

# ФІЗИЧНІ, ХІМІЧНІ ТА ІНШІ ЯВИЩА, НА ОСНОВІ ЯКИХ МОЖУТЬ БУТИ СТВОРЕНІ СЕНСОРИ

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## PHYSICAL, CHEMICAL AND OTHER PHENOMENA, AS THE BASES OF SENSORS

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### **EFFECT OF SUBSTRATE TEMPERATURE ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF AL-DOPED ZINC OXIDE THIN FILMS DEPOSITED BY LAYER-BY-LAYER METHOD AT MAGNETRON SPUTTERING**

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**Abstract.** Al-doped ZnO (AZO) thin films were deposited by magnetron sputtering layer-by-layer growth method on silicon and glass substrates at different substrate temperatures. The atomic force microscopy analysis shows that AZO films are very flat with average root-mean square roughness 2.3 nm. Energy dispersive X-ray spectroscopy analysis reveals that Al content in AZO films approx. 1 at. %. X-ray diffraction studies have shown that all aluminum doped ZnO films are polycrystalline ones having hexagonal wurtzite structure with *c*-axis oriented perpendicular to film plane (002). Optical

measurements showed that all as-grown films are highly transparent (84%) in the visible region of optical spectrum and have band gap energy within 3.34 - 3.41 eV testifying their good optical quality. The lowest value of electrical resistivity was  $1.7 \times 10^{-2} \Omega \cdot \text{cm}$  for AZO film deposited at substrate temperature 350°C.

**Keywords:** XRD, ZnO films, Al-doped, layer by layer method

## **ВПЛИВ ТЕМПЕРАТУРИ ПІДКЛАДКИ НА СТРУКТУРНІ, ОПТИЧНІ ТА ЕЛЕКТРИЧНІ ХАРАКТЕРИСТИКИ ЛЕГОВАНИХ АЛЮМІНІЄМ ТОНКИХ ПЛІВОК ОКСИДУ ЦИНКУ ОСАДЖЕНИХ МЕТОДОМ ПОШАРОВОГО МАГНЕТРОННОГО РОЗПИЛЕННЯ**

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**Анотація.** Леговані алюмінієм тонкі плівки ZnO (AZO) були вирощені на кремнієвих та скляних підкладках методом пошарового росту у магнетронному розпилюванні при різній температурі підкладки. Аналіз за допомогою атомно-силової мікроскопії продемонстрував, що плівки AZO є дуже гладкими з середнім значенням середньоквадратичної шорсткості 2,3 нм. В результаті проведення енерго-дисперсійного рентгенівського аналізу встановлено, що вміст алюмінію в плівках AZO становить приблизно 1 ат. %. Рентгенівські дослідження показали, що всі леговані алюмінієм плівки ZnO є полікристалічними з гексагональною структурою вюрциту з віссю *c* орієнтованою перпендикулярно площини плівки (002). Оптичні вимірювання показали, що всі вирощені плівки мають високу прозорість (84%) у видимій області спектра і мають ширину забороненої зони 3,34 - 3,41 eV, що свідчить про їх добру оптичну якість. Найнижче значення електричного опору становило  $1,7 \cdot 10^{-2} \text{ Ом} \cdot \text{см}$  для AZO плівки, вирощеної при температурі підкладки 350 °C.

**Ключові слова:** РДА, ZnO плівки, легування алюмінієм, пошаровий метод

## **ВЛИЯНИЯ ТЕМПЕРАТУРЫ ПОДЛОЖКИ НА СТРУКТУРНЫЕ, ОПТИЧЕСКИЕ И ЭЛЕКТРИЧЕСКИЕ ХАРАКТЕРИСТИКИ ЛЕГИРОВАННЫХ АЛЮМИНИЕМ ТОНКИХ ПЛЕНОК ОКСИДА ЦИНКА ОСАЖДЕННЫХ МЕТОДОМ ПОСЛОЙНОГО МАГНЕТРОННОГО РАСПЫЛЕНИЯ**

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**Аннотация.** Легированные алюминием тонкие пленки ZnO (AZO) были выращены на кремниевых и стеклянных подложках методом послойного роста в магнетронном распылении при разной температуре подложки. Анализ с помощью атомно-силового микроскопии показал, что пленки AZO являются очень гладкими со средним значением среднеквадратичной шероховатости 2,3 нм. В результате проведения энерго-дисперсионного рентгеновского анализа установлено, что содержание алюминия в пленках AZO составляет примерно 1 ат. %. Рентгеновские исследования показали, что все легированные алюминием пленки ZnO являются поликристаллическими с гексагональной структурой вюрцита с осью *c* ориентированной перпендикулярно плоскости пленки (002). Оптические измерения показали, что все выращенные пленки имеют высокую

прозрачность (84%) в видимой области спектра и имеют ширину запрещенной зоны 3,34 - 3,41 эВ, что свидетельствует о их хорошем оптическом качестве. Наименьшее значение сопротивления составило  $1,7 \cdot 10^{-2}$  Ом·см для пленки AZO, выращенной при температуре подложки 350 °С.

**Ключевые слова:** РДА, пленки ZnO, легирование алюминием, послойный метод

### *Introduction*

Transparent conductive oxides (TCO) having a wide band gap, high transparency and low resistance are popular materials for photovoltaic heterostructure solar energy cells, transparent conducting electrodes, window materials, displays, LEDs [1].

ZnO is II-VI semiconductor with *n*-type conductivity and wide direct band gap (3.2 eV at room temperature). It belongs to hexagonal crystal system with a point group of 6mm (Hermann-Mauguin notation) and space group  $C_{6v}^4$  ( $P6_3mc$ ) with high exciton binding energy (60 meV at room temperature) [2–6]. Doped by donor impurities (Al, Ga, In) zinc oxide is a promising material for future technologies of electronics and optoelectronics. In economic terms, aluminum is the most favorable donor impurity.

Zinc oxide doped by aluminum (AZO) have some advantages opposite to ITO: non-toxicity (on the stages of the production and application), the prevalence of raw materials in the Earth's crust, high stability to temperature changes, has a wide band gap that allows the material to be highly transparent (~ 85-95%) in a wide range of wavelengths, and low resistivity ( $\sim 2 \cdot 10^{-4}$  Ωcm) [7].

A variety of techniques such as DC [8] or RF magnetron sputtering [9], electron beam evaporation [10], pulsed laser deposition [11], spray pyrolysis [12], chemical vapor deposition [13] and sol-gel processing [14,15] have been successfully applied to prepare AZO films. Considering the application of flat panel displays such as Thin Film Transistor-Liquid Crystal Displays (TFT-LCDs) and Organic Light Emitting Displays (OLEDs), the sputtering method is most suitable for the industrial applications.

There are some papers with investigations of influence of process parameters on structural, optical and electrical properties of AZO films, and our main aim of this study, is to investigate the effect of applying the layer-by-layer method at

magnetron sputtering on structural and electrical properties changes of AZO films prepared at various substrate temperatures.

### *1. Experimental details*

AZO thin films were grown on Si (100) and glass substrates by radio frequency (r.f.) magnetron sputtering on vacuum equipment VS350 (SELM). The composite target of zinc (purity 99.99 %) with aluminum inserts (purity 99.99 %) have been used for films deposition. To improve the crystalline perfection of the AZO films and to maintain a constant growth rate we used a new approach in AZO magnetron sputtering, namely, the layer-by-layer growth method [16-18]. Using start-stop technique (i.e. introducing interruptions at film growth) Al-doped ZnO films were grown using three stages. Total time of deposition was 6 min. The substrate temperature  $T_s$  were changed from 150 to 350 °C. Other technological parameters such as r.f. discharge power (200 W), oxygen and argon gas pressures (0.05 and 1 Pa, respectively) and target-substrate distance (7 cm) were kept constant during films growth. So it has been provided AZO films growth in dependence on temperature of substrates.

The structural parameters were investigated by x-ray diffraction (XRD) using DRON-4 diffractometer, applying Cu-K $\alpha$  radiation ( $\lambda = 0.1542$  nm) at Bragg-Brentano theta-2theta configuration. Transmittance of AZO samples deposited on transparent glass substrates was investigated by DMR-4 spectrophotometer equipped with incandescent lamp as a light source and Si photodetector. The elemental analysis of AZO films was done by the ZEISS EVO 50 XVP SEM apparatus using energy dispersive X-ray spectroscopy (EDX) furnished with INCA 450 (OXFORD Instruments) analyzer. The grain size and a surface roughness (surface morphology) were measured with a Nanoscope III atomic force microscope (AFM) using a normal silicon tip (125  $\mu$ m) in Tapping Mode scanning the surface with an oscillating tip to its

resonant frequency (200–400 kHz). All measurements were carried out at room temperature (RT). The root-mean square (RMS) roughness of the surface is defined as  $RMS (nm) = [\sum (z_i - z_{ave})^2 / N]^{1/2}$ , where  $z_i - z_{ave}$  is the deviation of height from its average value in the scan area;  $N$  is the number of points. The grain radius and feature dimensions were evaluated using Gwyddion Program. The AZO film conductivities were measured by the four-probe method.

## 2. Results and discussion

The typical X-ray diffraction patterns of the AZO films deposited at different substrate temperatures on the glass and silicon substrates is shown on Fig. 1. The strong (0 0 2) peak of ZnO indicates that the deposited films have a  $c$ -axis preferred orientation due to self-texturing phenomenon [19]. No  $Al_2O_3$  phase was detected in the XRD patterns. Hopefully, aluminum replacing zinc substitutionally in the hexagonal lattice. Other peaks were not detected in the range 25-75 degrees. In order to investigate the dependence of structure on substrate temperature more clearly, we calculated the stress deformation  $\sigma$ , and the average grain size  $D$  based on the X-ray diffraction data. The stress deformation  $\sigma$  can be calculated by using the following formula [18]:

$$\sigma = -233 \cdot \frac{c - c_0}{c_0}, \quad (2.1)$$

where  $c$  is a lattice constant and  $c_0$  is an unstrained lattice period of ZnO (0.5206 nm). The average grain size  $D$  of the AZO films was estimated by Scherrer's equation:

$$D = \frac{0.9 \cdot \lambda}{FWHM \cdot \cos \theta}, \quad (2.2)$$

where  $\theta$  and  $\lambda$  are Bragg angle and X-ray wavelength, respectively.

Fig.2 shows the temperature dependences of the grain size and compressive stress on substrate temperature calculated from the data of Fig.1 using Eq. (2.1) and (2.2). It is interesting that the relationship between the grain size and stress in films follows the same tendency for films deposited on both types of substrates, i.e. the enlargement of grain size and the reduction of residual

stress with increasing of deposition temperature. An increase of substrate temperature leads to the decreasing of FWHM, i.e. improvement of crystal structure of AZO films. We suppose it is caused by better substitution of zinc by aluminum in cation sublattice, by reduction of deformation stresses and by enlargement of grain sizes. Such increase of grain size and relaxation of compressive stress during film growth were observed also in [20, 21].

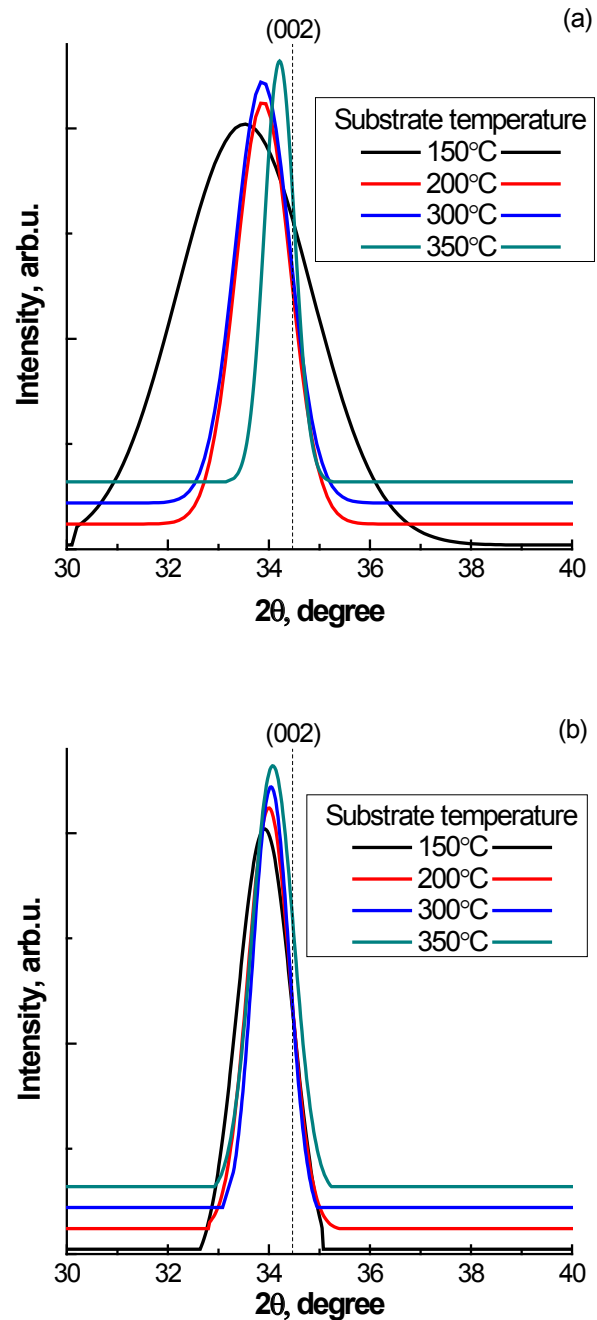


Fig. 1. X-ray diffraction patterns of AZO films deposited on a glass (a) and silicon (b) substrates

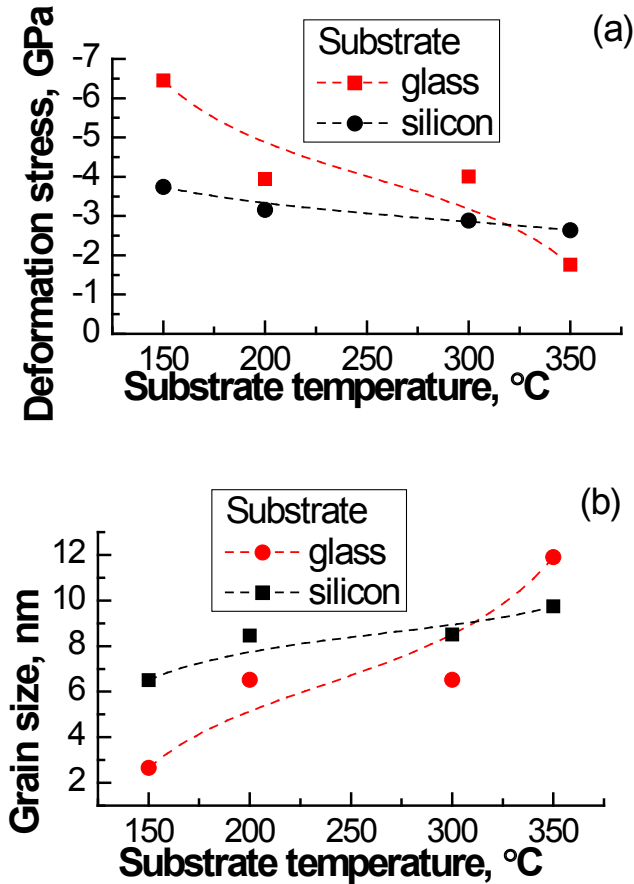


Fig. 2. The stress deformation (a) and grain sizes (b) for ZnO:Al films deposited on different substrate in dependencies on substrate temperature.

The surface morphology of AZO films deposited at different substrate temperatures present on Fig.3. AFM images reveal that the grain size slowly increase from 32 to 37 nm with enhancement of substrate temperature from 150 to 350 °C. The calculated root-mean-square (RMS) roughness of the AZO films have not similar tendency as changing grain sizes of AZO films: with increasing substrate temperature from 150 to 350 °C RMS changed as 1.56 nm, 2.14 nm, 3.38 nm and 2.13 nm, respectively. So far as we know, the large increase of surface roughness may cause deterioration of the electrical and optical properties [22]. But in our case RMS roughness of AZO films are practically similar. So the surface morphology cannot influence significantly on the structure, electrical and optical properties of the AZO films.

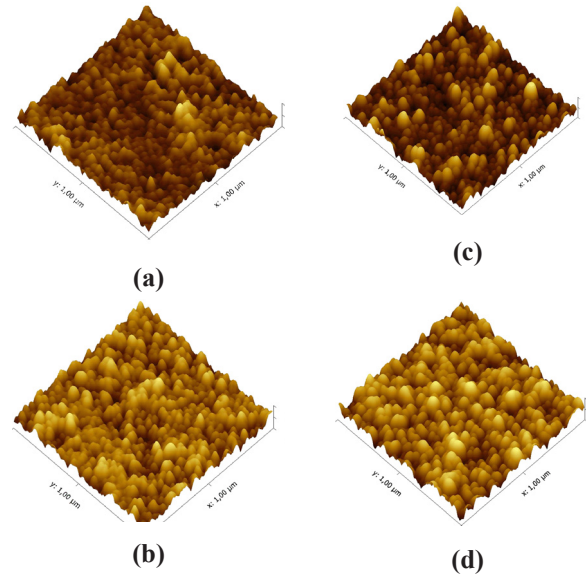


Fig. 3. AFM 3D images of surface morphology for ZnO:Al films deposited at different substrate temperatures: (a) 150 °C, (b) 200 °C, (c) 300 °C and (d) 350 °C.

The EDX spectrum one of AZO film is shown on Fig. 4. The presence of the Zn peak at about 1.010 keV, the Al peak at 1.490 keV and the O peak at 0.520 keV could be observed in the spectrum [23]. The Al content of the all films are nearly the same and equal to  $1 \pm 0.2$  at. %.

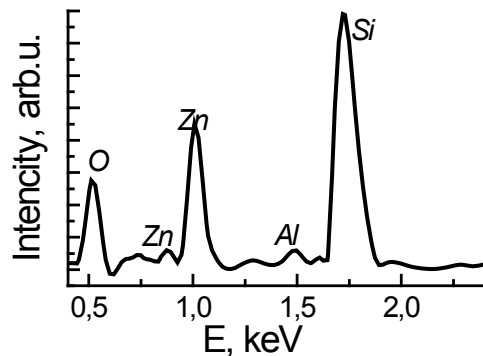
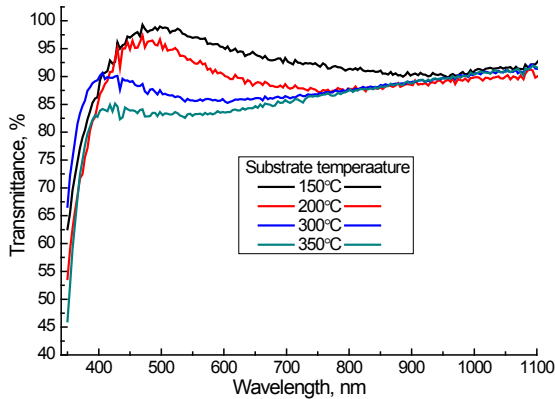


Fig. 4. Energy dispersive X-ray spectrum (EDX) of AZO films deposited on the Si substrate.

Fig.5 shows the variations of the optical transmittance of the AZO thin films as a function of the wavelength between 350 and 1100 nm with the deposition temperature. The films show optical transmittance not lower 84% in the visible range, which is important for many applications. The highest average transmittance 94% is observed for the AZO film deposited at 150 °C. Such varia-

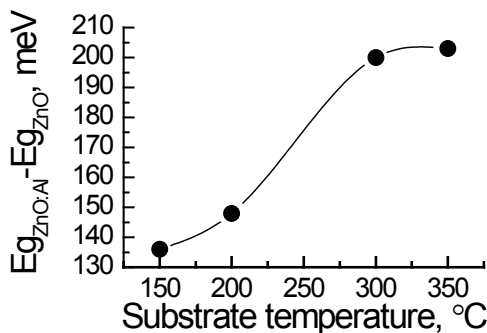


tion of optical transmittance in the visible region can be caused by the sample thickness changes, surface morphology and/or scattering by free carriers. In our case when all AZO films have similar thickness about 100 nm and RMS roughness the changing of optical transmittance in the visible region (Fig. 5) can be caused only scattering on free carriers.



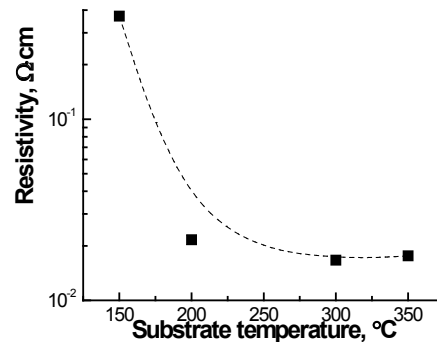
**Fig. 5. Optical transmittance of AZO thin films deposited at various substrate temperatures.**

The optical band gap energy ( $E_g$ ) of the films is obtained by extrapolating the linear part of the dependence  $(\alpha hv)^2 = f(hv)$  to zero, where  $\alpha$  – absorption coefficient. We see that the band gap of AZO films is increased from 3.34 to 3.41 eV with the increment of substrate temperature. For calculating of spectral shift we used  $E_g$  value 3.2 eV [24] of undoped-ZnO. Spectral shifts of the energy gap as a function of the substrate temperature is shown in Fig. 6. The shifts of the optical band gap might be ascribed to Burstein–Moss effect caused by an increasing free electron concentration due to the better entrance of aluminum impurity in zinc sublattice at higher temperatures of substrate.



**Fig. 6. Spectral shift of the energy gap vs substrate temperature.**

The resistivity of the AZO films prepared at different substrate temperatures shown on Fig.7. The resistivity of AZO films decreases with increasing substrate temperature because crystal perfection of films increase as we estimated using XRD analyze. The lowest value is  $1.7 \times 10^{-2} \Omega \cdot \text{cm}$  was obtained for AZO film deposited at  $T_s = 350^\circ\text{C}$ . This result is consistent with the conclusion expressed in Ref. [6] stated that higher substrate temperature is of advantage to increase the carrier concentration of AZO films. However, it should be noted that while Fig.6 demonstrate increasing of optical gap due to increasing of free carrier concentration as substrate temperature raise from 200 to 300°C, Fig.7 demonstrate slightly changing in resistivity, suggesting that carrier mobility is decreased in the same temperature range. So there is enhancement in scattering of free carriers that appear also as decreasing of optical transmittance for AZO films in the visible region about 500 nm (see Fig. 5). Decreasing in carrier mobility can be connected with increasing the process of oxygen chemisorption on AZO film surfaces during film growth. Being increased oxygen chemisorption create a depletion layer on AZO film surface that lower carrier mobility [25]. This effect may be enhanced as the film thickness is decreased, especially character for thin (<100 nm) films. Grain boundaries with adsorbed oxygen are other effective traps for free carriers [26]. Another possible explanation for high resistivity ( $\sim 10^{-2} \Omega \cdot \text{cm}$ ) is the forming of small nanosized  $\text{AlO}_x$  or  $\text{Al}_2\text{O}_3$  clusters that cannot be seen in XRD data but could change resistivity in much. That is why the very low (but enough for high transparency) oxygen pressure is favorable to obtain high conductivity films at magnetron sputtering. The further optimization of deposition parameter is necessary to obtain resistivity as low as  $10^{-3} \Omega \cdot \text{cm}$ .



**Fig. 7. The dependence of resistivity of AZO films on substrate temperatures. (Dash line for eye).**

### 3. Conclusions

The effect of substrate temperature on structural, electrical and optical properties of AZO thin films was studied. Substrate temperature strongly affects the crystallization and lattice periods of AZO films. Relationship between the grain size and stress in films follows the same tendency for the samples deposited on both types of substrates (silicon and glass): the greater grain size is accompanied by the smaller internal stress at increasing substrate temperature. It is determined that the main mechanism which influences on optical transmittance in the visible region for thin AZO films with thickness 100 nm is increasing of the scattering processes. We suppose that higher substrate temperature is of advantage to increase the carrier concentration of AZO films due to better substitution of Zn by Al and increasing crystal structure perfection that lead to decreasing the resistivity of AZO films meanwhile the electron mobility deteriorate with increasing substrate temperature. For enhancement the conductivity of AZO films deposited by layer-by-layer method in magnetron sputtering the further optimization of technological parameters is needed.

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