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Research Article

Effect of Various Precursors on ZnO Thin Films by USP Technique

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Abstract

ZnO is one of the main materials used in thin film coating due to its low cost and advantageous properties. The aim of this study is to examine the optical, morphological and structural properties of zinc oxide thin films coated with ultrasonic spray pyrolysis(USP) technique. ZnO thin films were grown at 450°C using different precursor solutions such as zinc acetate and zinc nitrate. Glass substrate was used in these processes. 0.1M and 100 mL solutions were prepared. Growth orientations according to XRD patterns are (002). Bandgap values for zinc acetate and zinc nitrate were measured as 3.25 eV and 3.13 eV, respectively. In addition, as can be seen from the Debye-Scherrer calculations, the ZnO grain size of the films obtained with zinc acetate, which was chosen as the precursor salt, is almost the same as the film obtained with zinc nitrate, which was chosen as the precursor salt. Finally, the amount of oxygen in ZnO films varies depending on different solutions and zinc salts.

Keywords: Gas Sensor, Thin Film, ZnO Thin Film, Ultrasonic Spray Pyrolysis(USP).

USP Tekniği ile Çeşitli Öncülerin ZnO İnce Filmler Üzerindeki Etkisi

Öz

ZnO düşük maliyetinden ve sahip olduğu avantajlı özelliklerinden dolayı ince film kaplamada kullanılan başlıca malzemelerdendir. Bu çalışmanın amacı, ultrasonik sprey piroliz (USP) tekniği ile kaplanmış çinko oksit ince filmlerin optik, morfolojik ve yapısal özelliklerini incelemektir. ZnO ince filmler, çinko asetat ve çinko nitrat gibi farklı öncü çözeltiler kullanılarak 450°C'de büyütülmüştür. Bu işlemlerde cam altlık kullanılmıştır. 0.1M ve 100 mL çözeltiler hazırlanmıştır. XRD desenlerine göre büyüme yönelimleri (002) şeklindedir. Çinko asetat ve çinko nitrat için bandgap değerleri sırasıyla, 3.25 eV ve 3.13 eV olarak ölçülmüştür. Ayrıca Debye-Scherrer hesaplamalarından anlaşıldığı üzere öncü tuz olarak seçilen çinko asetat ile elde edilen filmlerin ZnO tane boyutu öncü tuz olarak seçilen çinko nitrat ile elde edilen filmle hemen hemen aynıdır. Son olarak ZnO filmlerdeki oksijen miktarı farklı çözeltilere ve çinko tuzlarına bağlı olarak farklılık gösterir.

Anahtar Kelimeler: Gaz Sensörü, İnce Film, ZnO İnce Film, Ultrasonik Sprey Piroliz(USP).

1. Introduction

Today, the increasing need for semiconductors has triggered the growth of the semiconductor industry. The rapid growth of this industry; has led to the development of compact devices

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with high performance, flexibility and low cost. Products in nanotechnology contain very small particles and also show some advantageous properties. Therefore, it is one of the new and active areas in thin film technology. Because this technology allows the deposition of very thin layers of semiconductor material. Produced materials; exhibits new properties that will benefit electrical, chemical, mechanical and optical aspects. Thin film can be defined as a very thin layer of material deposited on a substrate. This very thin layer of material usually has a thickness ranging from 10 nm to 1-2 μm. Although the deposition process can be physical or chemical, it occurs by the regular condensation of ions, molecules or vapors. Thin films are deposited on a wide variety of substrates. The substrates can be in amorphous, monocrystalline or polycrystalline forms. Thin films and bulk materials have different properties. While a bulk material is stable, the properties of a thin film may vary depending on the quality of the surface. These features can be improved with some modifications. For example, the quality can be increased by doping change, thickness change or various surface treatments. However, multilayer thin films may exhibit unknown properties. With thin film technology, raw materials can be used more efficiently. Thin films deposited using nanotechnology have been used in sensors, photovoltaic devices, batteries, and information storage devices in recent years(Özgür et al., 2005; Nalwa, 2001; Sheu et al., 2008; Hosono, 2007; Patil et al., 2011; Bari et al., 2013; Lin and Wu, 2010; Zhou et al., 2007; Walsh et al., 2008). In particular, oxide-based semiconductors such as ZnO, silicon, GaN, gallium arsenide and others remain popular(Vyas, 2020). In addition, ZnO is the priority material for nanoelectronic devices due to some of its properties. Some of these features are: optical, electrical, magnetic and most importantly gas detection(Wasa et al., 2004). The different nanostructures of ZnO include nanorods, nanowires, nanotubes and nanostrips. Single-crystal ZnO can be used to manufacture high-performance electronic and optoelectronic devices. Because in this way, low-defect epitaxial films are obtained. It can be deposited on a variety of substrates using conventional thin-film deposition methods such as sputtering, thermal evaporation, and sol-gel(Özgür et al., 2005). Since the processing temperature of ZnO nanostructures is low, inexpensive substrates such as glass and plastic may also be preferred. In addition, the optical and electrical properties of ZnO allow for post-deposition treatments such as doping, surface treatments, and annealing. It can be selected as a transparent conductor for near-UV emission and detection. Because it is an n-type transparent material with high electrical conductivity and a direct band gap(Vyas et al., 2020). ZnO has a wide band gap of 3.3 eV and a low resistivity of 5×10^{-4} Ω·cm(Agrawal et al., 2013). Transparent Conductive Oxides (TCOs) are often doped metal oxide layers used in optical surfaces such as photovoltaic panels, architectural and transmission glass, and interactive devices such as touch panels. Chemical inertness and high transparency are the main factors contributing to the TCO selection(Engle, 2021). Transparent conductive oxide (TCO) films are used in many optoelectronic devices. Each parameter involved in the process affects various material properties such as crystal quality(Arnou et al., 2014). TCO thin films have been crucial in the design of existing devices in sensors, photovoltaics, microelectronics, and opto-electronics(Benzarouk et al., 2019). Currently, the most widely used TCO is indium-doped indium oxide (ITO). This is because this type of material offers a great combination of high transparency and high electrical conductivity. Unfortunately, because indium is a rare element, an alternative TCO material was needed. In this context, zinc oxide (ZnO) has become an alternative metal oxide(Arnou et al., 2014). Because ZnO thin films are abundant in nature. They are also non-toxic. The reasons why it is often preferred among other TCO materials is that it has many advantages. These advantages can be listed as follows: High optical transmittance in the visible region, high chemical stability, high thermal stability(Arnou et al., 2014; Benzarouk et al., 2019). The USP technique is simple, cheap and suitable for pure production. For this reason, the process of preparing ZnO films by spraying an aqueous solution has been popular in recent years. Many studies have focused on the effect of different precursor solutions on some properties of ZnO thin films(Benzarouk et al., 2019). Also although months have passed, doped ZnO nanoroads seem to have higher sensitivity and stability than pure ZnO nanoroads(Kasapoğlu et al., 2021). As we mentioned before, ZnO has attracted attention among many metal oxide materials. In addition to other advantages, it has physical properties such as good piezoelectric behavior and high electron mobility. Undoped and doped n-type ZnO are used in TCO application areas. Apart from simple and multifunctional chemical deposition methods, magnetron sputtering, pulsed laser, and plasma-assisted molecular beam epitaxy are known vacuum-based deposition techniques for producing ZnO thin films. Silar, spray pyrolysis, chemical bath deposition and sol-gel methods are the most prominent among the non-vacuum process thin film deposition techniques(Tumbul, 2019). Vacuum deposition systems require high installation costs. So avoiding these techniques can reduce production costs. Ultrasonic spray pyrolysis (USP) is a low-cost, simple atmospheric deposition technique and can be applied to vacuum-based systems(Arnou et al., 2014; Ynineb et al., 2013). Among the many deposition techniques mentioned, USP is the most suitable even for the preparation of doped oxide thin films. Because in addition to being simple and inexpensive, it can be easily adapted to large area accumulation(Supriyono et al., 2015). TCO conventional materials such as In2O3, SnO2, ZnO and CdO have been extensively studied. These properties have created an opportunity to be used as a transparent front contact material in solar cells and for ZnO films to be a potential candidate for photosensors, gas sensors, optoelectronic and photocatalytic applications(Atay et al., 2019). Being preferred in light emitting diodes (LEDs), laser diodes, solar cell, photodetectors, electronic devices, optoelectronic and photocatalytic applications, it offers a wide range of uses considering both energy platforms and environmental factors. Especially when it comes to sensor applications, it is necessary to increase the sensitivity of ZnO, and for this reason, many studies have been done. Research has shown that increasing the surface area of the material by itself can be a solution. That is, making a larger surface allows to obtain an advantageous ZnO nanostructure. For this, it is necessary to manipulate the structure itself in a certain way(Ramadhani et al., 2014). In general, the physical properties of ZnO are related to its microstructure. Depending on the precursor materials chosen, the morphology of ZnO can be controlled. One of the advantages of the pyrolytic decomposition of its precursors in this context is that crystallographic orientations can be taken over by the resulting ZnO. Hence, the microstructure of ZnO can be divided into hexagonal plates or prisms (Figure 1)(Yuki et al., 2015).

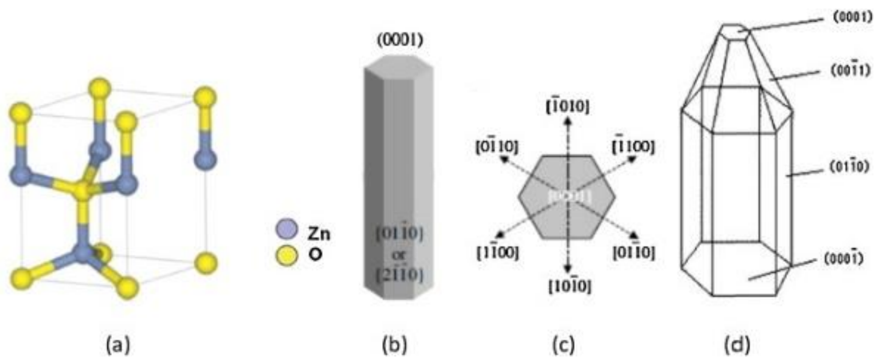


Figure 1. Unit cell of ZnO crystal structure(Skompska and Zarebska, 2014)

The character of the selected doping element varies according to certain conditions. These conditions are: the adsorption of oxygen during the deposition process, the film deposition temperature and the post deposition annealing atmosphere. Therefore, the opto-electrical properties of ZnO depend on the conditions both during and after deposition(Agrawal et al., 2013). USP; The simplicity of the experimental setup, the ability to add the material at desired rates, and the ability to produce homogeneous, cheap and easy in large areas(Malik et al., 2015; Bilgin et al., 2010; Lalasari et al., 2018; Kaleli et al., 2019). As a USP solution-based inexpensive method, it offers the possibility to easily adjust the deposition parameters depending on the desired material properties. In addition, the USP is both material-efficient and can be manufactured in a wide range(Arnou et al., 2014). ZnO nanoparticles can be obtained even at the lowest reaction temperature. Thanks to effective sintering, ZnO porous particles formed by the aggregation of ZnO nanoparticles were prepared at higher temperatures. The results showed that the properties of ZnO particles can be controlled by changing the reaction temperature in the ultrasonic spray pyrolysis method(Ebin et al., 2012).

In this paper, by using different precursors the structural, morphological and optical properties of zinc oxide thin films were investigated. At low temperatures, other atoms can form instead of oxygen. 450 °C degrees was preferred to obtain the oxide film.

2. Material and Methods

Ultrasonic spray pyrolysis technique is preferred because it is more economical than other techniques, it is suitable for intervention in the production process, there is no need for a vacuum environment for thin film production. It allows the coating of large surfaces and the production process can be followed step by step.

Three steps are followed to apply this method, which is a thin film production technique:

- Cleaning Step
- Solution Preparation with deionized water
- Thin Film Production by USP method

Glasses washed with soapy water are then exposed to ethanol and propyl alcohol solutions. Afterwards, the drying process is carried out.

2.1. Precursor Zinc Nitrate

In this process, 0.1 Molar and 100 mL solution was prepared using 2.972 g of zinc nitrate with a molecular weight of 297.2 g to be grown at 450°C for an hour on glass substrate using the spray pyrolysis. (0.01 mol $Zn(NO_3)_2.6H_2O$:2.972 g)

2.2. Precursor Zinc Acetate

In this process, 0.1 Molar and 100 mL of solution were prepared using 2.1949 g of zinc acetate with a molecular weight of 219.49 g to be grown at 450°C for an hour on glass substrate using the spray pyrolysis. (0.01 mol $Zn(CH_3COO)_2.2H_2O$:2.1949 g)

Spray nozzle with nozzle frequency 100 kHz was placed at a 45 degree angle of 30 cm from the table. 100 mL of solution was sprayed for 1 hour, the flow rate was 0.028 milliliters/second.

3. Experimental Results

X-ray diffraction (XRD), absorption and scanning electron microscopy (SEM) were used to examine the crystal structure and surface morphology analysis of the films, respectively.

3.1. Crystal Structure

XRD results showed that thin ZnO films were produced by ultrasonic sputtering technique. The main peaks of ZnO are visibled.

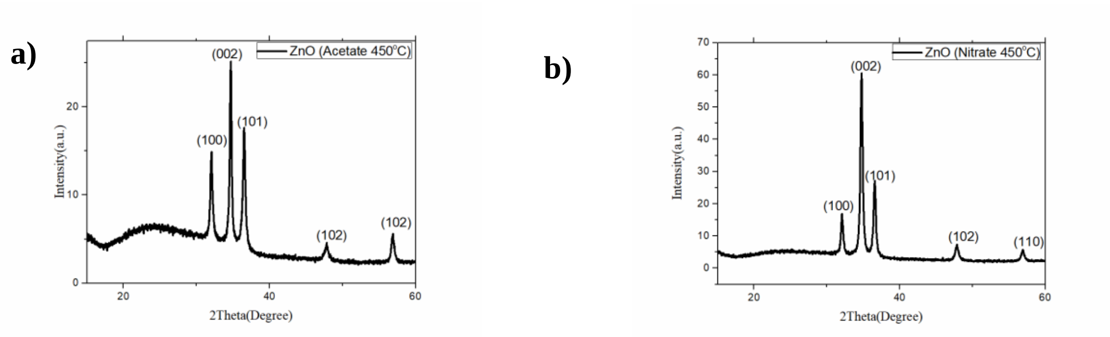


Figure 2. XRD graphs of ZnO a) Zinc Acetate b) Zinc Nitrate *(Reference Code: 01-079-0205)*

In Figure 2, different salt forms of zinc are used at constant temperature. Figure 3 shows the shift caused by these changed parameters. Both ZnO structures are in hexagonal structure and it is seen that they are oriented along the c axis (002) direction. In addition, as seen in Figure 3, the XRD peak intensities of the films obtained from nitrate salt solution are higher than acetate salt.

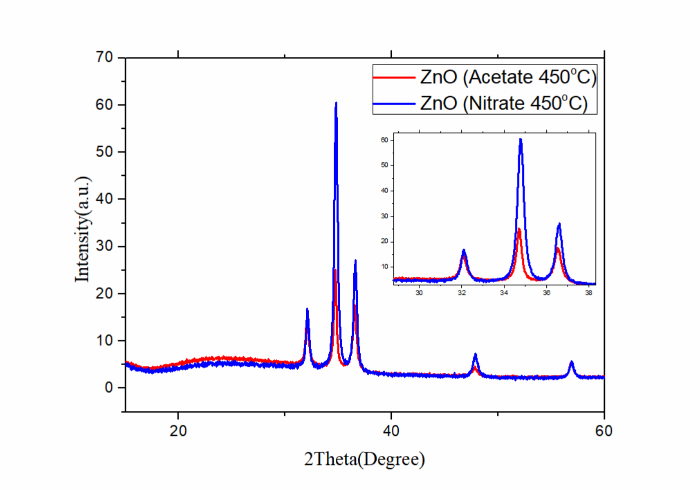


Figure 3. XRD graphs of Zinc Acetate and Zinc Nitrate at 450°C

Debye-Scherrer formula,

$$D=0,94* \lambda/ \beta\cos\theta \quad (1)$$

where λ is the wavelength (λ = 1.5405 Å), β is the full width at half maximum (FWHM) of the considerate peak and θ is the corresponding Bragg's angle. As seen in Table 1, the grain size values of the samples grown from different precursors according to the Debye-Scherrer method calculated in Equation 1 are approximately the same. However, with a slight difference, grain size of zinc acetate is larger than the grain size of zinc nitrate according to the average grain size values. Average of grain sizes for zinc nitrate and zinc acetate are 19,72 nm and 19,88 nm, respectively.

Table 1. Crystal size of thin films

	Zinc Nitrate		Zinc Acetate	
2 θ	β	D(nm)	β	D(nm)
32,10	0,36	22,4	0,37	22,3
34,75	0,38	21,6	0,31	26,1
35,59	0,40	20,8	0,44	18,6
47,88	0,54	16,1	0,67	12,8
56,93	0,51	17,7	0,46	19,6

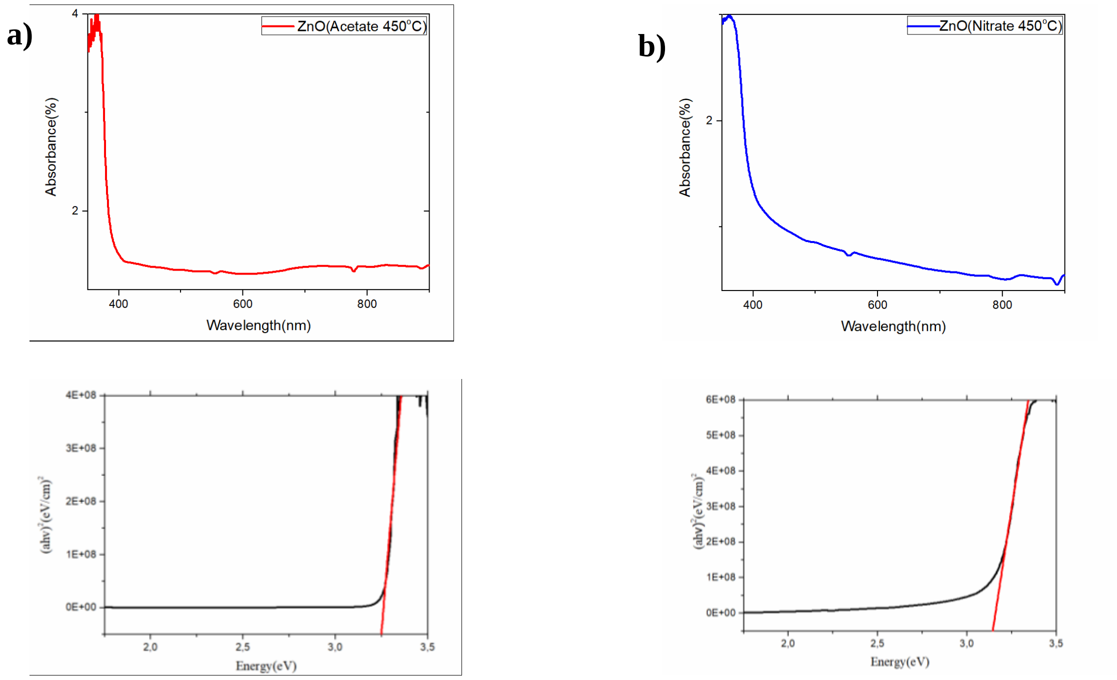


Figure 4. Absorption measurements, bandgap plots of ZnO films at 450°C

a) Zinc Acetate b)Zinc Nitrate

As seen in Figure 4, the absorption graphs differ according to the salt component used in the solution, and there is a remarkable change in the size of the band gap.

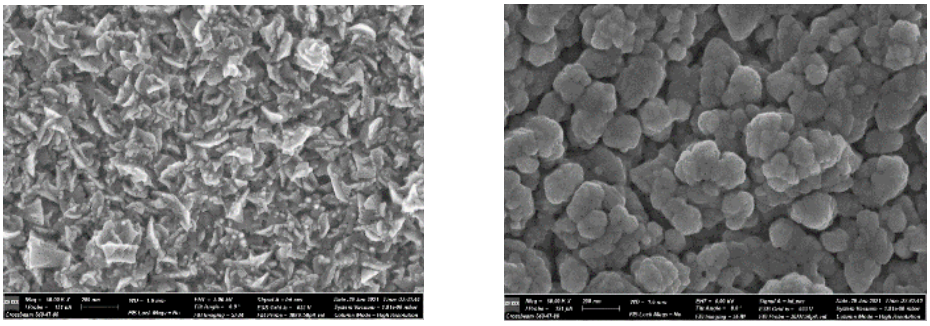
The optical band gap (E_g) values were determined from the commonly known equation (for n=0.5) :

$$ahv = A(hv-E_g)^{(1/n)} \quad (2)$$

The band gap of the thin film obtained with salt containing acetate is around 3.25 eV, while the band gap gap of the films obtained with salt containing nitrate is around 3.13 eV. The band gap values above were calculated according to Equation 2.

3.2. Surface Morphology

As can be seen from the SEM image (Fig. 5), it is seen that the grain size of the ZnO structure obtained with zinc nitrate salt is similarly the structure made with zinc acetate salt, and the difference in XRD peak intensity supports this situation.



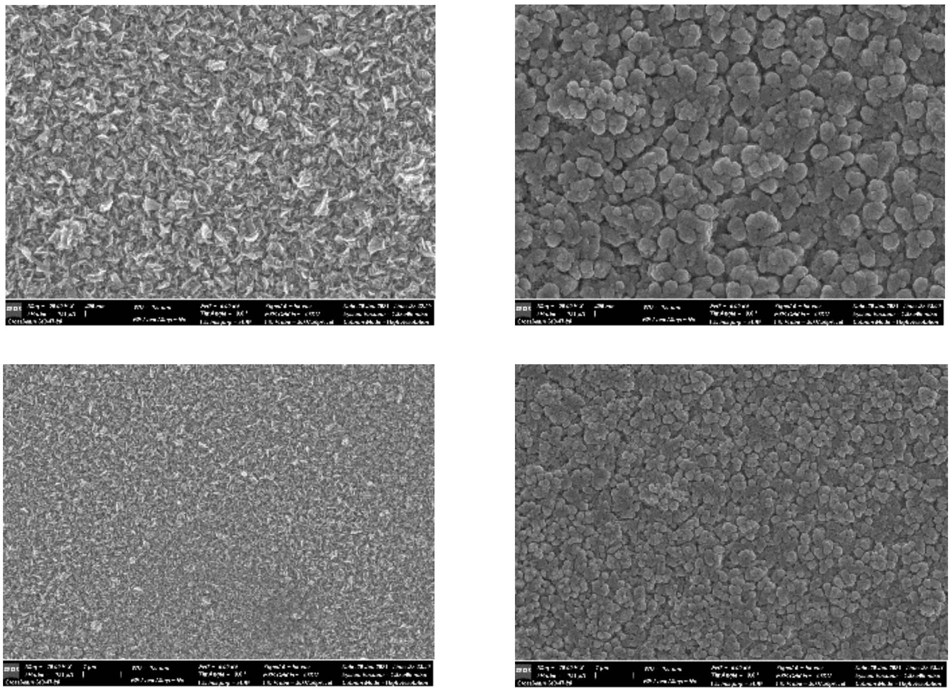


Figure 5. SEM micrographs of ZnO films (200nm-400nm-1μm) a)Zinc Acetate b) Zinc Nitrate

4. Conclusion

Thin ZnO films can be produced by ultrasonic spray coating. It is possible to produce gas sensors on transparent surfaces without losing their transparency. However, transparency-performance optimization should be made between sensor performance and film thickness. Performance-transparency optimization should be made especially in order to produce gas sensors without losing transparency. In our study, it has been observed that thin ZnO films can be produced by ultrasonic spray coating. ZnO thin films were produced at 450°C for two hours using the spray pyrolysis technique. Deposits were made on glass substrates.

Film prepared with zinc acetate solution has higher transmittance compared to films prepared with other zinc precursors. The calculated band gap of the ZnO films obtained using different precursor salts is lower than the band gap of the bulk ZnO crystal. It has also been observed that it is strongly affected by stress(Lehraki et al., 2020).

The precursor zinc acetate and precursor zinc nitrate used in these processes are 0.1M and 100 mL. The morphological features of the prepared films were analyzed. The bandgap values of the films obtained from zinc acetate and zinc nitrate precursor solutions were 3.25 eV and 3.13 eV, respectively. In addition, differences in crystal shapes were observed when the precursor solutions were changed. In the USP technique, both the cost is low and the parameters can be changed easily. The crystal size and surface morphology of the structures obtained by ultrasonic spray pyrolysis are promising for the preparation of a sensitive gas sensor.

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