Laser energy effect on the properties of ZnS thin films prepared by PLD technique

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Abstract

Zinc sulfide (ZnS) thin films were deposited on glass substrates using pulsed laser deposition technique. The laser used is the Q-switched Nd: YAG laser with 1064nm wavelength and 1Hz pulse repetition rate and varying laser energy (700mJ-1000mJ) with 25 pulse. The substrate temperature was kept constant at 100°C. The structural, morphological and optical properties of ZnS thin films were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscope (AFM) and UV-VIS spectrophotometer.

Key words

ZnS thin film, PLD, surface roughness.

Article info

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تاثير طاقة الليزر على خصائص الاغشية الرقيقة لكبريتيد الزنك المحضرة باستخدام تقنية الترسيب بالليزر النبضي

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الخلاصة

الاغشية الرقيقة لكبريتيد الزنك (ZnS) نميت على قواعد زجاجية باستخدام تقنية الترسيب بالليزر النبضي. الليزر المستخدم هو ليزر النيديميوم ياك النبضي (Nd: YAG) الذي يعمل بتقنية عامل النوعية ذو طول موجي (1064nm) و معدل تكرار نبضة (1 Hz) و بطاقات ليزر متغيرة (700mJ-1000mJ) مع 25 نبضة. درجة حرارة القاعدة بقيت ثابتة عند $100\ ^0C$. الخصائص التركيبية، الشكلية و البصرية لاغشية كبريتيد الزنك الرقيقة درست باستخدام حيود الاشعة السينية (XRD) ، المجهر الالكتروني الماسح (SEM)، مجهر القوة الذرية AFM و مقياس الطيف الضوئي UV--VIS.

Introduction

Zinc sulphide belongs to II-VI group compound material with large direct band gap between 3.4-3.7eV depending upon composition. It is potentially important material to be used as an antireflection coating for heterojunction solar cells [1], light emitting diode [2, 3], and other optoelectronic devices such as blue light emitting diode [4], electro luminescence devices and photovoltaic cells which enable wide application in the field of displays [5,6], sensor and laser [7]. In recent years ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counter parts. Therefore much effort has been made to control the size, morphology and crystalline of ZnS thin films. There has been growing

interest in developing techniques for preparing semiconductor nano particles and films.

Experimental

ZnS thin films were deposited by using the pulsed laser deposition technique. The chamber was evacuated to a base pressure of (10^{-3} mbar) at a substrate temperature of 100^{o}C. Q-switched Nd: YAG laser with a wavelength of 1064 nm with different laser energies (700mJ-1000mJ) and fixed number of pulses (25 pulse) was used; the focal length for the lens was about 13cm with a repetition rate of 1 Hz. The distance between the target and the substrate was kept at 2.5 cm. Fig.1 shows the setup of PLD. After deposition, the structural, morphological and optical properties of ZnS thin films were characterized with X-ray diffraction (XRD), atomic force microscope (AFM) and UV-VIS spectrophotometer.

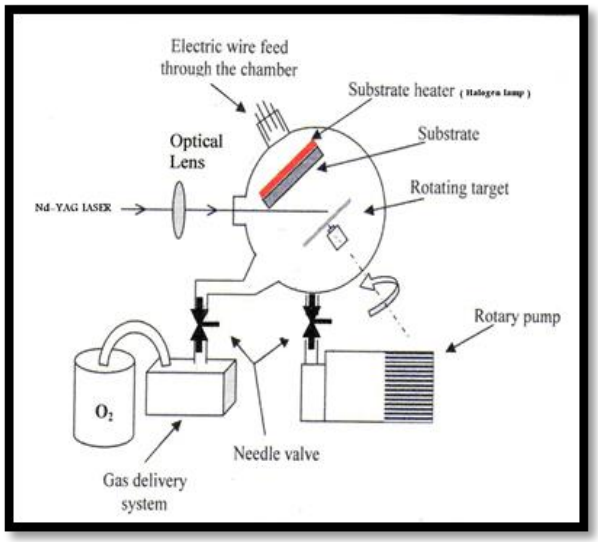


Fig.1: PLD setup.

Results and Discussion

1. Optical Properties

Optical properties of ZnS thin films were determined from the transmission, absorption and reflection measurements in the range of 300-800 nm. Figs. (2-4) show the variation of optical transmittance, absorbance and reflectance as a function of wavelength for the films prepared at different laser energies (700mJ, 800mJ, 900mJ & 1000mJ). From the graphs, it appears that ZnS thin films have a higher transmission and lower absorption as the laser energy decreased .In fact, increasing the fluency means delivering more energy that implies ablating larger amount of material, because of the plasma plume becomes more intense and the ZnS particles cloud becomes bushy. Most likely, this means that big particles will be present due to longer growth time and to the high probability of deposited particles muster. In other words, atoms and nanoscale particles deposited under laser radiation tend to muster during and after the laser pulse. This reality leads to generate of larger particles that becomes more distinguished when the density of the ZnS particles increases further with increasing the fluency. Maximum transmission was reached in the near IR region approximately 80%.

Absorption coefficient (α) associated with the strong absorption region of the films was calculated from absorbance (*A*) and the film thickness (*t*) using the relation [9]:

$$\alpha = 2.3026\, A / t \qquad (1)$$

The absorption coefficient (α) was analyzed using the following expression for near-edge optical absorption of semiconductors:

$$(\alpha\, h\nu) = \mathrm{K}\,(h\nu - E_g)^{n/2} \qquad (2)$$

Where: K is constant, E_g is the separation between the valence and conduction bands and n is a constant that is equal to 1 for direct band gap semiconductors. The band gap values were determined from the intercept of the straight-line portion of the $(\alpha h\nu)^2$ against the $h\nu$ graph on the $h\nu$ axis Fig.5.

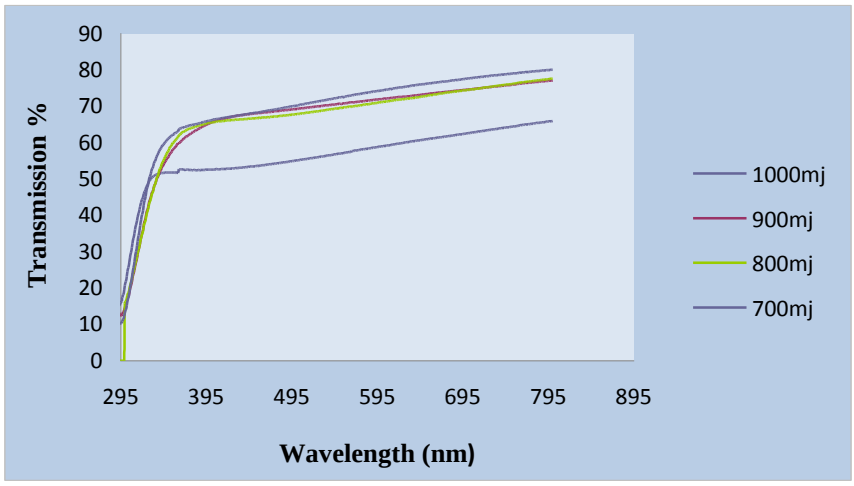


Fig.2: Optical transmission as a function of wavelength for ZnS/glass at different laser energy.

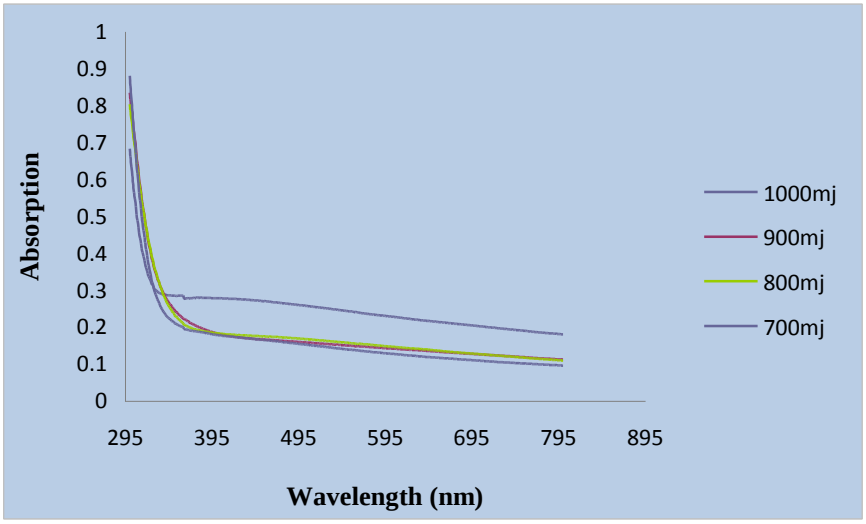


Fig.3: Optical Absorption as a function of wavelength for ZnS/glass at different laser energy.

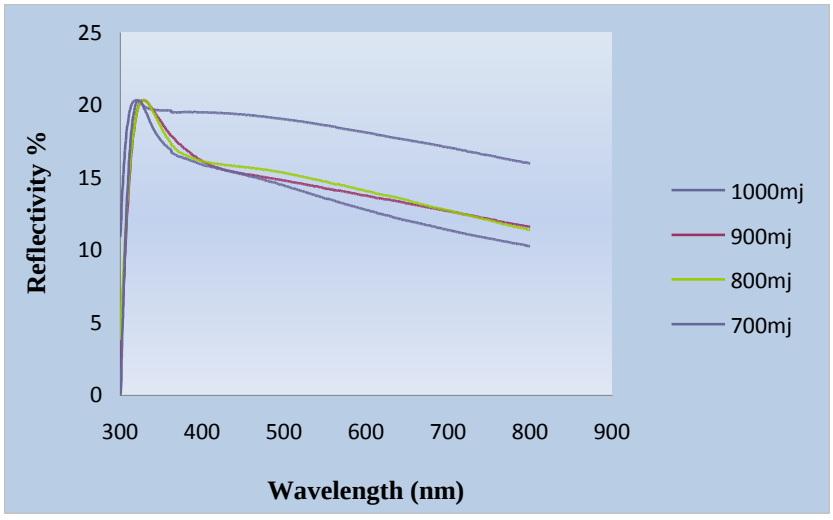


Fig.4: Optical reflectivity as a function of wavelength for ZnS/glass at different laser energy.

The linear part shows that the mode of transition in these films is of direct nature. The calculated band-gap value of the films was between (3.75-3.85) eV. The band-gap values are higher than bulk value of ZnS (3.68 eV) because of quantum confinement of ZnS nanocrystals.

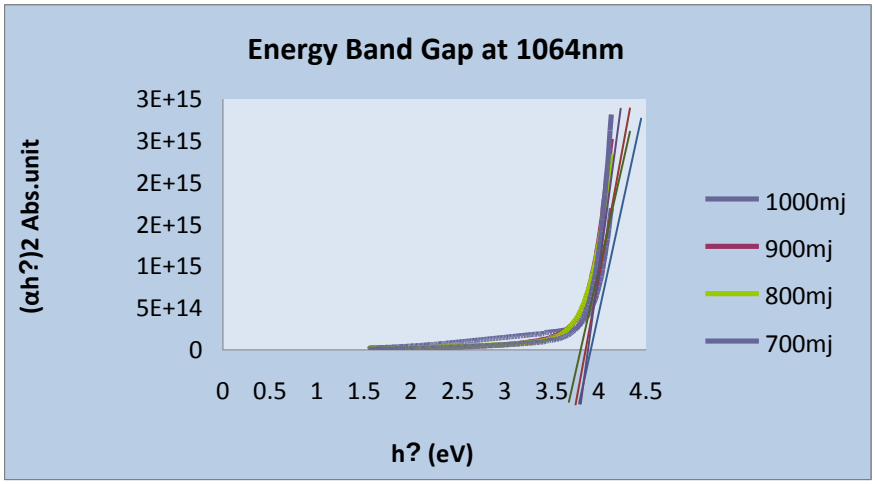


Fig.5: Optical energy band gap for ZnS/glass at different laser energy.

2. Structural and morphological properties

2.1 XRD studies

All the deposited ZnS films were white, homogeneous with a good adherence to the substrate. Generally ZnS material has the hexagonal, wurtzite type structure or cubic, zinc blend-type structure. X-ray diffraction patterns of ZnS thin films prepared at different laser energy (1000 &700) mJ are shown in Fig. (6 a &b). It shows that phase present in the deposited films belongs to the hexagonal wurtzite structure with reflections from (008), (104) planes and (008) plane at laser energy (1000mJ & 700mJ) respectively. The grain size of the nanocrystalline films is estimated using the Scherrer formula [9].

$$D = K \lambda / \beta \cos \theta \qquad (3)$$

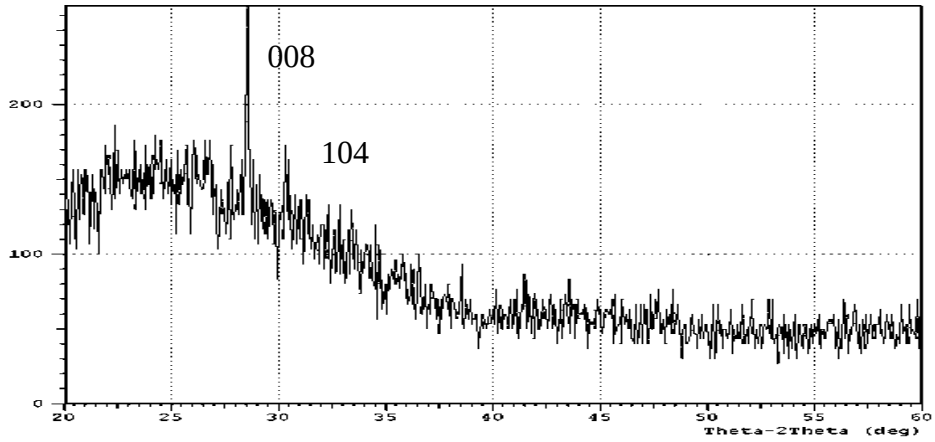
Where K is a constant taken to be 0.94, **λ** the wavelength of X-ray used (**λ** = 1.54056 A °) and **β** the full width at half maximum. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystals of very

small size. The grain sizes were found to be within the range of 33.8-71.7 nm.

2.2 SEM analysis

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Fig. (7) shows a picture of ZnS powder observed by SEM. The particle size from the SEM is found to be in the range of 210 nm.

a)



b)

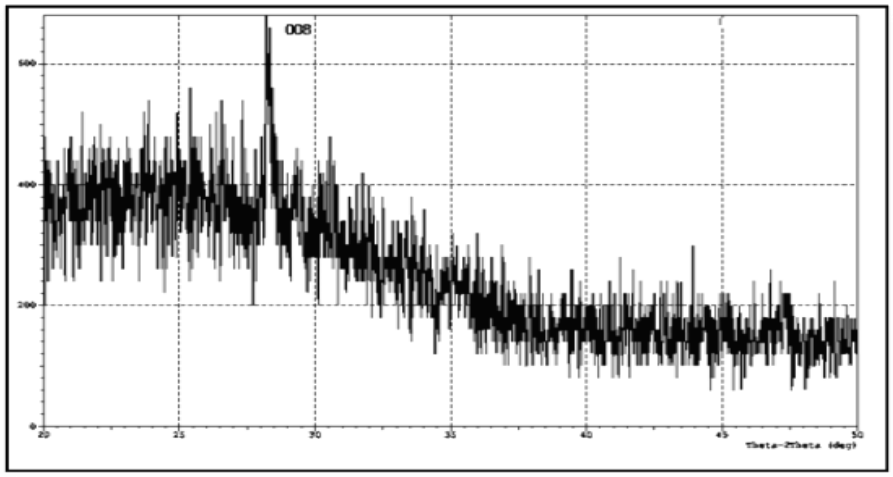


Fig.6: XRD diffraction pattern of ZnS a) at laser energy 1000mJ and b) at laser energy 700mJ.

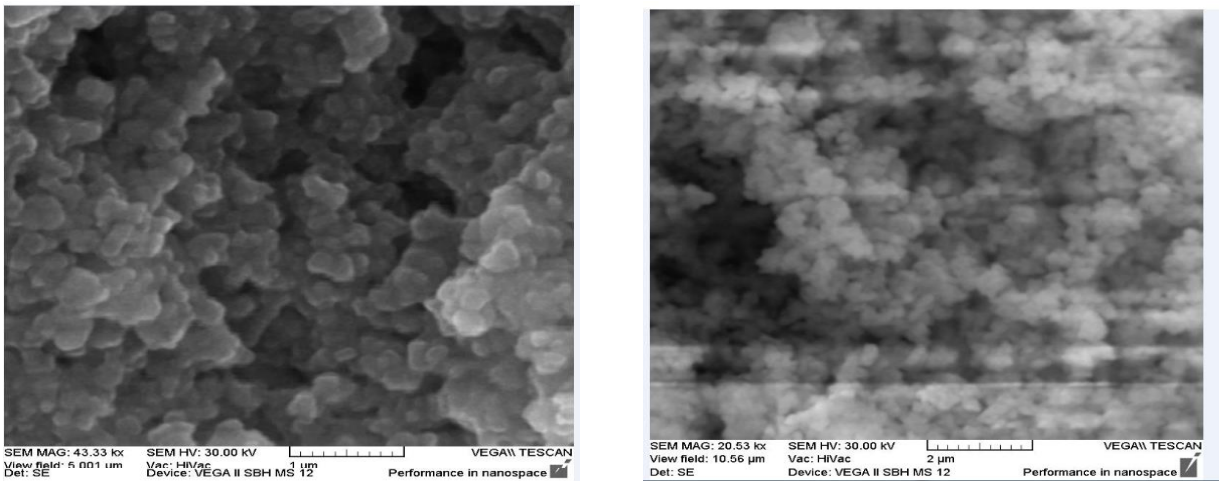


Fig.7: SEM picture of ZnS powder.

2.3 AFM analysis

AFM images which have been taken to the samples are shown in Fig. (8 a, b&c) which corresponding to the 1000Mj 900mJ and 700mJ samples respectively. The surface roughness and grain size were tabulated in Table 1.

Table 1

Energy (mJ)	Surface roughness (nm)	Average diameter (nm)
700	1.77	54.79
900	0.353	130.46
1000	1.14	92.77

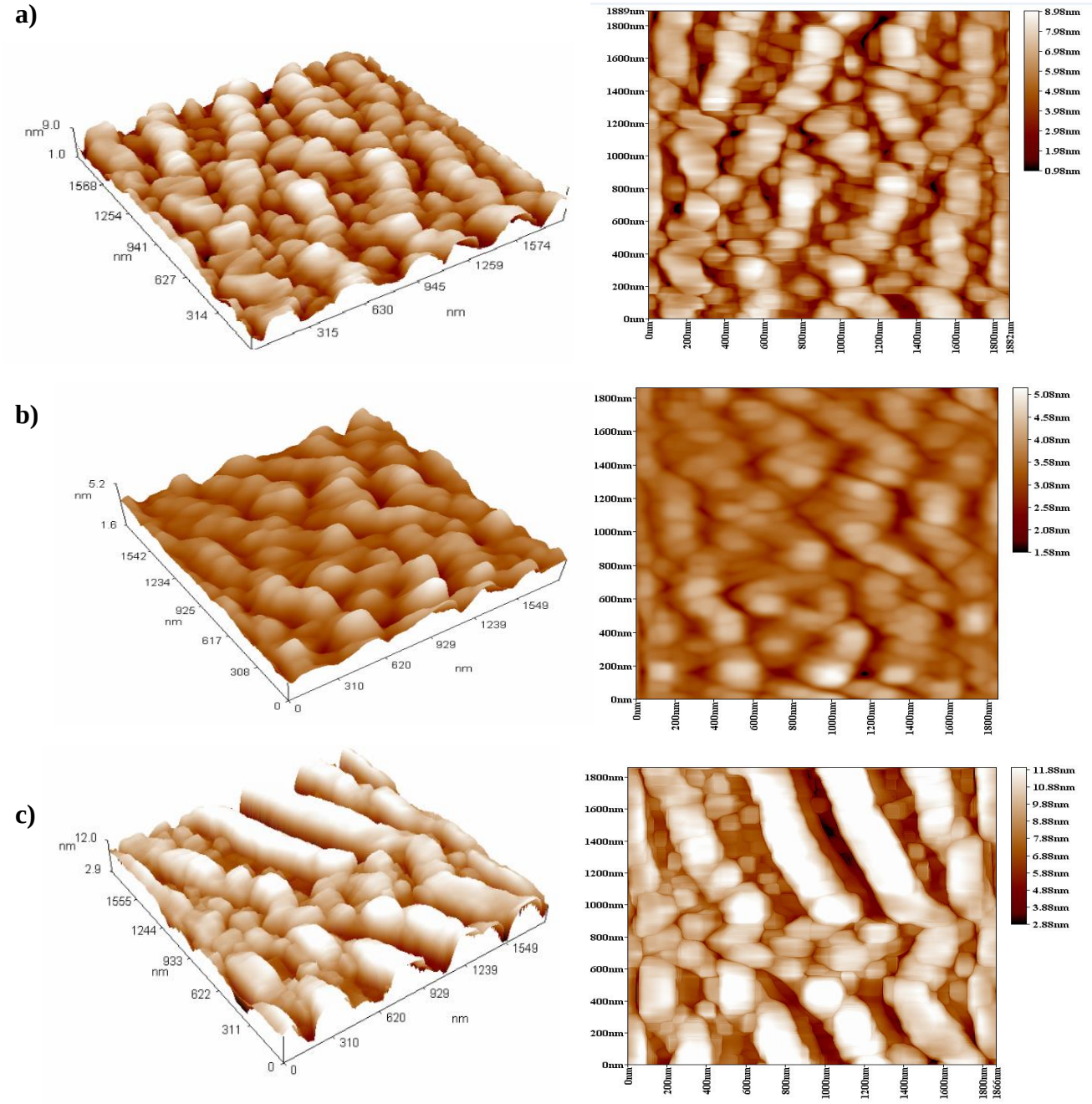


Fig.8: AFM images at a) 1000mJ, b) 900mJ and c) 700mJ.

Conclusions

Thin films of ZnS prepared by PLD technique are found to be nanocrystalline. The crystallite sizes measured by XRD studies are found to be within 33.8-71.7 nm. XRD shows that samples are of wurtzite hexagonal phase which is important for device performance. SEM studies showed irregular distributions of particles with particle size at a range of 210nm. The films were found to have high transmittance in the range of 65% and 80% in the UV–VISNIR regions; hence, they could be effective as thermal control window coatings for cold climates and antireflection coatings. The films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, and this fact supports the formation of nanocrystallites in these films.

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