Effect of solution pH on CdO thin films prepared by perfume atomizer spray pyrolysis method

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Abstract: Nano crystalline cadmium oxide (CdO) thin films have been deposited on glass substrates using perfume atomizer spray pyrolysis method on glass substrate at 200^0C at different pH values. X-ray diffraction and scanning electron microscope studies confirmed the cubic structure of the deposited CdO films. The CdO films were polycrystalline in nature with cubic crystal structure showing preferential orientation along (111) direction. The UV studies showed that the CdO films prepared have an average optical transmittance of ~60% and the optical band gap varied from 2.38 to 2.57 eV for pH solutions of 7, 8 and 9, respectively. The effect of pH on the film thickness, grain size and Photoluminescence studies were also made and analyzed.

Keywords: Thin films, X-ray diffraction, Thickness, Transmittance, Photoluminescence.

1. Introduction

Transparent Conducting Oxide (TCO) films are of most significant interest in terms of technological applications such as flat panel displays, smart windows, light emitting diodes, heat reflectors, photovoltaic devices and sensors [1 - 3]. Among various conducting oxide films, Cadmium Oxide (CdO) is an important n-type semiconducting material from the combination of group II and group VI. CdO has high electrical conductivity, high optical transmittance in the visible region of the solar spectrum [4] and also has promising applications in a wide range of fields such as photo detector hetero junctions, solar cells, phototransistors, transparent electrodes, catalysts and gas sensors [5–10]. For last few decades various techniques such as Chemical Vapor Deposition, Sputtering, Chemical Bath Deposition, Sol-gel, SILAR, Thermal Evaporation, Layer by Layer Assembly, Sol-gel Spin Coating, Activated Reactive Evaporation, Metal Organic Chemical Vapour Deposition (MOCVD), Pulsed Laser Deposition and Spray Pyrolysis techniques are employed for the preparation of CdO thin film [11-29]. In these techniques, Spray Pyrolysis technique is a simple and low cost chemical method for the preparation of thin films with large surface area. The structure, morphology and optical behavior of the film depend on pH, temperature and reagent concentrations. The variation of precursor solution pH affects the hydrolysis and condensation behavior of the solution, which, in turn, influences the structure of the resultant film, morphological and optical behavior of the films. In this paper, the effect of pH on the structural, morphological and optical properties of CdO films prepared by perfume atomizer spray pyrolysis deposition method was investigated.

2. Experimental Details

The intrusion detection model can be grouped into three models. They are Statistical model, Data mining model and CdO films have been prepared by using Cadmium Acetate Dihydrate [$Cd(CH_3(COO)_2)$. $2H_2O$] as a source material of Cd and double distilled water was used as solvent. Spray solution of 50 ml was prepared with 0.2 M precursor concentrations of Cadmium Acetate dehydrate. For the complex formation, an excess Ammonium Hydroxide solution (25%) was added slowly to reach different pH values (7– 9). The solution was stirred for 15 min to ensure the formation of homogeneous solution. The optimized deposition parameters such as substrate- spray nozzle distance (25 cm), spray angle (about 45º), spray time (3) and spray interval (30s) were kept constant. The resultant precursor solution was sprayed on the preheated substrate at constant temperature of 200º C and the optimized deposition parameters such as substrate-spray nozzle distance (25 cm),spray angle (about 45°), spray time (3 s) and spray interval (30 s) were kept constant. This procedure was repeated for various pH values of precursor solution such as 7, 8 and 9 on preheated substrate at 200ºC

The stylus profilometer (SJ-301, Mitutoyo) was used to measure thickness of the prepared film. X-ray diffraction patterns were recorded using Philips X Pert PRO X-ray diffraction system (Cu Kα radiation; K = 1.54056 Å). The optical transmittance spectrum in the wavelength region 190–900 nm was recorded using UV–Vis spectrometer (Shimadzu UV-1601). Room temperature luminescence spectrum was recorded using (SHIMADZU-5301) spectrofluorometer.

3. Result and Discussion

(i) Thickness studies:

The stylus profilometer used to measure the thickness of the prepared CdO thin film. The thickness was 0.41µm, 0.38 µm and 0.39 µm for pH 7, 8 and 9 respectively. The thickness of CdO film decreases with pH 7 to 8 and increases at pH 8 to 9. It reveals that the thickness increases or decrease with pH value of the solution.

(ii) Structural studies:

Figure.2, represent the XRD spectra of the CdO films prepared at different pH values. It clearly shows that the consistency of the diffraction patterns, and the presence of pure polycrystalline CdO thin film with a cubic (NaCl) structure (JCPDS card number: 05-0640 for CdO). The five peaks were obtained in the XRD spectra for the crystalline plane (111), (200), (220), (311) and (222) for different values of pH confirms that the cubic phase of the polycrystalline CdO films.

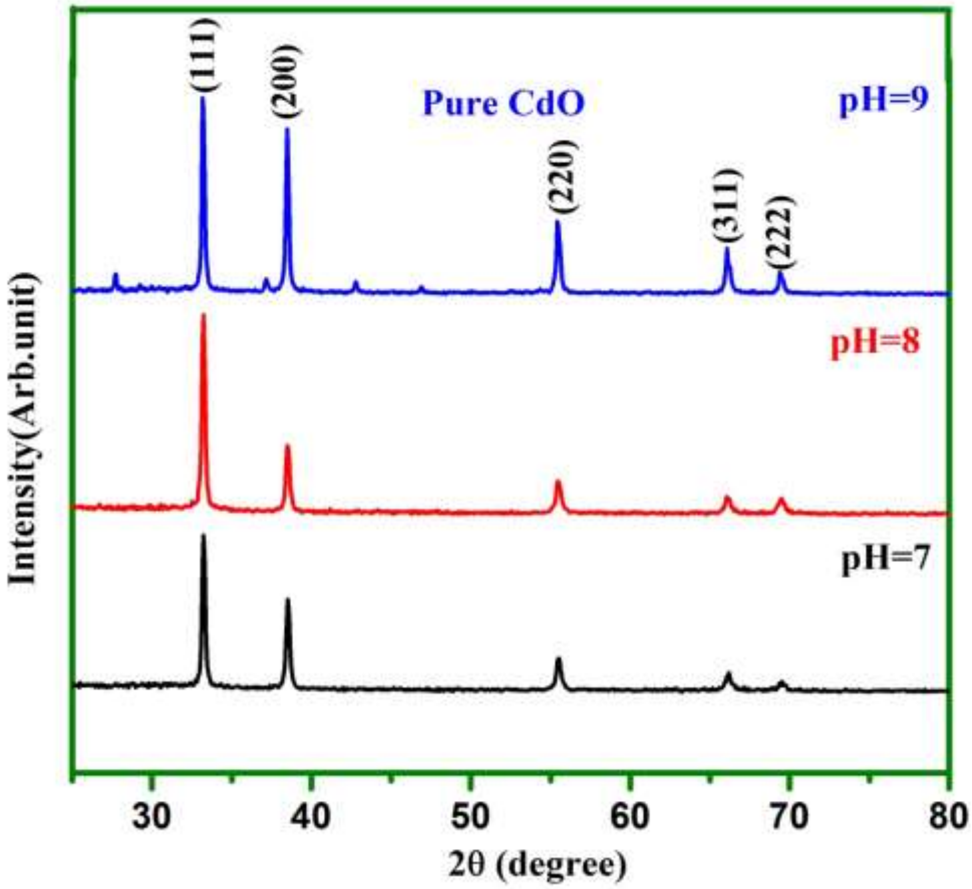

Figure 2: XRD pattern of CdO Thin films at different pH values

Solution pH	Film Thickness (t) μm	Crystallite Size (D) nm		Dislocation Density (δ) X 10^{14}	Strain (ε) X 10^{-3}	T.C	NRF
		D.S	W.H				
7	0.41	32.624	41.945	3.396	3.265	1.826	5.074
8	0.38	40.779	52.431	6.013	2.164	1.997	5.078
9	0.39	40.78	52.431	6.013	2.612	2.049	5.074

*Standard Lattice constant a = 4.694

Table 1: Structural parameter of CdO Thin films

The diffraction intensity increases with increasing pH value of the solution. The low intensity of the patterns, attributed to the small thickness of the film, is because of the low molarity of cadmium salt. This has made the number of (Cd^{+2}) ions insufficient to combine with all available (OH^-) ions in the solution. High (OH^-) ion concentration leads to a large amount of Cd(OH)2, which was produced as a precipitate in the solution, and hence a small film thickness in addition to a small amount of hydroxide which did not affect the intensity. The average crystallite size (D) of the CdO film was calculated from the following Scherrer's equation for the (111) plane [30].

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, k is a constant taken to be 0.94, λ is the X-ray wavelength, β is the full-width at half-maximum of the peak and θ is the reflection angle. The average crystallite size is also vary with the pH value. The preferred orientation along the (111) plane is, therefore, because of the controlled nucleation process associated with the low deposition rate. In other words, when pH values increase, film thickness decrease because of the higher (OH−) ion concentration, which gives colloidal precipitation during heating.

The Williamson-Hall equation according to UDM is given by [31]

$$\beta_{hkl}\cos\theta_{hkl} = \frac{k\lambda}{D} + 4\varepsilon\ \sin\theta_{hkl}$$

Dislocation density (δ) and strain (ε) for (111) plane was evaluated using the relations [32]

$$\delta = \frac{1}{D^2}$$

$$\varepsilon = \frac{\beta\cos\theta}{4}$$

The X-ray diffraction peak of films corresponding texture coefficient (T_C) was estimated using an expression [33]

$$T_c(h_ik_il_i) = \frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\left[\frac{1}{n}\sum\frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\right]^{-1}$$

Where I_0 - represents the standard intensity, I - is the observed intensity of ($h_ik_il_i$) plane and n is the reflection number. In order to study the structural properties of the material, the Nelson – Relay function (NRF) method is employed [34].

$$NRF = 0.5\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$$

As the solution pH increased, an increase in the crystallite size was obtained by using Debye- Scherer's formula and Williamson-Hall equation. These results confirm the beneficial effect of the aging time on the structural characteristics of the chemically sprayed CdO films. In this respect, it is well-known that, films with large crystallite is indicative of good quality films, which is very convenient for almost any application requiring good quality films, as is the case of the optoelectronic applications. The calculated crystallite sizes and other structural parameters are reported in Table 1.

(iii) SEM and EDAX studies:

The morphology and microstructure of prepared CdO film were examined by Scanning Electron Microscope (SEM). Figure 4 shows the SEM image of prepared CdO film at different pH values on the glass substrates at 200º C. It can be seen that all the substrates were fully covered and it clearly shows that the surface morphology slightly varies with different pH values. The film had small uniformly spherical grains and nearly uniform grains sizes spread throughout the surface and also some void and vacancies are there. Though a smooth morphology was achieved some smaller particles agglomerated randomly and it vary at different pH values. These SEM image confirms that surface morphology and grain size of the films could be controlled by pH value of precursor solution. The EDAX spectra of CdO film is shown in inset of Fig. 2 .and it confirms the presence of Cd and O elements in the starting solutions. These spectra show that the expected elements exist in the solid films

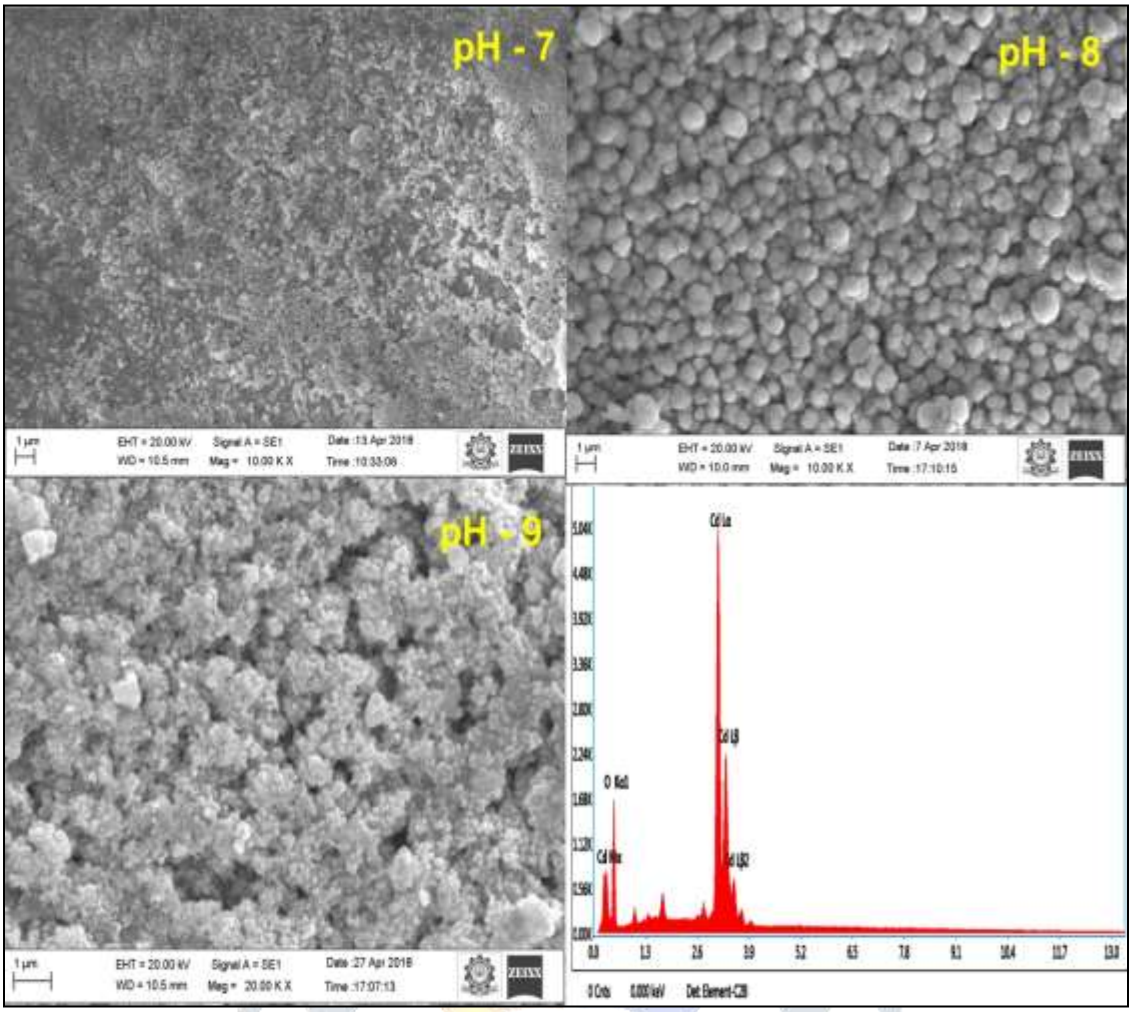

Figure 4: SEM and EDAX of CdO Thin films

(iv) Optical studies:

The transmittance spectra of CdO films prepared on glass substrate at different pH values is shown in Figure. 5. It reveals that the CdO films have an average optical transmission of 50- 60 % in UV- visible range.

The optical band gap (Eg) of the films was estimated from the transmittance data where the photon energy (hυ) and absorption coefficient (α) are related by the following equation [35]

$$\alpha h\nu = B(h\nu - E_g)^r$$

For allowed direct transition, the value of r = 1/2 and B is constant. The above equation can be rearranged as

$$\ln(\alpha h\upsilon) = \ln A + r\ln(h\upsilon - E_g)$$

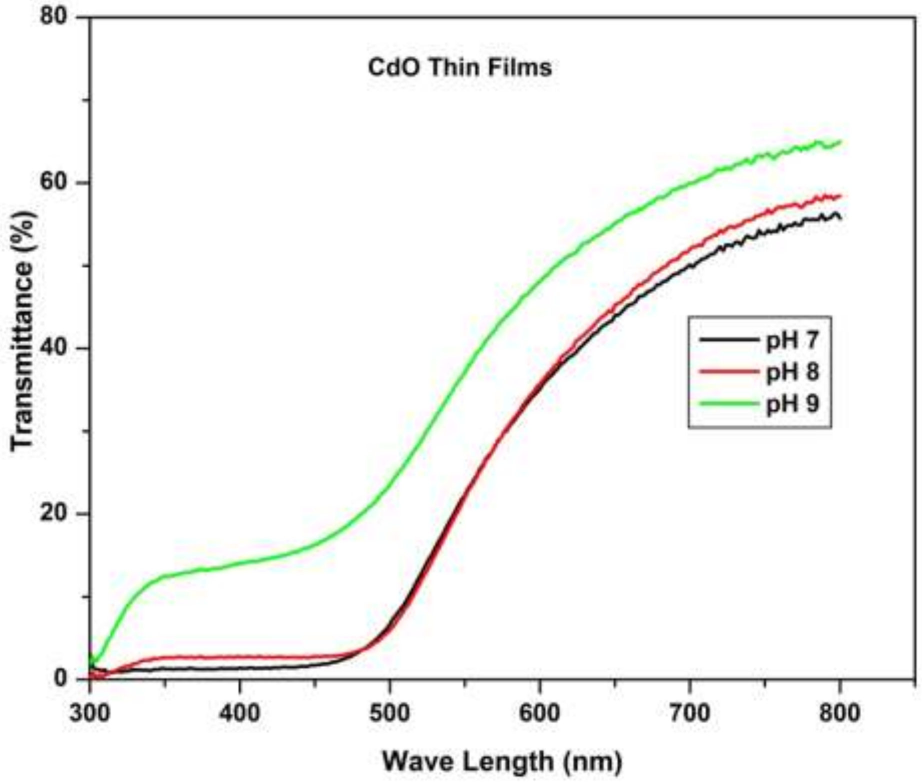

Figure 5: Transmittance spectra of CdO Thin films

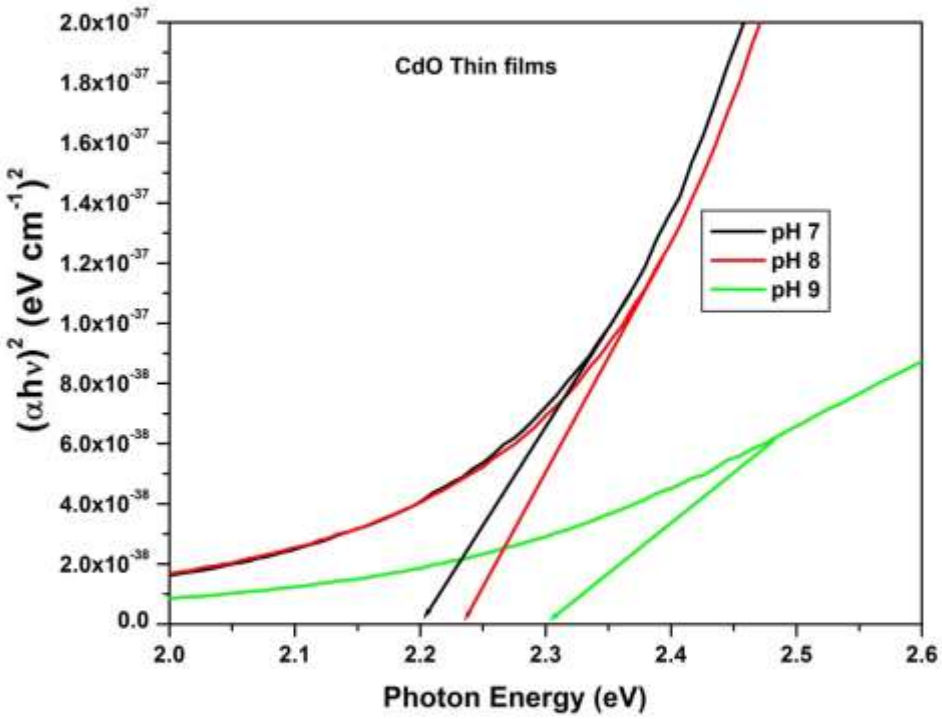

Figure 6: Tauc plot of CdO Thin films

A graph is plotted between $(\alpha h\upsilon)^2$ against hυ to calculated the band gap of prepared CdO film .Figure 6 shows the Tauc plot of CdO thin film at different pH value The Eg value. It was found to that the band gap increases with a increase of pH value from 7 to 9. The energy gap values of CdO films varied from 2.2 to 2.3eV and confirm the dependence on the pH value of the solution. The optical band gap of the CdO film obtained inthis work is in good agreement with those reported in [36–38].

iv) Photo Luminescence studies:

The photoluminescence (PL) spectra of CdO films measured in the visible region at room temperature was shown in Figure 7. The PL spectroscopy at room temperature displays various peaks. PL intensity around 521.2 nm which corresponds to the orange region of the electromagnetic spectrum changes with increasing saccharin concentration. The intense emission around 521.2 and 380.31 nm might be attributed to the combination of the electrons from the conduction band and holes from the valence band [39]. The PL measurements show that the pure CdO film has weak luminescence behavior, but it can interact with other materials to realize its applications in luminescent devices. Actually, this fact is not valid for nanoparticles [40]. As the saccharin concentration increases, the intensity of peak emission also increases. As a result, the number of defect sites decreased with increasing saccharin concentration which is approved by the PL signals. Also, the band structure changes due to the change in the concentration of saccharin. As seen in Figure6, the shifting in the optical band gap of CdO films can be explained by pH which may be attributed to change in grain size [41–43]. There have been suggestions that a distribution of grain sizes may be responsible for this [44, 45].

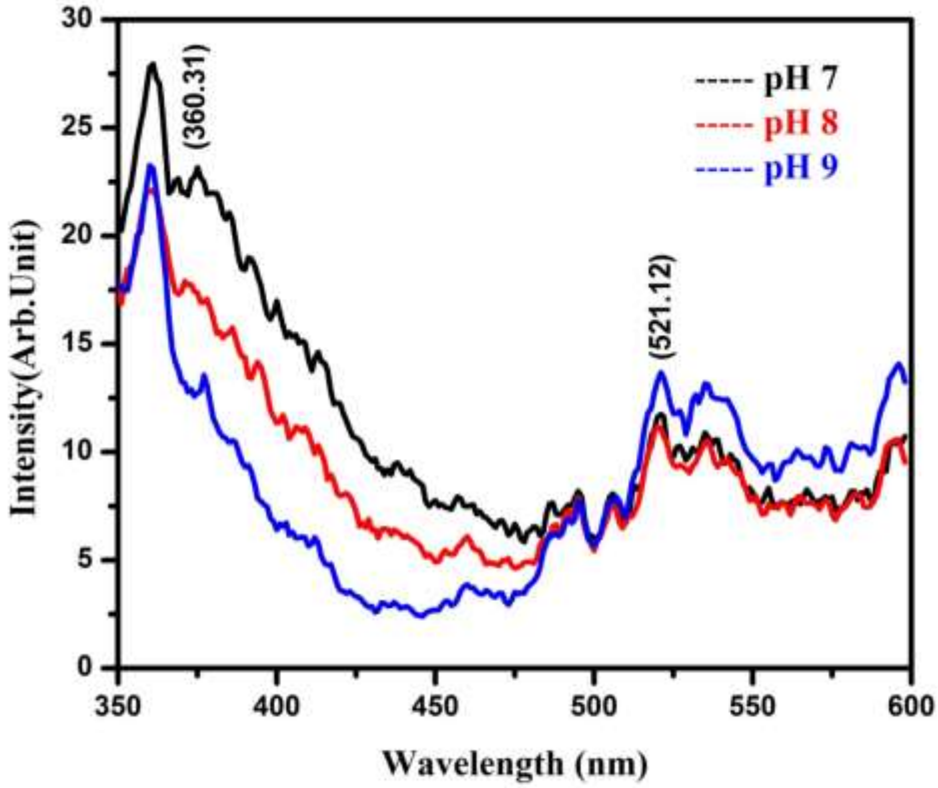

Figure 7: Photoluminescence spectra of CdO Thin films

4. Conclusion

This paper shown that the pH of a solution has a considerable influence on the structural, morphological and optical properties of nanostructured CdO thin films grown by perfume atomizer spray pyrolysis technique. XRD results confirmed that the films synthesized at different pH values are polycrystalline in nature and the intensity of the (111) plane is increased with pH. Optical characteristics revealed that the band gap increased with the increase of pH values. The SEM images confirm the influence of pH in structural change. EDAX analysis conforms that the presence of the constituents Cd and O. The PL spectra reveals that the slight variation with different pH values. These results are confirm the structural, morphological and optical properties of prepared CdO film and can control and improve the characteristics of CdO film for suitable device fabrication.

5. References

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