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# Effect of gas-timing technique on structure and optical properties of sputtered zinc oxide films

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**Abstract**

Zinc oxide thin films were prepared by the RF magnetron sputtering using a gas-timing technique whereby the flow of argon into the sputtering chamber was controlled by an on–off sequence. With this technique, polycrystalline ZnO thin films on glass substrates have been achieved without any thermal treatment of the substrate. In addition, the RF power and the gas-timing sequence can be fine-tuned to produce the hexagonal structure of ZnO thin films. X-ray diffraction (XRD) measurements confirm a (0 0 2) plane oriented wurtzite structure ZnO thin films. The optimized conditions for this hexagonal structure are an RF power of 30 W and an on–off gas-timing sequence of 50:2 s. The root mean square surface roughness of ZnO thin films measured by atomic force microscopy are in the range of 6.4–11.5 nm. The optical transmittance of ZnO thin films is over 85% in the visible range.


*Keywords:* A. Films; B. Grain size; C. Optical properties; Zinc oxide

## 1. Introduction

Zinc oxide (ZnO), one of the most important binary II–VI compounds, is a direct wide-band-gap semiconductor of wurtzite structure. Its minimum energy gap is ~3.2 eV at room temperature and ~3.44 eV at 4 K [1,2]. The remarkable properties of ZnO are large bond strength, good optical quality, extreme stability of excitons, and excellent piezoelectric properties. Consequently, ZnO has been actively studied in various fields, with potential applications in many technological domains, such as transparent conducting electrodes in display devices and solar energy cells, surface and bulk acoustic wave devices (SAW), optical-wave guide and acoustic-optical devices, and light-emitting diodes (LEDs) and laser diodes (LDs) [3–8]. Another advantage of zinc oxide relative to other materials is its low price, placing it as a strong candidate for industrial applications. A number of techniques have been employed for fabricating ZnO thin films, including chemical vapour deposition, sol–gel, spray-pyrolysis, molecular beam epitaxy, pulsed laser deposition, vacuum arc deposition, and magnetron sputtering [9–15]. Nonetheless, there remain difficulties in growing stable and high quality ZnO films.

One of the most important deposition techniques for ZnO thin films is the RF plasma sputtering, which permits deposition at low temperature, and gives better adhesion, larger coverage and higher film density than other methods. However, the quality of the films with regards to the crystal structure depends strongly on the sputtering conditions, such as RF power, sputtering pressure and target-to-substrate distance. In a special technique called gas-timing, the flow of the sputtering gas is deliberately controlled by an on–off sequence. This technique has been applied to our sputtering system to obtain high quality crystalline thin films at low RF power and at room temperature. Another major advantage of this technique is that the high quality crystalline thin films can be achieved without any annealing treatment after deposition. In our previous work, this technique has been successfully applied to the AlN and InN system [16].

In this work, zinc oxide thin films were prepared by the RF magnetron sputtering onto glass substrates using the gas-timing technique. The films were characterized by the X-ray diffraction (XRD) measurements, the atomic force microscopy

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(AFM) and the optical transmittance spectroscopy. The influence of processing parameters on the structural and optical properties of the films was investigated.

## 2. Experimental procedure

The ZnO sputtering deposition was conducted with an Edwards AUTO 306 plant equipped with a RF magnetron sputtering set. The sputtering target was ZnO with 99.99% purity. The substrate holder was kept at room temperature during the sputtering process. The main adjustable process parameters were the RF power and the sputtering gas pressure. A quartz crystal microbalance was employed to monitor film thickness during deposition. The chamber was evacuated to $5.0 \times 10^{-7}$ mbar. The target-substrate distance was 50 mm. An on–off gas-timing sequence was used to control the flow of argon into the sputtering chamber. This was realized by a mass flow controller with an external control program. The flow rate of argon during the 'on' sequence was fixed at 9 sccm (standard cubic centimeters per minute). Fig. 1 depicts the gas-timing sequence of argon gas that flows for 50 s then stops for 2 s.

Prior to the deposition, the glass substrates were cleaned by the piranha process, which should remove any organic residues. The standard piranha solution was a 3:1 mixture of $H_2SO_4$ (95%) and $H_2O_2$ (30%). Glass substrates were boiled in the solution, rinsed by de-ionized water, and thoroughly dried by nitrogen gas.

The RF plasma sputtering conditions are listed in Table 1. The thickness of the deposited ZnO thin films were all set at 200 nm. After the sputtering process, the film thickness was measured by a profilometer (TENCOR, Alphastep 500). The crystallinity of the films was investigated by X-ray diffractometer (Bruker, D8) using Cu Kα with the radiation wavelength (λ) of 0.154056 nm. The optical transmittance spectroscopy was performed with a single beam UV–Vis spectrophotometer (Thermo electron corporation, Heliosα). The RMS roughness and the surface morphology of films were measured by the Atomic Force Microscope (Seiko, SPA-400).

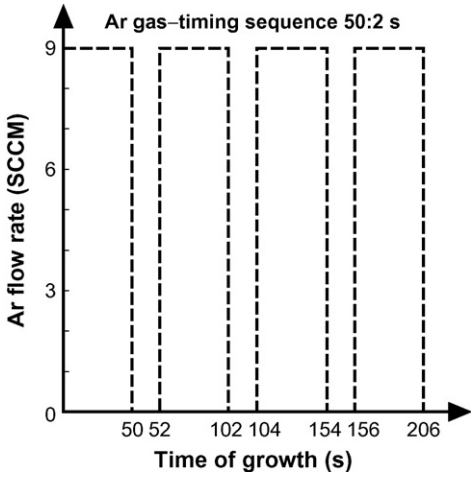


Fig. 1. Schematic representation of the 50:2 on–off gas-timing sequence of argon during sputtering deposition with a flow rate of 9 sccm (on) for 50 s and zero flow (off) for 2 s.

Table 1
Sputtering conditions used for deposition of ZnO thin films

| Deposition parameters | Conditions |
|---|---|
| Base pressure | $5.0 \times 10^{-7}$ mbar |
| RF power | 30, 50, 80, 120 W |
| Substrate-target distance | 50 mm |
| Substrate temperature | Unheated and uncontrolled |
| Sputtering pressure | $2.8 \times 10^{-3}$ mbar, argon gas activated |
| Ar flow rate | 9 sccm, fixed |
| Ar gas-timing (on:off) | 30:2, 40:2, 50:2, 60:2 s |

## 3. Results and discussion

For structural studies, the crystalline structure of the deposited films was investigated by the XRD technique. The XRD patterns of ZnO thin films deposited at different gas-timing sequences and RF powers indicate the difference in the crystalline quality. At the optimized argon gas-timing sequence of 50:2 s, the highest peak intensity for the (0 0 2) plane oriented wurtzite structure has been observed, as shown in Fig. 2a. A possible mechanism for this enhancement in the crystallinity is balanced between a specific gas-timing sequence

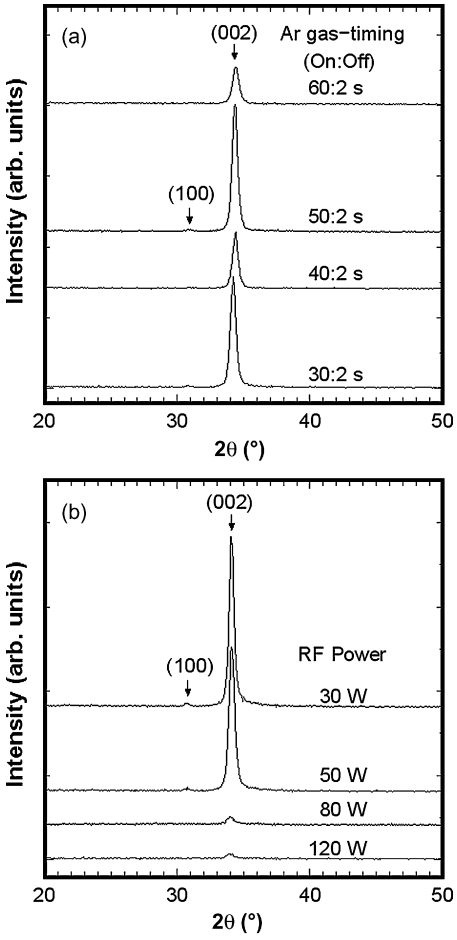


Fig. 2. X-ray diffraction patterns of ZnO thin films (a) deposited at different argon gas-timing sequences (30:2, 40:2, 50:2, 60:2 s) and 30 W RF power; (b) deposited at different RF power (30, 50, 80, 120 W) and the argon gas-timing sequence of 50:2 s.

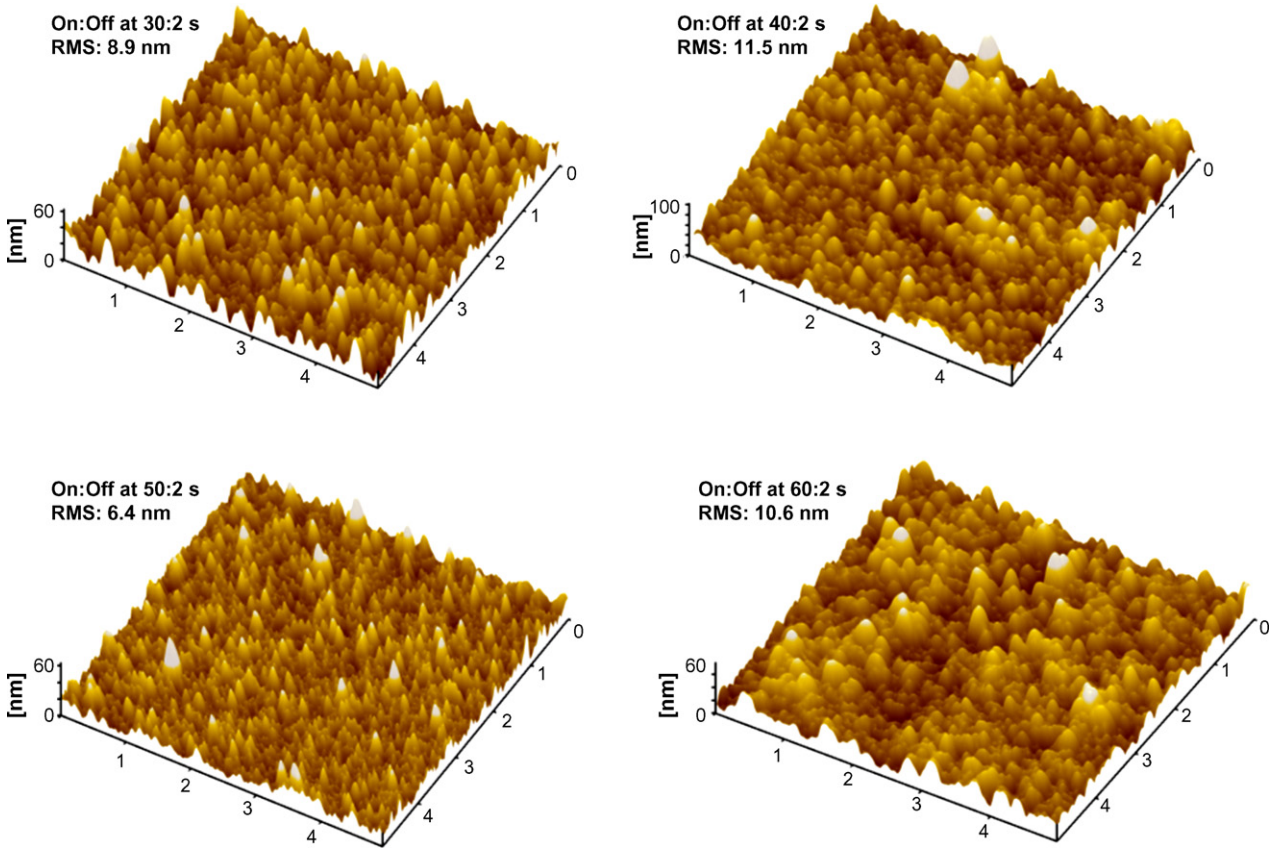


Fig. 3. AFM images (5 μm × 5 μm) of ZnO thin films deposited at different argon gas-timing sequences (30:2, 40:2, 50:2, 60:2 s) and 30 W RF power.

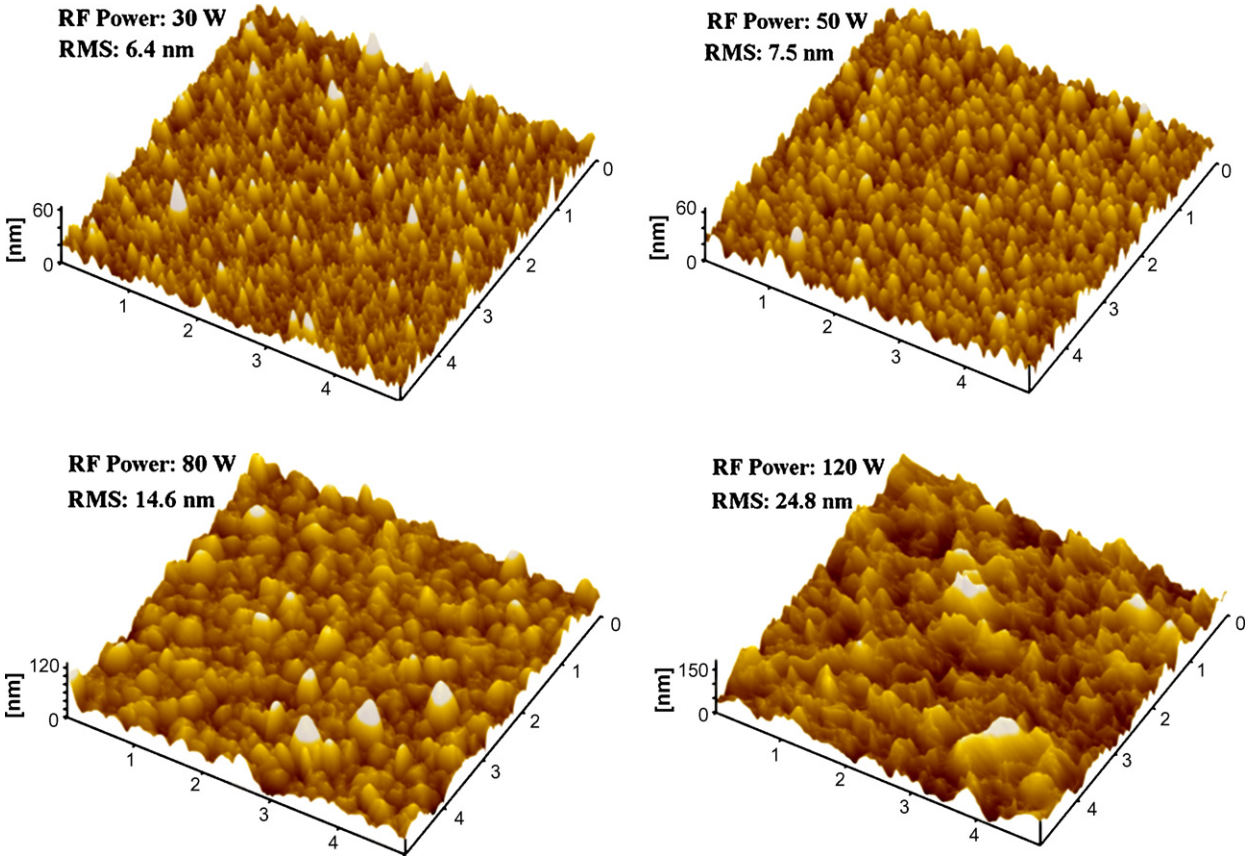


Fig. 4. AFM images (5 μm × 5 μm) of ZnO thin films deposited at different RF power (30, 50, 80, 120 W) and the argon gas-timing sequence of 50:2 s.

with the temporal characteristics of the nucleation and growth of ZnO thin films. In addition to the preferential (0 0 2) reflection, all the films exhibit a weak (1 0 0) reflection. Fig. 2b illustrates the XRD patterns of the ZnO films grown at different RF powers of 30, 50, 80 and 120 W. The gas-timing sequence for all the samples was 50:2 s. Strong XRD peaks in the (0 0 2) reflection, at around 34.2°, can be observed for all the samples. The intensity of the (0 0 2) peak also seems to decrease with an increase in RF power. The highest (0 0 2) peak intensity occurs at the RF power of 30 W. It should be noted that the plasma sputtering power of 30 W is sufficient for the growth of hexagonal ZnO thin films. Comparing to other plasma-based film deposition methods, the gas-timing technique requires lower RF plasma power levels [17]. In general, high RF power also induces faster reaction and more damages on the surface, resulting in a poor crystallinity of thin films.

The AFM images (5 μm × 5 μm) of ZnO thin films prepared at different argon gas-timing sequences and a fixed RF power of 30 W are shown in Fig. 3. The results indicate that the films have uniform morphology of possibly the polycrystalline nature, with a relatively small root mean square (RMS) surface roughness of less than 12 nm. Comparable roughness values have been found in other reports with sputtering deposition methods [18,19]. Fig. 4 shows the AFM images (5 μm × 5 μm) of ZnO thin films deposited at different RF powers and a fixed argon gas-timing sequence of 50:2 s. The surface morphology of the films for the AFM measurements implies that the grain size tends to be larger at higher RF powers [17,19]. Thus, at higher RF powers, an improvement of surface density is expected. On the other hand, the more energetic sputtered particles may induce higher surface roughness [18]. In addition, despite larger grain sizes, the films grown at high RF powers have low crystallinity, as suggested by the XRD measurements. For our results, the optimized conditions for a smooth and crystalline ZnO thin film are the sputtering power of 30 W and the argon gas-timing sequences of 50:2 s. The RMS surface roughness of the film deposited at these conditions is approximately 6.4 nm.

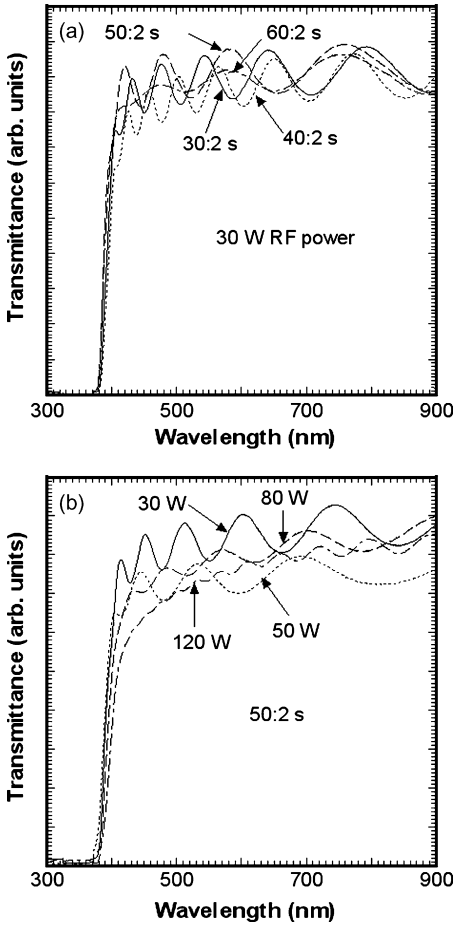


Fig. 5. Optical transmittance of ZnO thin films (a) deposited at different argon gas-timing sequences (30:2, 40:2, 50:2, 60:2 s) and 30 W RF power; (b) deposited at different RF power (30, 50, 80, 120 W) and the argon gas-timing sequence of 50:2 s.

The optical transmittance of the films has been measured in the wavelength range of 300–900 nm. As shown in Fig. 5a, the optical transmittance of the films grown at different gas-timing sequence conditions all exhibit an average transmittance in the visible range over 85%. Thus, the optical transmittance of these films has not been significantly influenced by the gas-timing method. Fig. 5b illustrates the optical transmittance of ZnO thin films deposited at different RF powers, which indicates that the transmittance gradually decreases with an increasing RF power. This characteristic may be caused by increased scattering, reflection and optical absorption of the films, owing to larger surface roughness and amorphous contents of the films deposited at higher RF powers [20]. The absorption coefficients, the film thickness, and the optical band gap ($E_g$) can be extracted from the optical transmittance spectra by using the unconstrained minimization algorithm [21]. The values of $E_g$ for the films deposited at various gas-timing sequences and RF powers are in the range ∼3.17 to ∼3.21 eV.

## 4. Conclusions

This work demonstrates that the gas-timing RF sputtering technique can be successfully applied to produce high quality polycrystalline zinc oxide thin films on glass substrates at room temperature and without any thermal treatment of the films. The optimized conditions for the wurtzite ZnO films have been found to be the RF power of 30 W and the gas-timing sequence of 50:2 s. The films deposited at these conditions also exhibit a small surface roughness, with the RMS value of less than 7 nm. Moreover, the films have high optical transmittance in the visible range of over 85%. The calculations of the optical band gap from the optical transmittance spectra give the band gap values for the films deposited at various gas-timing sequences and RF powers to be in the range ∼3.17 to ∼3.21 eV. With further studies, this technique may be applied to fabricate ZnO thin films at room temperature for transparent electronics such as transparent thin film transistors and flexible OLED displays.

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