

Research on Equipment of Magnetron Sputtering and Deposition of ZnO Films

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Abstract. The parts of magnetron sputtering system were given in the paper. Meanwhile, we analyzed the working theory of magnetron sputtering. After pure zinc oxide (ZnO) film was grown, N-doped films was Prepared in NH₃-O₂-Ar atmosphere using zinc as a target, and Al-doped and N+Al codoped ZnO films were grown by co-sputtering technique using zinc and aluminum as targets. AFM showed the crystal quality of the Films. The results of experiment demonstrate that high-quality films have been achieved by this technique, and research on ZnO films can be done by the equipment.

Keywords: magnetron sputtering, ZnO film, Atomic force microscope(AFM).

1. Introduction

Magnetron sputtering is a widely studied and relatively mature method for preparing thin film materials, which has advantages such as easy operation and controllable reaction conditions. It generally includes several methods such as DC sputtering, RF sputtering, magnetron sputtering, etc. However, in the process of localization of magnetron sputtering, there are always some problems that cannot be solved, such as multi target layout, substrate heating temperature, poor surface state of the film layer, and poor interfacial adhesion. Therefore, it is necessary to modify the magnetron sputtering instrument accordingly. At the same time, further in-depth research is needed on the principle of magnetron sputtering deposition of Films, in order to more effectively guide the transformation of magnetron sputtering instruments and improve the quality of Films. ZnO thin film is a direct bandgap wide bandgap thin film material, with a bandgap width of 3.37eV at room temperature and a bound exciton energy of up to 60meV [1]. ZnO is a suitable ultraviolet light emitting material for room temperature or higher, and can be widely used in gas sensors, ultraviolet band detectors, solar cell electrodes, and other fields [2-4].

Pure ZnO Films were prepared by single target sputtering using magnetron sputtering technology. RF and DC magnetron co sputtering were used to achieve effective doping (Al doping, N doping, Al+N co doping) in O₂-Ar and NH₃-O₂-Ar atmospheres, respectively, to obtain ZnO Films with good structural and electrical properties. The crystal properties and surface structure of the films were characterized using atomic force microscopy (AFM) and X-ray diffraction (XRD).

2. Component structure and original

2.1 Main technical indicators

According to the actual needs and technical requirements for depositing Films, relevant technical modifications have been made to the traditional magnetron sputtering instrument. The main technical indicators are as follows: (1) Volume of the vacuum chamber: ϕ 400mm $\times$ 370mm; (2) Extreme vacuum: 8×10^{-5} Pa; (3) Cathode target and target position: two targets, magnetic control target vertically adjustable, and adjustable distance from the substrate of 75-125mm; (4) Substrate holder: The maximum temperature is 650 °C, which can maintain a certain speed; (5) Power supply: two RF and two DC power supplies each; (6) Gas circuit: two mass flow meters and one automatic pressure control instrument; (7) Target material: size ϕ 60mm, with a maximum thickness of 6mm.

2.2 Component structure of equipment

The magnetron sputtering system for preparing ZnO films is shown in Figure 1. Mainly including: sputtering table, air circuit system, vacuum system, cooling system, and electric control cabinet. The sputtering chamber is vertical, and the electric lifting system opens the chamber cover. The base provides heating and rotating components to improve the growth environment of the film. There are three observation windows on the chamber to observe the operation of the magnetic control target and detect the emission spectrum of the glow discharge plasma.

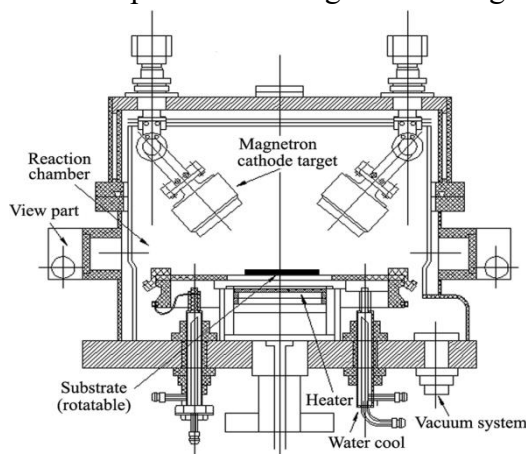


Fig. 1 Schematic diagram of magnetron sputtering system.

The RF power supply is a SY type 1KW RF power source with a frequency of 13.56MHz. The output power is continuously adjustable, and the RF power supply is combined with the SP-2 RF matcher. The impedance matching network regulates the incident power and reflected power of the RF entering the plasma. Because the extinction time of active particles in the plasma under radio frequency discharge conditions is much longer than that during the half cycle of excitation, the resulting plasma discharge is uniform, stable in performance, and has strong reactivity. Not only can it sputter metal targets, but it can also be applied to the sputtering of dielectric materials.

2.3 Principle of magnetron sputtering

When a solid surface is bombarded by molecules, atoms, or ions, many physical phenomena occur. The kinetic energy of colliding particles largely determines what phenomenon occurs. For low energy particles ($<10\text{eV}$), most interactions occur only on the surface of the target material. For particles with very low energy ($<5\text{eV}$), the interaction is mostly limited to the reflection and adsorption of the bombarding particles. Low energy particles exceeding the chemical bond binding energy of the target material ($5\text{-}10\text{eV}$) may experience migration or surface damage. When the particle energy is very high ($>10\text{keV}$), the bombarding ion will be embedded in the target material, which is the basis of ion implantation. When the energy of particles is between the two, two other phenomena will occur: (1) some of the energy of particles is transmitted to the target material in the form of thermal energy, resulting in lattice damage; (2) Another part of the energy causes atoms on the target surface to migrate, detach from the surface, and enter space (sputtering).

Magnetron sputtering is the use of the introduced orthogonal electromagnetic field to improve the ionization rate generated by electron collisions. By using magnetron sputtering, the current density on the target surface increases from about 1mA/cm^2 without a magnetic field to $10\text{-}100\text{mA/cm}^2$. Under the action of electric field E , electron e collides with argon atoms during its flight towards the substrate, causing it to ionize Ar^+ and a new electron e . The electron flies towards the substrate, and Ar^+ accelerates its flight towards the cathode target under the action of electric field E , and bombards the target surface with high energy, causing sputtering of the target material.

Spectral analysis technology has the advantages of simple operation, good selectivity, and high sensitivity, and is widely used for measuring plasma parameters. The characteristics of RF magnetron sputtering glow discharge are directly related to the internal state of the plasma. By

analyzing the emission spectrum of the plasma, the various components and spectral intensities inside the plasma can be intuitively understood, in order to achieve deterministic analysis of plasma parameters and real-time monitoring of the process of thin film material preparation, Figure 2 shows the glow discharge effect under different gas atmospheres during magnetron sputtering.

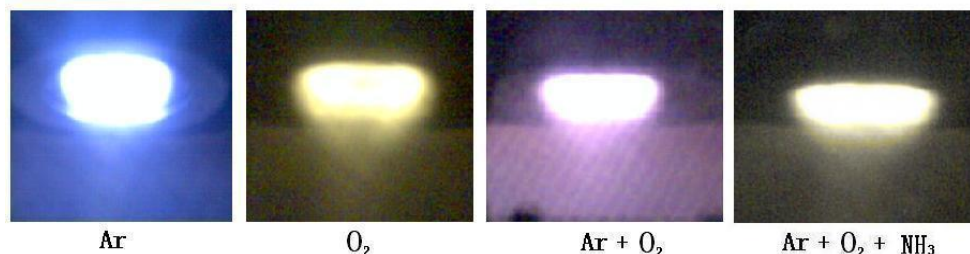


Fig.2 The pictures of glow discharge

3. Preparation of 3 ZnO Films

3.1 Experimental Equipment

ZnO Films were prepared using a self-designed RF magnetron sputtering system. There are two magnetron cathode targets in the vacuum chamber, each of which is cooled with water, with a diameter of 6cm. The installation thickness of the target material is less than 6mm. The magnetic control target is vertically adjustable, and the distance between the cathode target and the substrate plate is continuously adjustable within 75-125mm. A circular substrate plate with a diameter of 130mm is installed at the bottom of the vacuum chamber, which can rotate at an angular speed of 10-30r/min. At the same time, the substrate can be subjected to infrared heating, and the temperature range is adjusted between 200-650 °C through PLD. The substrate temperature can be detected by thermocouples. The sputtering system is equipped with two mass flow meters and one automatic pressure control instrument. The vacuum system consists of a 2XZ-4 rotary vane vacuum pump, an HTFB600 turbomolecular pump, and various valves. The opening and closing of the valve is controlled by the piston movement generated by the change in air pressure inside the small cylinder. The specific valve control can be operated through the corresponding buttons on the electric control cabinet. The RF power supply used is a SY type 500W crystal controlled RF power source, with a working frequency of 13.56MHz.

3.2 Cleaning of sputtering targets, gases, and substrates

The cleaning experiment of sputtering targets, gases, and substrates used metal zinc targets and aluminum targets, with a purity of 99.99% and a target diameter of 60mm. Argon is used as the sputtering gas, while oxygen, nitrogen, and ammonia are used as the reaction gases. Ar: purity greater than 99.999%; O₂, N₂, and NH₃: Purity greater than 99.996%, respectively.

The selection of substrate materials is crucial. The substrates we use mainly include quartz glass with a thickness of 1mm, a length of 5mm, and a width of 1mm; Before using the substrate, use acetone, alcohol, and deionized water to perform ultrasonic cleaning on the substrate before preparation. Heat and etch with a mixed solution of C (H₂SO₄): C (H₃PO₄)=3:1 for 10 minutes, then rinse with deionized water and dry with hot high-purity nitrogen gas for use.

3.3 Sputtering method for preparing Films

Before sputtering, place the cleaned substrate on a bracket in the vacuum chamber. Seal the vacuum chamber, turn on the power, turn on the mechanical pump, open the pre extraction valve to extract gas from the vacuum chamber, and achieve low vacuum. When the vacuum chamber pressure reaches below 8Pa, close the pre extraction valve, open the front stage valve, and start the molecular pump. When the molecular pump accelerates to a working frequency of 499Hz, open the

high valve between the molecular pump and the vacuum chamber, and the molecular pump operates. 30 minutes of suction can achieve the system's background vacuum of 8×10^{-4} Pa. While vacuuming, the substrate can be heated to a predetermined temperature. When preparing samples, gas is introduced from the two mass flow meters, and the flow rate is controlled by the mass flow meter to achieve the predetermined partial pressure of the gas in the vacuum chamber. When using the composite pressure control instrument, the automatic/manual switch is first set to automatic, and the pressure is set to the sum of the gases in the vacuum chamber. After opening the control valve, Turn the measurement/control switch on the composite pressure controller to the control direction, and the pressure will start to rise and stabilize at the set value to start sputtering. Before sputtering, the plate voltage potentiometer needs to be adjusted to the lowest position. Turn on the RF power source and preheat it for several minutes, turn on the board pressure switch, slowly adjust the board pressure to a specific value, repeatedly adjust the matching capacitors C1 and C2 until it lights up, then adjust the operating frequency to the required power, and adjust the matching capacitors C1 and C2 to make the reflected power as small as possible. After a few minutes of pre sputtering, start sputtering to prepare the sample.

Table 1 Experimental parameters of all the samples

sample	atmosphere (Total pressure 2Pa)	Target material	RF power	substrate temperature
Sample (a) (no-doped)	O ₂ :Ar=2:3	Zn	Zn-80W	450°C
sample (b) (N-doped)	NH ₃ :O ₂ :Ar=1:2:0.3	Zn	Zn-80W	450°C
sample (c) (Al-doped)	O ₂ :Ar=2:3	Zn Al	Zn-80W Al-20W	450°C
sample (d) (Al+N-doped)	NH ₃ :O ₂ :Ar=1:2:0.3	Zn Al	Zn-80W Al-20W	450°C

3.4 Single target sputtering preparation of ZnO Films

Figure 3 shows the AFM diagrams of samples (a) and (b), respectively. The average grain size of undoped sample (a) and N doped sample (b) is 100nm, and the grain size is relatively uniform. The surface smoothness of both is also good. The surface grain quality of the generated film is relatively high, and the adhesion between the film layer and the substrate is good.

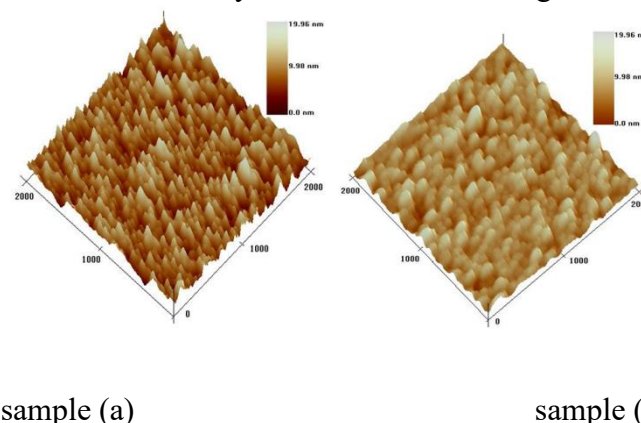


Fig.3 AFM images of ZnO films

Figure 4 shows the X-ray diffraction pattern of sample (a) ZnO thin film. two θ The high intensity diffraction peak at 34.42° originates from (0002) ZnO, with a half width at half height (FWHM) of 0.52° , respectively. No diffraction peaks in other crystal directions of ZnO crystals were observed in the figure, but only in the C direction. This indicates that ZnO Films grow preferentially along the C direction and have high crystal quality. At the same time, we found that

annealing treatment can improve the preferred orientation of the C-axis direction of the thin film grains and there is a trend of reducing the half width.

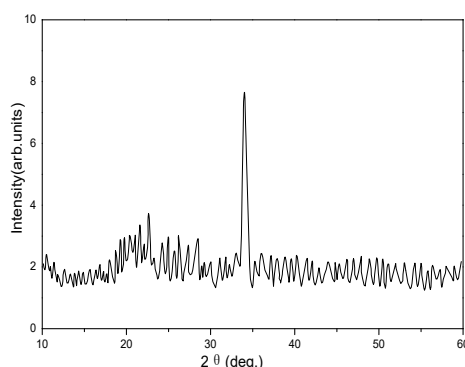


Fig.4 XRD of ZnO films

3.5 Double target co sputtering preparation of doped ZnO Films

Figure 5 shows the AFM diagrams of doped samples (c) and (d), respectively. It can be seen that the average grain sizes of samples (c) and (d) are 130nm and 150nm, respectively, with irregular grain shapes and obvious grain boundaries. Analysis suggests that ZnO-Al₂O₃ crystals were formed due to the incorporation of Al, which affected the grain shape. At the same time, we found that the surface roughness of (c) is about 20nm, but the surface roughness of Al+N co doped sample (d) is 10nm. We believe that this is mainly due to Al+N co doping, where N and Al replace the lattice positions of O and Zn respectively, eliminating some defects in the crystal and improving surface smoothness.

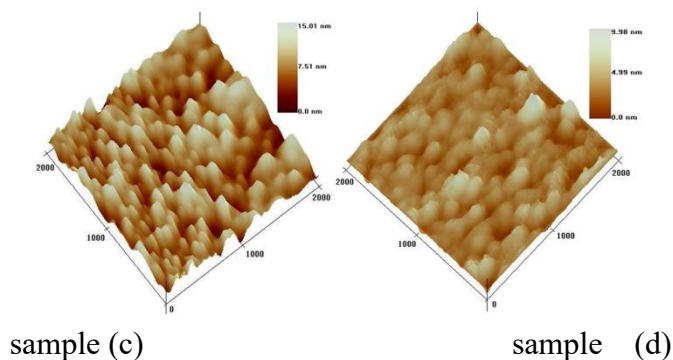


Fig.5 AFM images of ZnO Films

4. Conclusion

In response to practical needs, a technical transformation has been made to the traditional magnetron sputtering instrument, explaining the component structure of the designed magnetron sputtering system, and analyzing the working principle of magnetron sputtering. ZnO Films and doped samples were deposited on quartz substrates using magnetron sputtering method. AFM measurements were conducted on the crystal morphology of each sample at room temperature, and the measurement results showed that the prepared ZnO film had high surface quality. XRD testing and analysis indicate that the C-axis lattice constant of ZnO Films is slightly smaller than that of ZnO crystals, which is due to partial mismatch between ZnO and quartz substrates or tensile strain formed during the growth process. Some attempts have been made to achieve effective doping of ZnO Films using the dual target co sputtering method.

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