High-Efficiency Silicon Inverted Pyramid-Based Passivated Emitter and Rear Cells

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Abstract
Surface texturing is one of the most important techniques for improving the performance of photovoltaic (PV) device. As an appealing front texture, inverted pyramid (IP) has attracted lots of research interests due to its superior antireflection effect and structural characteristics. In this paper, we prepare high-uniform silicon (Si) IPs structures on a commercial monocrystalline silicon wafer with a standard size of 156 × 156 mm² employing the metal-assisted chemical etching (MACE) and alkali anisotropic etching technique. Combining the front IPs textures with the rear surface passivation of Al₂O₃/SiNx, we fabricate a novel Si IP-based passivated emitter and rear cell (PERC). Benefiting from the optical superiority of the optimized IPs and the improvement of electrical performance of the device, we achieve a high efficiency of 21.4% of the Si IP-based PERC, which is comparable with the average efficiency of the commercial PERC solar cells. The optimizing morphology of IP textures is the key to the improvement of the short circuit current $I_{sc}$ from 9.51 A to 9.63 A; meanwhile, simultaneous stack SiO₂/SiNx passivation for the Si IP-based n⁺ emitter and stack Al₂O₃/SiNx passivation for rear surface guarantees a high open-circuit voltage $V_{oc}$ of 0.677 V. The achievement of this high-performance PV device demonstrates a competitive texturing technique and a promising prospect for the mass production of the Si IP-based PERC.

Keywords: Si solar cell, MACE, Inverted pyramids, PERC, High-efficiency

Introduction
Improving efficiency is the eternal theme of the solar cell industry, which mainly focuses on two aspects: the optical performance and electrical performance. The front texturing technique is of importance for prompting the optical performance of the device. Inverted pyramid (IP) as an attractive light-trapping structure has attracted considerable attention due to its superior antireflection effect and structural characteristics [1–7]. To be specific, the incoming short-wavelength light in silicon (Si) IP undergoes triple or more bounces before being reflected away, possessing one or more bounces than that in traditional upright pyramids [7–9]. Meanwhile, this inverted pyramid-structured Si will avoid severe recombination losses faced by the nanostructured black Si [10–16] because of its big and open structural characteristic.

By employing the lithography inverted pyramid textures on the front surface and SiO₂ passivation of the rear surface, Green’s group [17] has successfully fabricated a 25.0% efficient passivated emitter and rear local-diffused solar cell (PERL) with an area of 4 cm². However, the lithography technique is not suitable for mass production because of its expense, low production-capacity, and incompatibility. Recently, many research interests turn to the metal-assisted chemical etching (MACE) large-area inverted pyramids since the MACE technique is simple, low-cost, large-area, and compatible with the current production line [14, 18–21]. For example, Jiang et al. [7] have reported inverted-pyramids nanostructure prepared by the MACE process followed by a post nanostructure rebuilding solution treatment and the
conversion efficiency of IPs based multi-crystalline silicon (mc-Si) solar cells in large size of 156 × 156 mm² wafers reached up to 18.62%. By utilizing Cu nanoparticles to catalyze chemical etching of Si, Yang et al. [8] have achieved 18.87% efficient IP-structured Si solar cells with a large area. Zhang et al. [9] have fabricated sc-Si solar cell with IP microstructure by modulated alkaline texturing combined with an optimized MACE method and have achieved a 20.19% efficient 1-μm-sized IP-textured device with a large area. So far, the performances of Si IP solar cell with a large area are not yet satisfied suffering from the large-area uniformity of IP morphology, the control of the IP feature size, and the passivation of the device. As a result, the front-optimized Si IP textures together with the rear passivation are expected to improve cell performance further.

In this paper, we successfully fabricated 21.4% efficiency Si IP-based passivated emitter and rear cells (PERC) with a standard solar wafer size of 156 × 156 mm² by combining the front optimized MACE IP textures with the simultaneous stack SiO₂/SiNx passivation for the Si IP-based n⁺ emitter and stack Al₂O₃/SiNx passivation for the rear surface. The key to high performance lies in the optical superiority of the IP textures and the reduced electrical losses by the simultaneous passivation of Si IP-based n⁺ emitter and rear surface. This novel Si IP-based PERC device structure and technique show a great potential in mass production of high-efficiency silicon-based solar cell.

**Methods**

The device structure of Si IP-based PERC is designed as follows: (i) The Si IP-based PERC n⁺ emitter is passivated by stack SiO₂/SiNx (PECVD) layers as shown in Fig. 1a. The Si IP textures have a good short-wavelength antireflection effect due to more opportunities of three or more bounces; meanwhile, the stack SiO₂/SiNx layer provides a further reduced reflectance and an excellent passivation effect for the Si IPs n⁺ emitter. (ii) The rear reflector is composed of stack Al₂O₃ (ALD)/SiNx (PECVD) layers and screen-printed Al as shown in Fig. 1a. Stack dielectric layers are designed to optimize the optical properties of long-wavelength by increasing inner rear reflectance while maintaining a good electrical passivation effect, which is attributed to the field-effect passivation of the fixed negative charges in Al₂O₃ layer and the chemical passivation of hydrogen atoms in SiNx film. In a word, both optical and electrical properties in this design are simultaneously considered to ensure a high performance of Si IP-based PERC.

Commercial 180-μm-thick 156 mm × 156 mm (100)-oriented crystalline silicon (c-Si), boron-doped (1–3 Ω·cm) p-type wafers were used as substrates. After the standard cleaning process, inverted pyramid textures were prepared on the surface of Si wafers as follows: (1) The cleaned Si wafers were immersed in the mixed solutions of AgNO₃(0.0001 M)/HF (4 M)/H₂O₂ (1 M) for 300 s, resulting in porous Si. (2) Si wafers with porous Si were etched in an NH₄OH:H₂O₂:H₂O = 1:1:6 (volume) solutions for 200 s to remove the residual Ag nanoparticles. (3) The wafers with porous Si were modified in an HNO₃:H₂O₂:H₂O = 4:2:1 (volume) solution to prepare nano-holes. (4) Inverted-pyramids textures were fabricated on the surface of Si wafer by anisotropic etching of 60 °C-NaOH solutions for 30, 60, and 90 s, respectively. POCl₃ diffuses for 40 min at 800 °C in the quartz tube furnace and then n⁺ emitter forms on the front of the wafer (M5111-4WL/UM, CETC 48th Research Institute). The sheet resistance of Si IP-based n⁺ emitter is 105-110 Ω·sq⁻¹. The selective emitter was fabricated on
the front surface of the wafer by laser doping (DR-SE-DY70, DR Laser). After the rear surface polished, SiO₂ passivation films were prepared by thermal oxidation on the front of silicon wafers. The Al₂O₃ passivation layers were deposited on the rear surface of wafer by ALD (PEALD-156, HUGUANG Scientific Instruments of Beijing) for \( \approx 30 \) min at 150 °C. The PECVD-SiNₓ layers were formed by the reaction of NH₄/SiH₄ (SC-TD-450C). Subsequently, the rear stack passivation layers of Si IP-based wafer were locally ablated by a 532-nm wavelength and 10-ps pulse length laser (DR-AL-Y60, DR Laser), in order to form the 50-µm width and 1-mm pitch local line openings. Finally, the Si IP-based PERC underwent the commercial screen-printing (PV1200, DEK) and co-firing process (CF-Series, Despatch), to form well Ohmic contacts and local BSFs.

The morphologies and structures of the samples were characterized with a JEOL JSM-6390LA scanning electron microscope. The lifetime of the minority carriers was measured by using a Sinton WCT-120. The absorption spectra were determined by FTIR (Tensor 27, BRUKER). The C-V curve is measured by an impedance analyzer (E4900A, KEYSIGHT). The photoluminescence and electroluminescence photos were taken by PL/EL imaging analysis system (LIS-R2, BTimaging). The reflectance spectra, as well as the IQEs and EQEs, were measured on the platform of quantum efficiency measurement (QEX10, PV Measurements). The electrical parameters of the solar cells were investigated by current-voltage (I–V) measurement under the illumination of AM1.5 (Crown Tech IVTest Station 2000). The cell efficiency was measured by using a BERGER Licht-technik Single Cell Tester.

**Results and Discussion**

Figure 2a–e shows the top-view SEM images of the different process steps for the silicon surface texturing. Figure 2a shows the 50–80 nm porous Si on the surface of Si wafer etched by MACE method in the mixed solutions of AgNO₃/HF/H₂O₂. Subsequently, the porous Si is modified by the isotropic etching in the mixed aqueous solutions containing HF/HNO₃ and turns to be nanohole structures with a diameter of 800 nm as shown in Fig. 2b. Finally, the micron inverted pyramids (IPs)
with different sizes (Fig. 2c–e) are obtained by sodium hydroxide in aqueous solution at 60 °C for 30, 60, and 90 s, respectively. From Fig. 2c–e, we can see that after alkali treatment, the IPs structure sizes for three etching time of 30, 60, and 90 s are ~1, 1.3, and 1.8 μm, respectively, meaning an increasing size of IP with the increase of alkali treatment time. Also, we notice that the IPs tend to collapse and transit to be the upright pyramids with the increase of the etching time. As known, the inverted pyramids have the advantage of light trapping over upright ones because light will undergo extra one or two bounces in inverted pyramids than that in upright pyramids. Therefore, the structures with shorter etching time are suitable for the light-trapping textures of PV devices because of the advantage in the short-wavelength antireflection. Figure 2f is the compared photos for different surface structures corresponding to Fig. 2a–e.

Now we turn to the optical properties of Si IP-strus. From the reflectance over the whole wavelength range of 300–1100 nm (Fig. 3a), we observe that the porous Si has a low reflection because of the excellent light-trapping performance of nanostructures [22–24]. For nanohole structures, the reflectance in the whole wavelength range has an obvious increase, which is attributed to the decrease of density and increase of feature size of nanoholes. After NaOH treatment for 30 s, benefiting from 3−4 bounces between the (111) planes of the IP, the IPs structures display lower reflection over the 300–1100 nm wavelength range, especially in the short-wavelength range of 300–500 nm. With the alkali etching time increasing, the IPs become larger and tend to be the upright pyramids, resulting in an increasing reflectance. When all samples were covered with the same stack SiO2/SiNx coating, the reflectance drop sharply by more than 10%, which is attributed to the combined reflectance from the optical interference of the stack SiO2/SiNx thin films and the surface structures. In this case, the reflection spectra of samples from different processes are mainly different in the wavelength range of 300–600 nm, which is caused by the difference of feature size of IPs. In particular, Si IP-strus covered by the stack SiO2/SiNx layers displays better short-wavelength antireflection ability than the others, indicating the excellent external quantum efficiencies (EQEs) in the short-wavelength range.

Furthermore, we calculate the average solar reflectivity \( R_{\text{ave}} \) (see Fig. 3b) over the wavelength range of 300–1100 nm and compare the reflectivity of Si IP-strus with other structures corresponding to different intermediate processes shown in Fig. 2a–c. \( R_{\text{ave}} \) can be calculated by the expression of

\[
R_{\text{ave}} = \frac{\int_{300\text{ nm}}^{1100\text{ nm}} R(\lambda) \cdot S(\lambda) \cdot d\lambda}{\int_{300\text{ nm}}^{1100\text{ nm}} S(\lambda) \cdot d\lambda}
\]

where \( R(\lambda) \) and \( S(\lambda) \) denote the measured reflectance and AM1.5 solar photon spectral distribution, respectively. As shown in Fig. 3b, the \( R_{\text{ave}} \)s of porous Si, nanoholes, IPs, and IPs with SiO2/SiNx coating are 8.22, 17.96, 15.18 (group 1—30 s)/17.35% (group 2—60 s)/20.3% (group 3—90 s), and 3.91% (group 1—30 s)/4.48% (group 2—60 s)/5.60% (group 3—90 s), respectively. The \( R_{\text{ave}} \)s show that the IP-strus have a better antireflection ability than nanoholes and show a decreasing trend with the increase of feature size. When IP-Strus are coated by the stack SiO2/SiNx layers, the lowest \( R_{\text{ave}} \) is 3.91%, revealing an ideal light-trapping structure for the PV device.

The stack SiO2 (~2 nm)/SiNx (~75 nm) passivation for the Si IP-based n+ emitter is an effective way for achieving well electrical performance of IP-based PERC and their passivation effect [1] and mechanism have been systematically studied in our previous work [14]. To show the electrical superiority of the stack Al2O3/SiNx passivation layers at the rear of our device, we
investigate the influence of the different annealing and light-soaking conditions on the effective minority carrier lifetime ($\tau_{\text{eff}}$) with respect to the injection level ($\Delta n$), as shown in Fig. 4a. Notice that the polished Si wafers have the bulk minority carrier lifetime of ~ 350 $\mu$s, and the stack $\text{Al}_2\text{O}_3/\text{SiN}_x$ layers are symmetrically deposited on both sides of polished Si wafers. The thickness of inner $\text{Al}_2\text{O}_3$ and the outer $\text{SiN}_x$ layer is estimated as ~ 3 and ~ 125 nm, respectively. Two annealing conditions are performed in the air atmosphere: 300 °C and 800 °C for 15 min. Then the wafers are illuminated at 25 °C under the full-wave ranged halogen lamp with a power intensity of 50 mW cm$^{-2}$ for 100 s. As can be seen from Fig. 4a, the 48 $\mu$s $\tau_{\text{eff}}$ (300 °C) and 126 $\mu$s $\tau_{\text{eff}}$ (800 °C) after annealing are much higher than the 22 $\mu$s $\tau_{\text{eff}}$ of the as-deposited $\text{Al}_2\text{O}_3/\text{SiN}_x$ passivated samples at the injection level of $1.2 \times 10^{15}$ cm$^{-3}$.

Importantly, the effective minority lifetime of annealed samples after 100 s of illumination are 230 $\mu$s and 150 $\mu$s, respectively, much higher than 126 $\mu$s and 48 $\mu$s before illumination, demonstrating a very clear light-enhanced c-Si surface passivation of $\text{Al}_2\text{O}_3/\text{SiN}_x$ layers. The charge trapping effect during light soaking [25–28] could be one of the main mechanisms for the light-enhanced c-Si surface passivation of $\text{Al}_2\text{O}_3/\text{SiN}_x$ films. As $\text{Al}_2\text{O}_3$ films are reported to have a negative fixed charge density [29–32], some of the excess electrons generated by light were likely to be injected or tunneled into trap states in the inner $\text{Al}_2\text{O}_3$ film, resulting in an increased level of field-effect passivation. Interestingly, the light-enhanced passivation effect at 300 °C annealing is better than that at 800 °C, meaning that light-soaking at a lower temperature annealing is a more effective way to the application of PV device.

To study the effect of the annealing process on the surface modification, we compare the Fourier transform infrared spectroscopic (FTIR) absorption spectra of the annealed samples with that of the as-deposition sample. Figure 4b manifests that the Si–N, Si–O, Si–H, and N–
H bonds correspond to the stretching absorption peaks at the wavenumbers of ~ 840, 1070, 2200, and 3340 cm⁻¹, respectively. We see that the densities of both the Si–N and Si–O bonds show an obvious increase after annealing; meanwhile, the density of the Si–H bonds increases slightly. The increases of the Si–O and Si–H bond density implies the decrease of the dangling bonds at the interface of Si/SiO₂, resulting in a better passivation effect [33]. Also, the annealing process promotes the density of Si–N bonds, indicating a more dense structure which can effectively prevent the out diffusion of H from entering into the environment instead of into Si bulk. However, for excessively high annealing temperature, the H in Si–H and N–H groups can escape from the bulk Si and the dielectric layers to the environment, which causes the decline of the passivation effect. The result of FTIR is consistent with that of the effective minority lifetime.

To further understand the difference of passivation mechanism between thermal annealing and light-soaking treatment, we analysis the density of fixed charges (Nᶠ) and the density of interface traps (Nᵣ) at the interface of Si and Al₂O₃ (ALD)/SiNx (PECVD) stack layers by using capacitance–voltage (C–V) measurements from a rigorous metal–oxide– semiconductor (MOS) model.

\[ N_f = \frac{Q_f}{S \times e} = \frac{C_{OX} \times (V_{MS} - V_{FB})}{S \times e} \]  

where the following expression can calculate \( V_{FB} \)

\[ V_{FB} = V_{MS} - \frac{Q_f}{C_{OX}} \]  

Note that \( S \) is the area of metal electrode, \( e \) is electronic charge, \( C_{OX} \) is the capacitance of dielectric film layer, \( V_{MS} \) is the difference of the work function between the metal electrode and p-type Si, and \( V_{FB} \) is flat band voltage.

Using the Lehovec method [34], we can obtain \( Nᵣ \) from the C–V curve:

\[ Nᵣ = \frac{(C_{OX} - C_{FB})C_{FB}}{3(\delta C/\delta V)_{FB}kTS} - \frac{C_{OX}^2}{(C_{OX} - C_{FB})Se^2} \]  

where \((\delta C/\delta V)_{FB}\) is the slope near-flat band and is taken as the absolute value, \( C_{FB} \), \( e \), and \( k \) are capacitance of MOS structure in a flat band, electronic charge, and Boltzmann constant, respectively.

It can be seen from Fig. 4c that the measured C–V curve of the Al₂O₃/SiNx stack layers shows obvious accumulation region, depletion region, and inversion region. According to the C–V curves and Eq. (2–4), we obtain the interface properties of the prepared MOS structures, as shown in Table 1.

| Sample                        | \( N_f/cm^2 \) | \( Nᵣ/cm^2/eV \) |
|-------------------------------|----------------|------------------|
| As-deposited                  | \(-4.3 \times 10^{11}\) | \(-3.89 \times 10^{11}\) |
| 300 °C annealing              | \(-2.26 \times 10^{12}\) | \(-8.59 \times 10^{11}\) |
| 300 °C annealing and light soaking | \(-2.87 \times 10^{12}\) | \(-8.68 \times 10^{11}\) |
| 800 °C annealing              | \(-1.04 \times 10^{12}\) | \(-4.32 \times 10^{11}\) |
| 800 °C annealing and light soaking | \(-1.65 \times 10^{12}\) | \(-4.65 \times 10^{11}\) |

The fixed negative charge densities show a significant increase by an order of magnitude after thermal annealing, meanwhile the interfacial states densities significantly decrease, indicating that annealing enhanced the chemical passivation and field-effect passivation of dielectric films. By further light-soaking treatment, the densities of interfacial states keep the same level, while the densities of fixed negative charges increase further. As mentioned above, some of the excess electrons generated by light were likely to be injected or tunneled into trap states in the inner Al₂O₃ film, which means that light soaking can enhance the field-effect passivation of the dielectric film. Although the value of \( Nᵣ \) is high, the sample by 300 °C annealing and 100 s light-soaking has the highest \( τ_{eff} \) of 230 μs due to the highest \( N_f \) of \(-2.87 \times 10^{12} \) cm⁻², meaning that field-effect passivation has an advantage over chemical passivation in this case.

Figure 4d shows the photoluminescence and electroluminescence photos of 1, 1.3, and 1.8 μm IP solar cells with the same passivation process. The brightness of the three groups of photos for both photoluminescence and electroluminescence keeps basically the same level, meaning that the three groups of solar cell devices perform equally well in the passivation of defects. That is to say, the passivation process determines the electrical performance of the solar cell instead of the feature size of IPs, which will be confirmed by the following output parameters of the fabricated solar cells.

Based on the excellent optical and electrical performance of the simultaneous SiO₂/SiNx stack layers passivated front Si IP-based n⁺ emitter and Al₂O₃/SiNx stack layers passivated rear reflector, we fabricated the Si IP-based PERC.

Figure 5a shows the internal quantum efficiencies (IQEs) and front surface reflections of the fabricated Si IP-based PERCs. We can observe that 30-s alkali-etching IP-based device (group 1—30 s) shows the lowest reflectance in the short wavelength of 300–600 nm due to its smaller feature size of IPs. Importantly, group 1—30 s has the highest IQEs in this wavelength range, and thus yields the highest external quantum efficiencies (EQEs) as shown in Fig. 5b. Also, the fabricated devices display almost the same EQEs in the long-wavelength range because of the same level of reflectance and IQEs in this
Therefore, group 1—30 s with smaller feature size possesses better output performance than the other two groups, which is further confirmed by the I-V and P-V curves of devices (see Fig. 5c). Figure 5d shows the \( \eta \) of our champion device reached 21.41%, as well as the \( V_{oc} \) of 0.677 V, \( I_{sc} \) of 9.63 A, and \( FF \) of 80.30%. By our knowledge, it is the highest \( \eta \) among MACE-IP-based solar cells. The inset of Fig. 5d is a photograph of the front and rear surface of the champion device.

Furthermore, Table 2 shows the detailed parameters of the fabricated devices. Obviously, the average \( I_{sc} \) (9.63 A) of the group 30 s device is higher than that of the other two groups, which lies in its best anti-reflection ability of front surface as mentioned above. The difference of \( I_{sc} \) mainly determines the output performances of the devices. Besides, the higher \( FF \) and the lower series resistance \( R_s \) guarantees the higher \( \eta \) of group 30 s. It is worth to note that all the average \( V_{oc}s \) of the Si IP-based PERCs are in the range of 674–676 mV, demonstrating that the same excellent passivation for the front and rear surface of all groups. Finally, benefiting from the gain of optical and electrical performance, we have successfully achieved the highest \( \eta \) of 21.4% of Si IP-based PERC solar cell.

### Conclusions

In conclusion, we optimize the morphologies of the MACE Si IPs structures and fabricate the novel Si IPs-based PERC solar cell with a standard size of 156 × 156 mm² by combining the stack SiO₂/SiNx layers coated IPs textures with the stack Al₂O₃/SiNx passivation of the rear surface. The optical properties show that the solar averaged \( R_{ave} \) of IPs textures coated by the stack SiO₂/SiNx layers can be up to 3.91%, revealing IPs an ideal...
light-trapping structure for PV device. Also, the electrical analysis shows that the polished rear surface passivated by the stack Al₂O₃/SiNx layers possess very high $\tau_{eff}$ of 230 $\mu$s due to the thermal and light-soaking treatment, demonstrating well-light-enhanced c-Si surface passivation of Al₂O₃/SiNx layers. FTIR measurements provide a further explanation for the high $\tau_{eff}$ of the rear surface passivated by the stack Al₂O₃/SiNx layers. Importantly, a high fixed charge density $N_f$ of $-2.87 \times 10^{12}$ cm$^{-2}$ is obtained by means of the C-V measurements, which reveals strong field-effect passivation of Al₂O₃/SiNx layers. Finally, benefiting from the excellent optical and electrical performance at the front Si IP-based $n^−$ emitter and rear reflector, we achieve the highest $\eta$ of 21.4%, as well as $V_{oc}$ of 0.677 V, $I_{sc}$ of 9.63 A, and $FF$ of 80.3%. The achievement of high-efficiency Si IP-based PERC provides IPs with an effective way to mass production of Si-based high-efficiency solar cells.

Abbreviations
PV: Photovoltaic; IP: Inverted pyramid; Si: Silicon; MACE: Metal-assisted chemical etching; PERC: Passivated emitter and rear cell; PERL: Passivated emitter and rear local-diffused solar cell; c-Si: Crystalline silicon; mc-Si: Multi-crystalline silicon; PECVD: Plasma-enhanced chemical vapor deposition; ALD: Atomic layer deposition; Si IP-str: Silicon inverted pyramid structured; $R_{av}$: Averaged reflectance; IQE: external quantum efficiency; $t_{neff}$: The effective minority carrier lifetime; $Q_n$: The injection level; FTIR: Fourier transform infrared spectroscopic; $N_d$: Density of fixed charges; $N_i$: Density of interface traps; C-V: Capacitance–voltage; IQE: Internal quantum efficiency; $V_{oc}$: Open-circuit voltage; $I_{sc}$: Short-circuit current; $FF$: Fill factor; $R_s$: Series resistance

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Authors’ contributions
K.G designed and performed the experiment, part of performance characterization, data processing, and manuscript drafting. Y.L gave help in the experiment and data processing. Y.F drew the device diagram. L.X.S gave help in calculating $N_d$ and $N_i$ at the interface between Al₂O₃/SiNx stack layers and Si YFZ, YPC, SZY, and YWY did the devices fabrication and part of the performance characterization of the samples. W.Z.S gave some help in writing the paper. Z.G.H gave the idea and the experimental guidance for the whole processes and modified the manuscript writing. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets supporting the conclusions of this article are included within the article.

Competing interests
The authors declare that they have no competing interests.

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