Research Article

Optical and Piezoelectric Properties of Mn-Doped ZnO Films Deposited by Sol-Gel and Hydrothermal Methods

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Received 30 June 2018; Revised 21 October 2018; Accepted 4 November 2018; Published 10 February 2019

Academic Editor: Ilaria Armentano

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Nowadays, multifunctional materials are of high interest due to their ability to be used in different applications by controlling one or two parameters (e.g., morphology and/or dopant). Zinc oxide is an intensive-studied material because of its large usability. Recently, we have shown that the conduction, transparency, and charge carrier concentration of ZnO can be controlled by changing the dopants, leading to promising materials as transparent conductive oxide films. In this work, sol-gel (SG) and hydrothermal (HT) methods were used separately or in combination in order to obtain ZnO films doped with Mn (1, 2, and 5%) for possible application in transparent optoelectronics or as piezoelectric materials. The manganese (Mn) dopant in the form of anhydrous manganese acetate was used to obtain Mn-doped ZnO films. ZnO hydrothermal (HT) growth was made on a previously ZnO seed layer, formed by sol-gel method. The Mn-doped ZnO films were deposited on microscope glass and on Pt/Ti/SiO2/Si substrates. A comparative characterization of the films for their structure, morphology, and optical and piezoelectric properties was achieved. SG films exhibit equiaxed nanoparticles, with diameters around 50 nm, while the films prepared by HT show a homogeneous morphology consisting of uniform 1D nanorods, sized about 30 nm diameter and 200–300 nm length. XRD diffractograms evidenced the presence of zincte phase (wurtzite structure hexagonally close packed), with an improvement in crystallinity of the HT films (compared with SG ones), which present a stronger tendency to be oriented along (002) plane (c-axis) at 2% at Mn. Spectroscopic ellipsometry shows that the films obtained by SG are much thinner than the ones obtained by HT and that the refractive index is increasing with the percent of dopant. The band gap energy was found to decrease with the Mn doping level from 3.28 eV (undoped ZnO) to 3.10 eV (ZnO doped with 5 at% Mn) for the samples deposited on Pt/Ti/SiO2/Si. The maximum transmission is found for the undoped ZnO film and decreases with Mn concentration but remains over 78% in the visible range. From the piezoelectric tests, it was found that the $d_{33}$ coefficient is much larger for the HT samples in comparison with the SG samples, especially for 2 and 5 at% Mn. The optical and piezoelectric results could be of interest for applications in optoelectronic or piezoelectric devices.

1. Introduction

ZnO is an n-type semiconductor with a large band gap of 3.37 eV at room temperature, high exciton binding energy of 60 meV, high transparency, and biocompatibility. It is nontoxic, abundant in nature, and chemically and mechanically stable [1].

Due to these properties, ZnO draws much attention and it can be used in a large variety of applications like solar cells [2], light-emitting devices [3], gas sensors [4, 5], piezoelectric devices [6], photocatalysis [7], DNA sequence detectors [8], and field emission transistors [9].

It is well known that by introducing a selective element into ZnO the properties of the semiconductor such as band...
gap or electrical conductivity can be controlled, and the carrier concentration for electronic applications can be increased [10]. Therefore, by tuning its properties, ZnO can have novel functionalities, and it can be a promising candidate for diluted magnetic semiconductors (DMS) in which one of the transition metal (TM) ions (e.g., Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Fe$^{2+}$) substitutes a fraction of the original atoms of the ZnO host lattice [11].

Among different transition metal (TM) doping ZnO, Mn$^{2+}$ has some advantages because of the relatively small ionic radii difference between Mn$^{2+}$(0.080 nm) and Zn$^{2+}$(0.074 nm), its high magnetic moment, and its half-filled 3d orbitals which facilitates its incorporation without altering the ZnO original structure [12].

Mn$^{2+}$-doped ZnO can be obtained by different methods such as RF magnetron sputtering [13], molecular beam epitaxy [14], sol-gel method [15–20], and hydrothermal method [21, 22].

Most synthesis techniques require expensive equipment and high temperatures, while both sol-gel and hydrothermal methods represent simple approaches, in which the composition can be controlled easily, the cost is reduced, and the obtained films are homogenously deposited.

The present work focuses on the synthesis by sol-gel (SG) and hydrothermal (HT) methods and complex characterization of Mn-doped ZnO thin films for several possible applications.

2. Materials and Methods

2.1. Film Preparation. To deposit the pristine and Mn-doped ZnO films, the chemical methods (sol-gel and hydrothermal) were used separately or in combination.

For the sol-gel method, the materials used were zinc acetate dihydrate Zn(CH$_3$COO)$_2$·2H$_2$O (Merck) and anhydrous manganese acetate Mn(CH$_3$COO)$_2$ (Merck) as source of zinc and manganese, respectively, absolute ethanol C$_2$H$_5$OH (Emsure) and methanol CH$_3$OH (Merck) as solvents, and triethanolamine C$_6$H$_{12}$N$_4$ (TEA, Merck) as stabilizer.

To obtain a solution of 0.1 M ZnO and Mn-doped ZnO, zinc acetate dihydrate was first dissolved in ethanol and homogenized at 50°C for 1 h. During the homogenization, TEA was added drop by drop. The molar ratio between zinc acetate: triethanolamine was 5:1. Then, the manganese (Mn) dopant in the form of anhydrous manganese acetate dissolved in methanol was added in the ZnO precursor as the Mn source (1 at%, 2 at%, and 5 at%). The mixture was stirred at 50°C for 1 h again to yield a clear and homogenous solution, which served as the coating solution after cooling to room temperature. Undoped ZnO precursor was prepared in the same way (without adding the manganese acetate).

The solution was deposited by dip coating (withdrawal speed of 50 mm/min, stationary time in solution 1 minute). To obtain the desired thickness 1–10 layers were deposited. An intermediary thermal treatment at 500°C/5 min was applied after each deposited layer and one final treatment at 500°C/1 h.

For hydrothermal (HT) deposition, firstly, a thin undoped ZnO seed layer was deposited by sol-gel method on the Pt/Ti/SiO$_2$/Si substrates.

The starting materials were zinc nitrate hexahydrate Zn(NO$_3$)$_2$·6H$_2$O (Merck) and hexamethylenetetramine—HMTA, C$_6$H$_{12}$N$_4$ (Merck). The dopant source of manganese was manganese acetate dissolved in methanol.

As in a typical synthesis process, zinc nitrate was mixed with HMTA and bidistilled water at room temperature and then was added a various quantity of dopant (1 at%, 2 at%, and 5 at% Mn). The mixed solution (of 0.05 M concentration) was magnetically stirred and then transferred into a Teflon-lined stainless steel autoclave along with the substrates which were vertically immersed into the reaction solution. The reaction temperature was kept at 90°C/2 h. Subsequently, the substrates were washed with bidistilled water and dried at 500°C/1 h.

For structural and morphological characterization and piezoelectric measurements, the films were deposited on Pt/Ti/SiO$_2$/Si substrate, while the optical transmission measurements were made on films deposited on microscope glass substrate.

2.2. Film Characterization. Structural (XRD), morphological (AFM and SEM), optical (SE), and elemental characterization (EDX, XRF) and piezoelectric measurements of the nanostructured films were correlated with technological parameters and annealing temperature.

Scanning Electron Microscopy (SEM) was done using a high-resolution microscope, FEI Quanta 3D FEG model, at an accelerating voltage of 20 kV, in high-vacuum mode with Everhart-Thornley secondary electron (SE) detector coupled with energy-dispersive X-ray (EDX) analysis.

Atomic Force Microscopy (AFM) measurements were carried in noncontact mode with XE-100 (Park Systems), using sharp tips with apex radius of less than 8 nm (PPP-NCHR from Nanosensors). The XEI (v.1.8.0) image processing program developed by Park Systems was used for image displaying and roughness evaluation.

X-ray Diffraction (XRD) patterns were recorded using a Rigaku Ultima IV multifunctional diffraction system. The equipment was set in asymmetric diffraction geometry ("thin films method"), with parallel beam (PB) optics, and operated at 40 kV and 30 mA, using Cu Ka ($\lambda = 1.5406$ Å) radiation. Measurements were performed in continuous scan mode, with a scan speed of 1°/min and a step width of 0.02° (2θ), at a fixed incident angle, $\alpha$, of 0.3°. Data were collected over the 2θ range from 25 to 75°. The crystalline phase identification was done by PDXL software, connected to the ICDD PDF-2 database.

Elemental analysis of the samples was carried out using a wavelength-dispersive X-ray fluorescence (WDXRF) spectroscopy method, on a Rigaku ZSX Primus II spectrometer equipped with an X-ray tube with Rh anode, 4.0 kW power, with front Be window (30 µm thickness). The XRF result was analyzed using EZ scan combined with Rigaku SQX fundamental parameter software (standard less) which is capable of automatically correcting all matrix effects, including line overlaps.
Spectroscopic ellipsometry (SE) measurements were performed in air at room temperature, using a J.A.Woollam Co. VASE® ellipsometer for UV–vis–NIR range. The data analysis was done using commercially available WVASE32™ software package [23].

Optical Transmission measurements were performed on the same apparatus at normal incidence of light (transmission mode).

The piezoelectric parameters ($d_{33}$, capacitance, and dielectric loss) were measured with PiezoMeter System PM300 from Piezotest Pte. Ltd. (Singapore). The measurement was made by metallization of the films on top and backside. Further, the condenser-like structure is clamped between the electrodes of the apparatus and a low-frequency force is applied. The electrical signal from the sample is collected and compared with a built-in reference.
The obtained piezoelectric parameters are $d_{33}$, capacitance ($C$), and dielectric loss (Tanδ).

3. Results and Discussion

Sol-gel (SG) and hydrothermal (HT) Mn-doped ZnO films thermally treated at 500°C/1 h were characterized in order to establish the morphological, structural, optical, and piezoelectric characteristics.

3.1. SEM and EDX on SG and HT Films. The original surface of the Si substrate, with a coating of Pt (i.e., the substrate used for piezoelectric tests), before deposition of the ZnO film, is shown in the inset in Figure 1(a). After first sol-gel deposition of zinc oxide, the surface appears decorated with a discontinuous coating made of zinc oxide islands (Figure 1(a)–1(c)).

The tilted image of the sample after the first deposition (Figure 1(c)) shows in more details some of these islands, of a darker colour, that extend over hundreds of nm, on
Figure 3: SEM micrographs (a, b, c, d) and EDX spectra (e) Mn (1%); (f) Mn (2%); (g) Mn (5%) of Mn-doped ZnO films prepared by HT method.
top of the Pt nanocrystalline layer, without forming a connected network, rather a dotted surface. Furthermore, these oxide dots fill the holes and irregularities of the Pt layer, leading to the flattening of the surface, although keeping a texture of similar scale with the diameter of Pt nanoparticles (~20 nm). After 10 depositions, SEM micrographs show the formation of continuous and homogeneous films (Figure 1(d)–1(f)) which cover totally the substrate. The films are polycrystalline, made of a single layer of equiaxed nanoparticles, with diameters around 50 nm. The image from a scratch done in the film (Figure 1(d)) shows the nanorange thickness of the film section.

The effect of Mn content on the films was analyzed also by EDX. Compositions up to 5 at% of Mn showed similar, one phase, microstructure (Figure 2(a)–2(c)), and nanoparticle size (Figure 2(d)–2(f)). EDX spectra detected the presence of Mn dopant (Figure 2(g)–2(i)), indicating the incorporation of Mn in the ZnO films prepared by SG.

The SEM images of the films prepared by HT method show a homogeneous morphology that consists of uniform 1D nanorods, sized about 30 nm diameter and 200–300 nm length (Figure 3(a)–3(d)). EDX spectra detected the presence of Mn dopant (Figure 3(e)–3(g)).

3.2. Atomic Force Microscopy on SG Films. The surface morphology of Mn-doped ZnO films prepared by sol-gel method is ideal to be examined by AFM because they are smooth and uniform, in contrast with the surface of the ZnO films prepared by HT method which are formed by micrometric rods. For more details, two types of AFM images will be presented by scanning larger areas of 5 × 5 μm² (Figure 4) and lower areas of 2 × 2 μm² (Figure 5).

The images scanned at larger scale (Figure 4) are useful to check the uniformity and possible defects of deposition while the images recorded at lower scales (Figure 5) emphasize the morphology of the films (constituting grain shape

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**Figure 4:** 2D AFM images at the scale of 5 × 5 μm² for undoped (a) and Mn-doped ZnO films (c–d) with 10 layers prepared by SG method.
and dimensions. It can be seen from Figure 4(a)–4(d) that the surface of the films is highly uniform without defects as cracks or exfoliations.

The films are adherent to the substrate, continuous, and homogenous and all samples have a granular morphology with nanometric-sized grains and small roughness. The root-mean-square (RMS) roughness was found to be in the range of 2.88–3.85 nm with Mn doping content $x = 0.00$ (Figure 4(a)), 0.01 (Figure 4(b)), 0.02 (Figure 4(c)), and 0.05 (Figure 4(d)), respectively. The AFM images recorded at the scale of $2 \times 2 \, \mu m^2$ (Figure 5) suggest the columnar growth of the undoped and Mn-doped ZnO films, as shown from the appearance of the protruding nanoparticles at the surface, a tendency which is rather known for the ZnO-based films [25].

Figure 6 shows the decreasing of the roughness from undoped to doped ones, the lowest roughness values being registered for the ZnO films doped with 2% Mn. It is suggested that doping with 2% Mn leads to better compacted microstructure as a result from AFM investigations, in agreement with the XRD results.

3.3. XRD of SG and HT Films. The XRD diffractograms (Figure 7) evidenced the presence of zincite phase, ZnO,
According to ICDD file no. 00-036-1451. Zincite has a wurtzite structure, with hexagonal close packing, belonging to hexagonal crystal system, and P63mc (186) space group. In addition to zincite phase, only platinum phase, Pt, was noticed, which belongs to the substrate. No manganese-based compounds were detected within the detection limits of the instrument. This observation suggests that the films are single-phase ZnO, with manganese ions incorporated in the zincite structure, as dopants, without changing the hexagonal wurtzite structure. Therefore, in order to emphasize the Mn content, the samples were supplementary analyzed by XRF and XPS methods.

In Table 1, the unit cell parameters and crystallite size determined by XRD analysis.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Deposition method</th>
<th>$a = b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>S-G</td>
<td>3.2444</td>
<td>5.1802</td>
<td>18.7</td>
</tr>
<tr>
<td>ZnO + 1% Mn</td>
<td></td>
<td>3.2364</td>
<td>5.1898</td>
<td>13.8</td>
</tr>
<tr>
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<td></td>
<td>3.2390</td>
<td>5.1808</td>
<td>17.1</td>
</tr>
<tr>
<td>ZnO + 5% Mn</td>
<td></td>
<td>3.2372</td>
<td>5.1900</td>
<td>13.2</td>
</tr>
<tr>
<td>ZnO + 1% Mn</td>
<td></td>
<td>3.2505</td>
<td>5.2027</td>
<td>15.4</td>
</tr>
<tr>
<td>ZnO + 2% Mn</td>
<td>HT</td>
<td>3.2500</td>
<td>5.2030</td>
<td>17.5</td>
</tr>
<tr>
<td>ZnO + 5% Mn</td>
<td></td>
<td>3.2497</td>
<td>5.2065</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Figure 7: XRD diffractograms of Mn-doped ZnO films, prepared by (a) SG and (b) HT methods.

Table 1: Unit cell parameters and crystallite size determined by XRD analysis.

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In Table 1, the unit cell parameters and crystallite size evolution of ZnO phase are presented. The narrow full width half maxima (FWHM) of the thin films prepared by hydrothermal method compared to FWHM of the films prepared by sol-gel method indicates an improvement in crystallinity of these thin films [26].

The thin films prepared by hydrothermal method present a stronger tendency for the crystallites to be oriented along (002) plane (c-axis) but less oriented for 5 at% Mn-doped ZnO sample, which is associated with the lattice disorder and strain induced in the ZnO lattice by the substitution of Zn²⁺ ions to larger ionic radius of Mn²⁺ ions [16].
Also, the unit cell parameters are not influenced by the different amounts of dopant and these are close to the indexed values (ICDD file no. 00-036-1451); the small differences may be attributed to statistical errors.

The films obtained by sol-gel method are rather random than oriented, with unit cell parameters smaller than the indexed values. It is worth mentioning that for both methods the 2 at% Mn-doped ZnO thin film samples present larger crystallite size than the other doped samples. According to Fujihara et al. [27], by increasing the dopant amount from 2 at% to 5 at% of manganese, the concentration of zinc in the system reduces. As a consequence, the diffusivity is decreased in ZnO that may suppress the grain growth. According to Neogi et al. [28], increasing the dopant amount may generate a retarding force on the grain boundaries that impedes the movement of the grain boundary and turning in a gradual decrease of the crystallite size with increasing manganese concentration.

3.4. X-Ray Fluorescence (XRF) on SG Films. The XRF investigation was realized to ascertain the elemental composition of Mn-doped ZnO film with the doping concentration of 5 at%.

In the XRF investigation, the signals of Mn were identified as Ka (2θ = 62.95°) and Kβ (2θ = 56.62°) spectral lines. The Mn content was 4.84 at% (% error of 3.2) in good agreement with its theoretical amount suggesting the incorporation of Mn into ZnO lattice.

3.5. Spectroscopic Ellipsometry (SE). Measurements were carried out with 5 nm steps in the 300–1700 nm spectral range, for 70° and 75° incidence angles. The ellipsometric WAVE32™ software package was used to evaluate the thickness, d, and refractive index, n, of the films from the Ψ and Δ ellipsometric experimental spectra. According to [29], it is not possible to gain information by SE from substrates placed below metal films thicker than 50 nm. Because Pt thickness is 200 nm, in the modelling of ellipsometry data we assumed that the light beam could not reach to the layers below Pt in the complex substrate Pt/Ti/SiO2/Si. Therefore, the Pt layer is taken into account as substrate when building the optical two-layer model, which was used for the data analysis. This model consisted of Pt substrate/ZnO/surface roughness and the optical constants of Pt from the software list of materials were used accordingly [30]. In order to determine the thickness d and the refractive index n of the ZnO film, ellipsometric data were fitted by means of the Cauchy equation in the nonabsorbing spectral region. The surface layer was modelled by Effective Medium Approximation (EMA) theory [31] and it was assumed that it consisted of a combination of 50% voids and 50% ZnO. The deposition parameters, the thickness, and roughness of the films together with the Mean Squared Error (MSE) of the fit are presented in Table 2. An important observation is that the films obtained by the SG method are much thinner (even with 10 layers) than the ones obtained by the HT method (1 layer). All the samples present a small roughness of just a few nanometers (Table 2). Also, the Mean Squared Error (MSE) values that can be observed in Table 2 show a good quality of the fit. For the HT samples, the MSE values are slightly larger because of the complex structure of HT ZnO films that are more difficult to be modelled.

Spectroscopic ellipsometry (SE) underlined the influence of the manganese dopant on the optical properties of the ZnO layer. The variation of the refractive index for the S-G samples doped with 1, 2, and 5 at% Mn deposited on the Pt/Ti/SiO2/Si substrate was obtained by SE (Figure 8). As one can see, the refractive index is increasing with the increase in Mn concentration and the highest refractive index is obtained for the samples with 5% Mn dopant.

The band gap energy Eg was estimated assuming a direct transition, using Tauc’s relation [32]. The obtained results show that with the increasing of the dopant concentration from 0 to 1, 2, and 5 at% Mn, the energy band gap of the investigated films is gradually decreasing while the values for n at 550 nm are increasing. This evolution is presented in Figure 9 for the films deposited on the complex Pt/Ti/SiO2/Si substrate. Such dependence of the band gap energy is in good agreement with the literature data [33] and could be related to the defects induced by manganese doping in ZnO [34].

![Figure 8: Effect of dopant amount on the refractive index for ZnO films prepared by SG method.](image-url)
3.6. Optical Transmission of SG Films. The transmission measurements were done by SE in the 340–800 nm wavelength ranges with a 10 nm step on SG films deposited on microscope glass substrate. One can see that all the samples are transparent in the visible spectral range with the highest transmission of more than 80%, indicating a good optical quality of the SG films with low absorption losses. The maximum transmission in the visible range was found for the undoped ZnO film. The obtained data showed a slight decrease of the transmission with the increase of the dopant from 1 to 5 at% Mn (Figure 10), in accordance with other work [35].

The decrease in optical transmission may be associated with the loss of light due to oxygen vacancies and to the scattering at grain boundaries [36]. In literature [35], this behavior of transmission is explained by the introduction of Mn defect states within the forbidden bands and as a consequence, the incident photons are absorbed to a higher degree.

3.7. Piezoelectric Measurements. Piezotest measurements were made on the obtained films using a PiezoMeter System PM300, using modified electrodes, as proposed for thin films clamping by Southin et al. [37]. The values of $d_{33}$ parameter (which is a material coefficient representing charge per unit force in the direction of polarization), dielectric capacitance ($C$), and dielectric loss ($\tan \delta$) have been measured for SG and HT samples (Figure 11). Even that the absolute values are relatively low (which may be due to the measurement
system which is recommended for bulk-type ceramics), the obtained results are qualitatively discussed. The piezoelectric measurements were done at a frequency of 95 Hz, a dynamic force of 0.05 N, and a static force of 10 N. As we can see from Figure 11, the $d_{33}$ coefficient is much larger for the HT samples in comparison with the SG samples, for 2 and 5 at% Mn. The same tendency could be observed for the capacitance, which is much larger for the HT samples in comparison with the SG ones (17.3 ± 2.5 pC for SG films in comparison with 202 ± 4 pC for 1 and 5 at% Mn and 545 ± 10 pC for 5 at% Mn). No dielectric loss was measured (within the error limit of the device used for measurements) for the SG films, while the largest dielectric loss (~0.93 ± 0.05) was observed also for 2 at% Mn. However, the largest piezoelectric effect was noticed for the films doped with 2 at% Mn, prepared by the HT method.

Most probably, the largest values of $d_{33}$ obtained for the samples prepared by HT method could be related to the presence of Mn$^{3+/4+}$ inside the ZnO matrix, which is essential for obtaining a significant piezoelectric effect [38]. This hypothesis is in good agreement with the literature data [39] which shows the oxidation of the Mn$^{2+}$ (from the used reagent) to Mn$^{3+/4+}$ in aqueous solution used in the HT preparation method.

### 4. Conclusions

The obtained Mn-doped ZnO SG films are continuous, homogenous, adherent to the substrate, without defects (as cracks or exfoliations), and have granular morphology with nanometric-sized grains and small surface roughness (3-4 nm).

The Mn-doped ZnO HT films show also a homogeneous morphology but consist of uniform 1D nanorods, sized about 30 nm diameter and 200–300 nm length and are more rough and thicker (with one order of magnitude) than SG ones. EDX analysis detected the presence of the dopant even for the lowest quantity of 1 at% Mn in both film types and XRF confirms that the quantity of Mn found in the film is in good agreement with the intended one.

The refractive index increases with Mn content, proving a densification of the film with the insertion of the dopant and a small decrease of the optical band gap.

The variation of band gap energy values with the Mn dopant percent provides the possibility to further use the obtained thin films in different optoelectronic applications that require the band gap modulation.

ZnO SG films doped with Mn show a smaller piezoelectric response than ZnO-HT films due to the facts that their thickness are one order of magnitude smaller than that of the HT films and that Mn$^{2+}$ could oxidize to Mn$^{3+/4+}$ in aqueous solution used in the HT preparation method.

### Data Availability

The data used to support the findings of this study are included within the article. More information could be obtained from the authors upon request.

### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

### Acknowledgments

This work was supported by the M-ERA.Net 12/2015 grant. Project EU (ERDF) and the Romanian Government that allowed the acquisition of the research infrastructure under POS-CCE (Project INFRAANOCHEM—no. 19/01.03.2009) are also acknowledged.

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