Effect of annealing process in tuning of defects in ZnO nanorods and their application in UV photodetectors

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Abstract

ZnO nanorod (NR) arrays were grown by a simple two-step chemical bath deposition method. The as-deposited NRs were then annealed at different temperatures (300, 400 and 500°C) for two time durations (1 and 5 h). The NRs were studied by scanning electron microscopy, photoluminescence spectroscopy, X-ray diffraction and two-point electrical test. Finally, ultraviolet (UV) detection properties of samples as an active layer in UV photodetector devices were evaluated. The structural results showed that the sample annealed at 400°C had the best crystallinity. Furthermore, it was seen that the optical transparency and band gap of NRs increased with increase of the annealing temperature up to 400°C and then decreased at 500°C. The electrical resistance decreases with increment of the annealing temperature due to intensive desorption of oxygen molecules from the surface of ZnO NRs. The UV detection results proved a meaningful relevance of UV detection properties with the density of defects and quantity of oxygen molecules absorbed on the surface. ZnO NRs annealed at 300°C for 1 h had the highest photosensitivity of ~300 and photoresponsivity of 2.067 A/W which make it suitable for the practical applications.

Keywords: Zinc oxide, Nanostructures, Vacancy, Ultraviolet detector.

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1. Introduction

ZnO has unique optoelectronic properties like direct wide bandgap (3.37 eV) with hexagonal wurtzite structure, large free-exciton binding energy (60 meV), strong cohesive energy of 1.89 eV, high optical gain (300 cm^{-1}) and high mechanical and thermal stabilities [1,2]. Due to these exclusive characteristics, it is expected that ZnO has efficient utilization in different scientific and industrial applications such as integrated optical devices, antireflection coatings, liquid crystal displays, light-emitting diodes, laser diodes, chemical sensors, solar cells [3-6].

Meanwhile, not only pure ZnO takes into account as a highly transparent in the visible and near infrared region of the electromagnetic spectra, but also, it is an attractive stuff for ultraviolet (UV) sensing owing to its optical band gap value (almost lies in the boundary of ultraviolet and visible light). Therefore, ZnO is known as a liable candidate for fabrication of a simple UV photodetectors (PDs). PDs operating in the UV region are important devices that can be used in many commercial and military applications, such as ozone layer monitoring, flame detection and missile warning systems [7,8], etc.

Considering the various restrictions of pure ZnO layer as an UV-detector such as low sensitivity and long time of response, various works have been carried out to optimize it as an efficient PD device [9,10]. Among the various modifications, the surface modification of ZnO nanostructures is accounted as an attractive way because of the diversity of fabrication methods for these nanostructures, their large surface availability, excellent optoelectrical, physical and chemical properties [11].

Hydrothermal is known to be a simple, low temperature, and cost-effective large-area deposition technique. In general, ZnO nanostructures fabricated by this method have a larger

number of defects due to a low growth temperature ($<100\text{ }^{\circ}\text{C}$) [12]. It is well known that the defect chemistry of ZnO is complex, with a range of oxygen or zinc defects of varying charges and with concentrations that are interdependent on each other [13]. The typically fabricated photodetectors based on as-grown ZnO nanorod (NR) arrays contain a considerable number of defects which lead to low response to UV light. Annealing process is one of the most important methods that can strongly affect the properties of ZnO nanostructures. Panda et al. [14] reported that ZnO sensor device became more sensitive to UV light after annealing. The concentration of defects in ZnO NR arrays undergoes a considerable change through annealing. On the other hands, the annealing, as a surface treatment process, can remove surface defects and contamination and modify surface absorption and desorption of oxygen molecules, thereby improving the surface condition of ZnO [11]. In this regard and since the UV photoconductivity is governed by the surface conditions of the NR arrays, effective annealing methods should be developed to reduce the number of defects and improve the surface quality of the prepared ZnO NR arrays. It is known that the photoconduction in the ZnO nanostructures is controlled by oxygen adsorption and desorption on the surface [15]. Therefore, annealing process can improve the photosensitivity as well as photoresponse of ZnO NRs due to surface modification and structural improvement. Various groups have put efforts to enhance the performance of UV-detectors based ZnO nanostructures [15]. Chen et al. [16] reported an amazing photoresponsivity for ZnO thin films grown by the sol–gel method and crystallized at 700°C in a pure oxygen atmosphere. Dhara et al. [15] reported the major improvement in UV photosensitivity and faster photoresponse from vertically aligned ZnO nanowires by means of rapid thermal annealing at 700°C in Ar gas ambient. Also, Mamat et al. [11] fabricated MSM (metal-semiconductor-metal) UV PDs using Al-doped ZnO NR arrays that were annealed at

different atmospheres. They observed the higher photosensitivity for oxygen-annealed ZnO NRs.

It can be seen that the density of anionic vacancies on the surface of ZnO NRs plays an important role in the surface oxygen adsorption and desorption during UV irradiating and that is the objective of this study to find the best annealing temperature for fabrication a practical ZnO NRs based UV-detector. Therefore, to achieve an optimized UV sensitive material, we synthesized ZnO NRs by hydrothermal method and then annealed at various temperatures followed by a rapid cooling down in air. Afterwards, the structural, optical, electrical and UV photodetection properties of ZnO NR samples were investigated.

2. Experimental details

2.1. Preparing ZnO seed layer

The ZnO seed layer was coated onto the glass substrates by sol–gel spin-coating method as follows: Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was used as a starting material. Ethanol and diethanolamin (DEA) were used as the solvent and stabilizer, respectively. The obtained mixture was stirred at 60°C for 20 min to yield a clear and homogeneous solution, which then served as the coating source after being cooled down to room temperature. The glass substrates were first cleaned by detergent, then in acetone, ethanol and deionized water by using an ultrasonic bath. Finally, the glass substrates were rinsed with deionized water and dried. The coating solution was dropped onto the glass substrate and rotated at 3000 rpm for 30 sec. After spin-coating, the films were dried at 180°C for 10 min in an oven to evaporate the solvent and to remove organic residues. This coating/drying procedure was repeated for five times to ensure uniform coverage of glass substrate with a uniform layer of ZnO. The films were then annealed at 450°C for 1 h in air by a tube furnace.

2.2. Growing ZnO NRs

In the second step, the ZnO NRs were grown by a hydrothermal process. The solution for growing the ZnO NRs was prepared by mixing the zinc nitrate hexahydrate (0.001 M) with NaOH (0.1 M). The glass substrates with the seed layer were immersed into the resultant solution and then heated at 70°C for 1.5 h.

For removing residual salt on the surface, ZnO NRs grown on the substrate were washed with deionized water. Finally, ZnO NRs were annealed in air at various annealing temperatures of 300, 400 and 500°C for different time durations (1 and 5 h) and then cooled down to room temperature.

2.3. Sample characterizations

The crystallographic structure of ZnO NRs was analyzed by X-ray diffractometer (XRD, X'Pert PRO, Philips) with wavelength of 0.154059 nm. The morphology of the synthesized ZnO NRs and ZnO seed layer were characterized by scanning electron microscopy (SEM, VEGA, TESCAN) and atomic force microscopy (AFM Image (NT-MDT)). The optical characteristics of the samples were characterized using an UV-visible spectrophotometer (Jasco v570). The photoluminescence (PL) properties of the synthesized NRs were investigated using a PL spectrophotometer (PL-Perkin-Elmer LS55) equipped with a 450W Xe lamp as an excitation source operating at 325 nm.

2.4. Photodetector device fabrication and characterization

For PD fabrication, the inter-digitized Au electrodes (thickness 70 nm) were deposited on ZnO NR samples by RF & DC magnetron sputtering system (Yar Nikan Saleh Co., Iran) using a shadow mask. The fingers of the contact electrodes had 10 mm length, 1 mm width and interspacing between electrodes was 1 mm. The active area of the whole device was $10 \times 10 \text{ mm}^2$. The image of Au/ZnO NR/Au based PD is shown in Fig. 1. The current–voltage (I–V) characteristics were measured by sweeping the bias voltage from 0 to 21 V. The UV

photoresponse properties of NR PDs were measured at room temperature in air and under an 8 W Philips black UV-light lamp with 350-400 nm range of illumination. Also, the dependence of photosensitivity as a function of optical power density was measured at different distances of UV lamp to the samples.

<Fig. 1>

3. Results and discussion

3.1. SEM and AFM analysis

The AFM image of seed layer prepared using spin-coating is shown in Fig 2(a). After heat treatment of spin-coated ZnO thin film at 450°C, a seed layer was formed on the glass substrate. This layer includes the nanograins with number density of $\sim 4 \times 10^8 \text{ cm}^{-2}$, average peak height of 19 nm and root mean square roughness 2.2 nm. In next step, this seed layer was used for growth of ZnO NRs. Fig 2(b) shows the SEM image of the hydrothermally grown NRs annealed at 500°C. The length of NRs is in the range of 1 μm [2], and their diameter is in the range of 40-60 nm.

It has been reported that the use of seed layer on the substrate results in an improved vertical orientation of the NRs in hydrothermal conditions [17]. When the concentration of Zn^{2+} and OH^- exceed supersaturation, ZnO nuclei are formed on the substrate surface [18]. With increasing temperature, these complexes become dehydrated and heterogeneous nucleation of ZnO crystals takes place at the interface between substrate and solution and consequently causes to growth of ZnO NRs [19].

<Fig. 2>

3.2. XRD analysis

The XRD patterns of ZnO NRs with different annealing temperatures (300, 400 and 500°C) for 1 h are shown in Fig. 3. All patterns exhibited a dominant peak corresponding to the (002)

direction of ZnO. It is clear that all ZnO NRs have the hexagonal wurtzite structure with a preferential orientation along the c-axis (perpendicular to the substrate). The XRD results obtained from patterns have summarized in table 1. It can be seen that the intensity as well as full width of half-maximum (FWHM) of (002) peak are dependent on the annealing temperatures. The intensity of (002) diffraction peak first increases (up to 400°C) and then decreases with increasing of annealing temperature to 500°C. It is clear that with increasing the annealing temperature from 300°C to 400°C, the crystallization of the ZnO samples was developed by a sufficient supply of thermal energy and then that began to deteriorate at 500°C. The reduction of crystallinity in the sample annealed at 500°C may also be attributed to terrible desorption of oxygen molecules of ZnO surface and formation of non-stoichiometric ZnO [16]. Therefore, there is an optimum annealing temperature for improving the crystallinity of the ZnO NR arrays. Above the optimum annealing temperature (400°C), point defects in the form of oxygen vacancies will be created [12].

<Fig. 3>

<Table 1>

3.3. UV-visible spectroscopy analysis

Fig. 4(a) shows the transmittance spectra of ZnO NRs annealed at different temperatures for 1 h. With increasing the annealing temperature to 400°C, the average transmittance increases in visible light range, which can be attributed to the improvement of structure in ZnO samples [20]. This may be due to decrease the density of grain boundaries because of grain growth and consequently reduce optical scatterings of visible light [20]. Therefore, higher optical transmittance can be obtained by annealing during the grain growth process, which is suitable for growing ZnO transparent films [21]. The optical absorption edge has a tendency to shift to a lower wavelength with the increase of the annealing temperature up to 400°C and then it decreases with temperature increasing to 500°C. It is well identified that the optical

absorption determines the optical band gap of ZnO NRs which has a direct band gap [14]. The optical band gap of ZnO NRs annealed at temperatures of 300, 400 and 500°C was found to be 3.1, 3.2 and 2.9 eV, respectively (Fig. 4(b)). Typically the blue shift of the absorption edge of the ZnO NRs is associated with an increase of the carriers concentration and the movement of Fermi level into the conduction band where block the lowest states in the conduction band, well known as the Burstein-Moss effect [22,23]. This is opposed with what Ma et al. [20] reported for ZnO thin films. They observed the shifting optical band edge to longer wave lengths as the annealing temperature shifted from room temperature to 700°C and described it according to the quantum confinement effect due to diameter increasing. On the other hands, the reduction of transparency of sample annealed at 500°C can be attributed to its metallic nature after annealing at this temperature [24]. Similarly, Seo et al. [25] reported the reduced band gap of non-stoichiometric oxide semiconductor films caused by the sub-oxide states associated with the oxygen vacancies. Also, Sendi et al. [26] observed a reduction in bandgap of the ZnO nanostructures when the annealing temperature was increased up to 650°C. Therefore, it can be concluded that increasing the annealing temperature to above the optimum temperature causes to strong desorption of surface oxygen molecules.

<Fig. 4>

3.4. Photoluminescence analysis

Fig. 5 shows the PL spectra of the ZnO NRs annealed at different temperatures for 1 h. In the PL spectra, two emission peaks are observed in the samples. The near-band-edge emission at the UV region of ~400 nm (~3.1 eV) was attributed to free-exciton recombination. It was reported that the UV emission band of ZnO nanostructures occurs in the range of 3.10 eV to 3.37 eV [27]. Other is a broad peak related to the deep-level emission at the visible region, which usually indicates the presence of structural defects and impurities. In the different

literature, a variety of defects at different energies for ZnO nanostructures were reported, including oxygen vacancy, zinc vacancy, antisite oxygen, antisite zinc, interstitial oxygen, and interstitial zinc [20].

<Fig. 5>

The UV peak is associated with free-exciton recombination across the band gap. Its intensity becomes higher when there are less recombination traps within the band gap [13]. The PL peak intensity decreased with increasing annealing temperature above 300°C. This trend indicates that annealing at the high temperatures causes to increase defects, particularly surface oxygen vacancy concentrations through desorbing oxygen species of surface ZnO NRs. However, the UV emission intensity in ZnO NRs after annealing depends on the two competition processes, one is to release the surface attached chemical elements which will enhance the UV emission intensity, and the other is the creation of the deep level defects which will reduce the UV emission intensity [28-30].

3.5. Electrical analysis

The current-voltage (I-V) characteristics of the Au/ZnO NRs/Au MSM PDs were measured in the dark (Fig. 6(a)) which indicated an ohmic behavior for all of the samples with Au electrodes [23]. The resistance of the ZnO NRs annealed at different temperatures was obtained using I-V curves (Fig. 6(b)). The dark resistance were calculated to be 0.80, 5.01, 0.53, 0.071 and 0.038 MΩ for the samples annealed at 300 (1 h), 300 (5 h), 400 (5 h), 500 (1 h) and 500°C (5 h), respectively. It is obvious that resistance of the ZnO NRs annealed at 300°C is very high compared to other samples. While, annealing at higher temperatures significantly decreases the resistance of the NR arrays. The resistance of ZnO NR samples is depended on concentration and mobility of electronic carriers, which they are dependent on

physical properties such as degree of crystallinity, grain size, stoichiometry and lattice defects.

<Fig. 6>

In general, the reduction of grain boundaries with increasing the annealing temperature (in the annealed samples at 400 and 500°C) may cause to decrease the resistance of ZnO NRs [22]. In fact, the formation of larger crystallites during annealing process causes to reduce the charge carrier scattering probability. Furthermore, electron mobility also increased along with the annealing temperature which could occur due to the reduction of grain boundary scattering for electron transport [31].

With annealing in air at 300°C, a high density of oxygen ions would be adsorbed on the surface of NRs which increases the resistance of the NR arrays. During the annealing process, oxygen could also diffuse into the NR arrays, which induces a high density of acceptor-like defects (i.e., Zn vacancies and oxygen antisites) [11]. This condition results in the compensation of donor-like defects (i.e., oxygen vacancies and Zn interstitials formed in growth process) and depletion of the carrier density [11]. Oxygen vacancies act as donor impurities and provide n-type doping to the material. High density of sub-gap states associated with the oxygen vacancies provides a metallic behavior. The annealing compensates the oxygen vacancies and eliminates the mid-gap levels for which the conductivity decreases [14].

The lower resistance for the samples annealed at 400°C and 500°C can be described by loss oxygen adsorption on the surface of NRs where the stoichiometry of ZnO is deteriorated and resistance of ZnO NRs decreases [32,33]. This is similar with the results reported by Lupan et al. [34] when ZnO NRs were annealed with rapid thermal annealing method. The desorption of the large number of chemisorbed oxygen species at the surface of prepared zinc oxide

samples causes to the increment of the electron concentration on the surface and improves the conductance. Ogata et al. [35] observed that in ZnO thin films, after annealing above 500°C, the electron carrier density increased. They ascribed this increase to the formation of interstitial zinc and oxygen vacancy due to the evaporation of oxygen.

The conductivity of ZnO is controlled by the concentration of interstitial zinc ion and oxygen vacancy [30]. Zhaoyuan and Li [36] also reported the annealing temperature as a key factor in controlling the balance between the adsorption and desorption of oxygen atoms in ZnO films. At higher temperatures, the rate of desorption overtakes the rate of adsorption, which is due to the significant weakness of the Zn-O binding. The annealing at 500°C leads to the formation of non-stoichiometric defects and results in an ionic charge imbalance that makes ZnO naturally conductive even without intentional doping [2], in agreement with optical results. As the annealing temperature is around 400°C, thermal energy is not enough to totally break the Zn-O binding and just makes it weak to some extent, which is not an appropriate situation for accepting oxygen and other atoms from the annealing atmosphere; but ZnO structure is well-prepared to disrobe oxygen from grain boundaries that make a reduction in the defect density and improve crystallinity [37]. As a result of the oxygen desorption from grain boundaries due to decrease in electrical resistance [37]. Therefore, the analysis of the dark I-V characteristics of the ZnO NRs annealed at 300°C clearly indicates the presence of high density of trap centers on the surface of ZnO NRs, while the trap density is significantly reduced in the used annealing method at temperatures higher than 400°C like rapid thermal annealing processed ZnO nanostructures [15].

3.6. UV photodetection analysis

Fig. 7 depicts the photocurrent of the UV photodetectors prepared using the ZnO NR arrays that were annealed at different temperatures for duration times of 1 and 5 h. The photodetection tests were performed using a dark UV-A light with optical power density of

208 $\mu\text{W}/\text{cm}^2$ and a series circuit with bias voltage of 10V. Under UV illumination, the current rapidly increased and then gradually became saturated. It is clear that the photocurrent of the sample annealed at 300°C for 1 h shows the highest photocurrent value of 0.43 mA. Amazingly, the PD based on ZnO NR array annealed at 300°C for 5 h shows the lowest photocurrent value of 0.063 mA.

<Fig. 7>

In the dark, ZnO NRs adsorb oxygen molecules on their surface by donating free electrons and producing adsorbed oxygen ions (O_2^-). Thereby, a space charge region near the surface of NRs forms with much lower electron concentration. The gradient of charge carrier in this depletion layer causes to existence of an electric field in width of this region and band bending. When the NRs are irradiated with UV light, electron-hole pairs are generated at the ZnO NRs. The photogenerated holes recombine with the adsorbed oxygen ions on the surface and release oxygen molecules. At the same time, the desorption of adsorbed oxygen ions on the NRs surface leaves photogenerated electrons in the conduction band, thereby increases the conductivity (known as photocurrent).

From the photocurrent graph, the photoresponsivity of the PDs was estimated using the following equation [9]:

$$\text{photoresponsivity} = \frac{I_{ph} - I_{dark}}{P_{op}} \quad (1)$$

where I_{ph} is the photocurrent, I_{dark} is the dark current, and P_{op} is the optical power of the UV source. It is obvious that the sensor based on ZnO NRs annealed at 300°C for 1 h has a higher photoresponsivity (2.065 A/W) than the other samples (Fig. 7(b)). Although the photocurrent value of PD annealed at 500°C is relatively high, but this PD exhibits a lower responsivity value (0.28 A/W) because of its high dark current value.

The sensitivity of the PDs, which is defined as the photocurrent to dark current ratio, was calculated for all of the devices (shown in Fig. 7(b)). The results indicate that the PD based on ZnO NR array annealed at 300°C for 1 h has the highest sensitivity (~300). The highest sensitivity of the 300°C annealed sample in air is due to the significant reduction of the dark current value and increment of photocurrent as compared with the other samples through existence of much value of Zn interstitials formed in growth process. The significant reduction in the dark current value is correlated with more adsorbed oxygen on the NR arrays, which increases the resistance of the sample, as shown by the I-V measurement results. The sensitivity of the sensor has been reported to be correlated with the oxygen adsorption and desorption processes [11]. On the other hand, the photocurrent value of the ZnO NR array based UV PDs could be attributed to the high concentration of Zn interstitials. According to Bera et al. [38], when ZnO with a high concentration of Zn interstitials are irradiated with UV light, the photogenerated excitons could interact with the Zn interstitials, which results in ionization of Zn interstitials. When Zn interstitials are ionized, more free electrons are generated in the conduction band, which increases the photocurrent of the PD. Increasing of annealing temperature ($\geq 400^\circ\text{C}$) causes to decrease the concentration of Zn interstitials and therefore decreases the photocurrent [11]. The calculations have indicated that zinc interstitials are shallow donors, but unstable; they have high formation energies and very low migration barriers, in agreement with experimental results of irradiated samples [1]. Wang et al. [39] reported the significant interstitial zinc diffusion at high annealing temperature.

On the other hand, the adsorption of oxygen on the NR surface causes the existence of a non-conductive barrier or a surface depletion region and thus, an upward band bending. The width of this barrier in NR arrays may differ after annealing at different conditions. For example, Mamat et al. [11] considered effect of annealing in different atmospheres on the band

bending of the as-grown Al-doped ZnO NR arrays. They observed that the oxygen-annealed NRs have the most depleted surface region due to the large amount of adsorbed oxygen, followed by the air-annealed sample. Also, they observed the lower photocurrent in oxygen-annealed Al-doped ZnO NRs compared to the other annealed samples. According to our results, the NR arrays annealed at 300°C have the most depleted surface region due to the large amount of adsorbed oxygen [11].

According to the space charge model, L_d (a Debye length) can be expressed by [40]:

$$L_d = (\epsilon k T / q^2 n_c)^{1/2} \quad (3)$$

where ϵ is the static dielectric constant, k is the Boltzmann's constant, T is the absolute temperature, q is the electrical charge of the carrier, and n_c is the carrier concentration. When the annealing temperature increases, the electron concentration (n_c) increases due to desorption oxygen species from NR surface. Therefore, the Debye length (depletion layer) decreases through increasing of electron concentration and UV photodetection properties are weaken.

In Fig. 8 the photocurrent of the samples annealed at 300°C for 1 and 5 h were shown. It is clear that response of PDs is repeatable well. However, annealing at 300°C temperature in air caused to the improvement of the ZnO stoichiometry and adsorption of high density of surface oxygen ions. During the annealing process, vacant sites in the ZnO lattice, which resulted from the evaporation of OH groups from the nanorod surface, were immediately replaced by oxygen from the environment which results in the increase of the nanorod resistance.

<Fig. 8>

4. Conclusions

In this work, the ZnO NR arrays were prepared by a two-step chemical bath deposition method and annealed at various temperatures and its optimized state as an UV-detector was obtained. The XRD results showed that annealing increases the crystallinity and crystallite size of ZnO NRs. It was discerned that vacancies tend to be decreased to 400°C thermodynamically leading to the considerable increment in crystallinity. The breakings of the surface oxygen bonds and desorption of them at higher temperatures due to the deterioration of ZnO crystallinity. The PL results explained that intensity of UV peak decreases with increasing of annealing temperature where can be attributed to the surface defects due to desorption of surface oxygen ions. Moreover, the electrical measurements showed that annealing at 300°C caused to increase resistance due to increasing of surface oxygen ions. The ZnO NRs annealed at 300°C for 1 h had the highest photosensitivity of ~300 and photoresponsivity of 2.067 A/W which is liable for practical applications.

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Fig captions:

Fig. 1. The image of Au/ZnO NRs/Au based PD.

Fig. 2. a) AFM image of the ZnO seed layer and b) top view SEM image of the ZnO nanorod arrays grown on the glass substrate.

Fig. 3. XRD patterns of ZnO NRs annealed at different temperatures for 1 h.

Fig. 4. A) Transmittance spectra and b) $(\alpha h\nu)^2$ vs. $h\nu$ curves of the samples at different annealing temperatures for 1h.

Fig. 5.a) The PL spectra of the annealed ZnO NRs at different temperatures for 1 h.

Fig. 6. a) The dark current-voltage characteristics for the ZnO NRs annealed at different temperatures for 1 and 5 h and b) The electrical resistance of the samples at dark and under UV illumination.

Fig. 7. a) The time-dependent photocurrent characteristic of the photodetectors under UV-light irradiation and b) the photosensitivity and responsivity of the samples.

Fig. 8. Photocurrent of the samples annealed at 300°C for 1 and 5 h at several cycles as long with the variations of rise and recovery times.

Table caption:

Table 1. The XRD analysis results of the samples.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Table 1

Sample	Peak position of (002) (°)	FWHM (°)	Intensity peak	d-spacing (nm)	Grain size (nm)	a (nm)	c (nm)
300	34.39232	0.1081	4562.807	0.26058	50	0.32603	0.52115
400	34.40457	0.1057	6495.418	0.26049	55	0.32574	0.52097
500	34.36959	0.1082	4869.701	0.26074	60	0.32535	0.52149