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Growth of n-type ZnO thin films by using mixture gas of hydrogen and argon*

Zhou Xin(周 新), Wang Shi-Qi(王世奇),
Lian Gui-Jun(连贵君), and Xiong Guang-Cheng(熊光成)†

Department of Physics, Peking University, Beijing 100871, *China*

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High-quality oxide semiconductor ZnO thin films were prepared on single-crystal sapphire and $LaAlO_3$ substrates by pulsed laser deposition (PLD) in the mixture gas of hydrogen and argon. Low resistivity n-type ZnO thin films with smoother surface were achieved by deposition at 600°C in 1Pa of the mixture gas. In addition, ferromagnetism was observed in Co-doped ZnO thin films and rectification $I-V$ curves were found in p-GaN/n-ZnO and p-CdTe/n-ZnO heterostructure junctions. The results indicated that using mixture gas of hydrogen and argon in PLD technique was a flexible method for depositing high-quality n-type oxide semiconductor films, especially for the multilayer thin film devices.

Keywords: ZnO, PLD, heterostructure
PACC: 7280E, 7155G, 7340L

1. Introduction

In the recent decade, wide-gap semiconductors, especially oxide semiconductors have attracted much attention due to their potential applications according to theoretical calculations and experimental researches.[1−5] ZnO, with a room-temperature band gap of 3.37eV, is transparent to visible light and impervious to ultraviolet.[6] More importantly, after being doped by some magnetic elements (Co, Fe, Mn, etc), the ZnO thin film exhibits room-temperature ferromagnetism, which makes it a candidate for "spintronic" devices.[7] Various techniques have been adopted for the deposition of ZnO thin films, such as metal organic chemical vapour deposition (MOCVD),[8] molecular beam epitaxy (MBE)[9] and pulsed laser deposition (PLD).[10]

The n-type ZnO films were mostly prepared in high vacuum environment for the consideration of low resistivity, which is often attributed to the native defects, such as oxygen vacancies and zinc interstitials.[11] For the PLD technique, however, deposition in high vacuum does not merely produce oxygen vacancies in thin films. One of the most obvious characteristics of the PLD technique is that the surface of the film is bombarded by the high-kinetic-energy ablation particles, which may cause disorder of film growth. This drawback will be serious when the film is deposited in ultrahigh vacuum environment. The bombardment by high-kinetic-energy ablation particles is a key problem for epitaxial growth of high-quality films, especially in preparing devices with heterostructure interfaces.

We present a simple and flexible method, using a mixture gas of hydrogen and argon in the PLD for overcoming the bombardment problem, because we believe that the argon could decrease the kinetic energy of the ablation particles, and the hydrogen would lead to the enhancement of electrical conductivity. In this article, we describe the growth of epitaxial n-type ZnO thin films in the mixture gas of hydrogen and argon. As expected, the mixture gas is proved to be helpful for both producing oxygen vacancies and reducing particle bombardment. Therefore, low resistivity with smooth surface can be achieved in the n-type ZnO films. In addition, rectification $I-V$

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†E-mail: ssxgc@pku.edu.cn

curves are obtained in p-GaN/n-ZnO and p-CdTe/n-ZnO heterostructure junctions. The results indicate that using the mixture gas of hydrogen and argon is a convenient method for depositing high-quality oxide semiconductor films.

2. Experiment

In this work the ZnO target was prepared from high-purity ZnO powders sintered at 1000°C for 12h. The mixture gas of hydrogen (10%) and argon was used in the PLD. A laser repetition rate of 6 Hz with an energy density of 130 J/m^2 was applied. The distance between the target and the substrate was about 3 cm. Thin film growth was carried out at different substrate temperatures (from 500 to 700°C) under a variable gas pressure (from 0.1 to 10Pa). The thickness of the thin film after 6 minute deposition was about 75nm.

3. Results and discussion

The structure properties of the grown films were characterized by x-ray diffraction (XRD). Figure 1 shows the pattern of XRD $\theta - 2\theta$ scans of ZnO thin films deposited on sapphire and $LaAlO_3$ substrates. Three strong peaks can be found in Fig.1(a) from Al_2O_3 (006) and from ZnO (002) and (004) at 2θ=34.425° and 72.625°, respectively. No impurity peak is detected. The sharp and intense peaks observed indicate that the thin films are highly crystallized with c-axis normal to the surface, which is confirmed by the low value of the full width at half maximum of the rocking curve recorded around the peak of (002). XRD ϕ scans indicate that the ZnO films exhibit epitaxial single crystalline structure. The lattice constant of the c-axis epitaxial ZnO film is calculated to be c=0.5210nm, which is close to the reported value in Ref.[12]. It is interesting that highly oriented ZnO films can be obtained by using α-Al_2O_3 single-crystal substrates. Figure 1(b) shows XRD $\theta - 2\theta$ scans of a ZnO thin film deposited on an α-Al_2O_3 single-crystal substrate. The single ZnO (110) peak at 56.675° indicates that the film is highly [110] oriented, although the α-Al_2O_3 single-crystal substrate surface is in nearly cubic orientation. From the ZnO (110) peak position, the calculated a=0.3290nm is close to the reported value in Ref.[12]. It is more interesting that the ZnO thin films deposited on single-crystal perovskite $LaAlO_3$ (001) substrate are highly crystallized. Figure 1(c) illustrates the $\theta - 2\theta$ scan of a ZnO thin film deposited on a $LaAlO_3$ (001) substrate. Only [102] and [110] oriented growth directions are observed in the ZnO thin film. XRD measurements indicate that under the growth of our deposition conditions the ZnO thin films deposited on sapphire and $LaAlO_3$ substrates are in preferred orientation.

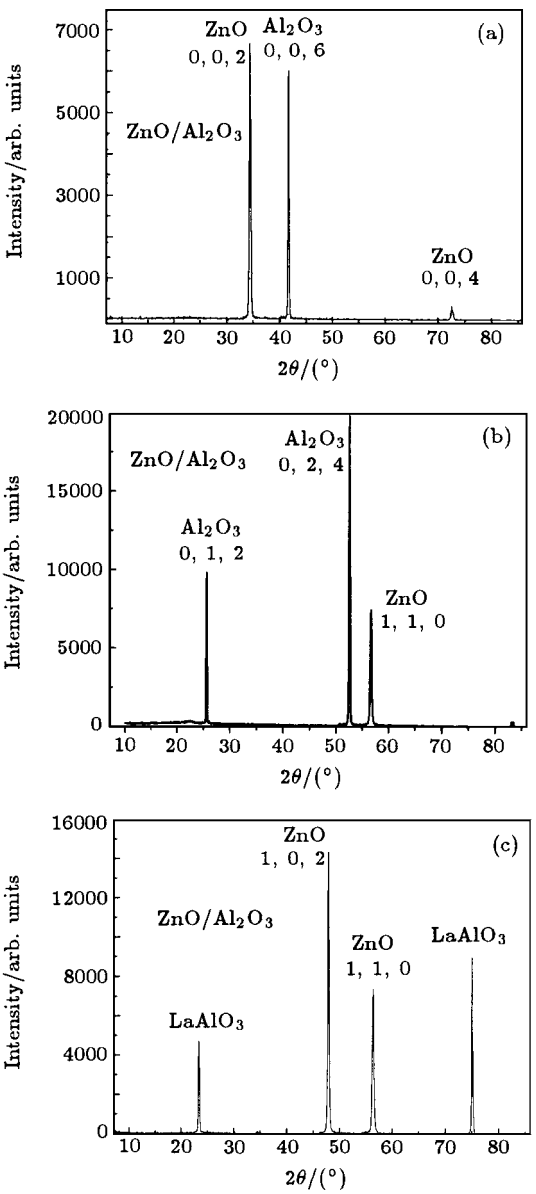


Fig.1. XRD of ZnO thin films. The substrates are (a) sapphire with (001) surface, (b) sapphire with (012) surface and (c) $LaAlO_3$ with (001) surface, respectively.

The surface morphology of the ZnO thin films grown at various substrate temperatures were characterized by atomic force microscope (AFM). Figures 2(a) and 2(b) exhibit the micrographs of epitaxial ZnO thin films grown in the mixture gas of hydrogen and argon at substrate temperatures of 600°C and 700°C, respectively. It can be seen that the epitaxial ZnO

thin film grown at 600°C has a fairly smoother surface. Figure 2(c) is the AFM image of ZnO thin film deposited on GaN/Al_2O_3, which shows a relatively rougher surface than the surface of ZnO grown on sapphire substrate due to the lattice mismatch between ZnO and GaN.

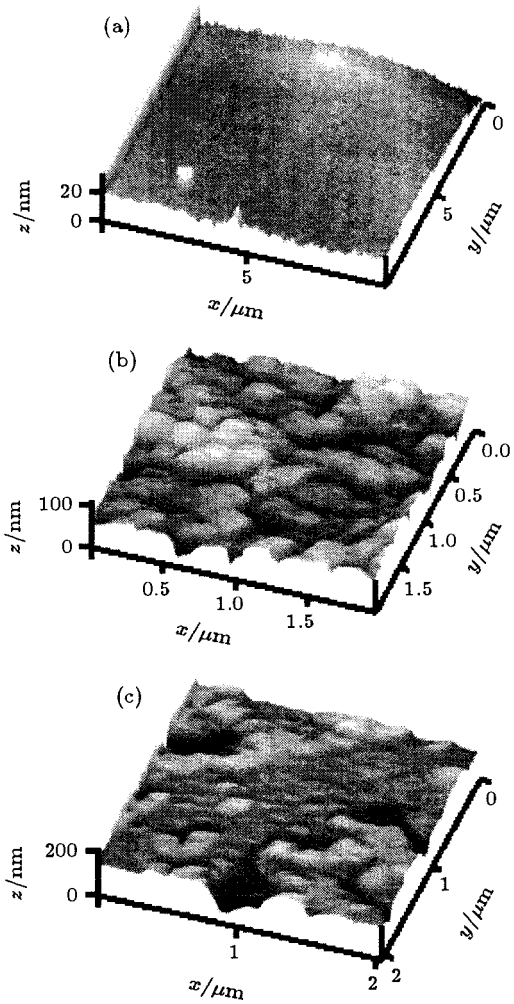


Fig.2. AFM images of ZnO thin films. The substrates are sapphires with the temperature of 600°C and 500°C for Fig.2(a) and 2(b), respectively; Figure 2(c) is the AFM image of ZnO deposited on GaN/Al_2O_3.

Low-resistivity ZnO thin films (15.2mΩ·cm at room temperature) with smoother surface can be obtained by deposition at 600°C at 1Pa of the mixture gas. The n-type carrier density of the ZnO thin films deposited in these conditions is about $1.0\times10^{20}/cm^3$ measured by conventional Hall method. All of the conductive ZnO thin films are highly transparent. Figure 3 shows the optical transmittance spectrum of ZnO thin film measured at room temperature. In the visible and near-infrared region (400–900nm) the transmittance is over 95%, which is higher than most of the reported values.[13–15]

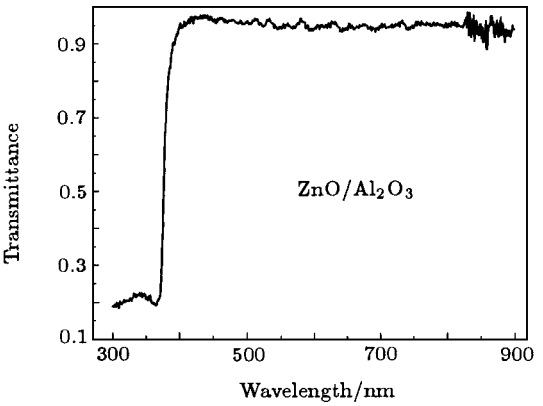


Fig.3. Optical transmittance spectrum of a ZnO thin film at room temperature.

Using the deposition conditions, Co-doped ZnO thin films demonstrate a ferromagnetic to paramagnetic transition at about 346K from $M-T$ curves measured by superconductor quantum interference device (SQUID) under a field of $\sim 4\times10^5$A/m (5000 Oe). Figure 4 shows the hysteresis loop of Co-doped ZnO thin film at room temperature (300K). The saturation magnetization is about 400emu/cm^3 in the field of $\sim 4\times10^5$A/m and the coercive field (H_c) is less than $\sim 4\times10^3$A/m (50 Oe). The magnetic behaviours cannot be attributed to the contribution of Co clusters, as reported in Ref.[16], since we argue that reducing the particle bombardment would not be favourable to the formation of Co clusters. Using the mixture gas of hydrogen and argon, the n-type ZnO thin films were deposited on p-type GaN and CdTe films for constructing heterostructure junctions. Rectification $I-V$ curves were obtained in p-GaN/n-ZnO and p-CdTe/n-ZnO heterostructure junctions, as demonstrated in Fig.5. These results indicate that using the mixture gas of hydrogen and argon in PLD is an effective technique for depositing high-quality n-type ZnO thin films and heterostructure devices.

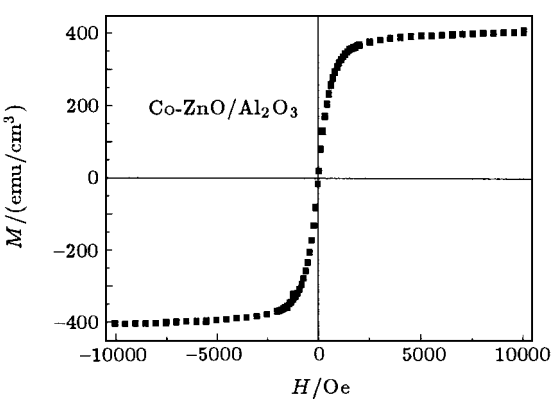


Fig.4. Magnetization vs field curve of a Co–ZnO thin film at 300K.

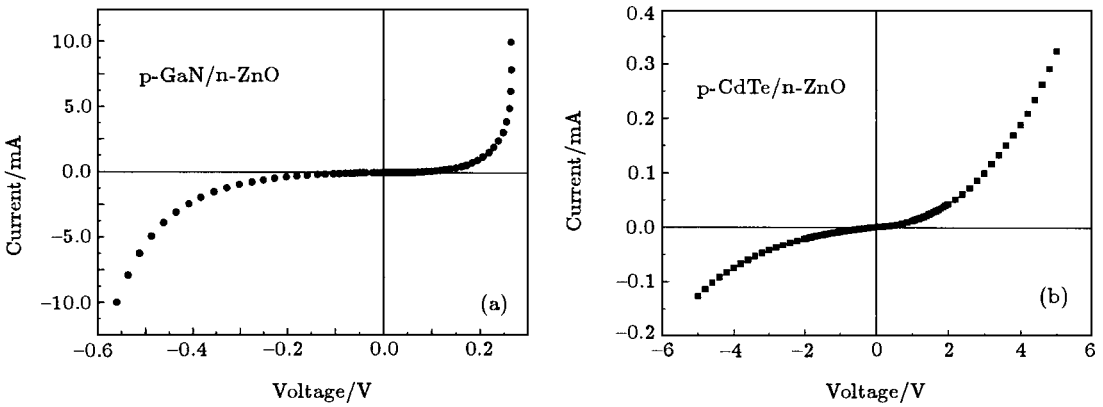


Fig.5. Current–voltage curves of a p-GaN/n-ZnO (a) and a p-CdTe/n-ZnO (b) heterostructure junctions.

4. Conclusion

In summary, the structure of ZnO thin film could be improved with the help of mixture gas of hydrogen and argon since it reduces the particle bombardment. Besides, the increase of the oxygen vacancies on account of the hydrogen leads to the enhancement of electrical conductivity. Thus, high-quality ZnO thin film with low resistivity could be obtained. Moreover, room temperature ferromagnetism of Co-doped ZnO, p-GaN/n-ZnO and p-CdTe/n-ZnO heterostructure junction demonstrates that the credit of using mixture gas needs further investigation.

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