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Microwave-assisted low temperature fabrication of ZnO thin film electrodes for solar energy harvesting

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Abstract

Metallic Zn thin films were electrodeposited on fluorine-doped tin oxide (FTO) glass substrates and oxidized under air by conventional radiant and microwave post-annealing methods to obtain ZnO thin film electrodes. The temperature of each post-annealing method was varied systematically and the photoelectrochemical (PEC) performance of electrodes was evaluated. The best photocurrent density achieved by the conventional radiant annealing method at 425 °C for 15 min was 93 μA cm⁻² at 1.23 V vs. NHE and the electrode showed an incident photon-to-electron conversion efficiency (IPCE) of 28.2%. X-ray diffractogram of this electrode showed that the oxidation of Zn to ZnO was not completed during the radiant annealing process as evident by the presence of metallic Zn in the electrode. For the electrode oxidized from Zn to ZnO under microwave irradiation, a photocurrent of 130 μA cm⁻² at 1.23 V vs. NHE and IPCE of 35.6% was observed after annealing for just 3 min, during which the temperature reached 250 °C. The photocurrent was 40% higher for the microwave annealed sample; this increase was attributed to higher surface area by preserving the nanostructure, confirmed by SEM surface topographical analysis, and better conversion yields to crystalline ZnO. Overall, it was demonstrated that oxidation of Zn to ZnO can be accomplished by microwave annealing five times faster than that of conventional annealing, thus resulting in a ~75% power saving. This study shows that microwave processing of materials offers significant economic and performance advantages for industrial scale up.

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1. Introduction

Post-annealing of materials using microwave radiation is emerging as a novel and innovative technology as it has various advantages over conventional radiant annealing. They include: very rapid heating rates, greatly reduced processing time and temperature, preservation of nanostructures, improved mechanical properties, better product performance, etc [1]. Recent trends have been to process semiconductor thin films under microwave radiation as it provides new approaches for enhancing the physical, chemical, and photoelectrochemical (PEC) properties of materials as well as providing economic benefits through significant energy savings [2]. It has also been proven that microwave annealing is a promising alternative method to conventional radiant annealing, as it opens up a new research strategy for engineering semiconductor material properties while keeping the specifically engineered texture and nanostructure unaltered for use in a range of applications such as solar energy harvesting and energy storage devices (PEC cells, solar cells, batteries, supercapacitors) [3,4].

Zinc oxide (ZnO) is one of the most widely used materials to fabricate such devices. It is also extensively used as a photoelectrode in PEC cells because it has a wide bandgap with lower photoresistivity, higher chemical stability and greater carrier mobility [5]. The majority of deposition methods for ZnO, such as electrodeposition, [6] metal–organic chemical vapor deposition (MOCVD), [7] aerosol assisted chemical vapor deposition (AACVD), [8] chemical bath deposition, [9] spray pyrolysis [10], and screen printing [11] involve a post-annealing step after film fabrication. These steps improve the inter-particle and particle-substrate adhesion, crystallinity, and thus conductivity of the film [12]. Post-annealing under air also helps to oxidize remaining metallic Zn or Zn containing precursors present in the film [13]. At the same time, post-annealing steps can cause collapse of the specifically engineered nanostructure, reducing the porosity and surface area of the film, which in turn affects the final device performance [3,4]. This effect is more pronounced when using conventional radiant annealing as the method for post-annealing, due to non-uniform heat distribution. In conventional radiant annealing, the thermal energy is transferred to the material from the exterior, creating a temperature gradient [14]. Microwave annealing overcomes this through absorption of the microwave energy evenly throughout the volume of the material (also known as volumetric heating). Since the surface loses energy by radiation, the core of the material is usually hotter and the temperature profile is typically the inverse of that seen in conventional radiant heating [14].
The microwave absorbing characteristics of materials are related to the dielectric and magnetic properties such as electric permittivity ($\varepsilon$) and magnetic permeability ($\mu$), and the extent of heat generation by absorbed energy is determined by the loss tangent (tan $\delta$) of the material. Therefore, when microwaves are in contact with materials of different dielectric properties, they will selectively couple with the higher loss tangent material and generate heat.

The interaction of microwaves with matter is quantified by the two complex physical quantities; dielectric permittivity, $\varepsilon$, and permeability (magnetic susceptibility), $\mu$ [15]. In reality, the permittivity and permeability are complex quantities which are defined as $\varepsilon' \mu'$, respectively, as shown in Eqs. (1) and (2), [16]

$$\varepsilon' = \varepsilon' - i\varepsilon'' = \varepsilon_0 \left( \varepsilon' - i\varepsilon'' \right) \quad (1)$$

$$\mu' = \mu' - i\mu'' = \mu_0 \left( \mu' - i\mu'' \right) \quad (2)$$

where $\varepsilon'$ is the dielectric constant which represents the time-independent polarizability of a material in the presence of an external electric field, that is to say it measures the resistance encountered when forming an electric field in a medium. $\varepsilon''$ is the dielectric loss or loss factor of the material, and indicates the time-dependent component of the permittivity which quantifies the ability of the material to convert absorbed energy into heat. $\varepsilon_r$ is the relative permittivity of the material which is the ratio of the permittivity of a substance to that of free space or vacuum. $\varepsilon''_0$ is the effective relative loss factor, $\mu$ is the magnetic permeability, $\mu_r$ magnetic loss factor, $\mu_0$ the permeability of free space ($\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$), $\mu_r$ is the relative permeability of the material, and $\mu''_0$ is the effective relative magnetic loss factor.

The ratio of the dielectric loss to the dielectric constant is known as the loss tangent (tan $\delta$) or dissipation factor which is given in Eq. (3), [17]

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

The angle $\delta$ represents the phase lag between the polarization of the material and the applied electric field. The loss tangent is an indicator of the ability of the material to convert absorbed energy into heat. In order for microwaves to interact with the material, a balanced combination of a moderate dielectric constant (to permit adequate penetration) and a high loss tangent (for higher energy to heat conversions) is required [18]. The reported dielectric constant and loss tangent values of ZnO are 3.430 and 0.0529 respectively [3]. This demonstrates the heat generation ability of ZnO by absorbing microwave radiation [3]. This ability is not unique to ZnO, in fact most semiconductor materials have the ability to absorb microwaves and generate heat. In a recent study, the effect of microwave annealing on the PEC properties of TiO$_2$ thin films was compared with conventional radiant annealing. It was found that microwave-assisted post-annealing helped to improve the electrode performance by three times [4]. Similarly, Yarahmadi et al. [19] claimed that a significant enhancement of PEC performance could be achieved by using microwave-assisted annealing for the fabrication of $\alpha$-Fe$_2$O$_3$ thin films, with significant energy savings up to 60% when compared to conventional radiant annealing. The effect of microwave and conventional radiant annealing has been studied on ZnO nanorods by Bhatti et al. [3] and they found that microwave radiation caused sintering between individual rods, resulting in them bundling up into new rods with larger diameters, without significantly affecting the hierarchical rod structures. Apart from the abovementioned literature, to the best of our knowledge, there are very few reports on the use of microwave radiation for post-annealing of semiconductor thin films for electronic and optoelectronic device fabrication.

In this study for the first time, we have compared the effects of conventional radiant and microwave annealing methods on the oxidation of electrodeposited Zn to ZnO. The PEC performance of ZnO electrodes oxidized by the two annealing methods was studied. We demonstrate a 40% increase in the photocurrent density when using microwave radiation to oxidize Zn to ZnO compared to that of the radiantly annealed films. Also better conversion yields and faster processing times at lower temperatures were achieved with microwave annealing; features that are highly desirable for large-scale industrial production of ZnO based electronic and optoelectronic devices.

2. Materials and methods

2.1. Electrodeposition of metallic Zn films

Fluorine-doped tin oxide (FTO) glass substrates (FTO, TEC8, Pilkington Glass, Ltd, St Helens UK) were cut to 1 $\times$ 2 cm$^2$ slides and were cleaned via a series of 15 min sonications in 2-propanol, acetone, ethanol and deionized water (resistivity = 18.2 M$\Omega$) and finally stored in absolute ethanol. A 1 mM stock solution of aqueous Zn(NO$_3$)$_2$ was prepared by dissolving the appropriate amount of Zn(NO$_3$)$_2$ - 6H$_2$O (reagent grade, Sigma Aldrich, Dorset, UK) in 100 mL deionized water. The electrochemical deposition of Zn films was performed in a three-electrode configuration where the FTO was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The deposition area of the film was maintained at 1 cm$^2$. A potential of $-1.25$ V vs. Ag/AgCl was applied for 1800s. This resulted in a gray metallic Zn film on the FTO conducting surface. The films were then washed by deionized water and left in air to dry.

2.2. Post-deposition annealing

The oxidation of Zn to ZnO was studied using both conventional radiant and microwave annealing. Conventional radiant annealing was carried out in a tube furnace (MTF-10-25-130, Carbolute, UK) with a ramp rate of 15 °C/min to its desired temperature. Both ends of the tube were left open to allow air to flow in. After annealing, the furnace was turned off and the samples were allowed to cool in the tube furnace until they reached room temperature. Microwave assisted annealing was performed using a microwave oven (Microwave research Applications Inc. BP-211/50, USA) operating at 2.45 GHz frequency with a maximum power of 3000 W. The Zn films were annealed using the microwave furnace until the sample reached the desired temperature. The heat loss during annealing was minimized by covering the sample with insulator blocks. The temperature of the annealed films was monitored using an infrared temperature probe (Mikron InfraRed Inc. MG7/ MG7S series, USA) with an error of $\pm 5 ^\circ\text{C}$.

2.3. Characterization

The PEC performance of the annealed ZnO films was measured using a three-electrode configuration in 1 M Na$_2$SO$_4$ aqueous electrolyte (pH 5.7), with Ag/AgCl as the reference electrode and Pt wire as the counter electrode. For analysis of the results the reference potentials were converted to NHE using $E_{\text{HNE}} = E_{\text{AgCl}} + 0.059 \text{pH} + E_{\text{AgCl}}$ where $E_{\text{AgCl}} = 0.1976$ V at 25 °C [20]. The potential of the photoelectrode was controlled using a computer-controlled software and a potentiotstat (microAutoLab, type III, Windsor Scientific Limited, Berkshire, UK). The electrodes were illuminated through the electrolyte side and the illumination was set to 1 cm$^2$. The illumination source was an AM 1.5 class A solar simulator (165 – 300 solar simulator, Solar Light Co., Inc., PA, USA) equipped with a 300 W xenon lamp. The intensity of the light was calibrated at 100 mW/cm$^2$ using a class II pyranometer (PMA2144, Solar Light Co., Inc., PA, USA) equipped with a digital photometer (PMA2100, Solar Light Co., Inc., PA, USA).

The microstructure and surface morphology of the thin films were investigated using a field emission gun scanning electron microscopy (FEG-SEM, Jeol, Hertfordshire, UK) at an accelerating voltage of 5 kV.
and working distance of 5 mm. The phase and crystallinity of the as-deposited and annealed ZnO films were studied using Bruker D8 XRD, operating with monochromatic Cu Kα (λ = 1.54Å) radiation and PSD detector. The incident photon to electron conversion efficiency (IPCE) was obtained by measuring the incident photon flux using a 75 W xenon lamp connected to a monochromator (TMc300, Bentham Instruments Ltd., Berkshire, UK). The light was calibrated using a silicon diode. Photocurrent spectra were measured at 1.23 V vs. NHE using a combination of a lock-in amplifier (Bentham 485, Bentham Instruments Ltd., Berkshire, UK) and a custom built potentiostat.

3. Results and discussion

3.1. Material characterization

Metallic Zn was electrodeposited on conducting glass substrates and further annealed by conventional radiant or microwave annealing methods. The phase and crystallinity of the films were studied by XRD. Fig. 1 shows the XRD diffractograms of as-deposited, conventionally annealed and microwave annealed samples. The peaks at 26.9, 34.1, 38.1, 51.9, 54.9, 61.9, and 65.9° correspond to the (110), (101), (200), (211), (220), (310), and (112) reflections of F:SnO2 on the substrate. The XRD reflections of electrodeposited Zn (Fig. 1a) confirmed that the sample consists only of Zn with a hcp crystal structure with a preferred orientation in the (101) direction. The films were subjected to radiant annealing at 425 °C for 15 min in air, during which the as-deposited Zn is converted into ZnO with wurtzite crystallites of (100), (002), (101), (102), (103), (200), and (110) orientations. The corresponding ZnO wurtzite film at 250 °C for 3 min shows only ZnO reflections, indicating the complete oxidation of Zn to ZnO. The corresponding ZnO wurtzite crystallites with (100), (002), (101), (102), (103), (200), and (110) reflections are more intense and well-defined than in the conventional radiant annealed films. This indicates a higher degree of crystallinity in the microwave annealed films compared to the conventionally annealed samples. This clearly indicates that microwave annealing is a more efficient way of oxidizing Zn to ZnO compared to the conventional radiant annealing due to the volumetric heat generation. According to previous literature reports, the thermal conversion of Zn to ZnO has required temperatures ranging from 500 to 900 °C [21-27] however, the data shows that by use of microwave processing, complete conversion can be achieved at 250 °C in 3 min.

![Fig. 1. XRD diffractograms of (a) electrodeposited Zn, (b) conventional radiant annealed at 425 °C for 15 min and (c) microwave annealed at 250 °C for 3 min. The (101) peak of Zn is shown with an arrow. The standard XRD reflections of SnO2, Zn and ZnO are also shown.](image)

The thickness of the electrodeposited Zn film was determined by taking a cross-sectional FEG-SEM image, which is shown in Fig. 2: it shows that the thickness of the Zn film is around 2 μm.

The impact of the annealing method on the morphology of the nanostructure was studied using FEG-SEM. Fig. 3 shows the surface morphology of as-deposited and radiant annealed films at different temperatures. The surface of as-deposited Zn is shown in Fig. 3a which is comprised of structures with a broad size distribution in the nanometer size range. The particle shape is more or less spherical with some cluster/agglomeration between the particles. The larger particles are spatially distributed on the surface, which is further surrounded by a blanket of clustered/agglomerated small Zn particles. The post-annealing of Zn films resulted in oxidation and sintering which leads to various morphological changes of the film depending on the annealing temperature, as shown in Fig. 3b-d. At 425 °C (Fig. 3c) the ZnO nanostructure adopts a cauliflower-like structure with a high apparent surface area. Heating at a higher temperature of 600 °C resulted in agglomeration and sintering of the nanostructure (Fig. 3d), resulting in relatively low apparent surface area.

Images of the surface morphology for as-deposited and microwave annealed films at different temperatures are shown in Fig. 4. A significant change in the film morphology is not observed when electrodeposited Zn is oxidized to ZnO under microwave annealing. It shows that the porous structure of electrodeposited films is retained until the annealing temperature reached 250 °C (Fig. 4c). The XRD and SEM results conclude that porous nanostructured crystalline ZnO thin film electrodes can be obtained by annealing electrodeposited Zn films at 250 °C under microwave radiation. Evidence of particle agglomeration and sintering begins to be observed at a microwave annealing temperature of 300 °C (Fig. 4d). The SEM images demonstrate that microwave annealing preserves the nanostructure of the film compared to radiant annealed films due to its rapid and volumetric heating capabilities. This phenomena agrees well with our previous observations for TiO2 and α-Fe2O3 [4,19].

3.2. Photoelectrochemical characterization

One of the main goals of semiconductor photoelectrochemistry has been to increase the photocurrent of the electrodes under illumination, which would increase product yields for the photoelectrochemical reaction in question i.e. water splitting to produce oxygen and hydrogen gas. There are two main strategies to improve the photocurrent of electrodes: (1) introduction of surface catalysts which can reduce the overpotential required for the photoelectrochemical reaction and as well as increase the rate of charge transfer from the bulk to the interface; and (2) by production of highly nanostructured materials with well defined geometries such that the dimensions are matched with the minority charge carrier diffusion length so as to enhance the
probability that they reach the interface before they recombine [28,29]. Microwave processing is very interesting in this context, because compared with conventional radiant annealing, it can preserve the nanostructure, which is essential to provide a high photocurrent [4, 19]. Photoelectrochemical (PEC) studies were carried out for the oxidized ZnO electrodes by conventional radiant and microwave annealing methods. The current density-potential plots of ZnO electrodes obtained by annealing electrodeposited Zn films using conventional radiant and microwave annealing methods at different temperatures are shown in Figs. 5 and 6 respectively. The inset in the respective figures shows the photocurrent densities acquired for conventional radiant and microwave annealed electrodes at 1.23 V vs. NHE as a function of annealing temperature. As shown in Fig. 5, the photocurrent density reached its maximum value of 93 μA cm\(^{-2}\) at 1.23 V vs. NHE, for the electrodeposited Zn films annealed at 425 °C for 15 min by conventional radiant annealing. Further annealing up to 600 °C resulted in the reduction of the photocurrent density to 38 μA cm\(^{-2}\). This was most likely due to a reduction in the surface area caused by sintering of the nanostructure; this is confirmed by the respective SEM images in Fig. 3c and d. The samples annealed at temperatures lower than 400 °C showed that negligible photocurrent with a relatively higher dark current may be due to the presence of unconverted Zn in the film (data not shown).

![SEM images of (a) electrodeposited Zn, conventional radiant annealed Zn electrodes at (b) 400 °C, (c) 425 °C, and (d) 600 °C.](image1)

![SEM images of (a) electrodeposited Zn, microwave annealed Zn electrodes at (b) 180 °C, (c) 250 °C, and (d) 300 °C.](image2)
Fig. 6 shows the chopped (i.e. light and dark) photocurrent densities of ZnO electrodes attained by microwave annealing Zn films at different temperatures. The photocurrent densities of the microwave annealed electrodes increased until the annealing temperature rose to 250 °C. Microwave annealing at temperatures higher than 250 °C resulted in lower photocurrents, most likely due to reduction in surface area caused by sintering and agglomeration of the nanostructure, as evidenced by the SEM images (Fig. 4). The electrode annealed at 180 °C under microwave radiation showed a photocurrent density of about 73 μA cm⁻² at 1.23 V vs. NHE, while the electrode annealed at 250 °C showed a much higher photocurrent density of 130 μA cm⁻² at 1.23 V vs. NHE.

Fig. 7 compares the highest PEC performance obtained for conventional radiant and microwave annealed electrodes. The inset of the figure represents the highest photocurrent density obtained at 1.23 V vs. NHE. The figure indicates that highest photocurrent density obtained for the ZnO electrode annealed using microwave annealing (i.e. 130 μA cm⁻²) was 40% higher than the highest photocurrent density attained for the conventional radiant annealed electrode which was 93 μA cm⁻².

The increase in the photocurrent density of ZnO electrodes achieved by microwave annealing compared with conventional radiant annealing could be attributed to three possible factors — an increase in crystallinity, efficient oxidation of Zn to ZnO and higher internal surface area of the film. Evidence for these factors has already been seen in the XRD and SEM images. The IPCE plots for the highest performing ZnO electrodes acquired by microwave and conventional radiant annealing at 1.23 V vs. NHE are compared in Fig. 8. An IPCE of 28.2% and 35.6% was observed for conventional radiant and microwave annealed ZnO electrodes respectively. The estimated photocurrent density by integrating the IPCE spectra is in close agreement with the observed photocurrent density of both electrodes.

The benefit of using microwave radiation as an alternative to the conventional radiant annealing method was evaluated according to the method used by Saremi-Yarahmadi et al., where the authors constructed a temperature-time profile to estimate the energy consumed during each annealing process [19]. It was found that microwave annealing requires only 25% of the energy needed for conventional radiant annealing while operating at nearly one tenth of the maximum power level. Moreover, the microwave method also produced ZnO electrode...
with 40% higher photocurrent density than that of the conventional radio frequency annealed electrode. The microwave annealing method could be easily adopted for the large scale (batch or continuous) processing of thin films — such large scale microwave technology already exists in the industry [30–32].

4. Conclusions

The oxidation of electrodeposited Zn to ZnO was conducted using microwave and conventional radiant annealing methods at various temperatures and comparisons were drawn. A 40% higher photocurrent (at 1.23 V vs. NHE) was achieved for the microwave annealed film compared to the conventional radiant annealed counterpart. This improvement in the PEC properties was attributed to higher surface area, phase purity and crystallinity of ZnO electrodes achieved by the microwave annealing method. It was found that the higher temperatures used in the radiant annealing result in sintering of the nanostructure which reduces the overall surface area. Notably, in contrast to conventional radiant annealing, microwave annealing preserves the nanostructure of the electrodes due to the difference in the heating mechanism (i.e. volumetric heating). Microwave annealing also allows complete oxidation of metallic Zn to ZnO five times faster than in conventional radiant annealing. The techno-economic impact was considered by assessing the overall energy usage. This evaluation shows that the microwave annealing method offers energy savings of up to ~75%, which would make it highly desirable for industrial scale up.

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