Nitrogen-doped CuAlO₂ Films Prepared by Chemical Solution Deposition

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Abstract. N-doped CuAlO₂ thin films were prepared by chemical solution deposition and annealed at different temperature in nitrogen ambience. Single phase N-doped CuAlO₂ thin films can be obtained by annealing the films at 1000 °C. Crystallization quality of the film was improved by increasing annealing temperature. XPS measurements showed the N has successfully incorporated into the CuAlO₂ thin films. Above results show that the chemical solution deposition was an effective way to prepare the N-doped CuAlO₂ thin films which can be used in optoelectronic devices.

1. Introduction

Due to its potential application in light emitting diode, solar cells, flat panel displays, gas sensors, and touch panels, transparent conducting oxides (TCOs) has received widespread attention recently[1-5]. Most of the TCOs were n-type with better conductivity than that of the p-type TCOs. Such as ZnO, SnO₂, In₂O₃, Ga₂O₃ [6-9]. However, these materials were difficult to obtain better conductivity p-type TCOs. The n-type and p-type TCOs should have better conductivity for fabricating p-n junction devices. Therefore, the application of these materials in optoelectronic device was limited. P-type TCOs CuAlO₂ with visible transmittance of 70% and conductivity of 0.95 S·cm⁻¹ was obtained by Kawazoe in 1997 [10]. However, Due to the low acceptor defects concentration and high acceptor ionization energy, the CuAlO₂ has a lower hole concentration [11]. Therefore, many methods were used to enhance the conductivity of CuAlO₂ [12-16]. Doping is an effective way to enhance the conductivity of p-type CuAlO₂, such as N, Ag, Mg and Ni doping [17-20]. For the atomic radius and electronegativity of N is similar to O, N was considered to be a better dopant for CuAlO₂. The CuAlO₂ thin film with better conductivity was obtained by adjusting N-doping concentration [17]. CuAlO₂ films have been prepared by using different methods, such as radio frequency magnetron sputtering [21], pulsed laser deposition (PLD) [10], and chemical solution deposition (CSD) [19, 22], etc. Due to its mass production, large-area coating, easy setup, and low cost, chemical solution method became an effective way to fabricate CuAlO₂ films.

Since there have no related reported about the N-doped CuAlO₂ prepared by using CSD, in this paper, the CuAlO₂ with N-doping fabricated by CSD was studied.

2. Experiment Methods

CSD was used to fabricate the CuAlO₂ with N-doping on c-plane sapphire substrates. For fabricating CuAlO₂, citric acid monohydrate, aluminum nitrate (99%), and cupric nitrate (99%) were used. Diethanolamine (99%) and ethylene glycol was used as nitrogen source and solvent, respectively. The molar ratio of cupric nitrate to aluminum nitrate was kept at 1.0. In order to obtain a better mixed solution, the mixture was stirred continuously for 4 hours. The coating solution concentration was 0.25...
M. The c-plane sapphire substrate was cleaned by sonication in acetone, ethanol and water and dried with a gently nitrogen stream. The prepared solutions were spin-coated with 3000 rpm for 20 s on c-plane sapphire substrates. The solvent and remove organic residues were evaporated by preheated for 10 min at 300 °C in a quartz tube furnace. Eight cycles of spin-coating and preheating were used to obtain a certain thickness. Finally, different temperatures (800 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C) were used to anneal the samples for 3 h in the flow of nitrogen gas with 200 mL/min. The furnace temperature was natural cooling to room temperature. The thickness of the as-grown N-doped CuAlO$_2$ films were about 380 nm.

X-ray diffraction (XRD) with Cu $K\alpha$ radiation was used to examine the structures of the N-doped CuAlO$_2$ films before and after annealing. Al$_2$O$_3$ (0006) peak at 41.68 ° was used to calibrate he XRD diffraction peaks. For Raman scattering spectrum measurement, polarized light from the 488 nm line of an Ar$^+$ ion laser was used. X-ray photoelectron spectroscopy (XPS) measurements were performed by an ESCALAB 250 XPS instrument with Al $K\alpha$ (hv =1486.6 eV) X-ray radiation source.

3. Results and Discussion

Figure 1 shows the XRD diffraction patterns of N-doped CuAlO$_2$ films before and after annealing at different temperatures. The peaks located at 28.75 ° and 41.68 ° were corresponding to the (110) and (0006) diffraction peaks of c-plane sapphire substrates. The as-grown films have several weak diffraction peaks, indicating that the as-grown samples were amorphous phase which can be attributed to the low growth temperature and the failure to reach the crystallization temperature of CuAlO$_2$. A diffraction peak located at 59.61° was found after annealing at 800 °C, which can be attributed to the (511) diffraction peak of CuAl$_2$O$_4$ (PDF# 73-1958). Several diffraction peaks located at 15.72 °, 31.67 °, 36.79 °, 37.74 °, 48.34 ° and 66.15 ° were found in the CuAlO$_2$ films after annealing at 900 °C and 1000 °C, which correspond to the diffraction peaks of CuAlO$_2$ (003), (006), (101), (012), (009) and (0012), respectively, indicating that the textured growth of $R3m$ CuAlO$_2$ (PDF# 75-2398 and 75-2360). Two additional diffraction peaks related to the (002) and (110) of Al$_2$O$_3$ were found located 19.04 ° and 20.62 °, respectively, indicating that the CuAlO$_2$ films were polycrystalline contain little Al$_2$O$_3$. The diffraction peaks related to Al$_2$O$_3$ disappeared and only (003), (006), (009), (0012), (101), (012) and (110) diffraction peaks of CuAlO$_2$ appears (PDF# 75-2398 and 75-2360) after annealing at 1100 °C, indicating that a single phase of CuAlO$_2$ polycrystalline film was obtained. Those patterns of the film show that the thin film tend to be grown in (001) direction. Cu$^{2+}$ related diffraction peaks were not observed. The main phases of the annealed film were CuAlO$_2$ phase, suggesting that the nitrogen atmosphere prevents the oxidation of Cu$^+$ ion. It shows that higher annealing temperature is beneficial to the formation of CuAlO$_2$ phase and Cu$^+$. The main reason is that CuAlO$_2$ belongs to high temperature phase and the formation of Cu$^+$ needs high temperature. With increasing the annealing temperature, the intensity and full widths at half maxima (FWHM) of the diffraction peak (003), (006), (009) and (0012) of the CuAlO$_2$ show increases and decreases, respectively, which indicated that the crystallization quality of the film was improved by increasing annealing temperature. Annealing process makes the atom in the films obtain enough energy to diffuse through point defects into the lattice sit, and further improve the crystalline quality of the film. With the increase of annealing temperature, the diffraction peaks related to CuAlO$_2$ disappeared, but the diffraction peaks of Cu$_2$O (111) and (311) appeared at 36.41 ° and 61.42 ° (PDF# 78-2076), which indicated that the decomposition of CuAlO$_2$ polycrystalline films occurred at high temperature.
Figure 1. X-ray diffraction patterns of the as-grown and annealed N-doped CuAlO$_2$ films annealed at different temperatures.

CuAlO$_2$ has a delafossite structure and belongs to the $R\bar{3}m$ space group (D$_{3d}$ symmetry). Each primitive cell of CuAlO$_2$ has four atoms, which produces 12 phonon modes, three of which are acoustic and nine optical. The vibration mode can be expressed as follows: $\Gamma' = A_{1g} + E_g + 3A_{2u} + 3E_u$. Only the $A_{1g}$ and $E_g$ modes is Raman active. Therefore, it can also be written as: $\Gamma' = A_{1g} + E_g$. $A_{1g}$ and $E_g$ mode represents the vibration of Cu-O bond along c-axis and a-axis, respectively.

Figure 2 shows the room temperature Raman spectrum of N-doped CuAlO$_2$ films before and after annealing at different temperatures were acquired using a 488 nm laser. It can be found that no Raman peaks related to CuAlO$_2$ were found in the as-grown film and the film after annealing at 800 °C, indicating that the as-grown and annealed films have no CuAlO$_2$ phase due to the low growth and annealing temperature. Two Raman peaks at 418 cm$^{-1}$ and 767 cm$^{-1}$ appeared in the Raman spectrum at high annealing temperatures which can be attributed to the $E_g$ and $A_{1g}$ modes, respectively. These positions agree well with the other research results [23]. The intensity of these two Raman peaks increase with increasing annealing temperature, indicating that the crystalline quality of the CuAlO$_2$ was improved with the increase of annealing temperature. While annealing at 1200 °C, the Raman peaks located at 418 cm$^{-1}$ and 767 cm$^{-1}$ in the Raman spectrum become weaker and disappear, respectively. The 295 cm$^{-1}$ Raman peaks belong to the $A_g$ mode of CuO. The Raman peaks located at 216 cm$^{-1}$ and 630 cm$^{-1}$ in the Raman spectrum which correspond to the second-order Raman-allowed mode and the infrared-allowed mode of Cu$_2$O [23-25], respectively, indicating that the decomposition of CuAlO$_2$ polycrystalline films occurred at high temperature which was consistent with XRD measurements.
Figure 2. Raman spectrum of the as-grown and annealed N-doped CuAlO$_2$ films annealed at different temperatures.

Figure 3. XPS spectrum of the (a) Cu 2p and (b) N1s lines of the as-grown and annealed CuAlO$_2$ film annealed at 1000 °C.

Figure 3 show typical Cu 2p spectrum of the as-grown CuAlO$_2$ and the CuAlO$_2$ after annealing at 1000 °C. In XPS spectrum, the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ related peaks were found at 932.6 eV and 952.7 eV, respectively [26]. It was also can be found that in the as-grown CuAlO$_2$ film, as inset in figure 5(a), the shake-up satellite of Cu$^{2+}$ was also found, indicating that Cu$^{2+}$ appears in the films. After annealing at 1000 °C, the peaks related to Cu$^{2+}$ nearly disappeared, as shown in figure 3(a), indicating that more Cu$^{2+}$ were converted into Cu$^{1+}$ due to the high annealing temperature. Therefore, single phase CuAlO$_2$ film with better crystalline quality was obtained, which agree well with the results of XRD and Raman measurements. In order to clarify the change of N content in the CuAlO$_2$ film after annealing, XPS was used to measure the N content in the film before and after annealing at 1000 °C, as shown in figure 3(b). The N content in the film before and after annealing were about 2.32% and 1.17%, respectively. It can be found that the N content show decreases after annealing due to the high temperature which will further effect the optical-electrical properties. How to prevent the N escape from film during annealing process at high temperature is a very important research topic. Therefore, work to solve the escaping of N at higher temperature is underway. The solution to the escaping of N will lay a solid foundation for obtaining CuAlO$_2$ films with high hole concentration and low resistivity.
required in optoelectronic devices.

4. Conclusions
N-doped CuAlO$_2$ thin films were prepared by chemical solution deposition and annealed at different temperature in nitrogen ambience. N has successfully incorporated into the CuAlO$_2$ thin films using chemical solution method. Crystallization quality of the film was improved by increasing annealing temperature. Single phase N-doped CuAlO$_2$ thin films can be obtained by annealing the films at 1000 °C. These results show that the chemical solution method was an effective way to fabricate the N-doped CuAlO$_2$ films which can be used in optoelectronic devices.

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6. References

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