  $[H]/[SiH_3]$  is preferable for crystalline formation. These results suggest that higher crystallinity films are obtained in downstream region. Figure 4 shows dependence of intensity ratio from  $Si^*$ (288.1nm) and  $SiH^*$ (414.0nm)  $I_{Si^*}/I_{SiH^*}$  on  $H_2$  dilution ratio  $R$ . The  $I_{Si^*}/I_{SiH^*}$  gives information on the electron temperature  $T_e$ . The ratio  $I_{Si^*}/I_{SiH^*}$  decreases with increasing  $R$ . The ratio in the upstream region is almost the same as that in the downstream region. Therefore, the electron temperature in the upstream region is almost the same as that in the downstream region.

### 4. Conclusions

We have measured the volume fraction of (220) crystalline orientation crystals of  $\mu c$ -Si:H thin films with and without nano-particles deposited by the multi-hollow discharge plasma CVD method. The (220) orientation of the films without nano-particles is higher than those with nano-particles. These results suggest that incorporation of nano-particles tends to suppress (220) orientation crystal growth.

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