INLINE MICROWAVE-EXCITED PLASMA DEPOSITION OF THIN AMORPHOUS SILICON LAYERS

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ABSTRACT: Intrinsic hydrogenated amorphous silicon (a-Si:H(i)) passivation layers with a thickness < 7 nm were deposited by an industrial scale inline deposition technique with a very high dynamic deposition rate of around 35 nm*m/min. An implied open circuit voltage near an injection level of one sun of 714 mV on flat mono-crystalline silicon wafers was achieved. The a-Si:H(i) layers were characterized by spectral ellipsometry, infra-red spectroscopy and the quasi-steady-state-photo-conductance method. The highest passivation quality for the inline microwave excited plasma enhanced chemical vapor deposition (MW-PECVD) of a-Si:H(i) layers was achieved at deposition temperatures of 325 - 350 °C. Due to the high deposition temperature no additional annealing is necessary to improve the passivation quality. The layer roughness and the band gap of the deposited a-Si:H(i) layers decrease, as well as the Si-H_2 concentration with an increased deposition temperature. A hydrogen dilution of the deposition plasma can be advantageous for the passivation quality of a-Si:H(i) layers at lower temperatures, but detrimental for higher temperatures. Furthermore, a hydrogen dilution was obtained as a method to change the band gap and the surface roughness of the deposited a-Si:H(i) layers. The growth dynamic of the inline deposited a-Si:H(i) layers was studied and a formation of silicon di-hydrid was found to build the initial layer of growing a-Si:H(i) films, as already observed for static deposited a-Si:H(i) in the literature earlier. The inline deposition of these thin a-Si:H(i) layers is the first step to produce silicon heterojunction solar cells by a complete inline process.

Keywords: Amorphous silicon, a-Si, Deposition, SHJ, Heterojunction, Inline, Microwave, PECVD

1 INTRODUCTION

The most important requirement of thin intrinsic hydrogenated amorphous silicon (a-Si:H(i)) layers for silicon heterojunction (SHJ) solar cells is a high passivation quality, to obtain the biggest advantage of these type of solar cell, a very high open circuit voltage above 700 mV. Another advantage of this cell structure is the complete low temperature manufacturing and very short fabrication time for a complete solar cell. By using inline deposition methods with high deposition rates for the fabrication of SHJ solar cells, an improvement of the throughput can be realized. The very high deposition rate of the used micro-wave plasma enhanced chemical vapour desposition (MW-PECVD) system is around 30 times higher as the conventional parallel plate PECVD method [1]. But this advantage demands a very good process control, to achieve high quality a-Si:H(i) passivation layers in deposition times shorter than 3 s.

Whithin this study the capability of a high-throughput inline PECVD (Plasma-Enhanced Chemical Vapour Deposition) system for the deposition of thin a-Si:H(i) passivation layers for SHJ solar cells will be evaluated. In the past, thick a-Si:H(i) layers with a high passivation quality were already deposited by this technique [2]. However, the passivation quality of thin a-Si:H(i) layers (< 10 nm) is much more sensitive to additional effects like the interface layer formation [3], the roughness of the substrate or the chamber cleanliness, and therefore the deposition parameters must be adapted.

A challenge which must as well be taken into account is the very high base pressure of the used inline MW-PECVD system, of around 1×10^{-2} mbar. In comparison to the base pressure of conventional small lab-type PEVCD systems this is a factor of 1000 higher. As known from the literature [4], this can cause a high impurity contamination in the deposited a-Si:H(i) films of around 10^{21} cm^{-3} of oxygen and 10^{20} cm^{-3} of nitrogen [4].

2 EXPERIMENTAL

The plasma in the used inline PECVD system (SiNA, Roth&Rau) is excited by electromagnetic radiation in the microwave range at a frequency of 2.45 GHz, which is coupled in a linear antenna. The plasma width is about 100 x 20 cm^2. The wafers are placed on multi-crystalline dummy wafers on a carbon carrier with a width of 90 cm, which passes through the plasma zone with a velocity v.

The deposition of the a-Si:H(i) layers was performed symmetrically on both sides of p-type mono-crystalline float zone (FZ) silicon wafers with shiny etched surfaces and a <100> crystal orientation with a specific resistance of about 0.5 Ωcm, a wafer thickness of 250 μm and an area of approximately 20 cm^2. Before the deposition, the wafers were cleaned by a 1 minute etching step in a 1 % HF solution. The resulting a-Si:H(i) layer thickness was in the range of 6.5 ± 0.5 nm. Silane (SiH$_4$) and hydrogen (H$_2$) are used as precursor gases for the a-Si:H(i) deposition. The varied deposition parameters are the temperature (T) and the hydrogen gas flux ($[H_2]$). The constant deposition parameters are shown in the following table.

Table I: Constant PECVD parameters for the inline deposition of a-Si:H(i) films.

$[SiH_4]$ (sccm)	P_{eff} (kW)	p (mbar)	v (cm/min)
300 ± 2.1	1.1 ± 0.05	0.25 ± 0.025	600 ± 1

With $[SiH_4]$ as the silane gas flux, P_{eff} the time average power of the microwave plasma source, p the pressure in the PECVD reactor during the deposition and the velocity v of the carrier to vary the thickness of the a-Si:H(i) layer. The homogeneity of the deposition is

investigated by distributing wafers on several positions on the carrier.

By using the quasi-steady-state photo conductance (QSSPC) technique, the implied open circuit voltage ($V_{oc,implied}$) at a minority carrier density near one sun was derived [5]. The QSSPC measurements where performed directly after deposition, thus no additional annealing step was performed, since no mentionable effect was seen. Spectroscopic investigations in the NUV-VIS (spectral ellipsometry, SE) and IR (Fourier transformed IR spectroscopy, FTIR) wavelength range are performed, to evaluate the thickness and the roughness as well as the optical parameters and the composition of the a-Si:H(i) films. The Tauc-Lorentz model which is used for the SE, yields furthermore the dielectric function of the measured layer and the optical band gap E_g [6]. The surface roughness, d_{rough}, of the deposited films were obtained by using the effective medium approximation (EMA) by Bruggemann, with the assumption of a mixture of 50 vol.% of bulk a-Si layer and 50 vol.% void, in the ellipsometric model [7]. The entire a-Si:H(i) layer thickness results thereby to

$$d_{\text{a-Si:H(i)}} = d_{\text{Tauc-Lorentz}} + d_{\text{rough}}/2, \qquad (1)$$

where $d_{\text{Tauc-Lorentz}}$ is the bulk a-Si:H(i) layer thickness extracted from the Tauc-Lorentz ellipsometry model.

3   RESULTS

A: Temperature Variation

In Figure 1 the influence of the deposition temperature on $V_{oc,implied}$ for a pure silane plasma and a hydrogen diluted plasma is shown.
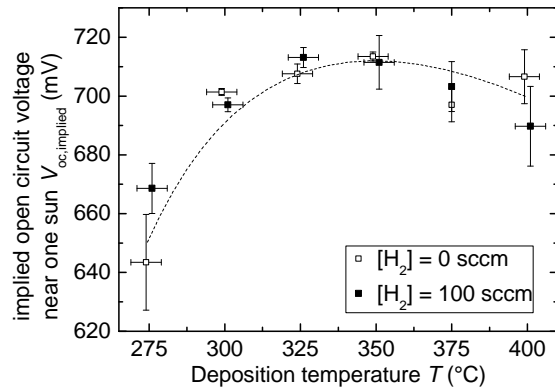

Figure 1: Influence of the deposition temperature and hydrogen dilution on $V_{oc,implied}$ for a-Si:H(i) lifetime samples.

The maximum $V_{oc,implied}$ of ca. 714 mV is obtained in a temperature range of 325-350 °C. For temperatures lower than 325 °C a decrease of $V_{oc,implied}$ can be observed, as well as for a temperature of 400 °C. A hydrogen dilution with 100 sccm has no significant effect on $V_{oc,implied}$. As known from the literature, a too low as well as a too high deposition temperature leads to an increased defect density of a-Si:H(i) films [8]. This can be the explanation for the decrease of $V_{oc,implied}$ at 275 °C and 400 °, respectively.

For the samples in Figure 1 the a-Si:H(i) layer roughness (d_{rough}) was obtained by SE. As can be seen in Figure 2, there is a steady decrease of the layer roughness with the temperature. A hydrogen dilution of 100 sccm

can yield a further decrease of the layer roughness. The temperature effect on the roughness can be explained by a higher thermal mobility of the species on the c-Si surface [9]. The very high roughness at lower temperatures could also be a possible explanation for the sharp decrease of the implied voltage at 275 °C (cf. Figure 1). For a a-Si:H(i) layer thickness of 6 nm, the resulting a-Si bulk layer thickness, $d_{\text{Tauc-Lorentz}}$, gives roughly 4.5 nm (s. Eq. 1), which is probably too low for a proper passivation. Another explanation for the decreased passivation quality at 275 °C deposition temperature can be the formation of voids in the a-Si:H(i) bulk material [8]. This can cause an increased defect density because of dangling bonds at internal void surfaces.
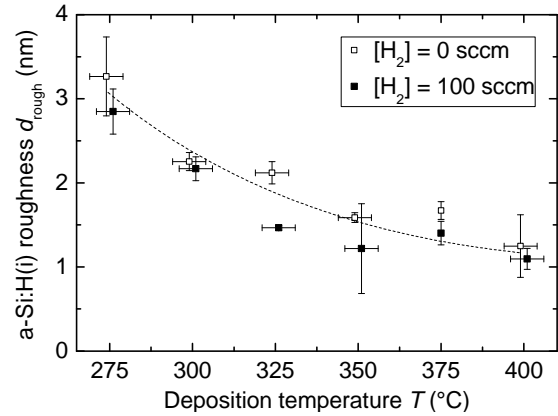

Figure 2: Influence of the deposition temperature and hydrogen dilution on the a-Si:H(i) layer roughness.

In Figure 3 the change of the band gap E_g, extracted from the ellipsometric model, of a-Si:H(i) layers with the deposition temperature is shown. E_g decreases with increasing temperature, and adding hydrogen tends to result in a decrease of E_g, too. The increased band gap for the low temperature deposited films could hint to a higher defect density within the a-Si:H(i) film, as seen in the literature [10]. The increased E_g of the samples at 375 °C deposition temperature is probably due to the higher oxygen contamination, seen by FTIR measurement, within the layer after a chamber opening for maintenance. As known from the literature oxygen can increase the band gap which is again due to an increased defect density within the a-Si:H(i) layer [10]. Therefore the samples can be considered as outliers.
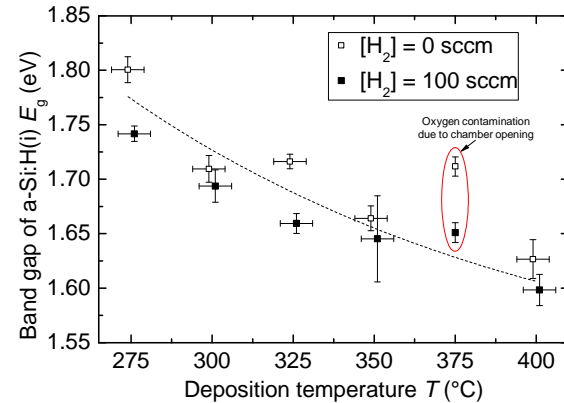

Figure 3: Influence of the deposition temperature on the band gap of the a-Si:H(i) layer at two different hydrogen dilutions (the red encircled outliers at 375 °C are due to

an oxygen contamination within the chamber after opening for maintenance).

In Figure 4 the FTIR spectra of a-Si:H(i) layers deposited at different temperatures can be seen. The silicon di-hydride (Si-H$_2$) absorption declines with increased deposition temperature, as well as E_g. The effect of the deposition temperature on the band gap was shown in the literature earlier, and a correlation between the band gap and the di-hydride concentration in the a-Si:H(i) layers was found [11]. As known from the literature, the presence of Si-H$_2$ compounds hint to an increased void formation within the a-Si:H(i) bulk layer [14]. This supports the assumption that the reduced passivation quality at lower deposition temperatures (s. Figure 1) is due to an increased defect density within the a-Si:H(i) layer which is owing to void formation.
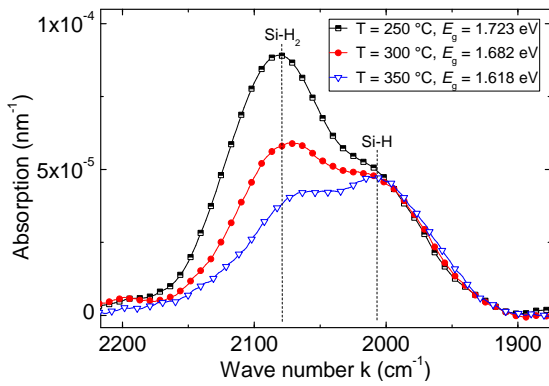

Figure 4: Influence of the deposition temperature on E_g and the Si-H$_x$ absorption obtained by FTIR measurements of a-Si:H(i) deposited wafers.

B: Hydrogen dilution

In Figure 5 a more detailed investigation on the effect of hydrogen dilution on $V_{oc,implied}$ at two deposition temperatures is shown.
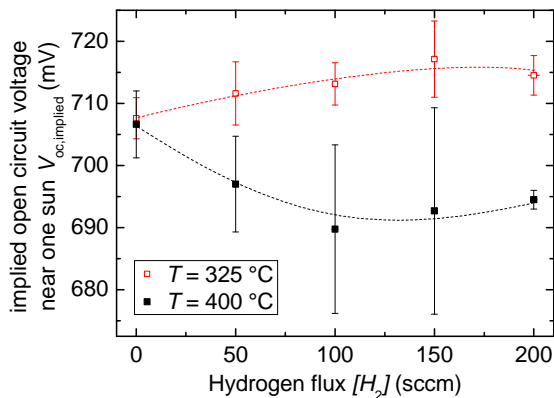

Figure 5: Influence of the hydrogen dilution for two deposition temperatures on $V_{oc,implied}$ for a-Si:H(i) deposited wafers.

Neither for a deposition temperature of 325 °C nor for 400 °C a significant effect of hydrogen dilution on $V_{oc,implied}$ can be seen. However, an opposite trend can be observed for a temperature of 325 °C and a higher temperature of 400 °C. At 325 °C, the addition of hydrogen tends to result in a higher $V_{oc,implied}$, whereas at 400 °C $V_{oc,implied}$ declines. A possible explanation for that

can be an increased micro crystallinity at higher temperatures and for a hydrogen dilution of the plasma [8], which is known to reduce the passivation quality [12].

From Figure 2, an effect on the surface roughness by the addition of hydrogen can be estimated. For a more detailed investigation of this effect, the roughnesses of the samples from Figure 5 were obtained by SE, and are shown in Figure 6.
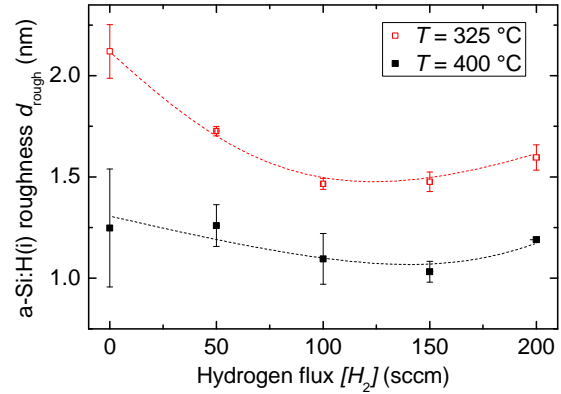

Figure 6: Influence of a hydrogen dilution at 325 °C and 400 °C deposition temperature on the a-Si:H(i) layer roughness.

The lowest surface roughness is achieved at a hydrogen flux of 100-150 sccm for both, 325 °C and 400 °C deposition temperature. For a higher hydrogen flux of 200 sccm, the roughness slightly increases, which is a known effect for high H$_2$ dilluted SiH$_4$ plasmas and can be due to a microstructure of the deposited layer [13]. There also can be seen, that the roughness of films deposited at 400 °C is lower than for layers deposited at 325 °C, which validates the data from Figure 2. Though, the smoothening effect of hydrogen is stronger pronounced for the deposition temperature of 325 °C than for 400 °C. One explanation for this can be the surface diffusion controlled smoothening at higher temperatures [9] which is obviously not mentionable increased by adding hydrogen. At lower deposition temperatures possibly the surface is rough enough, due to a reduced surface diffusion, so that hydrogen can reduce the roughness.
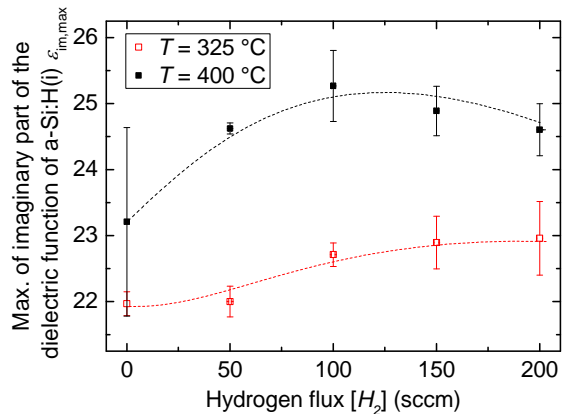

Figure 7: Influence of the hydrogen flux during a-Si:H(i) deposition on the maximum of the imaginary part of the dielectric function ($\varepsilon_{im,max}$) of a-Si:H(i) layers deposited at two different temperatures.

It is not clear yet which effect causes the decrease of the roughness with the addition of H_2 to the plasma (s. Figure 6), but what can be said is that a hydrogen dilution changes the morphology of the deposited a-Si:H(i) layer. From spectral ellipsometry the maximum of the imaginary part of the dielectric function, $\varepsilon_{im,max}$, can be derived. As can be seen in Figure 7, $\varepsilon_{im,max}$ increases with an addition of hydrogen. This indicates a more dense material as known from literature [14], and this again can be the reason for the abatement of the surface roughness by adding hydrogen to the plasma.

As already seen in Figure 3, the influence of a hydrogen dilution on E_g is worth mentioning. Therefore, a more detailed investigation on the effect of hydrogen dilution on E_g for three deposition temperatures is shown in Figure 8. At the lowest temperature of 325 °C, the influence of a hydrogen dilution on E_g is greater than for the higher temperatures. The band gap for a-Si:H(i) layers deposited at 375 °C is fairly in between them at 325 °C and 400 °C. At 400 °C no significant change in E_g can be observed for a hydrogen flux greater than 50 sccm. This is also the case for 325 °C at a hydrogen flux greater than 150 sccm. For 375 °C one can also suppose that there is at least a smaller change of E_g for a hydrogen flux greater than 100 sccm. It seems that a plateau of constant E_g is shifting towards higher hydrogen fluxes for lower deposition temperatures.
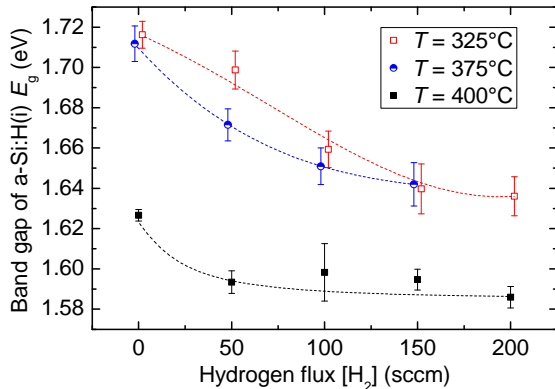

Figure 8: Influence of the hydrogen dilution on E_g for three different deposition temperatures

C: Growth Dynamics

In Figure 9 the cross section of the plasma source with a conveying wafer is shown. Since the wafer passes through the plasma, the film grows on the surface exposed to the plasma.
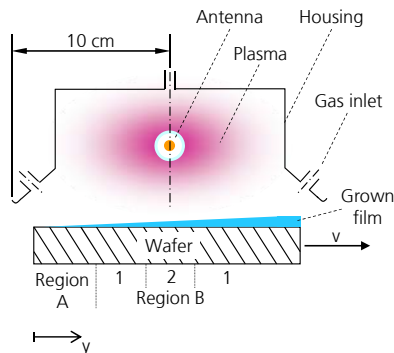

Figure 9: Schematic of the growth of an a-Si:H(i) layer by passing the plasma source.

The deposition starts in region A. In region B the bulk film is deposited. In Figure 10 the initial growth of the film can be observed. SE measurements were performed on a wafer as shown in Figure 9. The refractive index of the initial layer is 2.25 and it increases strongly with the layer thickness ($d_{a-Si:H(i)}$), up to a value of 4. It seems that the refractive index gets down below the antenna (Region B-2). After the antenna is passed, the refractive index of the layer remains constant but the layer thickness continues to rise.
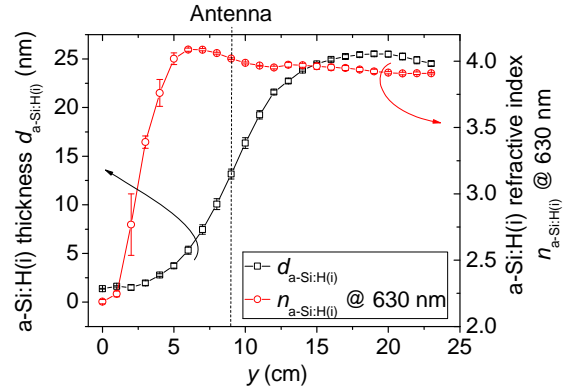

Figure 10: Formation of an a-Si:H(i) film by passing the plasma source obtained by SE, as shown in Figure 9.

Figure 11 shows the FTIR absorbance spectra of the growing film from Figure 9 in the range of k = 1900 to 2400 cm^{-1}. At a thickness of 1.5 nm, IR absorption at around 2100 cm^{-1} can be identified. This can be interpreted as absorption by Si-H_2 configurations [15]. With increasing layer thickness the Si-H_2 absorption rises. At a thickness of 2.9 nm another absorption peak at around 2008 cm^{-1} appears. This can be due to absorption by a Si-H compound [15]. As reported earlier [3], the presence of Si-H_2 can be understood as an interface layer formation on the c-Si surface, whereas the increasing Si-H amount represents high quality compact a-Si:H(i) material [16].
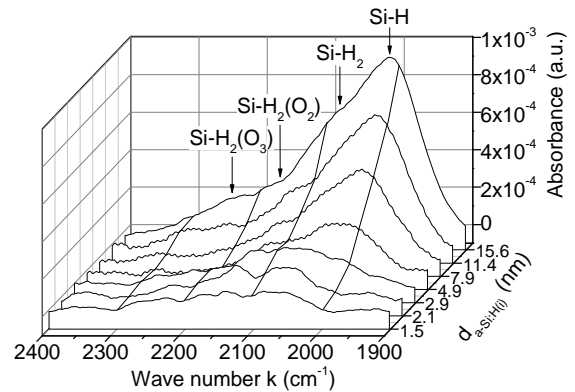

Figure 11: Evolution of the a-Si:H(i) composition by passing the plasma source obtained by FTIR measurements of the samples from Figure 10.

In the upper graph, the presence of oxygen related absorption at k = 2185 cm^{-1} (Si-$H_2(O_2)$) and k = 2250 cm^{-1} (Si-$H_2(O_3)$) can be seen [17, 18]. This contamination is due to the high base pressure of the used PECVD system, which correspondence to an air leakage, as already mentioned [4].

4 SUMMARY

It was shown that a deposition of thin amorphous silicon layers with very high deposition rates is possible on an industrial scale PECVD system. The deposition temperature which provides the best passivation quality is in the range from 325 to 350 °C. An increase of the deposition temperature changes the morphology and the electrical properties of the a-Si:H(i) layer. A decrease of the silicon di-hydride absorption in the FTIR spectra was observed by increasing the deposition temperature. The layer roughness and the band gap, measured by spectral ellipsometry, is reduced by increasing the temperature and an addition of hydrogen to the plasma. The imaginary part of the dielectric function shows a densification of the a-Si:H(i) layer by increasing the temperature and a dilution of the plasma with hydrogen. It was found that a hydrogen dilution causes no significant change of the passivation quality, but can be detrimental at higher deposition temperatures, probably due to a micro crystalline structure of the a-Si:H(i) layer or to an increased defect density. The low passivation quality at lower deposition temperatures can be either due to an increased surface roughness or to a higher defect density of the layer, obtained by the increased band gap. An increased absorption of $Si-H_2$ compounds, seen by FTIR, for a-Si:H(i) layers deposited at lower temperatures supports the assumption of an increased defect density due to void formation within the layer. The analysis of the a-Si:H(i) growth dynamics on a c-Si surface obtained an interface layer which consists of silicon di-hydride, as already seen in the literature for static deposited a-Si:H(i) films.

5 ACKNOWLEDGMENTS

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