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Fabrication and Characterization of Al Doped ZnOThin Film Using Spin Coating Deposition System

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Abstract:*Al doped zinc oxide (ZnO) thin film was fabricated on glass substrate using spin coating method at different rotation speed. Two samples were prepared at 2% Al with 4000 revolutions per minute (rpm) & 5000 rpm deposition speeds respectively. Then their structural, morphological and optical characteristics were investigated. The thicknesses for both were measured (100 nm) by using stylus profilometer. X-ray diffraction was used to determine the surface morphology and crystallinity. Grain size was also calculated from Bragg's angle. SEM image showedthat surface morphology was affected by doping concentration.From the SEM image rough surface with a few numbers of scattered grains was observed which proved the crystalline nature.Various optical parameters such as absorption coefficient, band gap, refractive index and extinction coefficient werestudied using transmittance and reflectance spectral data in the photon wavelength of 310 nm to 2500 nm. High transparency was found in visible and infrared regions in the range from 75% to 85%. Absorbance was shown as the opposite nature of transmittance response. Optical band gaps of 3.275 eV and 3.11 eVwere found respectively for sample-1 and sample-2.*

Keywords: *ZnO, Thin film, Annealing temperature, Surface morphology, Optical band gap*

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I. Introduction

In future solar power may be one of the important energy sources. Thin film solar cell is the most efficient device to extract solar power. Not only in the solar cell but also in other sector such as semiconductor devices, light crystal displays, integrated circuits, telecommunications, transistors, light-emitting diodes, compact discs, memories, lithography etc. thin film is playing a vital role [1-2].ZnO is a group II-VI semiconductor thin film with a hexagonal wurtzite crystal structure. It has direct wide band gap (3.2 eV) [3] of low electrical resistivity and high optical transmittance characteristics within the visible range.Elements from group II and III metal ions such as In, Al, Ga, Cu, Cdetc. have been doped with ZnO to enhance its structural, optical and electrical properties [3-6].

Al is one of the important impurities with light weight and abundant in nature. It was reported that in terms of optical transparency enhancement and bandgap shift of AZO thin film Al played a major role [7]. Different techniques have been used by scientists to prepare and investigate various properties of Al doped ZnO(AZO) thin film [8-9]. It has been reported that the optical band gap of Al_2ZnO_4 is in the range of 3.14 - 3.32 eV[10]. For the optical transmission in visible and infrared region it has been studied widely to use in practical fields such as solar cells [10], flat panel display electrodes surface acoustic devices, optical waveguide [11], gas sensors etc. In this work spin coating method was selected for its various advantages [12].

II. Material and Methods

AZO thin film was deposited on glass substrate. The substrate was cleaned very carefully with the following things such as glass cleaner, acetone, detergent, de-ionized water, ultrasonic bath and dry pump.

ZnO precursor solution was made by dissolving zinc acetate di-hydrate in the solution of ethanol and di-ethanolamine at room temperature. Both zinc acetate di-hydrate and di-ethanolamine had the molar ratio 1. The concentration of zinc acetate was 0.1M. Then the solution wasstirred at 60ºC to obtain a clear and homogeneous solution and cooled to room temperature. The solution was filtered and aged for 24hours at room temperature.Al at 2%was added to the ZnO precursor solution. After that the solution was stirred at room temperature for 2 hours. For 2% doping, the ratio of Zn and Al was 100:2 and the calculated formula was $Al_{0.02}Zn_{0.98}$.

AZO (Al at 2%) thin film was deposited on glass substrate and two differentsamples were prepared. Puddles of AZO solution were dropped on glass substratesand placed in vacuumsection of spin coater machine.

Two rpm such as 4000 rpm and 5000 rpm were selected. Rotating time was set for 30 seconds and count was set for 4 times for every sample. 50 bar nitrogen vacuum was maintained through the spin coatingdeposition process.The samples were annealed at 300ºC for 15 minutes. Annealing process was done in vacuum section. Thewhole process was repeated again.

Thickness of AZO samples was measured by usingstylus profilometer (Model: DektakXT).RIGAKU UltimaIV X-ray Diffractometerwith theCu Ka radiations (λ = 1.54059 Å)was usedtodetermine X-ray diffraction patterns.Grain size was measured from Scherrer's formula [13]

$$D = \frac{0.9\lambda}{\beta\cos\theta_B}$$

Where λ is the wavelength of radiation, θ_B is the Bragg's angle at where XRD peak is found and β is full width at half maximum (FWHM).

SEM machine (Model: JSM 6010LA) was used to take image which helped to obtain surface morphological characteristics. Opticalproperties of the thin films were also investigated withthe help of UV-Visspectrophotometer in the photonwavelength range from 310 nm to 2500 nm. Transmittance was measured from the following equation

$$T = \frac{\text{transmitted intensity}}{\text{incident intensity}} \times 100\%$$

Absorption co-efficient (α) was measured as

$$\alpha = -\frac{\ln T}{t}$$

Where, t is the thickness of the sample.

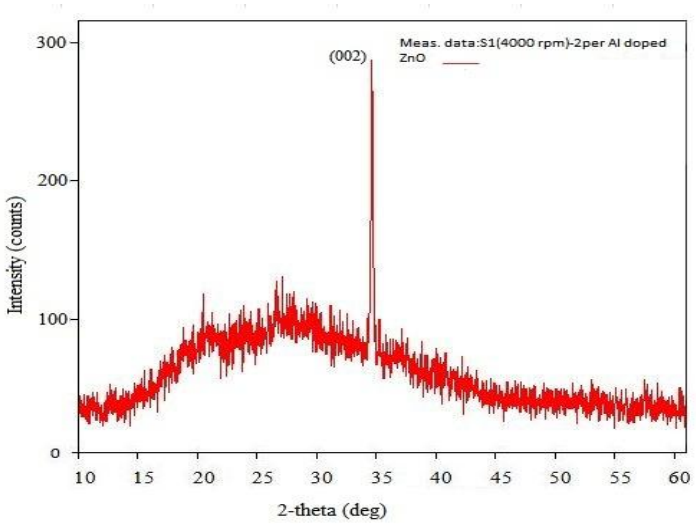
Optical bandgap was measured from the following energy, α is absorption co-efficient and A is the optical constant.

$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$

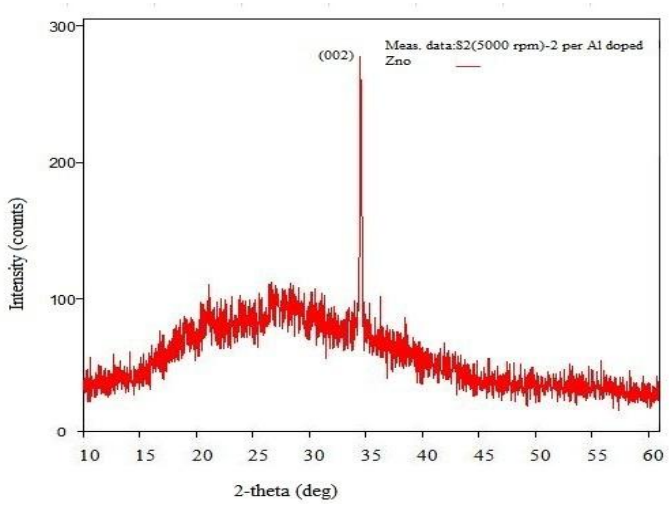
III. Results and Discussion

III A. XRD Analysis of the Thin Films

The thickness measured for both films was 100 nm. X-ray diffraction pattern of both AZO film are shown in Fig. 1. It is found that both have a sharp peak at (002) plane which reveals that both thin films are likely of crystalline hexagonal structure [14]. According to Bragg's equation the grain sizes were calculated and tabulated at table1.



(a)



(b)

Figure 1.XRD pattern of AZO thin film for (a) Sample-1 (4000 rpm) anb (b) Sample-2 (5000 rpm)

Table1.$2\theta_B$, FWHM and grain sizes for Sample-1 and Sample-2

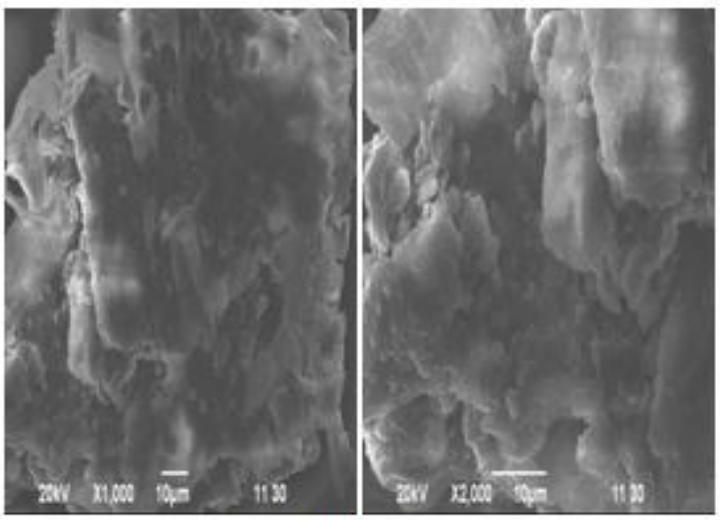
Thin Film	$2\theta_B$ (deg)	FWHM (deg)	Grain Size (nm)
Sample-1	34.34	0.363	0.401
Sample-2	34.44	0.306	0.476

IV. OPTICAL PROPERTIES

SEM images are shown in Fig. 2 for both samples. Film surfaces are not fully uniform and covered with the slightly inhomogeneous deposited material. It looks like a rough surface with a few numbers of scattered grains and without pores. These scattered grains prove the crystalline nature [9].

Another important optical property reflectance has been studied for both the AZO samples deposited on glass substrate using UV-Vis-NIR Spectrophotometer. The reflectance investigation has also been done in the range from 310 nm to 2500 nm. In Figures 3 and 4 the reflectance response against wavelength and the photon energy have been shown respectively. Different reflectance values have been found for different samples in different regions. Both the samples have given some irregular values of reflectance up to 940 nm. In the region from 380 nm to 700 nm (visible region) reflectance first has increased and then decreased.

From Fig. 4 it is clear that the reflectance value has started to increase from 0.5 eVand both the samples have achieved the maximum valueat 0.7 eV (1780 nm). Then it has started to decrease. The higher values have been found in the region for 0.5 eV to 2.5 eVand the lower responses for 2.5 eV to 4 eV. At starting point the reflectance values have been found 6.79% and 5.62% (at 310 nm and 4 eV) and at last 10.92% and 12.31% (at 2500 nm and 0.5 eV) for sample-1 and sample-2 respectively.



(a) Sample-1

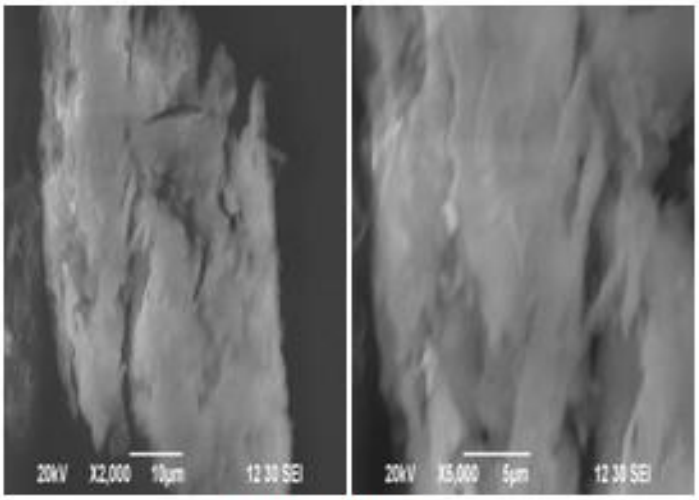


Figure 2. SEM images of AZO thin films for (a) Sample-1 (4000 rpm) anb (b) Sample-2 (5000 rpm).

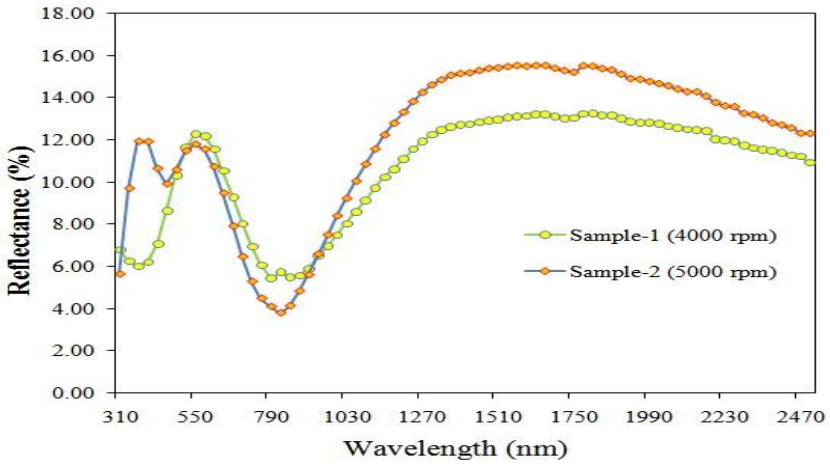


Fig 3: Reflectance (%) of AZO samples (different rpm) with respect to wavelength

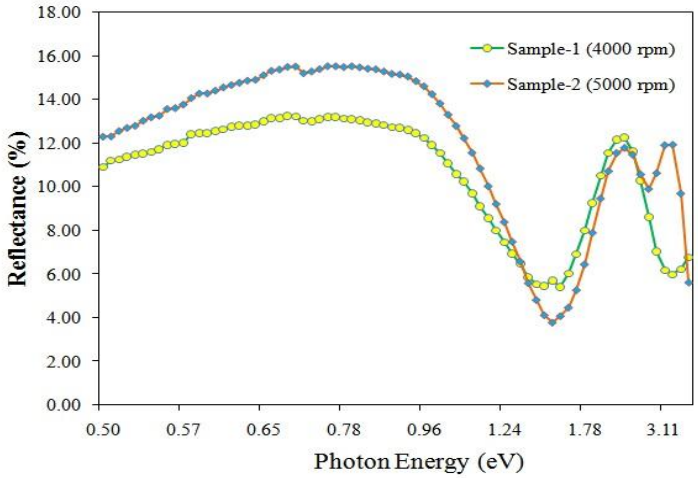


Fig 4: Reflectance (%) of AZO samples (different rpm) with respect to photon energy

Crystalline structure is more clearfor sample-1 than for sample-2. Percentage transmittance is shown in Fig. 5 in the region of wavelength 310 nm to 2500 nm. Transmittance increases with the increase of wavelength. In the visible and infrared regions transmittance is about 80% to 85%. But in the ultraviolet region it is very low. Absorption characteristic shows the opposite nature of transmittance which depicts in Fig. 6. It is decreasing

with the increase of wavelength and gives a consistent value beyond 700 nm. Low absorption at visible and ultraviolet regions indicates higher transmission. From 400 nm to downward values absorption increases rapidly which indicates the position of optical band gap [15].By plotting$(\alpha h\gamma)^2$ versus $h\gamma$(Fig. 7)for AZO thin film bandgap is determined. Band gaps for sample-1 and sample-2 arefound 3.275 eV and 3.11 eV respectively [15]. It is seen that band gap value of Sample-2 is lower than that of Sample-1. So less energy is required to transmit electron from valence band to conduction band for Sample-2. It also indicates that transmittance of Sample-1 is greater than that of Sample-2.

The extinction coefficient, K is the imaginary part of the complex index of refraction which is also related to the light absorption. Fig. 8 shows that the extinction coefficient increases with the increase of wavelength (nm). Fig. 9 shows the refractive index for different wavelengths and gives a higher value in the region from 700 nm to 2500 nm[16].

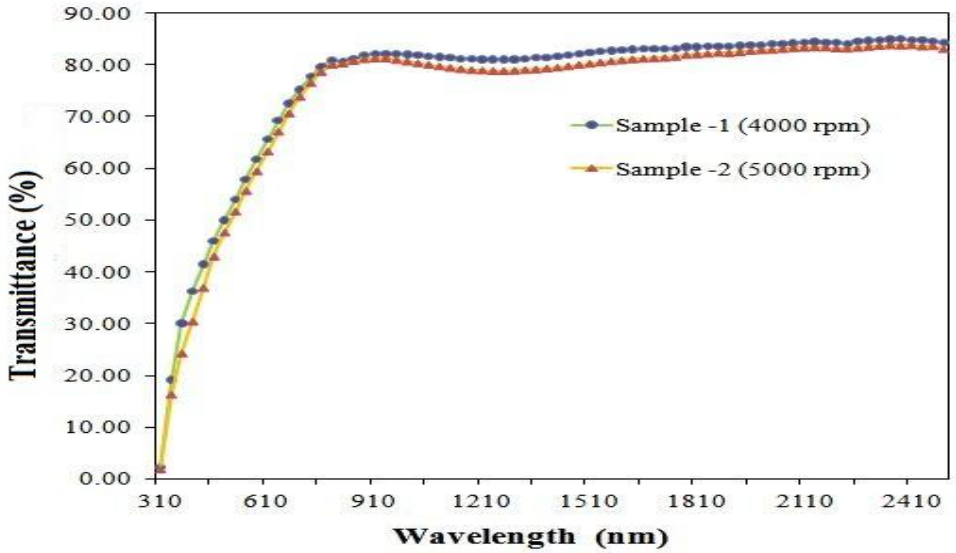


Figure 5. Optical transmittance of AZO thinfilms

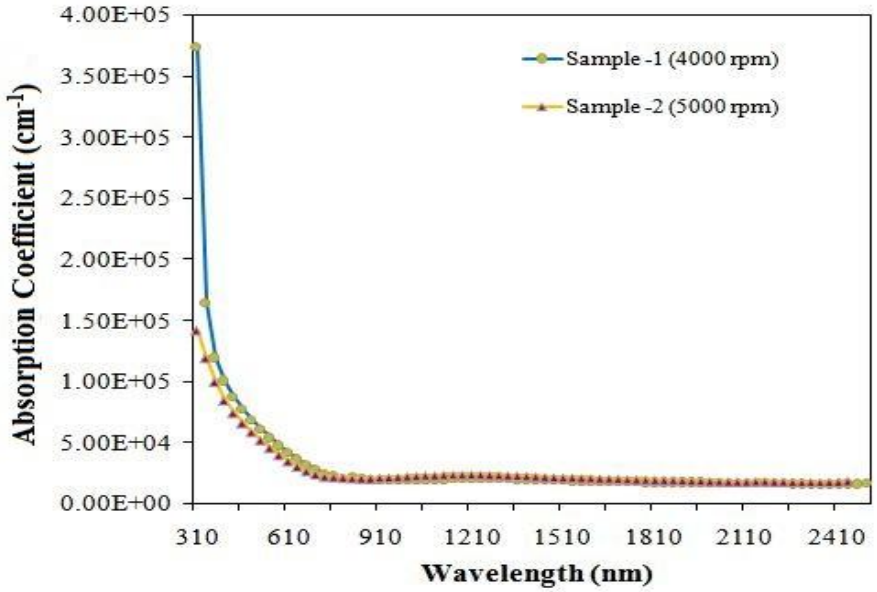
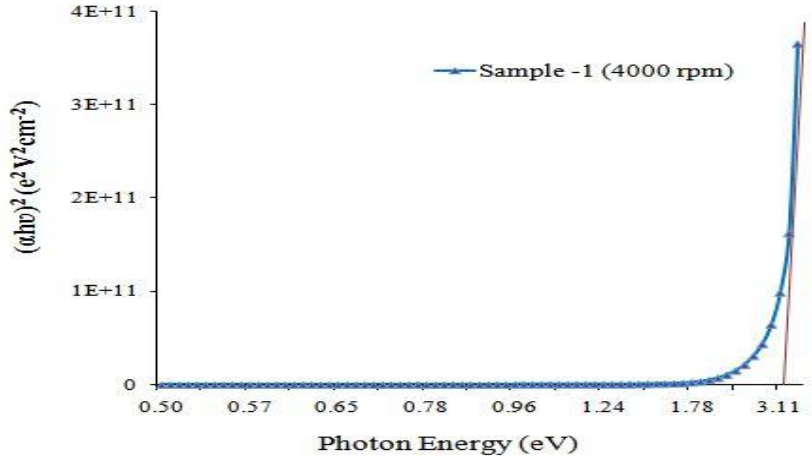
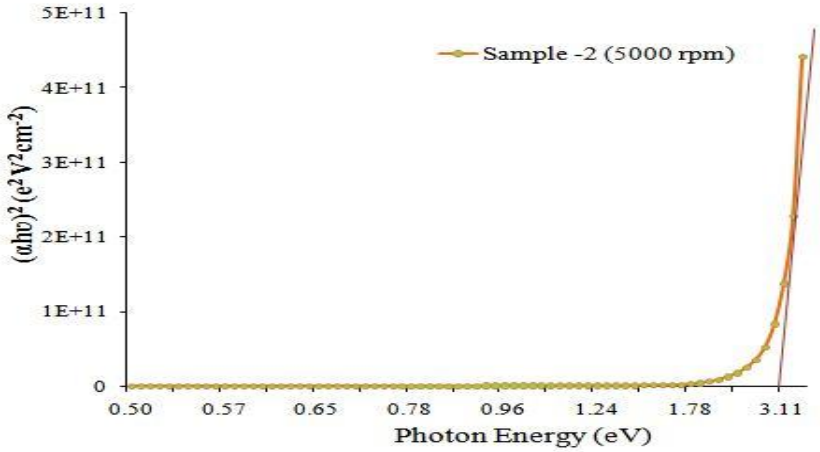


Figure 6. Absorption co-efficient of AZO samples (different rpm) vs. wavelength



(a) Sample_1



(b) Sample_2

Figure 7. Band gap plot of $(\alpha h\gamma)^2$ versus hγ for AZO thin films

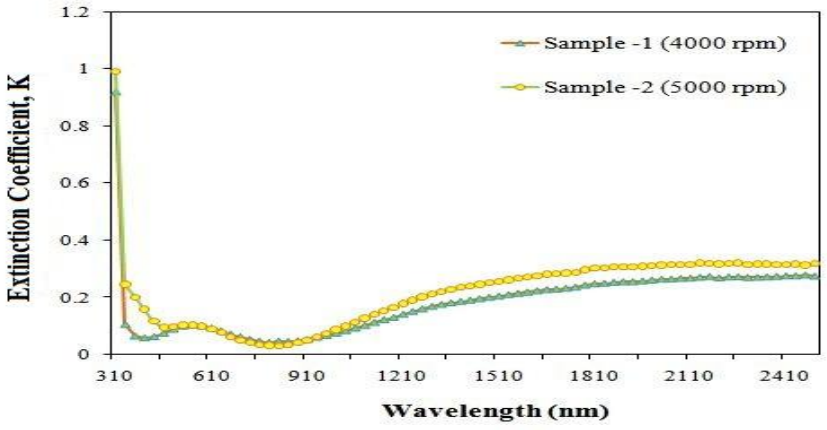


Figure 8. Extinction co-efficient of AZO samples (different rpm) vs. wavelength

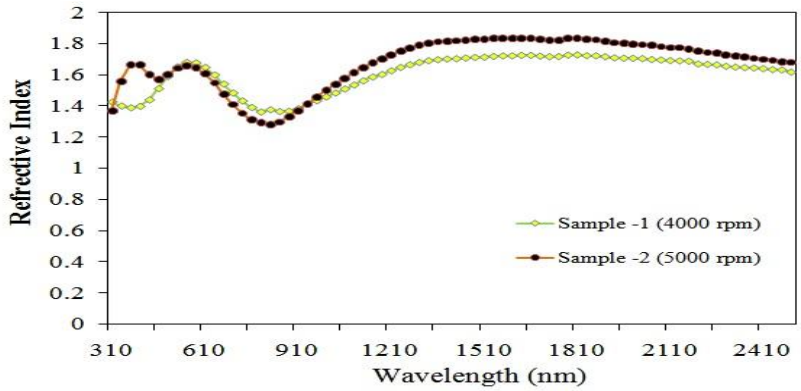


Figure 9. Refractive index of AZO samples (different rpm) vs. wavelength

V. Conclusion

AZO nanostructured thin films were prepared and synthesized onto glass substrate by spin coating method. From the diffraction peak of XRD pattern the crystalline nature was determined. Grain size was also measured. The optical characteristics were obtained within 310 nm and 2500 nm wavelength region. Maximum transmittance was found 85%.So it can be used as the transparent window layer in the solar cell. Optical bandgaps were measured 3.275 eV and 3.11 eV.

Acknowledgements

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