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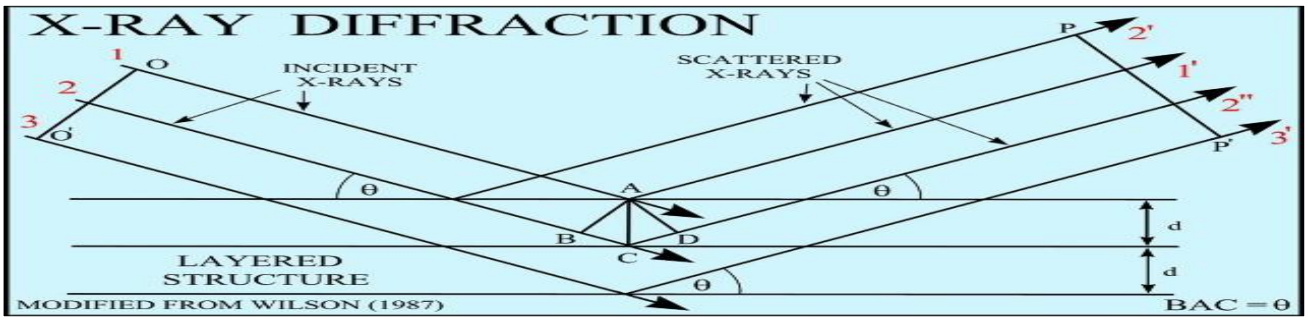

STUDIES ON THERMAL PROPERTIES OF ZINC SELENIDE THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION

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ABSTRACT

Zinc selenide films have been deposited on glass substrate by chemical bath deposition method. The structural properties of zinc selenide thin films have been investigated by X-ray diffraction techniques. The X-ray diffraction spectra showed that zinc selenide thin films are polycrystalline and have a cubic structure. The lattice parameter, grain size, microstrain were calculated and correlated with annealing temperature. The optical properties showed direct band gap values were found to be in the region of 2.62 to 2.78eV. All the films composed of minute grains was uniformly distributed on the surface. The electrical studies showed conductivity increases with increase in annealing temperature with n-type conductivity. The optoelectric and structural data discussed from the point of applications based on achieving high performance devices.

KEYWORDS : *X-ray diffraction, Optical absorption, Thin film materials.*

1. INTRODUCTION

Among these compounds, zinc selenide can be prepared in both n-and p-type forms.[1] Due to its very wide transmission range and high optical quality, it is used to manufacture optical components, mirrors, lenses etc. for infra-red lasers. More progress has been achieved in fabrication of blue-green light emitting diodes, photo-sensors, luminescent devices, photoelectrochemical cells, thin film transistors, etc.

[2-5] Ultra-violet (UV) imaging technology finds a lot of applications in the fields of UV astronomy, environmental and biological science, as well as in medical instrumentation. It is well known that II-VI wide band gap semiconductor enjoy the advantages of being highly resistive and UV light sensitive [6].

A very attractive method for deposition of zinc selenide thin films, due to possibility of large area deposition at low cost is the chemical bath deposition method. [7] Chemical deposition of zinc selenide has been reported in the literature from aqueous alkaline medium using sodium selenosulphate, selenourea and dimethylselenoura as selenide ion source.[8-12] The photoelectronic and other properties of zinc selenide thin films are highly structure sensitive, which in turn can heavily influence the device performance. The structural properties are strongly dependent on the deposition parameter. [5, 13]

Thermal treatment is necessary for fabrication process of several kinds of opto-electronic devices. The role of thermal annealing process is very important in achieving high performance devices. Therefore, studies of annealing effect on the surface, the structure and optical properties play a very important role in enhancing device efficiency. [14-15]

In the present investigation we describe the effect of annealing on zinc selenide films grown on glass substrates by chemical bath deposition. Structural, morphological, optical, compositional and electrical properties of annealed sample were study.

2. EXPERIMENTAL DETAILS

All the chemicals used for the deposition were analytical grade. It includes zinc sulphate heptahydrate, tartaric acid, liquor ammonia, hydrazine hydrate, sodium sulfite and selenium powder. All the solutions were prepared in double distilled water. Sodium Selenosulphate (Na_2SeSO_3) solution was prepared by the following the method reported earlier.[16] The commercially available, non-conducting glass slides of dimensions 26mm x 76mm x 2mm were cleaned by washing with chromic acid followed by rinsing in acetone and finally with double distilled water before use.

In actual experimentation, 10 mL (0.2 M) zinc sulphate heptahydrate solution was taken in 100mL beaker. 2.5mL (1 M) tartaric acid, 25mL (2.8 M) ammonia, 25mL (2%) hydrazine hydrate and 10mL (0.25 M) sodium selenosulphate were added in the reaction bath at room temperature. The pH of the reactive mixture is 11.45. The beaker was kept in oil bath. The non-conducting glass substrate were mounted vertically on a specially designed substrate holder and rotated in the reaction mixture with a speed of 55±2 rpm. The temperature of the bath was then allowed to increases slowly upto 333 K. After 120 minutes (2hr) the slides were removed, washed several times with double distilled water, dried naturally preserved in a dark desiccator over anhydrous $CaCl_2$. The resultant films were homogenous, well adherent to glass substrate. The films were annealed at 348K, 423K and 473K for 3 hours.

3. SAMPLE CHARACTERIZATION

The X-ray diffraction study of annealed zinc selenide film was carried out in the range of the diffraction angle 10^0-80^0 with Cu $K\alpha_1$ radiation using Philips PW-1710 diffractometer (λ=1.54056Å). The electrical conductivity of annealed zinc selenide thin film was measured using a 'dc' two-probe method. A quick drying silver paste was applied at the ends of the film for ohmic contact purpose. For the measurements of conductivity, a constant voltage of 30V was applied across the sample. The current was noted at different temperature. Maintaining a temperature gradient along the length of a film performed thermoelectric power measurements and the potential difference between the points separated by a 1cm was recorded with a digital microvoltmeter. A calibrated thermocouple probe (chromel-alumel, 24 gauge) with a digital indicator was used to sense the working temperature. The optical absorption measurements were made in the wavelength range 350-850 nm by using a Hitachi-330 (Japan) UV- VIS-NIR double beam spectrophotometer at room temperature. Placing an identical, uncoated glass substrate in the reference beam made a substrate absorption correction. The analysis of the spectrum was carried out by computing the values of absorption at every step of 2 nm. A 250MK-III Stereoscan (USA) scanning electron microscope (SEM) was used for the microscopic observations. Compositional analysis for zinc was carried out with an atomic absorption spectrophotometer using Perkin-Elmer 3030, USA.

4. RESULTS AND DISCUSSIONS

4.1 XRD Studies

The XRD pattern at room temperature of as grown as well as annealed at zinc selenide thin films are shown in Fig. 1, the corresponding data is shown in Table No. 1. Zinc selenide can be grown with either hexagonal, wurtzite type structure (JCPDS 15-105) or the cubic zinc blende type structure (JCPDS 37-1463). The as deposited film with poor crystallinity, since no well resolved peaks were observed except a small intensity peak at d value 3.275 Å (111). Annealing of film at 348K increases the intensity of the above peak with development of new peak at d = 2.842 Å (200). Annealing at 423 K introduces further peaks at d = 2.008 Å (220). Annealing at 473K gives new peaks at d = 1.691 Å (311) and d = 1.635 Å (222). The diffused background is due to amorphous glass substrate and also to some amorphous phase present in zinc selenide thin films. The peak intensity increases with increases in temperature. The annealed film shows increase in crystallite size due to annealing.

It is observed that all zinc selenide thin films are polycrystalline having face centered cubic zinc blende structure irrespective to their annealing temperature. All films show the most preferred plane (111) in addition to other (200) and (220) prominent reflections. No other peak besides these is observed which indicates the single phase cubic structure of the films. The constancy in the d value of prominent peaks shows that due to annealing, the material is neither shrinking nor expanding. Thus the cell symmetry is not changed by annealing. The lattice parameter was determined by using;

$$a = d\,(h^2+k^2+l^2)^{1/2} \text{ ----------1.1}$$

It is found that the lattice parameter decreases smoothly from 5.6741 to 5.6601 Å. as annealing temperature increases. The variation of lattice parameter with annealing temperature is shown in Fig. 2. The change in lattice constant for chemical deposited thin film over bulk clearly suggests that the film grains are strained which may be due to nature and concentration of the native imperfections changing.

The crystallite size (D) is calculated using Debye-Scherrer formula, [17] from the full width at half maximum (FWHM) β,

$$D = K\lambda/\beta\cos\theta \text{----------1.2}$$

Where terms have usual meaning. The average crystallite size was calculated by resolving the highest intensity peak i.e. (111) plane. It is found that crystallite size increases from 128 to 158 Å. as the annealing temperature increases. The variation of crystallite size with annealing temperature is shown in Fig.3. The origin of the strain is related to lattice misfit who in turn depends upon the deposition conditions. The microstrain (ε) developed in the films were calculated from the equation;

$$\varepsilon = \beta\cos\theta/4 \text{----------1.3}$$

Where β is the full width at half maximum of (111) peak. As the annealing temperature increases, the microstrain decreases. This is due to the predominant recrystallization process in the polycrystalline thin films and due to the movement of interstitial zinc atoms from inside the crystallites to its grain boundary which dissipate and lead to a reduction in the lattice imperfection. [18-19].The variation of microstrain with annealing temperature is shown in Fig.4.

4.2 Optical Characterization

The optical absorption spectra of as deposited as well as annealed samples at room temperature were obtained in the range of 350 to 850 nm and shown in Fig. 5. The optical studies show that the films are highly absorptive ($\alpha \times 10^4$/cm). The spectra showed that absorption edge for the annealed samples shifted towards lower than that for the as deposited samples. The value of absorption coefficient increases with increase in annealing temperature .The data were properly studied in the vicinity of an absorption edge on

the basis of three dimensional model to estimate the band gap value. The simplest form of the equation obeyed near and above absorption edge are; [20]

$$\alpha h\nu = A\,(h\nu - E_g)^n \text{ ----------1.4}$$

Where A is constant depending upon the temperature, phonon energy, etc. For allowed transition n = ½ and for allowed indirect transition n = 2. A plot of $(\alpha h\nu)^2$ with hν is shown in Fig.6. Extrapolation of the linear portion of curve at energy axis gives the optical band gap. The band gap was found to be 2.78 eV for as deposited sample and 2.62 eV for annealed sample at 473K.The decrease in band gap with annealing temperature is probably to increase in grain size, leading to reduction in density of grain boundary trapping centre and improved crystallinity of the films.

4.3 Morphological Study

Scanning electron microscopy (SEM) is an excellent method to study morphology of the sample. The SEM micrograph of 'as deposited' and those 'annealed' at 473 K are shown in Fig.7 at 10,000X magnification. 'As deposited' zinc selenide thin film is homogenous, without cracks or pinholes and well cover to the glass substrate. From the micrograph, it is clearly seen that the film, composed of minute grains, was uniformly distributed over a smooth homogenous background that may correspond to amorphous phase of zinc selenide thin film. In annealed film, the grains are more distinct and of bigger size. The increase in grain size leads to decrease in the grain boundaries. The presence of fine background is an indication of one step growth by multiple nucleations. The average grain size of 'as deposited' as well as annealed samples is reported in table 1.

4.4 Electrical and thermoelectrical Properties

The dark electrical conductivity of as deposited and annealed zinc selenide film on non-conducting glass slide was determined by using a 'dc' two probe method, in the temperature range 300-525K. At room temperature the specific conductance was found to be in the order of 10^{-8} to 10^{-7}(cm)-1, which agrees well with the earlier reported value. [22]The values of specific conductance at 300 and 525 K are reported in Table 3.The low value of conductivity for as deposited film may be due to low crystallinity and small thickness of the film. The electrical properties of polycrystalline thin films are mainly depend upon their structural characteristics and composition.[23-24] A plot of log (conductivity) versus inverse absolute temperature for the cooling curve is shown in the Fig. 8. A plot shows that electrical conductivity has two linear regions, an intrinsic region setting at low temperature, characterized by small slope (300-350 K). High temperature region is associated with extrinsic conduction due to the presence donor states. The activation energy is calculated using exponential form of Arrhenius equation. The activation energies decreases with increase in annealing temperature while, specific conductance increases with increase in annealing temperature. This is probably due to decrease in band gap, improvement in grain size and decrease in grain boundary.

In thermoelectric power measurements, all the film shows n-type conductivity.

5. CONCLUSION

Zinc selenide thin film is homogeneous and uniform deposited using chemical bath method. The films were annealed at different temperature. Crystallographic and micrographic studies revealed presence of polycrystalline nature. Optical studies show that, as the annealing temperature increases the optical absorption coefficient increases. Temperature dependence of electrical conductivity showed the activation energy decreases with increase in annealing temperature. Thermoelectric power measurement shows n-type conduction.

Table Caption:

Table 1: Structural and morphological characterization of annealed zinc selenide thin film.
Table 2: Optical and electrical characterization of annealed zinc selenide thin film.

Figure Captions:

Fig. 1: XRD pattern of annealed zinc selenide thin film.
Fig. 2: Variation of lattice parameter with annealing temperature.
Fig. 3: Variation of crystallite size with annealing temperature.
Fig. 4: Variation of microstrain with annealing temperature.
Fig. 5: Absorption spectrum of annealed zinc selenide thin film.
Fig. 6: Plots of $(\alpha h\nu)^2$ with respect to photon energy.
Fig. 7: SEM micrograph of a) 'as deposited' b) 'annealed at 473 K' zinc selenide thin film.
Fig. 8: The variations of log (conductivity) with inverse temperature

Table No. 1

Sr. No.	Annealing temperature (K)	d –value(Å)		hkl plane	Grain Size (Å)		Cell parameter (Å)	Micro strain (10^{-3})
		Obs.	ASTM		XRD	SEM		
01	As deposited	3.276	3.271	111	128	134	5.6741	2.67
02	348	3.273 2.835	3.271 2.837	111 200	139	145	5.6699	2.60
03	423	3.271 2.830 2.004	3.271 2.837 2.004	111 200 220	147	153	5.6652	2.46
04	473	3.271 2.853 1.998 1.691 1.635	3.271 2.837 2.004 1.708 1.636	111 200 220 311 222	158	162	5.6601	2.29

Table No. 2:

Sr. No.	Annealing temperature (K)	Band gap (eV)	Activation energy (eV)		Specific conductance $(\Omega\ cm)^{-1}$	
			HT	LT	300 K	525K
01	As deposited	2.80	0.610	0.022	5.836×10^{-8}	6.142×10^{-5}
02	348	2.78	0.592	0.019	2.422×10^{-8}	8.426×10^{-4}
03	423	2.74	0.583	0.017	7.163×10^{-7}	1.001×10^{-4}
04	473	2.68	0.574	0.014	3.153×10^{-7}	1.375×10^{-3}

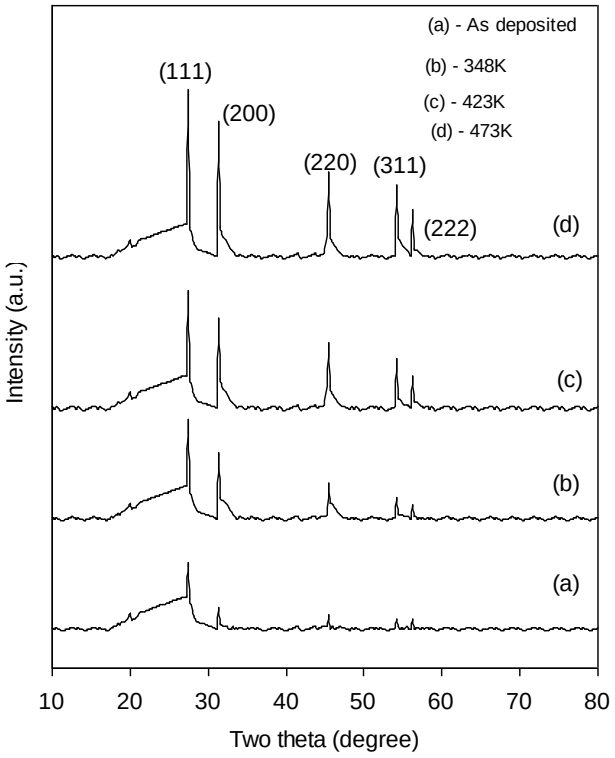

(a) - As deposited
(b) - 348K
(c) - 423K
(d) - 473K
(111)
(200)
(220)
(311)
(222)
(d)
(c)
(b)
(a)
Intensity (a.u.)
10
20
30
40
50
60
70
80
Two theta (degree)

Fig. 1

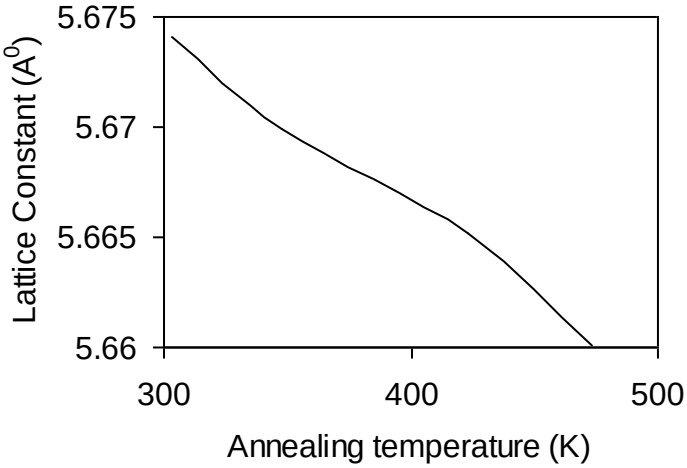

5.675
5.67
5.665
5.66
Lattice Constant (A0)
300
400
500
Annealing temperature (K)

Fig. 2

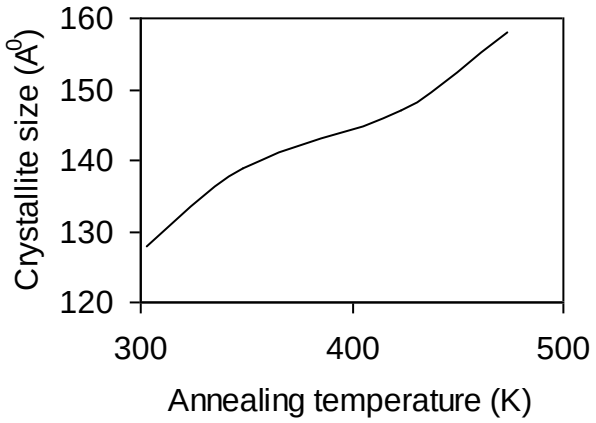


Fig. 3

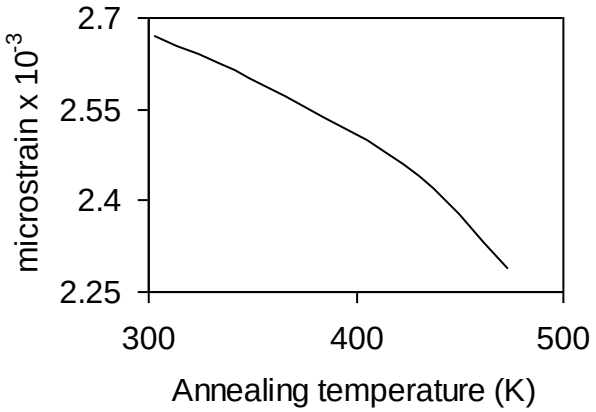


Fig. 4

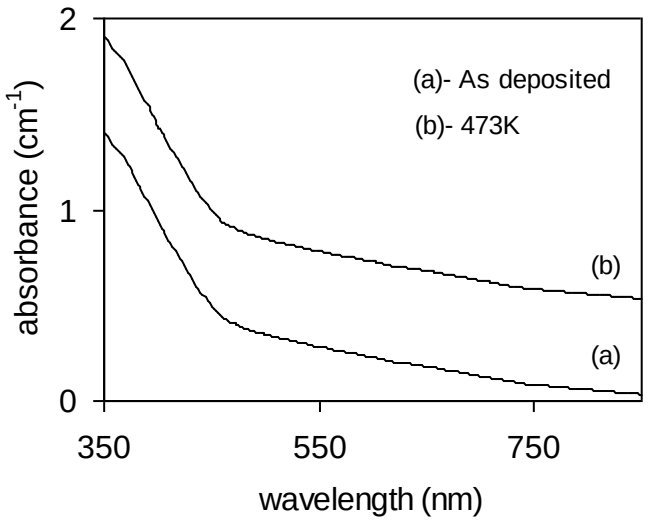


Fig. 5

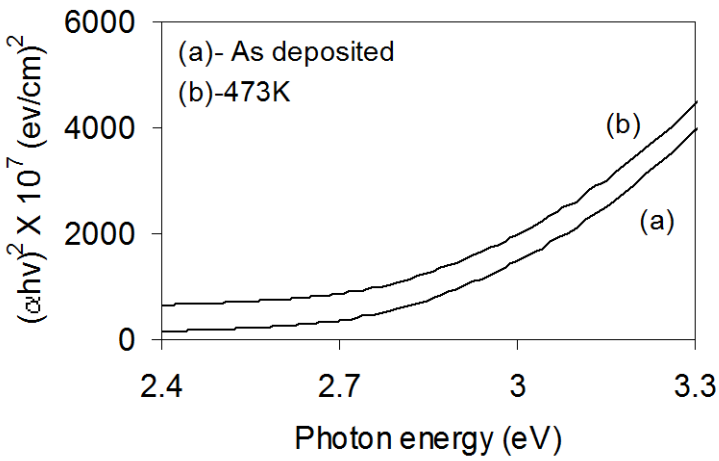
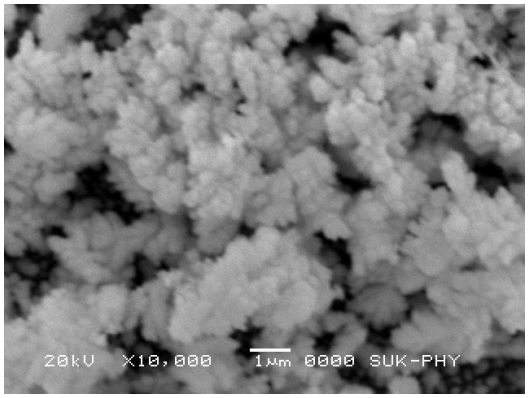
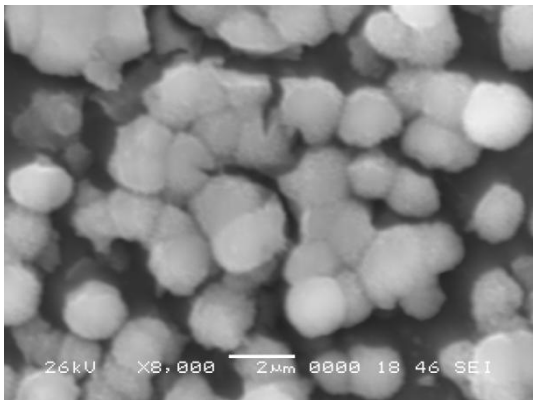

6000
4000
2000
0
(αhv)^2 X 10^7 (ev/cm)^2
(a)- As deposited
(b)-473K
(b)
(a)
2.4
2.7
3
3.3
Photon energy (eV)

Fig. 6


20kV X10,000 1μm 0000 SUK-PHY

(a)


26kV X8,000 2μm 0000 18 46 SEI

(b)

Fig. 7

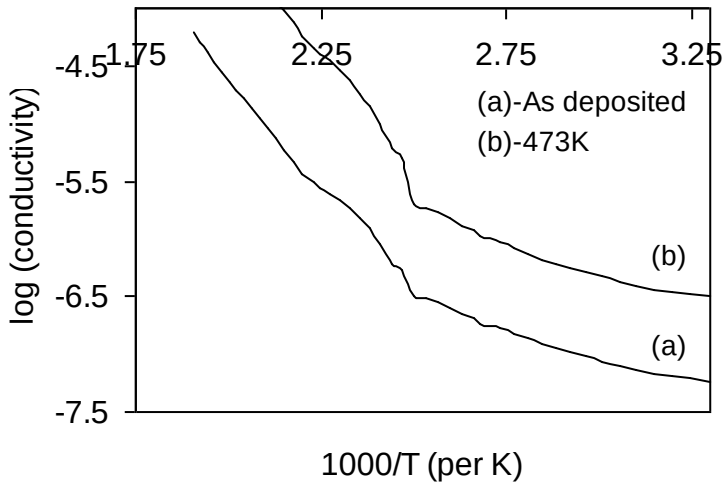


Fig. 8

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