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# Characterization and properties of $ZnO_{1-x}S_x$ alloy films fabricated by radio-frequency magnetron sputtering

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## ABSTRACT

A series of  $ZnO_{1-x}S_x$  alloy films ( $0 \le x \le 1$ ) were grown on quartz substrates by radio-frequency (rf) magnetron sputtering of ZnS ceramic target, using oxygen and argon as working gas. X-ray diffraction measurement shows that the  $ZnO_{1-x}S_x$  films have wurtzite structure with (002) preferential orientation in O-rich side ( $0 \le x \le 0.23$ ) and zinc blende structure with (111) preferential orientation in S-rich side ( $0.77 \le x \le 1$ ). However, when the S content is in the range of 0.23 < x < 0.77, the  $ZnO_{1-x}S_x$  film consists of two phases of wurtzite and zinc blende or amorphous  $ZnO_{1-x}S_x$  phase. The band gap energy of the films shows non-linear dependence on the S content, with an optical bowing parameter of about 2.9 eV. The photoluminescence (PL) measurement reveals that the PL spectrum of the wurtzite  $ZnO_{1-x}S_x$  is dominated by visible band and its PL intensity and intensity ratio of UV to visible band decrease greatly compared with undoped ZnO. All as-grown  $ZnO_{1-x}S_x$  films behave insulating, but show n-type conductivity for w- $ZnO_{1-x}S_x$  and maintain insulating properties for  $\beta$ - $ZnO_{1-x}S_x$  after annealed. Mechanisms of effects of S on optical and electrical properties of the  $ZnO_{1-x}S_x$  alloy are discussed in the present work. © 2010 Elsevier B.V. All rights reserved.

# 1. Introduction

ZnS and ZnO are important II-VI group wide band gap semiconductors, and have band gap of 3.68 eV and 3.30 eV at room temperature, respectively [1]. In addition, ZnS and ZnO are of extremely large exciton binding energy of 60 meV and 40 meV, respectively, so their excitons are thermally stable at room temperature. Thus they have attracted intense interest owing to their promising applications in short-wavelength light emitting diodes and laser diodes [2-4]. The alloying of ZnS and ZnO has been considered to be an interesting research for a long time. The  $ZnO_{1-x}S_x$ alloy is referred to isovalent impurities materials, due to S and O are isovalent elements. It is well known that isovalent impurities with a large electronegativity and atom size mismatch compared with the replaced atoms always strongly modify the electronic properties of the host crystal. The most prominent example is III-N-V semiconductor materials, such as,  $GaN_xAs_{1-x}$ , where N replaces Ga element in GaAs, founding that the energy band structure of GaAs is strongly affected by the isovalent N element [5]. A non-linear dependence of the fundamental band gap of GaAs on the N composition is observed in  $GaN_xAs_{1-x}$ , and this behavior is referred

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to band gap bowing. A band-anticrossing (BAC) model has been developed to explain these unusual effects [6,7]. In the BAC model, the anticrossing interaction between the localized N states and the conduction-band states of the host semiconductor modifies the electronic structure of the host compounds, which accounts for the band gap bowing effects.

Due to large mismatch of electronegativity and atom size between O and S, ZnOS alloy is expected to have large bowing parameter as GaNP and GaNAs. Based on theory calculation, the synthesis of  $ZnO_{1-x}S_x$  is quite difficult due to different crystalline symmetry of ZnS and ZnO, and the inferior stability of sulfur, which is vaporized at 373 K. Florian Janetzko and Jug [8] calculated the free enthalpy of mixing  $(\Delta M_G)$  of  $ZnO_{1-x}S_x$  at x=0.0208 to be 0.92 kJ/mol at T = 1000 K but negative at 2000 K, which implies that alloying of ZnO and ZnS is impossible at thermodynamic equilibrium state under relatively low temperature. However at the non-equilibrium states, the alloying of ZnS and ZnO may be performed. In the recent years, Yoo et al. [9] reported that  $ZnO_{1-x}S_x$ alloys  $(0 \le x \le 0.15)$  were synthesized by pulse laser deposition. Meyer et al. [10] also synthesized  $ZnO_{1-x}S_x$  by reactive sputtering in composition range of  $0 \le x \le 1$ . Recently, Persson et al. [11] reported that the valence-band (VB) offset  $E_{v}(x)$  of  $ZnO_{1-x}S_{x}$  increases strongly for small S content, whereas the conduction-band edge  $E_{c}(x)$  increases only weakly, according to density functional calculations of  $ZnO_{1-x}S_x$ . Based on this calculation, the acceptor levels in ZnO could be efficiently decreased due to the strong increase of

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the valence-band maximum (VBM) in  $\text{ZnO}_{1-x}S_x$  alloy, which probably may be an efficient way to enhance conductivity of p-type ZnO-based alloy. Moreover, we can also modulate the band gap of  $\text{ZnO}_{1-x}S_x$  by changing the sulfur content in  $\text{ZnO}_{1-x}S_x$ . The bandgap engineering of  $\text{ZnO}_{1-x}S_x$  may possibly optimize the performance of ZnO-based electronic and optoelectronic devices. Nowadays, poor efficient and unstable p-type ZnO has been a barrier which blocks the ultraviolet optoelectronic devices application of ZnO. We hope to achieve high quality p-type ZnO with low ionized energy of acceptor, through proper acceptor element doping in  $\text{ZnO}_{1-x}S_x$ alloys (x < 0.2). Consequently, it is very important to have a definite clear picture of the properties of  $\text{ZnO}_{1-x}S_x$  alloys.

In the present work,  $ZnO_{1-x}S_x$  alloy films were deposited on quartz substrates by radio-frequency (rf) magnetron sputtering technique. Their structures as well as optical and electrical properties were investigated.

#### 2. Experimental procedures

A series of  $ZnO_{1-x}S_x$  alloy films were deposited on quartz substrates using oxygen and argon as working gas by rf-magnetron sputtering technique. The target was a high pure (99.99%) ZnS ceramic. The quartz substrates were cleaned at room temperature in an ultrasonic bath using acetone, ethanol and de-ionized water for 10 min, respectively, and then blown dry by nitrogen. The vacuum chamber was evacuated to a base pressure of  $6 \times 10^{-4}$  Pa. The flow ratio of Ar to  $O_2$  was changed to obtain  $ZnO_{1-x}S_x$  alloy films with different S content. The films were grown for 2 h at substrates temperature of 573 K. All the as-grown samples were annealed for 20 min under Ar ambient in a temperature range from 773 K to 873 K.

X-ray Diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm) was used to characterize the structure of the films. Composition of the films was detected by Energy disperse spectroscopy (EDS). UV–VIS–NIR SCANNING spectrophotometer was used to measure the optical band gap. The photoluminescence (PL) measurement was carried out at room temperature by the excitation from a 325 nm He–Cd laser. The electrical properties were measured in the van der Pauw configuration by Hall effect measurement system at room temperature.

#### 3. Results and discussion

Fig. 1 shows the XRD patterns of the  $ZnO_{1-x}S_x$  films with different S concentration ( $0 \le x \le 1$ ). As shown in Fig. 1(a)–(c), one obvious preferential XRD peak is observed near diffraction angle of (002) peak of ZnO with wurtzite structure ( $34.42^\circ$ ) in the O-rich side ( $0 \le x \le 0.23$ ), and the diffraction angle of the (002) peak shifts from  $34.42^\circ$  of the ZnO to lower angle with the increasing S content. It is well known that ionic radius of S is larger than that of O ( $r_s/r_o = 1.39$ ) and that the calculated bond length  $\delta$ (Zn-anion) is 1.98 Å for Zn–O bond and 2.34 Å for Zn–S bond [11]. Obviously, lattice constants of *c*-axis will increase as S substitutes for O sublattice, leading to decrease in diffraction angle of the (002) peak. Therefore, it is concluded that the ZnO<sub>1-x</sub>S<sub>x</sub> alloy films are of wurtzite structure and preferentially oriented in (002) direction in the O-rich side, and denoted by w-ZnO<sub>1-x</sub>S<sub>x</sub>.

Fig. 1(g) shows XRD pattern of ZnS (x = 1), indicating that there are many diffraction peaks in the XRD pattern. In order to determine structure of the ZnS, its XRD pattern is given in diffraction angles of 20–80°, as shown in Fig. 2. The diffraction angles of XRD peaks are listed in Table 1. Results of Table 1 indicate that the diffraction angles of the peaks marked by  $\bullet$  in Fig. 2 are well consistent with XRD profile of ZnS with Zinc blende structure ( $\beta$ -ZnS) reported previously in literatures (JCPDS Card No. 77-2100). And the diffraction



**Fig. 1.** XRD patterns of annealed ZnO<sub>1−x</sub>S<sub>x</sub> with S content of (a) 0, (b) 0.12, (c) 0.23, (d) 0.47, (e) 0.77, (f) 0.85 and (g) 1.00. (▼) w-ZnO<sub>1−x</sub>S<sub>x</sub> (●) β-ZnO<sub>1−x</sub>S<sub>x</sub>.



**Fig. 2.** XRD pattern of ZnS. ( $\bullet$ )  $\beta$ -ZnS ( $\blacksquare$ )  $\alpha$ -ZnS.

#### Table 1

The X-ray diffraction data of peaks marked by ( $\bullet$ ) in Fig. 2 (Obs. denotes the observation results of  $2\theta$  (°) in the present experiment).

2θ (°) Obs.	2θ (°) β-ZnS	( <i>h k l</i> ) β-ZnS
28.55	8.531	111
33.01	33.062	200
47.42	47.455	220
56.24	56.308	311
59.01	59.030	222
69.37	69.370	400
76.61	76.650	331



**Fig. 3.** Plots of lattice constant and FWHM of the  $ZnO_{1-x}S_x$  alloy as a function of S concentration. (**■**) lattice constant of *c*-axis, (**●**) FWHM.

angle of the peak marked by I in Fig. 2 is closed to diffraction angle of (100) peak of ZnS with wurtzite structure ( $\alpha$ -ZnS). The intensity of the (100) peak is the strongest in XRD profile of  $\alpha$ -ZnS, but very weak in Fig. 2, implying that the amount of the  $\alpha$ -ZnS phase is very small in the film. It is well known that  $\beta$ -ZnS is stable thermodynamic phase at temperatures of below 1273 K, while  $\alpha$ -ZnS is unstable phase at temperatures of below 1273 K but stable at temperature higher than 1293 K [12]. Therefore, the ZnS film prepared at 573 K and annealed in high temperature should mainly consist of β-ZnS. Since rf-sputtering is a thermodynamic non-equilibrium process, a small amount of  $\alpha$ -ZnS phase may form at a relative low growth temperature, as shown in Fig. 2. However, with increasing substrate temperature, the  $\alpha$ -ZnS phase gradually disappears and the ZnS film consists of only  $\beta$ -ZnS. That is consistent with result reported by Zhang et al. [12]. Based on the above discussion, it is concluded that the ZnS film consists of  $\beta$ -ZnS and very small amount of  $\alpha$ -ZnS.

In the S-rich side  $(0.77 \le x \le 1)$ , it is found from Figs. 1(e) and (f) that only one peak is observed. And the diffraction angles of the peak are near to those of  $(1 \ 1 \ 1)$  peak of  $\beta$ -ZnS or  $(0 \ 0 \ 2)$  peak of  $\alpha$ -ZnS and decrease with increasing S content. Based on the above discussion, the peak should be due to  $(1 \ 1 \ 1)$  peak of  $\beta$ -ZnS, and the ZnO<sub>1-x</sub>S<sub>x</sub> films in the S-rich side are of zinc blende structure and have preferential orientation in  $(1 \ 1 \ 1)$  direction, which are denoted by  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub>. This is different from result reported by Meyer et al. [10], where they attributed the peak to  $(0 \ 0 \ 2)$  peak of  $\alpha$ -ZnS and concluded that the ZnO<sub>1-x</sub>S<sub>x</sub> films in the S-rich side were of wurtzite structure.

It is found in the present work that it is difficult to fabricate a single phase of  $ZnO_{1-x}S_x$  alloy with wurtzite or zinc blende structure in the intermediate S content (0.23 < x < 0.77), instead, phase segregation occurs and the  $ZnO_{1-x}S_x$  alloy is composed by w- $ZnO_{1-x}S_x$  and  $\beta$ - $ZnO_{1-x}S_x$  or amorphous  $ZnO_{1-x}S_x$  alloy, as shown in Fig. 1(d). That is due to that the free enthalpy of mixing of  $ZnO_{1-x}S_x$  alloy is positive [9] and solid solubility of ZnO in ZnS or ZnS in ZnO is limited even though in non-equilibrium thermodynamic process [13]. The structure of the  $ZnO_{1-x}S_x$  alloy in the intermediate S content obtained in the present work is very different from that reported by Meyer et al. [10], where the  $ZnO_{1-x}S_x$  alloy consists of a single phase of  $ZnO_{1-x}S_x$  alloy with wurtzite structure.

Fig. 3 shows the lattice constants and full width at half maximum (FWHM) of the  $ZnO_{1-x}S_x$  films comprised by a single phase of w- and  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> as a function of S concentration. The FWHM are determined by fitting the (002) peak with Gaussian fitting programme in OriginPro7.5. Since the XRD patterns of the w-ZnO<sub>1-x</sub>S<sub>x</sub> films are all (002)-peak preferential, the *a*-axis lattice constant cannot be calculated directly from the XRD data in present experiments. So, only lattice constant of *c*-axis is given in Fig. 2 for



**Fig. 4.** The absorption spectra of  $ZnO_{1-x}S_x$  films with various S concentration.

w-ZnO<sub>1-x</sub>S<sub>x</sub>. The variation of the lattice constants of ZnO<sub>1-x</sub>S<sub>x</sub> films differs from that of  $Mg_xZn_{1-x}O$ , which follows the Vegard's law, showing non-linear variation. That is consistent with the results reported by Yoo et al. [9]. The change of the FWHM is interesting. It does not change monotonously with S concentration, but decreases firstly and then increases with increasing S concentration for w- $ZnO_{1-x}S_x$ , and with decreasing S concentration for  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub>, respectively, as shown in Fig. 3. It is well known that FWHM is determined mainly by lattice stress and grain size. In the present work, grain size of alloy films is similar, so, the FWHM is determined mainly by lattice stress. Lattice stress of an alloy film comes from nonuniformity of composition as well as lattice and thermal mismatch between film and substrate. In order to understand change of the FWHM clearly, we only discuss the change of the lattice stress of  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> with O content here. When a small amount of S in  $\beta$ -ZnS is substituted by O to form  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> alloy, on the one hand, the substitution destroys lattice order of the  $\beta$ -ZnS lattice, bringing lattice distortion and stress, but the stress is small. On the other hand, the lattice disorder can relax lattice stress induced by lattice and thermal mismatch. The two effects on the lattice stress induced by the substitution may lead that the lattice stress of  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> decreases with increasing O concentration. However, if the O content in  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> is large, the lattice order of the  $\beta$ -ZnS will be destroyed seriously, the lattice stress will be determined mainly by the substitution, resulting in monotonous increase of the lattice stress with increasing O content. Based on the above discussion, it is deduced that the lattice stress may decrease with increasing O content firstly, then reach a minimum at some O content as the S in the  $\beta$ -ZnS is replaced by a small amount of O, and increase quickly as the a large amount of S are replaced of O. The change of the lattice stress will result in that the FWHM shows a similar change, as shown in Fig. 3. The change of the FWHM for w-ZnO<sub>1-x</sub>S<sub>x</sub> can also be explained by the mechanism mentioned above.

It is known that properties of the materials depend on their structure. In the present work, the structure of  $ZnO_{1-x}S_x$  films changes with the S content, which should lead to change of their properties. Fig. 4 shows the absorption spectra of the  $ZnO_{1-x}S_x$  films, from which optical band gap of the  $ZnO_{1-x}S_x$  films can be estimated. For the S-rich and O-rich  $ZnO_{1-x}S_x$  films (that is,  $\beta$ - and w- $ZnO_{1-x}S_x$ ), they consist of a single phase and have one absorption edge in the absorption spectra, so have one certain optical band gap. However, for the  $ZnO_{1-x}S_x$  alloy with S concentrations of 0.23 < x < 0.77, they are composed by  $\beta$ - and w- $ZnO_{1-x}S_x$  due to occurrence of phase segregation, so, their optical band gap should include that of  $\beta$ - and w- $ZnO_{1-x}S_x$ , no new optical band gap is



**Fig. 5.** S concentration dependent band gap energy of the  $ZnO_{1-x}S_x$  alloy. (**■**) experimental data, solid line: band gap bowing fitting line.

observed. Fig. 5 exhibits the sulfur content dependence of the optical band gap of the  $\beta$ - and w-ZnO<sub>1-x</sub>S<sub>x</sub> films, indicating that the band gap decreases for w-ZnO<sub>1-x</sub>S<sub>x</sub> and increases for  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> with increasing S concentration. It is also found from Fig. 5 that the band gap energy of the w-ZnO<sub>1-x</sub>S<sub>x</sub> decreases greatly when a small amount of S incorporate into ZnO, implying that the w-ZnO<sub>1-x</sub>S<sub>x</sub> is a suitable well-layer material for preparation of ZnO-based quantum well. It is well known that the band gap of isovalent semiconductor alloys (AB<sub>1-x</sub>C<sub>x</sub>) which deviate from linear dependence can be described as

$$E_{ABC}(x) = xE_{AC} + (1-x)E_{AB} - b(1-x)x$$
(1)

where  $E_{ABC}$ ,  $E_{AC}$  and  $E_{AB}$  are band gap of  $AB_{1-x}C_x$ , AC and AB semiconductors, respectively, and b is the optical bowing parameter [14,15]. For the  $ZnO_{1-x}S_x$  films, the optical band gap of ZnS and ZnO films measured in the present work by rf-sputtering are 3.6 eV and 3.3 eV at 300 K, respectively. By fitting the data of Fig. 5 with Eq. (1), the bowing parameter of the  $ZnO_{1-x}S_x$  alloy films is calculated to be about 2.9 eV, which is a little smaller than 3.0 eV reported previously [10]. The band gap bowing effect has been comprehensively studied for III–N–V alloys (e.g., GaAs<sub>1–x</sub>N<sub>x</sub>) [16,17].A band-anticrossing (BAC) model has been developed to explain these unusual effects. The intercrossing interaction between the localized N states and the conduction-band states of the host semiconductors contributes to the band gap bowing effect. The BAC model recently has also been applied in II-VI group ternary semiconductors, such as,  $ZnS_xTe_{1-x}$  and  $ZnSe_xTe_{1-x}$  [18,19]. However, research report about electronic structure of  $ZnO_{1-x}S_x$  is few. Persson [11] has recently reported the strong valence-band offset bowing of  $ZnO_{1-x}S_x$  alloy. His density functional (DF) calculation revealed that ZnS-like bonds in w-ZnO<sub>1-x</sub>S<sub>x</sub> films raised the valence-band maximum (VBM) greatly but raised the conductionband minimum (CBM) little when the sulfur content is at x < 0.3, leading to VB bowing. The strong increasing of VBM can be used to decrease the ionization energy of acceptors in ZnO, which is very important to enhance the efficiency of p-type doping of ZnO.



Fig. 6. PL spectra of the  ${\rm ZnO}_{0.97}{\rm S}_{0.03}$  and undoped ZnO film measured at room temperature.

To further investigate effect of S on the optical properties of the  $ZnO_{1-x}S_x$ , photoluminescence (PL) measurement was performed at room temperature for ZnO<sub>0.97</sub>S<sub>0.03</sub> and undoped ZnO films fabricated under the same condition, as shown in Fig. 6. No emission related to S impurity is observed in the PL spectrum. That is consistent with the Clas Persson's explanation of the energy band structure for  $ZnO_{1-x}S_x$ , where Zn–S dimmers hybridized with the ZnO-host state do not form localized states, instead, broaden the VB dispersion, yielding the bowing effect. Fig. 6 shows that the PL intensity of both UV and visible bands and the intensity ratio of the UV to visible band of the  $ZnO_{0.97}S_{0.03}$  are much smaller than that of the undoped ZnO, implying that many defects form as 3 at% S incorporate into ZnO. Many research groups have investigated the origin of the visible emission band at about 2.4 eV and attributed it to oxygen vacancies  $(V_0)$  [20–22]. Therefore, results of Fig. 6 indicate that a lot of  $V_0$  form as S incorporates into ZnO, leading that crystal quality becomes poor and PL intensity of the all emission band and intensity ratio of UV to visible decrease greatly. Similar result is also observed in S-doped ZnO nanowires prepared via chemical vapor deposition [21].

The incorporation of S into ZnO also affects electrical properties of the ZnO<sub>1-x</sub>S<sub>x</sub> alloys. It is found that all as-grown samples are insulating. After annealed, the w-ZnO<sub>1-x</sub>S<sub>x</sub> is conductive, while  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> is still insulating. Table 2 shows the Hall effect results measured at room temperature for the w-ZnO<sub>1-x</sub>S<sub>x</sub> and undoped ZnO films prepared under the same condition, indicating that all the films show n-type conductivity. But, the resistivity of the ZnO<sub>1-x</sub>S<sub>x</sub> (0.03  $\leq x \leq 0.16$ ) is larger than the undoped ZnO, and both carrier concentration and hall mobility are smaller than those of undoped ZnO. This may be due to poor quality of the ZnO<sub>1-x</sub>S<sub>x</sub> films induced by incorporation of S. As mentioned above, the incorporation of S into ZnO can give rise to formation of many V<sub>O</sub> defects, which aggravates the scattering of the electrons as well as trap electrons and localized them, leading to decrease in conductivity, electron concentration and Hall mobility.

#### Table 2

Electronic properties of w-ZnO<sub>1-x</sub>S<sub>x</sub> at room temperature.

Sample	Resisitivity ( $\Omega$ cm)	Carrier concentration (cm <sup>-3</sup> )	Mobility $(cm^{-2} V^{-1} S^{-1})$	Туре
ZnO	3.09	8.4E+17	2.48	n
ZnO <sub>0.97</sub> S <sub>0.03</sub>	5.99E+1	4.7E+16	2.23	n
ZnO <sub>0.94</sub> S <sub>0.06</sub>	4.00E+2	8.1E+15	2.00	n
ZnO <sub>0.84</sub> S <sub>0.16</sub>	5.29E + 1	6.8E+16	1.75	n

## 4. Conclusions

A series of  $ZnO_{1-x}S_x$  alloy films  $(0 \le x \le 1)$  were grown on quartz substrates by radio-frequency magnetron sputtering of ZnS ceramic target, using oxygen and argon as working gas. The  $ZnO_{1-x}S_x$  films have wurtzite structure with (002) preferred orientation in O-rich side (0 < x < 0.23) and zinc blende structure with (111) preferential orientation in S-rich side (0.77 < x < 1), but consist of two phases of w- and  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> or amorphous  $ZnO_{1-x}S_x$  alloy phase in the range of 0.23 < x < 0.77. The band gap energy of the films shows non-linear dependence on the sulfur content, with an optical bowing parameter of about 2.9 eV. The emission in the visible range is dominant in the PL spectra for the w-ZnO<sub>1-x</sub>S<sub>x</sub>. The annealed w-ZnO<sub>1-x</sub>S<sub>x</sub> shows n-type conductivity, while  $\beta$ -ZnO<sub>1-x</sub>S<sub>x</sub> shows insulating. Compared with undoped ZnO, PL intensity and intensity ratio of UV to visible band of the w-ZnO<sub>1-x</sub>S<sub>x</sub> decrease greatly, and its electrical properties also degenerate very much. That may be attributed to formation of a lot of  $V_0$  defects induced by incorporation of S into ZnO.

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