

## Research Article

# Effect of the CO<sub>2</sub>/SiH<sub>4</sub> Ratio in the p-μc-SiO:H Emitter Layer on the Performance of Crystalline Silicon Heterojunction Solar Cells

Jaran Sritharathikhun,<sup>1</sup> Taweevat Krajangsang,<sup>1</sup>  
Apichan Moollakorn,<sup>1</sup> Sorapong Inthisang,<sup>1</sup> Amornrat Limmanee,<sup>1</sup>  
Aswin Hongsington,<sup>1</sup> Nattaphong Boriraksantikul,<sup>2</sup> Tianchai Taratiwat,<sup>2</sup>  
Nirod Akarapanjavit,<sup>2</sup> and Kobsak Sriprapha<sup>1</sup>

<sup>1</sup> Solar Energy Technology Laboratory, National Electronics and Computer Technology Center, 112 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

<sup>2</sup> PTT Research & Technology Institute, PTT Public Company Limited, 70 Moo 2 Phahonyothin Road, Sanubtup, Wangnoi, Ayutthaya 13170, Thailand

Correspondence should be addressed to Jaran Sritharathikhun; [jaran.sritharathikhun@nectec.or.th](mailto:jaran.sritharathikhun@nectec.or.th)

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This paper reports the preparation of wide gap p-type hydrogenated microcrystalline silicon oxide (p-μc-SiO:H) films using a 40 MHz very high frequency plasma enhanced chemical vapor deposition technique. The reported work focused on the effects of the CO<sub>2</sub>/SiH<sub>4</sub> ratio on the properties of p-μc-SiO:H films and the effectiveness of the films as an emitter layer of crystalline silicon heterojunction (c-Si-HJ) solar cells. A p-μc-SiO:H film with a wide optical band gap ( $E_{04}$ ), 2.1 eV, can be obtained by increasing the CO<sub>2</sub>/SiH<sub>4</sub> ratio; however, the tradeoff between  $E_{04}$  and dark conductivity must be considered. The CO<sub>2</sub>/SiH<sub>4</sub> ratio of the p-μc-SiO:H emitter layer also significantly affects the performance of the solar cells. Compared to the cell using p-μc-Si:H (CO<sub>2</sub>/SiH<sub>4</sub> = 0), the cell with the p-μc-SiO:H emitter layer performs more efficiently. We have achieved the highest efficiency of 18.3% with an open-circuit voltage ( $V_{oc}$ ) of 692 mV from the cell using the p-μc-SiO:H layer. The enhancement in the  $V_{oc}$  and the efficiency of the solar cells verified the potential of the p-μc-SiO:H films for use as the emitter layer in c-Si-HJ solar cells.

## 1. Introduction

The crystalline silicon heterojunction (c-Si-HJ) solar cell with a thin intrinsic hydrogenated amorphous silicon (i-a-Si:H) layer is attracting increasing attention in photovoltaic research because it exhibits a higher conversion efficiency, lower temperature coefficient (TC), and potentially lower process cost compared to a conventional c-Si solar cell [1, 2]. Optical losses, such as reflection loss, absorption loss, and metallic shading loss, occur at the front side of the c-Si HJ solar cells. The high absorption coefficient of a-Si:H leads to high absorption in these thin layers, which eventually results in a decrease of short circuit current density ( $J_{sc}$ ) and solar cell performance. Thus, the absorption loss due to the

doped and a-Si:H layers at the front side, which perform as an emitter layer, is one of main issues to address for future cell improvement. Hydrogenated silicon oxide material is a good candidate for use as the emitter layer because it has a wide band gap and excellent passivation quality [3–6]. Moreover, doped silicon oxide films also exhibit a relatively high conductivity that is suitable for solar cell applications. Many researchers have developed doped amorphous silicon of n- and p-type (a-SiO:H) with a combination with i-a-Si:H to form an emitter layer on a p- and n-type wafer [7, 8], respectively. Hydrogenated microcrystalline silicon oxide (μc-SiO:H), which exhibits better electrical properties and lower optical absorption coefficients than a-Si:H, is also of interest and has high potential for use as the emitter layer [9].

The combination of the doped  $\mu$ -c-SiO:H and i-a-SiO:H layers for use as the emitter layer of the c-Si-HJ solar cell is attractive and worth investigating. Although the use of the p- $\mu$ -c-SiO:H in combination with i-a-SiO:H has been previously reported [10], there have only been a few reports of its use; moreover, there is still much room for the future optimization of this p- $\mu$ -c-SiO:H emitter layer for c-Si-HJ solar cell applications.

In this paper, we report the properties of the p- $\mu$ -c-SiO:H films and their performance as the emitter layer of c-Si-HJ solar cells with respect to the effects of the  $\text{CO}_2/\text{SiH}_4$  ratio. The changes in the photovoltaic parameters and quantum efficiency (QE) with a variation in the  $\text{CO}_2/\text{SiH}_4$  ratio for the p- $\mu$ -c-SiO:H depositions are discussed.

## 2. Experiments

**2.1. Deposition of p- $\mu$ -c-SiO:H Films.** The p- $\mu$ -c-SiO:H films were deposited onto soda-lime glass substrates using the 40 MHz very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) technique. Silane ( $\text{SiH}_4$ ), hydrogen ( $\text{H}_2$ ), and carbon dioxide ( $\text{CO}_2$ ) gases were used as reactant gases and 3%-hydrogen-diluted trimethylboron (TMB:B ( $\text{CH}_3$ )<sub>3</sub>) was used as a dopant gas. The  $\text{CO}_2/\text{SiH}_4$  ratio was varied between 0 and 0.5, while the deposition temperature, pressure, and power density were kept at 180°C, 500 mTorr, and 83 mW/cm<sup>2</sup>, respectively. The thickness of the films was kept at approximately 100 nm.

The dark conductivity ( $\sigma_d$ ) and activation energy ( $E_a$ ) of the films were measured in a coplanar configuration using an Al electrode. The optical properties and thickness of the films were evaluated by spectroscopic ellipsometry. Fourier transform infrared (FTIR) spectroscopy was used to estimate the concentration of oxygen (C[O] at.%) in the films. The structural properties of the films were characterized by Raman scattering spectroscopy. The crystalline volume fraction ( $X_c$ ) is determined by using the simplified empirical relation as follows [11]:

$$X_c = \frac{(I_{510} + I_{520})}{(I_{480} + I_{510} + I_{520})}, \quad (1)$$

where  $I_{480}$ ,  $I_{510}$ , and  $I_{520}$  denote the integrated intensity corresponding to the amorphous, intermediate, and crystalline phases in the material, respectively.

**2.2. Fabrication of Heterojunction Solar Cells.** c-Si-HJ solar cells with a structure of Al/Ag/ITO/p- $\mu$ -c-SiO:H/i-a-SiO:H/n-c-Si [Float Zone (FZ), 200  $\mu\text{m}$ , 3  $\Omega\text{cm}$ , (100)]/i-a-SiO:H/n-a-Si:H/Ag/Al and total cell area of 1 cm<sup>2</sup> (active area of 0.96 cm<sup>2</sup>) were fabricated. The schematic diagram of the c-Si-HJ solar cells is shown in Figure 1. We deposited the p- $\mu$ -c-SiO:H layer at a different  $\text{CO}_2/\text{SiH}_4$  ratio to investigate its performance as the emitter layer of the c-Si-HJ solar cells. Prior to the deposition of the Si:H alloy layers, the wafers were cleaned in ethanol and acetone ultrasonically for 10 min each (ethanol/acetone/ethanol) and then dipped in HF (5%) to remove the native oxide. The i-a-SiO:H and n-a-Si:H layers were prepared using the 60 MHz VHF-PECVD technique to thicknesses of approximately 5 nm and 30 nm,

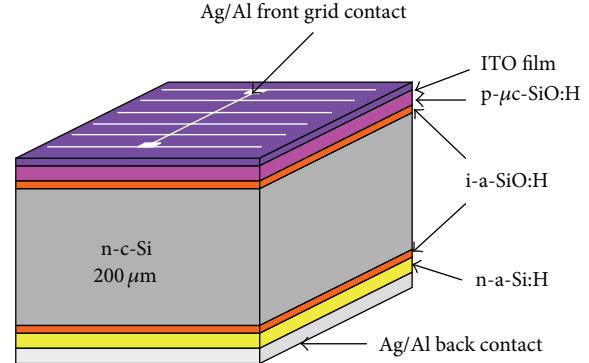


FIGURE 1: Schematic diagram of c-Si-HJ solar cells.

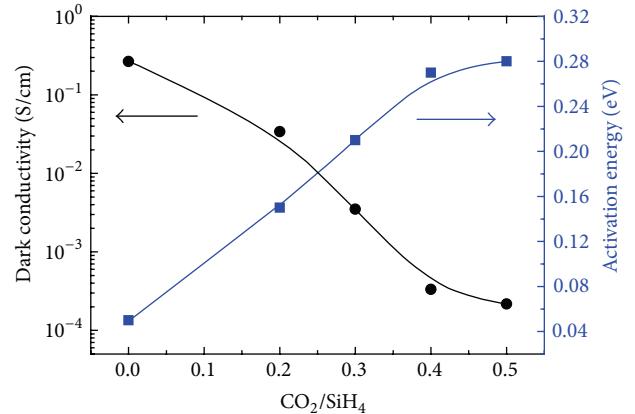


FIGURE 2: Dark conductivity ( $\sigma_d$ ) (indicated by ●) and activation energy ( $E_a$ ) (indicated by ■) of p- $\mu$ -c-SiO:H films as a function of the  $\text{CO}_2/\text{SiH}_4$  ratio. The lines are a guide to the eye.

respectively. The n-layer was doped by 3%-hydrogen-diluted phosphine ( $\text{PH}_3$ ). The fabrication temperature of the c-Si-HJ solar cells was kept at 180–200°C. Indium tin oxide (ITO) was deposited by RF magnetron sputtering. The front and back metal electrodes were prepared by thermal evaporation through shadow masks.

The photovoltaic parameters of the solar cells were investigated under standard test conditions (STC; AM1.5, irradiance 100 mW/cm<sup>2</sup>, and cell temperature 25°C) using a Wacom solar simulator [12]. The effective lifetime ( $\tau_{\text{eff}}$ ) of the passivated wafers was evaluated via a quasi-steady-state photoconductance (QSSPC) method (WT-120 Sinton instruments). The quantum efficiency (QE) of the solar cells was also characterized via a spectral response measurement technique.

## 3. Results and Discussions

**3.1. Effects of  $\text{CO}_2/\text{SiH}_4$  Ratio on the Properties of p- $\mu$ -c-SiO:H Films.** Figure 2 shows the  $\sigma_d$  and  $E_a$  of the p- $\mu$ -c-SiO:H films as a function of the  $\text{CO}_2/\text{SiH}_4$  ratio. It can be observed that  $\sigma_d$  decreased from  $2.7 \times 10^{-3}$  to  $2.2 \times 10^{-4}$  S/cm and that  $E_a$  increased continuously from 0.05 to 0.28 eV when the

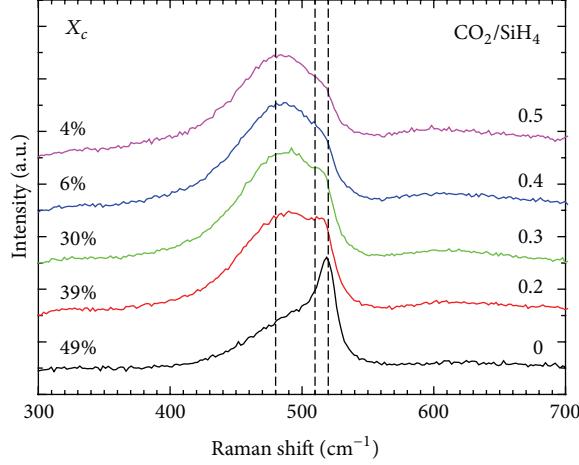


FIGURE 3: Raman spectra of p- $\mu$ c-SiO:H films with different  $\text{CO}_2/\text{SiH}_4$  ratios.

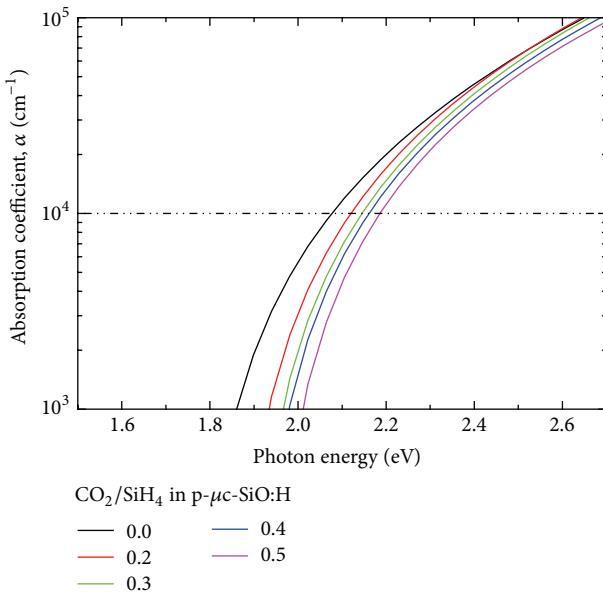


FIGURE 4: Absorption coefficient of p- $\mu$ c-SiO:H films with different  $\text{CO}_2/\text{SiH}_4$  ratios.

$\text{CO}_2/\text{SiH}_4$  ratio increased from 0.0 to 0.5. These changes are most likely due to an increase of the number of Si–O bonds in the films [13]. Figure 3 shows the Raman spectra of p- $\mu$ c-SiO:H films with different  $\text{CO}_2/\text{SiH}_4$  ratios. The crystalline volume fraction gradually reduced from 49% to 4% when the  $\text{CO}_2/\text{SiH}_4$  ratio was varied from 0.0 to 0.5 due to a phase transition from  $\mu$ c-Si(O):H to a-SiO:H.

The optical band gap ( $E_{04}$ ) (the photon energy value corresponding to an optical absorption coefficient of  $1 \times 10^4 \text{ cm}^{-1}$ ) of the p- $\mu$ c-SiO:H films was determined from absorption coefficient, as shown in Figure 4. We found that the optical absorption edges of p- $\mu$ c-SiO:H films with higher  $\text{CO}_2/\text{SiH}_4$  ratio shifted towards higher photon energy. With an increasing  $\text{CO}_2/\text{SiH}_4$  ratio, the optical band gap ( $E_{04}$ ) became wider, extending from 2.07 eV to 2.19 eV, which was

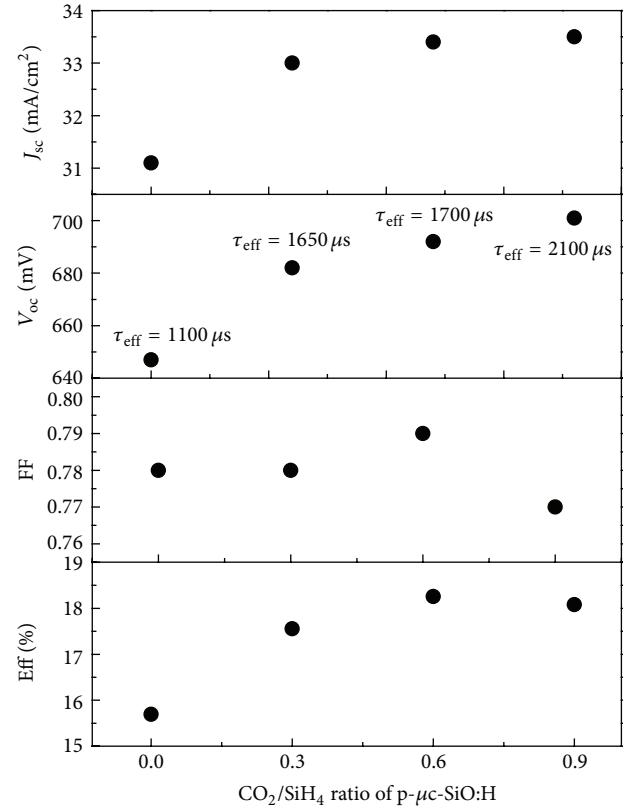


FIGURE 5: Photovoltaic parameters of the c-Si-HJ solar cells with p- $\mu$ c-SiO:H layers deposited at various  $\text{CO}_2/\text{SiH}_4$  ratios.

caused by the increased number of Si–O bonds in the SiO:H films [14, 15]. The variation of the oxygen concentration of the films was verified by the FTIR measurement. The derived oxygen concentration ranges between 0.5 at.% and 14.5 at.%, corresponding to the  $\text{CO}_2/\text{SiH}_4$  ranging from 0.0 to 0.5. According to the results, it is obvious that the  $\text{CO}_2/\text{SiH}_4$  ratio plays an important role in enhancing the  $E_{04}$  of the p- $\mu$ c-SiO:H films; however, a tradeoff between  $E_{04}$  and  $\sigma_d$  must be considered when the films are optimized for device fabrication.

**3.2. Effect of the  $\text{CO}_2/\text{SiH}_4$  Ratio in the p- $\mu$ c-SiO:H Emitter Layers on the Performance of c-Si-HJ Solar Cells.** To optimize the properties of the p- $\mu$ c-SiO:H as an emitter layer, we fabricated c-Si-HJ solar cells with the p layers deposited at various  $\text{CO}_2/\text{SiH}_4$  ratios. Figure 5 shows the photovoltaic parameters of the c-Si-HJ solar cells with the p- $\mu$ c-SiO:H layer deposited at various  $\text{CO}_2/\text{SiH}_4$  ratios, together with  $\tau_{\text{eff}}$  of solar cells, which was measured before the ITO layer deposition. The  $\text{CO}_2/\text{SiH}_4$  ratio for the p- $\mu$ c-SiO:H deposition was varied from 0.0 to 0.90, while the thickness of the film was fixed at approximately 25 nm. It is obvious that the  $\text{CO}_2/\text{SiH}_4$  ratio in p-layer strongly affects the c-Si-HJ solar cell performance. With an increasing  $\text{CO}_2/\text{SiH}_4$  ratio, the  $V_{\text{oc}}$  of solar cells increased from 647 mV to 701 mV, agreeing well with the enhancement of the  $\tau_{\text{eff}}$  from 1100 to 2100  $\mu$ s. This result clearly verified the excellent passivation quality of the

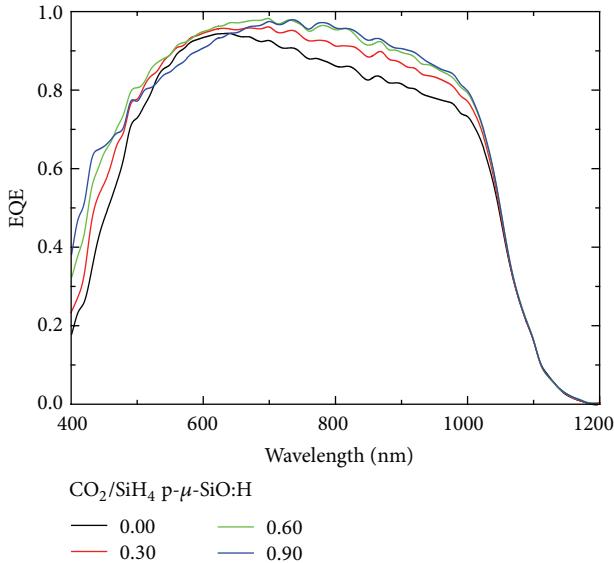


FIGURE 6: EQE of c-Si-HJ solar cells with various CO<sub>2</sub>/SiH<sub>4</sub> ratios for the p- $\mu$ c-SiO:H layer.

p- $\mu$ c-SiO:H emitter layer. However, the use of an emitter layer with a value of the CO<sub>2</sub>/SiH<sub>4</sub> ratio that was higher than 0.6 obviously caused a reduction of the FF due to an increase in the series resistance of the solar cells. The drop of the FF at high CO<sub>2</sub>/SiH<sub>4</sub> ratio led to a reduction of the cell efficiency.

The  $J_{sc}$  enhanced from 31.1 to 33.5 mA/cm<sup>2</sup> with an increasing CO<sub>2</sub>/SiH<sub>4</sub> ratio, which was due to the increase of the  $E_{04}$  of the p- $\mu$ c-SiO:H emitter layer. The external quantum efficiency (EQE) results shown in Figure 6 clearly indicated the enhancement of the spectral response over the entire wavelength region when the CO<sub>2</sub>/SiH<sub>4</sub> ratio for the p-layer deposition increases. These results suggest that the increase of the  $J_{sc}$  is attributed to an improvement of the optical confinement of the solar cells, which is mainly due to the properties of the p- $\mu$ c-SiO:H emitter layer. We achieved the highest efficiency of 18.3% with  $V_{oc} = 692$  mV,  $J_{sc} = 33.4$  mA/cm<sup>2</sup>, and fill factor = 0.79 (total area 1 cm<sup>2</sup>) from the cell using the p- $\mu$ c-SiO:H emitter layer. The J-V curve of the best cell is shown in Figure 7.

#### 4. Conclusions

The CO<sub>2</sub>/SiH<sub>4</sub> ratio for the p- $\mu$ c-SiO:H film plays a key role in controlling the structural, electrical, and optical properties of the films. The ratio also significantly affects performance of the c-Si-HJ solar cells when the p- $\mu$ c-SiO:H films are applied as the emitter layer. The experimental results demonstrated that the c-Si-HJ solar cells using the p- $\mu$ c-SiO:H emitter layer exhibit better performance compared to the cells using the p- $\mu$ c-Si:H layer (CO<sub>2</sub>/SiH<sub>4</sub> = 0). The improvement in the  $V_{oc}$  and the cell efficiency demonstrated the effectiveness of the p- $\mu$ c-SiO:H layer as the emitter layer of the c-Si-HJ solar cells. The highest efficiency of 18.3% with the  $V_{oc}$  of 692 mV was observed from the cell using the optimized p- $\mu$ c-SiO:H layer.

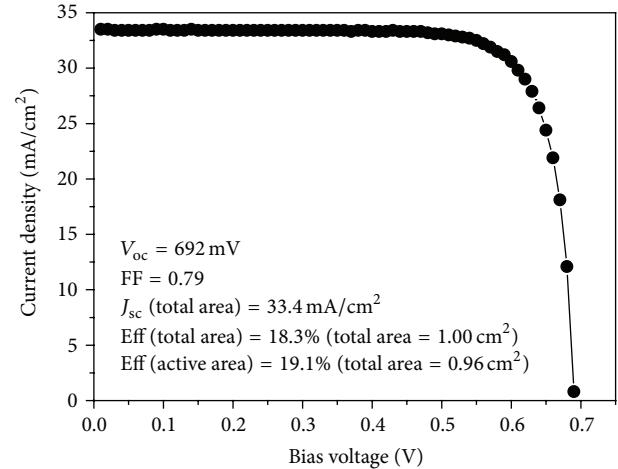


FIGURE 7: Illuminated J-V curve of the c-Si-HJ solar cell using the optimized p- $\mu$ c-SiO:H emitter layer.

Therefore, the use of the p- $\mu$ c-SiO:H can be considered to be an alternative to the p-a-Si(O):H emitter layer.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

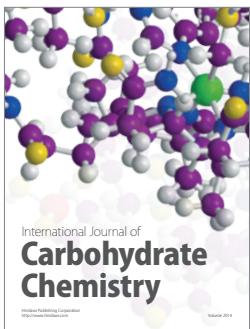
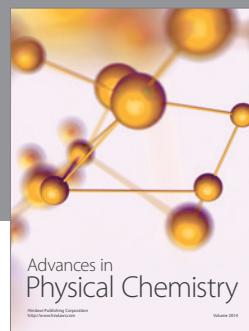
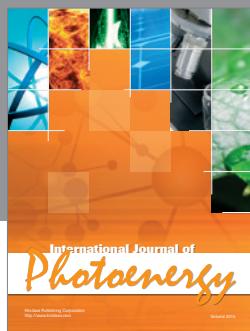
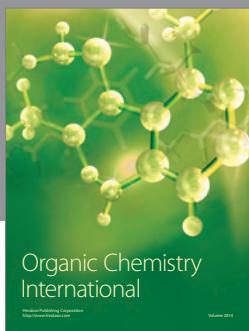
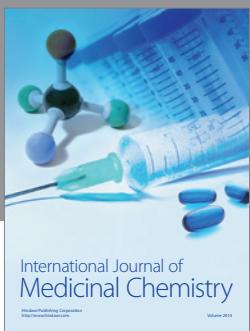
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