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Derejaw Gardew Dubale
Department of Physics, Hawasa University, Hawassa, EthiiopiaDebark, Ethiopia, wubetgardew@gmail.com

Tizazu Abza Abshiro
Department of Physics, Hawasa University, Hawassa, EthiiopiaDebark, Ethiopia, wubetgardew@gmail.com

Fekadu Gashaw Hone
Department of Physics, Hawasa University, Hawassa, EthiiopiaDebark, Ethiopia, wubetgardew@gmail.com

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Synthesis and Characterization of Copper Zinc Sulfide ($\mathrm{Cu_xZn_{1-x}}$S) Ternary Thin Film by Using Acidic Chemical Bath Deposition Method

Derejaw Gardew Dubale[*] *, Tizazu Abza Abshiro and Fekadu Gashaw Hone*

Department of Physics, Hawasa University, Hawassa, Ethiiopia

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Abstract: In this work, copper zinc sulfide **($\mathrm{Cu_xZn_{1-x}}$S)** ternary thin films with parameter "x" such that $0 \le x \le 0{:}13$ were successfully deposited on glass substrate by acidic chemical baths using EDTA as a complexing agent, zinc acetate and copper acetate as a source of Zn^{2+} and Cu^{2+} respectively and thioacetamide as source of S^{2-}. ZnS was deposited as a pure binary thin film. The band gap of ZnS thin film was increased from 3.8 eV to 4.05 eV for 4.7% Cu added to zinc sulfide. ZnS and $\mathrm{Cu_xZn_{1-x}}$**S** thin films were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and Optical Absorption Spectroscopy (UV-Vis). The effects of deposition concentrations of copper on the optical property of the CuZnS thin films were observed. The XRD studies revealed that pure zinc sulfide thin film cubic structure and all the CuZnS samples were crystallized in amorphous structure. The SEM studies determined the films grain size as spherical shape and the atoms in the film were networked to each other. When copper acetate was added to zinc acetate, they formed a solid solution after a long time by acidic chemical bath deposition. The band gap of pure ZnS thin film was 3.8 eV at deposition time of 1:30 hr with a pH of 3.5 and at deposition temperature of 75 75℃. The optical energy band gap of copper zinc sulfide was conducted at 2.1 eV by the above deposition condition. The films were adherent, transparent and uniform.

Keywords: Semiconductors, Copper zinc sulfide, Chemical Bath Deposition, Thin films, and Optical properties.

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1 Introduction

The starting point of what nowadays is called nanotechnology was marked in 1960 by a lecture of the physicist Richard Feynman entitled "There's plenty of room at the bottom". The ultimate goal of this idea was to arrange atoms one by one where we want them and to build more complex structures from the bottom-up using small building blocks. As of the National Nanotechnology Initiative, Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications [1]. Thin films possess unique properties which differ somewhat from the corresponding bulk materials. This is due to the fact that each atom in the film is very close to the surface and therefore may not have too many atoms surrounding it [2]. Thin film solar cells have many applications with the promise of better power-to-weight ratio than crystalline silicon devices. High efficiencies were quickly achieved, and several companies were established to commercialize this technology [3]. Semiconductors, which are materials with a fundamental energy band gap between that of a metal and an insulator, are the backbone of modern electronics because of their great flexibility in terms of allowing the control of electronic and optical properties [4]. Compounds formed from elements of the groups III and V of the periodic table (such as GaAs) has properties very similar to their group IV counterparts. In going from the group IV elements to the III-V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the

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[*] Corresponding author E-mail: wubetgardew@gmail.com

group. V atom. The ionicity causes significant changes in the semiconductor properties. It increases the Coulomb interaction between the ions and also the energy of the fundamental gap in the electronic band structure. The iconicity becomes even larger and more important in the II-VI compounds such as ZnS. As a result, most of the II-VI compound semiconductors have band gaps larger than 1 eV [5]. As an important II-VI semiconductor material, ZnS is chemically more stable and technologically better than other chalcogenides (such as ZnSe and CdS), so it is considered to be a promising host material. Transitional metal ions (e.g. 〖Mn〗^(2+) and 〖Cu〗^(2+)) and rare earth ions (e.g. 〖Eu〗^(2+)) have been incorporated into ZnS nanostructures by thermal evaporation,

sol-gel processing, co-precipitation, micro emulsion, etc [6]. II-VI semiconductors have attracted growing interest owing to their possible application in optoelectronics, they are important semiconductor materials for the development of various modern technologies of solid state devices. Zinc Sulfide have wide direct band gap of about 3.7 eV in the UV region. it is used as a key material for blue light emitting diodes and other optoelectronic devices such as electroluminescent displays, cathode luminescent displays and multilayer dielectric filters. There have been various studies on the bulk and thin film characteristics of ZnS including optical and electrical properties [7]. Whereas copper sulfide (CuS) is unlike that of ZnS, among the group of I-VI chalcogenide with a direct band gap of 2.5eV for bulk hexagonal wurtzite structure [8, 9]. Copper sulfide is important material for applications in p-type semiconductors and optoelectronics. This finds use in photo thermal conversion applications, photovoltaic applications solar control coatings and other electronic devices [2, 9, and [10]. In general, copper zinc sulfide ternary thin film is among the group I-II-VI in the periodic table. It is the co-deposition of the CuS and ZnS binaries. As well as its significance and its properties are dependent on the individual properties of the two binaries. Thin film is a layer of material ranging from fractions of a nanometer to several micrometers. The act of applying or depositing a thin film onto a surface or substrate is termed thin film deposition. "Thin" is a relative term, but most of the deposition techniques control the layer thickness within a few tens of nanometers. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film. [11]. Different deposition technique can be used amongst which are chemical bath deposition, vacuum evaporation, pulse laser, electro deposition method, spray pyrolysis, SILAR method, electron beam evaporation and many more. Most of these techniques are expensive and require a high controlled formation conditions. The solution growth technique otherwise called CBD technique which was adopted in this work for thin film from aqueous solutions is highly accepted in recent time because of its low cost, advantage, stress free to the environment [2, 12]

2 Experimental Details

Ternary copper zinc sulfide (CuZnS) thin film was prepared using chemical bath deposition method by the following procedure. During the preparation of the thin film, different materials were used. These materials are listed below. Beaker, Beam balance, Spoon, Different flasks with different volume, Glass substrate and substrate holder, PH machine, Syringe, Thermometer, Glove, Magnetic stirrer and tweezers, Stirrer holder/magnetic plate, Filter paper and Heat supply (heater). The reagents used to prepare the ternary copper zinc sulfide thin film are listed below.
Zinc acetate, copper acetate, thioacitamide, EDTA, HCL, nitric acid, magnetic, alcohol stirrers and beakers. The reagent solution prepared is summarized by the following table.

Table 1: Optimization of Copper Zinc Sulfide (CuZnS) with Time 1:30 hr.

Reaction bas	Deposition time	T(°C)	Zinc acetate	Copper acetate	EDTA	Thio acetamide	pH	Vol.(l)
Sample 1	1:30hr	75	0.1M 10ml	…	0.2M 2ml	1M 7ml	3.50	60
Sample 2	1:30hr	75	0.1M 10ml	0.025M 2ml	0.2M 2ml	1M 7ml	3.49	60
Sample 3	1:30hr	75	0.1M 10ml	0.025M 4ml	0.2M 2ml	1M 7ml	3.50	60
Sample 4	1:30hr	75	0.1M	0.025M	0.2M	1M 7ml	3.51	60

The deposition process is based on the slow release of Zn^{2+}, Cu^{2+} and S^{2-}ions in solution, which are then condensed on the substrate surface. The deposition of

CuZnS occurs when the ionic product of Zn^{2+}+Cu^{2+}+S^{2-}exceeds the solubility product of CuZnS. $[(CH_3COO)_2Cu;\ H2O]$ was used as the Cu^{2+} ions source, $[(CH_3COO)_2Zn;\ H2O]$ was used as Zn^{2+} and $(NH_2)_2CS$ provided S^{2-} ions. The expected chemical equation of the reaction for the deposition is given by: Thioacetate decomposition reaction for sulfide formation is:

H_3C: C(S) NH_2+2H_2 O →CH_3COOH+H_2S+NH_3 …1

H_2 S+H_2 O↔HS^-+H_3 O^+ … 2

The hydrosulfide ion again dissolves to sulfur ion:

HS^-+H_2 O ↔H_3 O^++S^(2-) … 3

The Zn^(2+) ion is released from zinc acetate dehydrate:

Zn〖(〖CH〗_3 COO)〗_2.2H_2 O↔〖Zn〗^(2+)+2〖CH〗_3 COO^-+2H_2 O … 4

The Zn^(2+)ion released from the zinc acetate dihydrate should be complexed by appropriate ligand in order to control the precipitation of ZnS.

The Cu^(2+) ion is released from copper acetate dihydrate:

Cu〖(〖CH〗_3 COO)〗_2.2H_2 O ↔〖Cu〗^(2+)+2〖CH〗_3 COO^-+2H_2 O … 5

The Cu^(2+) ion released from the copper acetate dihydrate should be complexed by appropriate ligand in order to control the precipitation of CuS. Then the ionic reaction of S^(2-)which is released from the hydrolysis of thioacetamide and both the Zn^(2+) released from the complexes forms a solid phase ZnS and the Cu^(2+) either as a thin film on the substrate or a CuZnS precipitate within the stock solution.

〖Cu〗^(2+) + 〖Zn〗^(2+) +S^(2-) → CuZnS … 6

The sulphide ions are released by the hydrolysis of thioacetamide, copper ions and zinc ions are from complexes which the solution of their precursors formed with EDTA. The copper ions, zinc ions and sulphide ions present in the solution combined to form CuZnS molecules which were deposited on the glass substrates.

3 Result and Discussion

3.1 Preparation of Mother Solution and Deposition of The Materia

To prepare 0.1M of zinc acetate 2.18392 g zinc acetate salt was dissolved in 100 ml of distilled water and to prepare 0.1 M of zinc acetate 2.18392 g zinc acetate salt was dissolved in 100 ml of distilled water. Thioacitamide was also prepared as like the above precursors. The above preparation was prepared by the following procedures; first, insert the glass substrate in nitric acid for 12 hours and then wash the beakers, the substrates, the magnetic stirrers by using distilled water. Next, dissolve the precursors with distilled water by different flask disks. Adjusting the pH machine and then read the pH value and immerse the washed substrate. This chemical bath also immersed into water bath and switch on the heat supply, insert the thermometer, record the initial time and final time. Finally wash the films by distilled water and leveling by appropriate symbols.

As we saw in the laboratory, the color of the solution was changed during preparation time. First, 10 ml of 0.1M zinc acetate was added to the beaker, the color of zinc acetate was clear before contaminated by of other sources. When adding 2 ml, 4 ml,6 ml of 0.025 M in samples with distilled water respectively copper acetate into the beaker, it was changed to yellow color. Next, 2ml of 0.2M with distilled water EDTA was added as a complexing agent; during this time, the solution became dark yellow compared with the first color. Finally 7ml of 1M thioacitamide was added in to preparing solution, at this time the color of the solution became clear. This color was dark compared to the color of zinc acetate. The total volume of the solution was 60 ml and we adjusted the pH of all samples to be 3.5. Then the solutions of all samples were heated for 1:30 hr. During heating time, the color also changed. After 25 minutes, it was looks like bright brown as we seen the first photo in Figure 1. Then after 40 minutes, it was changed dark brown as we seen the second photo. This was not the final color of the mother solution, after 1hr and 10 minutes it already changed to greenish as we shown the third photo in Figure 1. This color was existed up to the final time 1 hr and 30 minutes.

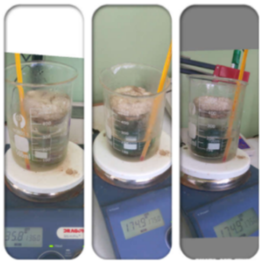

Fig. 1: Photo images of pure zinc sulfide and copper zinc sulfide solution samples.

After 1hr and 30 minutes the prepared thin film was observed to be as shown in Fig.1.

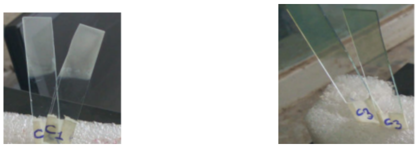

Fig. 2: Photo image of zinc sulfide thin film and copper zinc sulfide thin films on the substrate.

3.2 Structural Characterization

The structural characterization of pure zinc sulfide and copper zinc sulfide were determined by Bruker D8 diffractometer with Cu*kα* radiation (lambda=0.15406 nm). The experimental results were shown us, the structure of Zinc sulfide and copper zinc sulfide thin films nearly amorphous. This may be attributed to the thickness of the films since the films are very thin as visually observed by the naked eye. The films were very thin as shown in Figure 3.

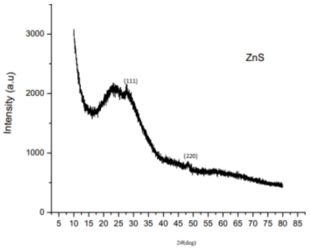

Fig. 3: XRD pattern of ZnS thin films deposited at 75*℃*.

The X-ray diffraction pattern of ZnS thin film shows two very weak peaks around 28 and at 48 degree over a wide hump. These show the nanocrystallinity or nearly amorphous nature of the films.There is no other impurity peaks. This shows the deposition of pure ZnS. The XRD pattern is matched to ZnS cubic structure (JCPDS file number 00-005- 05660) and the peaks were indexed as (111) and (220) planes of cubic ZnS structure.

When copper was added to zinc sulfide, the small peak was disappeared.

Therefore,the deposited films structure becomes amorphous. Before this work, many researchers reported the structure of zinc sulfide to be hexagonal and cubic which deposited in basic chemical bath deposition method. The XRD patterns of 4.7% Cu:ZnS and all the samples are shown in Fig.4.

As can be seen from Fig. 4, the peak at 28 degree becomes flattened as Cu concentration is increased. This implying decrease in creastallinity of the films.

We can conclude that, Zinc sulfide thin films had nanocrystalline nature however all the Cu:ZnS thin films have amorphous structure.

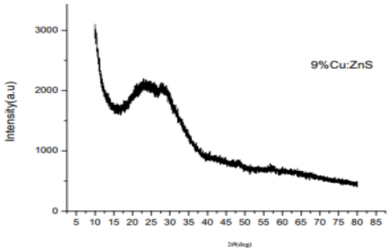

Fig. 4: XRD pattern of Cu ZnS thin films deposited at 75*℃*

3.3 Morphological Characterization

The morphology of Zinc sulfide thin film and Copper Zinc sulfide thin films were characterized by "JEOL-2300 Analysis Station". As we seen Fig. for pure zinc sulfide films and copper doped zinc sulfide films (9%) cover the substrate better than 4.7% copper doped zinc sulfide thin films. The two films of grain size were spherical and defined boundary condition. In general the grain sizes lack interconnection each other.

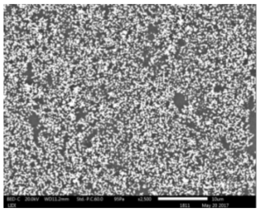

Fig. 5: morphological image of ZnS with concentration of Zinc 10 ml of 0.1 M in different magnification power.

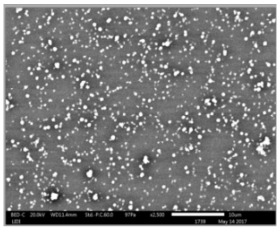

Fig. 6: The morphological structure of 4.7% Cu:ZnS thin films

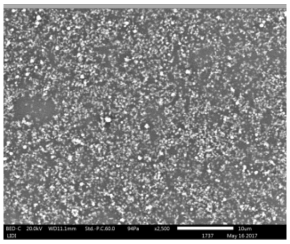

Fig. 7: The morphological structure of 9% Cu:ZnS thin films.

Now we can conclude the SEM of zinc sulfide and copper zinc sulfide thin films were spherical shaped grains with different grain sizes and uniformly distributed over a smooth homogenous background without visible defects such as cracks. The films were adherent and transparent.

3.4 EDX Analysis of the Films

From the XRD results, we have seen the formation of ZnS thin film. However, the EDX result does not show the existence of zinc in the films. This may be due to the free searching technique used in the EDX analysis which may make the percentage of zinc was below the detect level of the machine and may be replaced by sodium, since sodium and zinc have the same counts at 1 eV. The data indicated the presence of sulfur on the thin film of ZnS and both sulfur and copper on the thin film of CuZnS as shown in Figure 8.

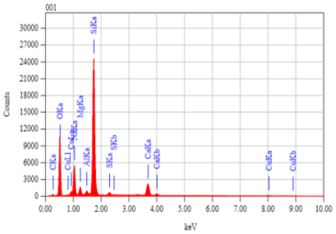

Fig. 8: Images of EDX spectrum of ZnS and 9% of Cu:ZnS

3.5 Optical Characterization

Energy band gap occurs between the conduction band and the valence band of a material. This energy band for any sample can also be determined by drawing graph of $(Ah\nu)^2$ versus the photon energy (hν) plot. The tangent line on the curve of $(Ah\nu)^2$ with the photon energy (hν) axis gives the value of the direct band gap. The optical characterization technique was determined the optical energy band gap of copper zinc sulfide thin films by "Berker Elmer Lambda 950 UV/Vis/NIR Spectrophotometer".

Figures 9-12 are plotted to determine the optical band gap of each sample.

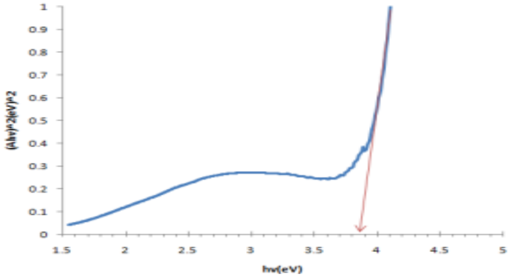

Fig. 9: plot of $(Ah\nu)^2$ $((eV)^2)$ Vs hν (eV) for ZnS thin films.

As we see the above plot (fig. 9), the band gap energy is obtained by extrapolating the linear portion of $(Ah\nu)^2$versus photon energy ($h\nu$) in eV, the optical analysis of the energy band gap is around 3.85 eV at pH of 3.5. This showed that the chemical bath is acidic bath. This experimental result is relatively comparable to the reported reviews; Manjulavalli and Kannan. (2015) [13], who reported the energy band gap of zinc sulfide was decreased from 3.96 eV to 3.84 eV with varying the concentration of zinc at ph of 9. This was basic bath. Also Ben Nasr et al. (2006) [14], were reported the energy band gap of zinc sulfide was 3.67 ev at pH of 11.5. Here the chemical bath was basic bath. Evidently our experimental value is appeared between the results of the above reviews. Therefore we could say the chemical bath is affected by pH value and nature of chemicals (precursors).

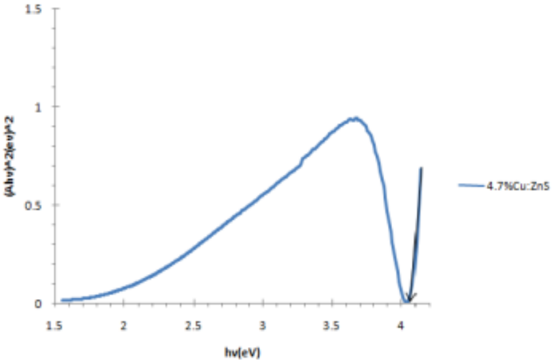

Fig. 10: plot of $(Ah\nu)^2$ $((eV)^2)$ versus hν (eV) for 4.7% Cu:ZnS thin films.

When we added 4.7% of copper acetate to the first sample zinc sulfide in Figure 10, the optical band gap determined from the UV-vis spectral studies showed that the band gaps are observed 4.05 eV. As understood, Figure 5.9 shows that the thin films are smaller than films in Figure 9 and Zinc sulfide was dominate the doped copper.

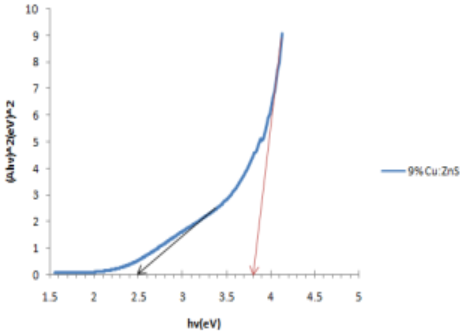

Fig. 11: plot of $(Ah\nu)^2$ $((eV)^2)$ versus hν (eV) for 9% Cu:ZnS thin films.

In Figure 11, the optical band gap determined two energy band gaps. These values are around 2.5 eV and 3.8 eV. As earlier reports, the first value is the optical energy band gap of copper sulfide (2.5 eV) and the second is the optical energy band gap of zinc sulfide (3.8 eV). These two results demonstrated that, the two binaries are not form a solid solution since the graph showed the two energy band gap separately. As we can see from the figure, the reaction of copper ion was faster than zinc ion.

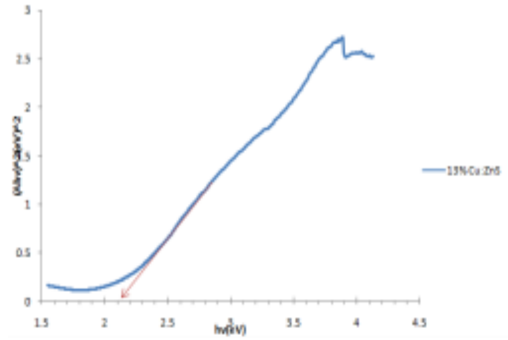

Fig. 12: plot of $(Ahv)^2$ $((eV)^2)$ versus hν (eV) for 13% Cu:ZnS thin films.

In Figure 12, the energy band gap is obtained around 2.1 eV. This shows that the thin films are made of a solid solution to each other. This result is in agreement with the expected energy band gap of copper zinc sulfide as stated earlier. Chidi Chukwuemeka Uhuegbu et al. (2008) [15], reported the optical band gap of copper zinc sulfide was obtained between 2.2.eV and 2.4 eV at average PH of 10.1. Thus we can conclude that the optical energy band gap of copper zinc sulfide was determined as in general from acidic chemical bath at pH of 3.5 deposited for 1:30 hr with temperature of 75°C. This film with this optical energy band gap will be used as solar cell applications. Here if we increased the concentration of copper and annealed the thin films again, we would get better thin films and small optical band gap.

4 Conclusions

Copper zinc sulfide Cu_x Zn_(1-x) ternary thin films were successfully deposited on glass substrate using 2 ml of 0.2M EDTA as a complexing agent, 7ml of 1M thioacitamide as a source of sulfur ion, (2ml, 4ml and 6 ml) of 0.025M copper acetate and 10ml of 0.1M zinc acetate as a source of copper ion and zinc ion respectively by acidic chemical bath deposition at a deposition time 1:30 hr in a pH of 3.5 as a reference of pure zinc sulfide. The deposition temperature of all samples was 75°C. During deposition process, the color of the chemical solution was nearly greenish color with increased concentration of copper. The optical analysis of the films was determined. The optical energy band gap of ZnS thin films were a wide direct energy band gap which UV/Visible spectrometry determined as 3.8 eV. The band gap of zinc sulfide was increased to 4.05 eV when we added 2ml of 0.025M of copper acetate (4.7%) to zinc sulfide. In the third sample 9% of Cu added, both the binary films were formed their own energy band gap. In this sample, the band gap of copper sulfide thin film was 2.5 eV and ZnS thin film was 3.8 eV. Finally the direct energy band gap of copper zinc sulfide (Cu_x Zn_(1-x)S) thin films were determined as 2.1 eV by 6 ml of 0.025 M copper acetate (13% Cu) and 10ml of 0.1M zinc acetate with composition of parameter "x" such that (0 ≤ x ≤ 0.13). At this band gap level, the precursors in the chemical bath were made a solid solution and agree each other to form one energy band gap. In this work the effect of Cu on Zn sulfide was observed in all characterizations of the film.

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