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Electrical Properties of DC Sputtered Titanium Nitride Films with Different Processing Conditions and Substrates

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ABSTRACT

Deposition of TiN_x film was conducted with a DC sputtering technique. The effect of the processing parameters such as substrate temperature, deposition time, working pressure, bias power, and volumetric flowing rate ratio of Ar to N_2 gas on the resistivity of TiN_x film was systematically investigated. Three kinds of substrates, soda-lime glass, (100) Si wafer, and 1 μm thermally grown (111) SiO_2 wafer were used to explore the effect of substrate. The phase of TiN_x film was analyzed by XRD peak pattern and deposition rate was determined by measuring the thickness of TiN_x film through SEM cross-sectional view. Resistance was obtained by 4 point probe method as a function of processing parameters and types of substrates. Finally, optimum condition for synthesizing TiN_x film having lowest resistivity was discussed.

Key words : TiN films, Ceramic coating, DC sputtering, Resistivity

1. Introduction

Titanium nitride film has excellent properties such as good wear resistance, high corrosion resistance, low friction coefficient, high conductivity and a bright, golden color. Owing to these properties, TiN has been widely used in protective and functional coatings on cutting tools, bearings, etc. In order to improve the lifetime and performance of industrial tools, TiN has been utilized as a protective coating.[1,2] The TiN layer has also been employed as a barrier material to inhibit diffusion of Al and Cu during high temperature processing as well as to promote adhesion of the ILD layer in microelectronics.[3] Due to high electrical conductivity and thermal stability of TiN film, TiN coating has recently been led to electrodes in microelectronic devices.[4] Furthermore, TiN coating on glass has been also popular for the production of decorative panels in architecture or solar glass in automotive industry. The reflected colors are silver, blue and whereas transmitted ones are brown and grey.[5] TiN film provides near-infrared reflectivity, which can provide high-performance rejection of solar heat in solar control glass.[6]

However, most of the researches concerning to the TiN_x film have been mainly focused on the issue of mechanical and chemical properties such as high hardness, wear-resistant durability and corrosion resistance enhancement. Therefore, few systematic works related to electrical conductivity of TiN_x film has been carried out. The effect of nitrogen content on electrical resistance of TiN_x films was investigated and its result suggested that optimum content of nitrogen makes highest resistivity.[7] It was also reported that annealed TiN_x films has higher sheet resistance than that of as-deposited one.[8] A few studies about electrical properties of TiN_x films were reported however, effect of substrate on the resistivity of TiN_x film has been rarely reported.

The purpose of this research is to investigate the effect of processing parameters of DC sputtering systematically on the electrical properties of TiN_x film. Three kinds of substrate, soda-lime glass, (100) Si wafer, 1 μm thermally grown (111) SiO_2 coated Si wafer were used. Processing variable were considered with substrate temperature, deposition time, working pressure, bias power and flowing rate ratio of Ar to N_2 gas. We try to explore the critical processing parameters and role of substrate to control the sheet resistance of TiN_x film. Consequently, suggest the optimum condition for synthesizing the high electrically conducting TiN_x film.

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2. Experimental Procedures

2.1. Deposition of TiN_x Film

Prior to deposition, substrates were cut 2 cm by 2 cm and cleaned in TCE with ultrasonic cleaner for 30 min and dried by N_2 atmosphere. Then, soda-lime glass, (100) Si wafer, 1 μm thermally grown (111) SiO_2 coated Si wafer were put

Table 1. Experimental Scope and Processing Variables in Detail

	Substrate temperature (°C)	Deposition time (min)	Working pressure (mTorr)	Power (W)	Ar:N_2 ratio (sccm)
Series 1	**40/100/200/300**	30	4	110	30:15
Series 2	40	**30/60/90/120**	4	110	30:15
Series 3	40	30	**4/8/12**	110	30:15
Series 4	40	30	4	**60/85/110**	30:15
Series 5	40	30	4	110	**40:10 30:10 30:15 20:20 20:30**

on the substrate holder at the same time. The TiN_x film was deposited by DC sputtering (High tech. Sanghai, China). Chamber was maintained below 5×10^{-6} Torr and filled with Ar and N_2 up to proper working pressure range. Entire experimental scope and each processing variables are summarized in Table 3.1. Five series of experiments were conducted and each series consisted of 3 or 4 experimental sets.

In order to investigate the effect of substrate temperature, TiN_x film was deposited at the temperature of 40, 100, 200 and 300°C for 30 min. In second series, deposition time was changed from 30 min to 120 min at an interval of 30 min. In third, working pressure during deposition varied at 4, 8, 12, mTorr. In fourth, bias power was changed 60, 85, 110 W and finally, in fifth, Ar to N_2 flowing rate ratio was systematically controlled described in Table 1.

2.2. Characterization of TiN_x Film

The phase of TiN_x film was analyzed by XRD peak pattern in the range from $2\theta = 30$ to 50°. The thickness of TiN_x film was determined by SEM cross-sectional view and the deposition rate was calculated. Resistance of the film was measured by 4 point probe method in order to compare intrinsic properties of deposited films. Three data points were obtained and average value was calculated.

3. Results and Discussion

3.1. Phase Analysis

After deposition of TiN_x film, phase was analyzed by XRD pattern in the range from $2\theta = 30$ to 50°. Fig. 1(a), (b), and (c) shows the X-ray diffraction pattern of TiN_x film on soda-lime glass, (100) Si wafer and 1 μm thermally grown (111) SiO_2 coated (100) Si wafer with different deposition temperature. All of the specimens have a common feature of peak shift as substrate temperature increases. Around 40°C, a major peak appeared at 42.5° which is diffracted from the (200) plane. However, 36.5° peak which is diffracted from the (111) plane, showed higher and sharper as the substrate temperature increases. It indicates the preferred orientation of TiN_x film changed from (200) to (111) and the crystallinity of the film increases. These phenomena can be explained impinging ions and atoms having higher energy at elevated temperature shows higher growth rate and lowest energy state. In case of TiN_x film, the direction of lowest energy is <111> direction. Compared to the specimen at higher temperature, at room temperature, in general, nucleation of TiNx film is <200> direction.[9] In the case of different substrate, there is one particular difference among the each specimen deposited at 40°C. The TiN_x film on soda-lime glass showed no peak at $2\theta = 36.5°$. On the contrary, both of TiN_x on (100) Si and (111) SiO_2 showed discrete peak intensity at the position. It means the structure of substrate influences the growth of depositing film. In case of amorphous structure like soda-lime glass, nucleation occurred only at original nucleating site.

In order to investigate the effect of the thickness of TiN_x film on the phase, deposition time was changed. Fig. 1(d), (e), and (f) shows the X-ray diffraction pattern of TiN_x film on soda-lime glass, Si wafer and SiO_2 wafer with different deposition time. Entire trend of peak position is very similar to Fig. 1(a), (b), and (c) in the sense of nucleation site and growth direction. As the deposition time increases, preferred growth of TiN_x film changed from <200> to <111> in order to lower the total energy and showed very high intensity at higher deposition time. Working pressure was changed from 4, 8, and 12 mTorr in order to analyze the effect of working pressure on the phase. As working pressure increases, the preferred orientation of the TiN_x film changed from <200> to <111> similarly to the previous Experimental series as shown in Fig. 1(g), (h), and (i). Peculiarly, the intensity of peak at 36.5° is almost same between that of 8 and 12 mTorr. Nucleation of TiN_x film depends on the working pressure and growth of the film saturates irrespective of increasing of working pressure. DC bias power varied 60, 85, and 110 W. At relatively low power, 60 W, no nucleation of crystalline TiN_x film was observed. At 85 W, small intensity to <200> direction was detected and finally, another nucleation to <111> appeared at 36.5°. From the result, nucleating site of TiN_x film is proven to be <200> direction and to be changed to <111> as the bias power increases. It is same trend with the substrate temperature and deposition time. Ar to N_2 flowing rate was controlled in order to study the effect of Ar to N_2 flowing rate on the phase. As the amount of N_2 relatively increases, the inten-

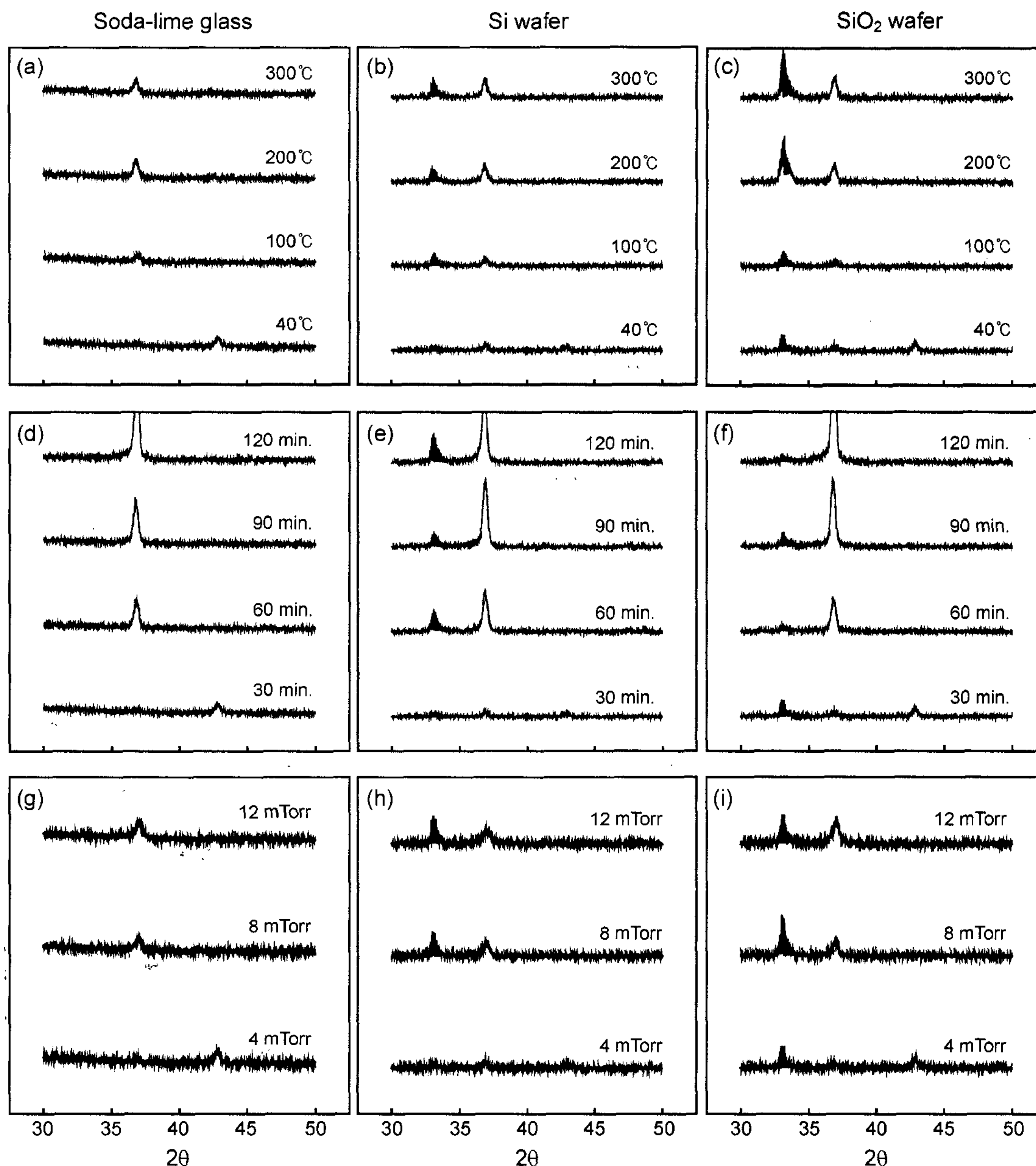

Fig. 1. X-ray diffraction patterns of TiN_x films on soda-lime glass, (100) Si wafer and 1 μm thermally grown (111) SiO_2 deposited at different processing conditions.

sity of the highest peak increases and except the case of $Ar:N_2 = 30:15$, all specimen showed the nucleation to <111> direction. In case of 30:15, both of nucleation to <200> and <111> appeared.

Films grown by PVD techniques have been reported to exhibit a preferred growth orientation. For TiN films a {111} orientation is commonly reported although both {200} and {220} orientations have also been found by some researchers.[9] The development of textures in PVD coatings occurs in three stages. At first, crystallites are nucleated on the substrate from the vapor phase. The distribution, orientation and size of the crystallites will depend on the nature of the substrate. Competitive growths are followed. Certain favorable oriented nuclei will grow faster into the vapor phase than will the remainder of the crystallites. However, these may not constitute the majority of the nuclei population. Finally, once a preferred orientation has achieved dominance, steady state growth will occur. The effect of preferred orientation on coating microstructure was clear to show faceted growth. The pyramidal end forms on the columns are likely to be the low energy {111} planes. Thinner coatings show {200} textures, indicating that this is the predominant orientation at nucleation. The hardness of thick coatings is found to be lower than that of thin coating, and this has been attributed to the increase in porosity towards the surface of the thicker coatings.

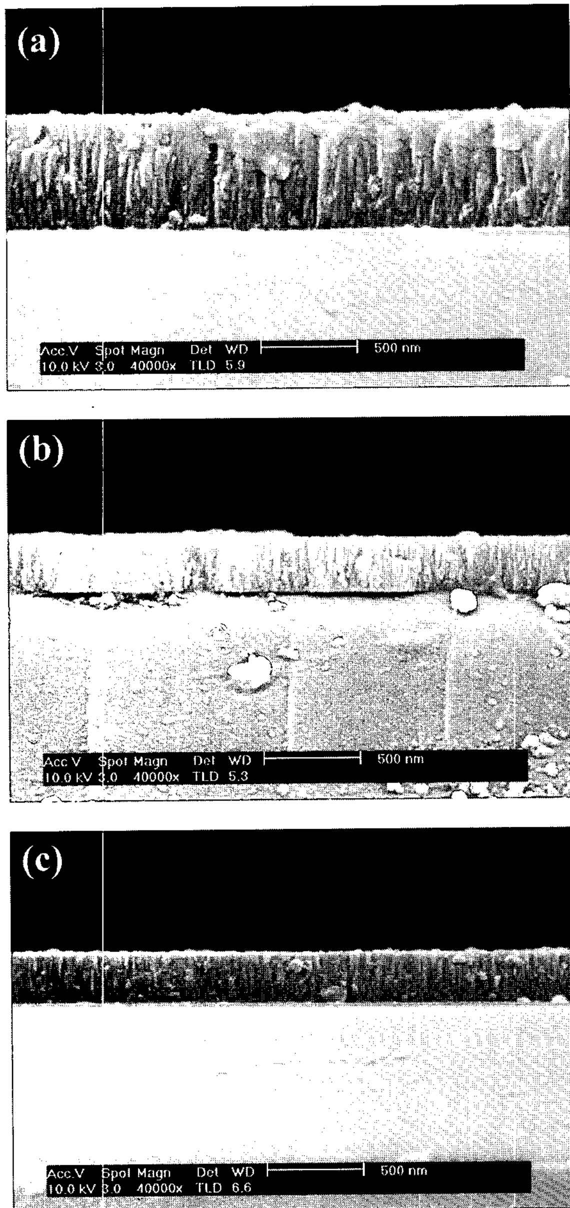

Fig. 2. SEM micrograph showing cross-sectional view of TiN_x film on (a) soda-lime glass, (b) (100) Si wafer, and (c) 1 μm thermally grown (111) SiO_2.

3.2. Deposition Rate of TiN_x Film

Deposition rate was calculated after measuring the thickness of TiN_x film by SEM cross-sectional view. The TiN_x films were distinguished clearly from the substrates. Fig. 2(a), (b), and (c) show the SEM micrograph showing the cross-sectional view of TiN_x film on soda-lime glass, on Si wafer and on SiO_2 wafer, respectively. Three points were measured and average value was obtained. The thickness of TiN_x film on soda-lime glass was measured and deposition rate was determined. Those of TiN_x film on Si and TiN_x film on SiO_2 show the similar trends with that of TiN_x on glass.

Deposition rate of TiN_x film increases as the substrate temperature increases as shown in Fig. 3(a). The highest rate was achieved at 300°C. The reason to show higher deposition rate at higher substrate temperature is considered as increased energy of the impinging ions and atoms promotes surface diffusion.[9] Consequently, deposition rate is linearly proportional to the substrate temperature. Deposition rate of TiN_x film increases as the deposition time increases as shown in Fig. 3(b). The highest rate was accomplished at the TiN_x film deposited for 120 min. In theory, the deposition rate should be equal irrespective of deposition time. However, in practice, the rate is different at the early and final stage. The reason to show higher rate at the higher time seems to be deposition of nonstoichiometric TiN_x film mainly due to poisoning of Ti target. Deposition rate of TiN_x film could be influenced by working pressure driven ionization efficiency as shown in Fig. 3(c). From 4 to 8 mTorr, deposition rate relatively decreases even though working pressure increases. It is probably caused by the decrease of ionization efficiency. Then, further increase of working pressure from 8 to 12 mTorr leads deposition rate to enhance. In this case, Ti ions and N ions in the TiN_x film contribute to the higher deposition rate in spite of decrease of ionization efficiency.

Deposition rate of TiN_x film is proportional to DC bias power as shown in Fig. 3(d). As bias power increases, plasma density could be enhanced. Accordingly, ionization efficiency becomes higher as the bias power increases up to certain level. Deposition rate of TiN_x film is strongly influenced by Ar to N_2 flowing rate ratio. As the volumetric amount of N_2 increases, the rate decreases. Deposition rate

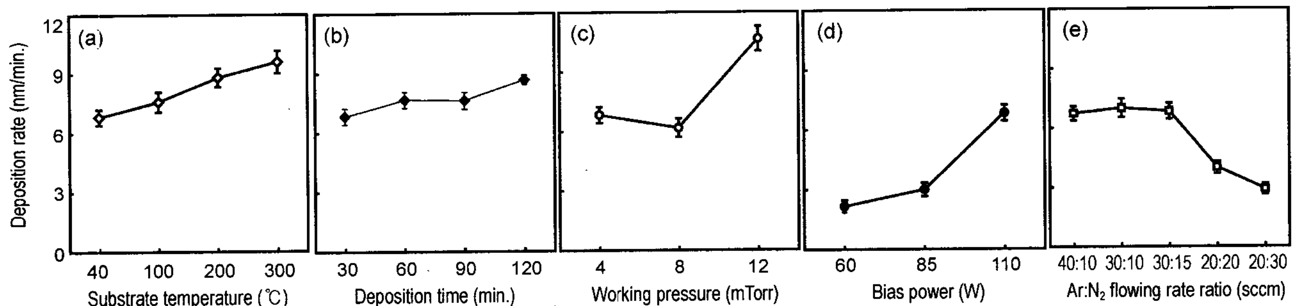

Fig. 3. Effect of processing conditions: substrate temperature, deposition time, working pressure, bias power, and Ar:N_2 flow ratio on deposition rate of TiN_x film on soda-lime glass.

shows the highest in the appropriate ratio like Ar:N_2 = 30:10 or 30:15. The reason to show maximum rate at the ratio range largely attributes to the increase of ionization efficiency.

3.3. Resistivity of TiN_x Film

Resistivity of TiN_x film was obtained by 4 point probe method. Fig. 4 shows the resistivity of entire TiN_x film. Resistivity was categorized by processing variables and types of substrate. In order to analyze the effect of processing parameter on the resistivity separately, the value of resistivity was plotted as a function of each variable and each substrate.

Fig. 4(a) shows the resistivity of TiN_x film as a function of substrate temperature. The lowest value was obtained at 300°C and the highest value at 100°C. It implies that to elevate the substrate temperature shows some advantages and some disadvantages at the same time. The primary reason to decrease sheet resistance contributes to smoothness of surface of TiN_x film as the substrate temperature increases. Fig. 4(b) shows the resistivity of TiN_x film as a function of deposition time. As the deposition time increases, the surface of TiN_x film becomes smoother. Consequently, the resistivity of the film decreases. This behavior is similar with the result of increasing substrate temperature. Fig. 4(c) shows the resistivity of TiN_x film as a function of working pressure. As the working pressure increases, the resistivity increases linearly. High working pressure results in smaller grain size and higher packing density. Consequently, resistivity of TiN_x film increases. Fig. 4(d) shows the resistivity of TiN_x film as a function of Ar to N_2 flowing rate ratio. Resistivity shows the highest value at the ratio of Ar:N_2= 30:10. As the ratio become closer to the extreme case like Ar:N_2=40:10 or 20:30, resistivity decreases mainly due to the Ti ion or N ion in the TiN_x film which promote conducting process easily.[9]

4. Conclusions

TiN_x film was deposited on different types of substrate by DC sputtering. Effect of five processing parameters on the electrical properties of TiN_x film was investigated. Resistivity of TiN_x film was strongly influenced by substrate temperature, deposition time, working pressure, bias power and Ar to N_2 flowing rate ratio. Based on the result, optimum condition for synthesizing TiN_x film having lowest resistivity is desirable. Higher substrate temperature over 200°C, longer deposition time, lower working pressure, higher bias power in a certain range, and appropriate Ar to N_2 ratio were required to achieve low resistivity of TiN_x film. However, the desirable processing conditions are reasonable in the sense of resistivity. Other properties such as the quality of deposited TiN_x film and deposition rate should be considered to determine the optimum processing.

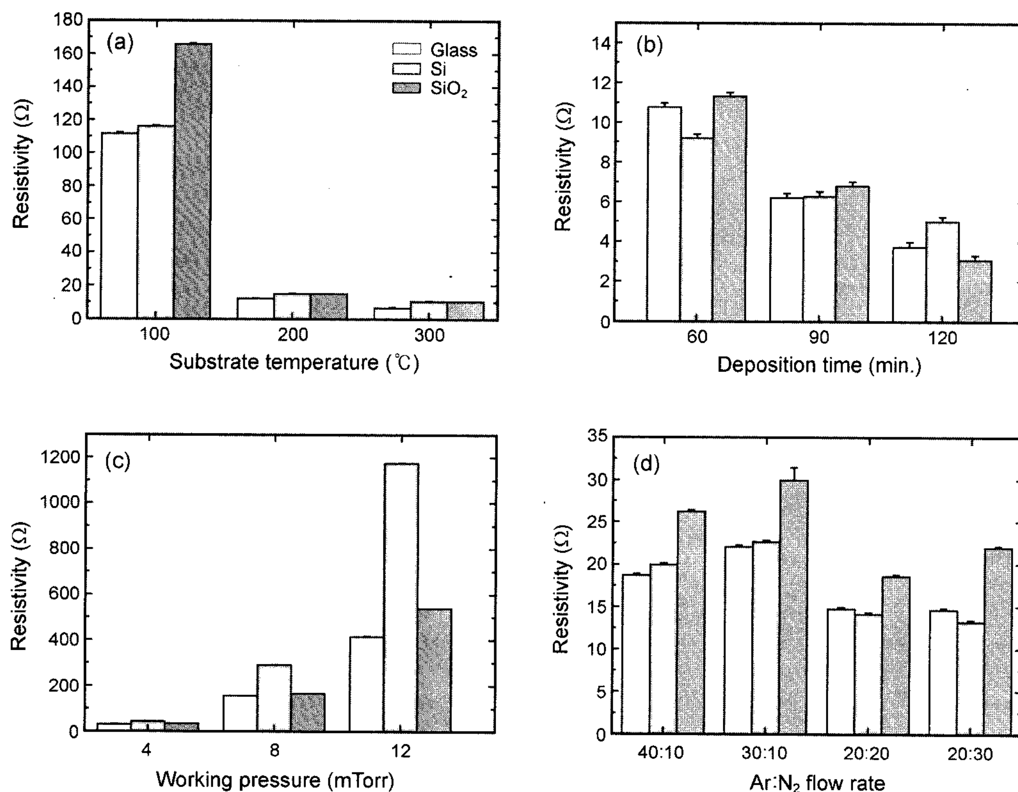

Fig. 4. Effect of processing conditions: substrate temperature, deposition time, working pressure, bias power, and Ar:N_2 flow ratio on resistivity of TiN_x film on soda-lime glass, Si and SiO_2 substrate.

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