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TUNING RESISTIVITY AND TRANSMITTANCE OF AZO FILMS THROUGH THE ELECTRO-CHEMICAL TREATMENT

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Aluminum-doped zinc oxide (AZO) films were prepared by radio-frequency magnetron sputtering from powder target, and the photo-electric properties of the films were tuned by the electrical and chemical interactions. The microstructure and photo-electrical properties of the films were characterized by Raman spectroscopy, X-ray diffraction (XRD), UV-visible spectrophotometer and Hall Effect apparatus. The results show both resistivity and transmittance of the AZO film treated under the electrical and chemical action decrease as the pH of the electrolyte decreases. At pH = 5, the photo-electric property of the treated AZO film is the most excellent. The resistivity is reduced to 3,7×10^{-3} Ω·cm from 7,1×10^{-1} Ω·cm of the as-prepared AZO film, and the transmittance is reduced to 90,1 % from 91,3 % of the as-prepared AZO film.

Key words: AZO film; electro-chemical treatment; properties; resistivity; transmittance

INTRODUCTION

The aluminum-doped zinc oxide (AZO) film is a kind of transparent conductive oxide film, and has many advantages such as abundant raw materials, low price, good thermal stability, low preparation temperature and little pollution. With its excellent electrical and optical properties comparable to that of the market-leading ITO (Sn-doped In_2O_3) film, AZO is a very promising material for prepar- ing opto-electronic devices, and would be widely used in touch screens[1], light-emitting diodes [2], thin film solar cell substrates [3] and so on.

Not all Al elements could be effectively doped in AZO thin films prepared by magnetron sputtering. Some invalid form is electrically neutral Al_2O_3 at grain boundaries, and others are compensated by other acceptor defects(O_i, $V_{Zn,}$ etc.)[4]. Therefore, the electri- cal properties of the film were not as good as expected. Studies have shown that subsequent heat treatment can significantly improve the electrical and optical properties of AZO films. For example, Osman Gürbüz et al. [5] studied AZO thin films deposited on a silicon dioxide annealing temperature of 400 °C have the lowest resistivity 9,40×10^{-5} Ω·cm. The film also exhibits good optical properties and high crystallinity. In the study of Oh et al. [6], when a sample was annealed at 500 °C in a mixture of N_2:H_2 (9:1) after deposited on sapphire at room temperature, its resistivity is 5,57×10^{-4} Ω·cm and transmittance is 91 – 96,99 % in the wavelength range of 400 – 1 100 nm. Jaehyeong Lee et al. [7] deposited aluminum- doped ZnO (ZnO:Al, AZO) films using a pulsed DC unbalanced magnetron sputtering system. The deposited AZO film was annealed in a N_2 atmosphere at different temperatures using a rapid thermal annealing apparatus. Studies have shown that as the annealing temperature increases from 300 °C to 500 °C, the resistivity of the film decreases from 1,63×10^{-3} to 9,9×10^{-4} Ω·cm.

In this paper, by the combination of electrical and chemical action, the reactive hydrogen are produced on the surface of AZO film as an electrode to reduce oxygen ions in AZO. The increased oxygen vacancy concentration could be used to manipulate the photo-electric performance instead of annea- ling heat treatment. Compared with heat treatment, the method conveniently operated in the simple equipment has a short working time, low cost and high efficiency.

EXPERIMENT

Using an AE600X type RF power source, the AZO film was prepared by a radio frequency magnetron sputtering from powder target which consisted of the pure 99,99 % ZnO and 99,99 % Al_2O_3 by metallic atomic ratio Al:Zn 3 %. Preparation process: the slide glass as a substrate was ultrasonic cleaned with acetone, alcohol and deionized water for 15 min, respectively. After dried by nitrogen, the slide glass was put into the vacuum chamber of the rig, which was evacuated to a base pressure lower than 3×10^{-3} Pa and then backfilled with 99,9 % argon gas to a working pressure of 0,1 Pa. The films were deposited by RF sputtering at 300 W for 70 min in deposition time.

The electro-chemical experiment was completed on the ITECH IT6720 digital control power supply. The AZO film was used as the cathode and the platinum electrode were the anode. The as-prepared films were

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treated as below: (1) Only under the electrical action (water as the electrolyte, no other ion inter- ference), adjusting the power supply voltage to 2 V, 5 V, 8 V; (2) Only under chemical action, immersing the sample in a zinc sulfate (Zn_2SO_4) solution that has been adjusted to a pH (without an external power source); (3) Combination of electrical and chemical action. The power supply voltage was 2 V, and the Zn_2SO_4 solution was used as the electrolyte. The pH was adjusted to 6, 5, 4, and 3 by adding HCl solution. The films at different conditions were treated for 5 minutes at 25 °C constant temperature in water bath.

The phase structure of the film was analyzed by a small angle diffraction module of X'Pert Pro X-ray diffraction (XRD). The Raman spectroscopy was investigated by XploRA PLUS. The transmittance of the film was measured by Lambda 900 ultraviolet- visible spectrophotometer. The electrical properties of the film were tested by using a SWIN Hall 8800 at room temperature.

RESULTS AND DISCUSSION

The AZO film is immersed in a mixed solution of zinc sulfate and hydrochloric acid, and the surface reacts:

$$2H^+ + O^{2-} = H_2O \tag{1}$$

The reactions of the anode and cathode in the electrical experiment are as follows:

Cathodic reaction:

$$2H^+ + 2e^- = H_2\uparrow,\ 2H^+ + O^{2-} = H_2O \tag{2}$$

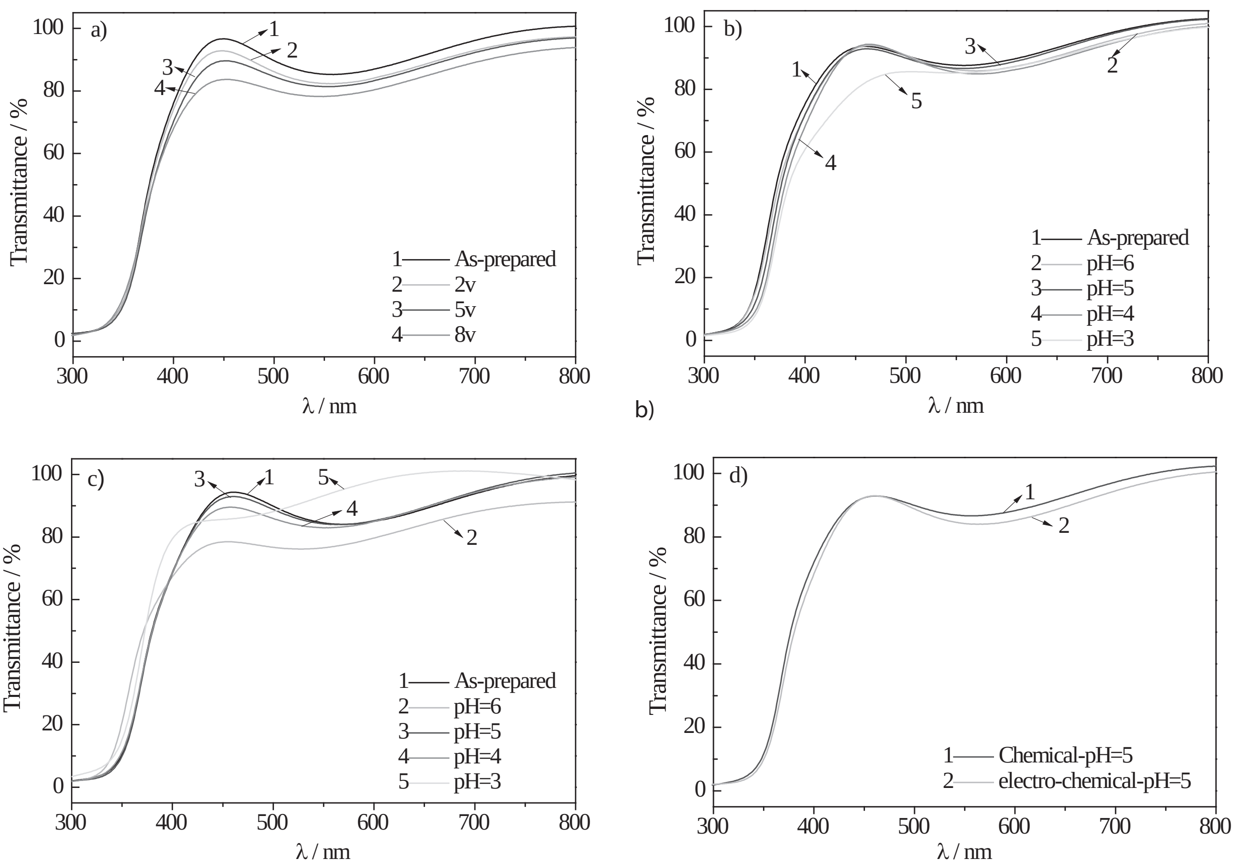
Anodic reaction:

$$H_2O - 2e^- = 1 / 2O_2\uparrow + 2H^+ \tag{3}$$

Due to the higher concentration of hydrogen ions in the higher acidic electrolyte solution, hydrogen ions preferentially acquire electrons under the action of concentration driving, and hydrogen is precipitated on the surface of the AZO film.

Optical properties

Figure 1 a) is the transmittance spectra of AZO films treated only under electrical action at different voltage. It can be seen that the original sample has the highest light transmit- tance, and the transmittance of the sample treated at 8 V voltage is the smallest. The average light transmittance in the visible wavelength range of 400 – 800 nm also reaches 85 % or more. As the voltage increases, the average light transmittance decreases gradually. This is mainly because the increas- ing voltage enhances the thermodynamic and kinetic behavior of the hydrogen ions in the solution, which more rapidly seized oxygen atoms on the surface of AZO film as the cathode, resulting in an increase in oxygen vacancies. The increase of lattice defects leads to a decrease in



a) b) c) d)

Figure 1 Transmittance spectra of AZO films treated under a) Electrical action; b) Chemical action; c) Electro-chemical action; d) Comparison between b) and c) light transmittance by an enhanced ability to light scattering.

Only under chemical action, as the pH of the solution decreases, the concentration of hydrogen ions in the solution increases, and the oxygen atoms in the AZO film are reduced, resulting in an increase in oxygen vacancies. As shown in Figure 1 b), an enhanced ability to scatter light, and a slight decrease in light transmission ability decrease slightly with the decreasing pH value. At the same time, the reduced oxygen in the AZO film cause the film much more metallic and band gap narrowing, and the absorption limit is shifted toward the long wave direction.

Figure 1 c) shows the transmittance curve of AZO films treated under both the electrical and chemical interaction. It can be seen that the transmittance curve of pH = 3 is abnormal, this is because the AZO film is severely etched when the acidity is strong. The light transmit- tance 88,8 % of AZO film treated at pH = 4 is slightly lower than 90,1 % at pH = 5. The concentration of hydrogen ions in the solution increases, and the oxygen ions in the film are easy to be reduced. The increasing Oxygen vacancies result in much more scattering light.

The change in the transmittance curve of AZO films treated under the electro-chemical action is more evident than that of the only chemical action. In order to investigate the additional effect of electrical action on the AZO film treated in chemical solution, a comparison between electro-chemical and chemical treat- ment in a zinc sulfate solution at pH = 5 is shown in Figure 1 d), the transmit- tance of the AZO film in the electro-chemical experiment is slightly lower, which also confirms that the synergistic effect of the chemical and electrical action on the AZO film is more remarkable than the chemical action.

Electrical property

As shown in Table 1, under the only electrical action, as the power supply voltage increases, the sheet resistance and resistivity of the experimental sample decrease. Because the electrons of the cathode increase by the increasing voltage, the rate of hydrogen evolution increases, and the ability to reduce oxygen ions is enhanced. Therefore, AZO film is much more metallic and conductive.

In the electro-chemical treatment, the resistivity of the AZO films are significantly different under the electrolytes with different acidic. When the pH of the electrolytes is lowered to 4, the resistivity reduces from $7,10\times10^{-1}$ Ω·cm of the as-prepared sample to $3,57\times10^{-3}$ Ω·cm. there are two reasons for this. One reason is that hydrogen ion in an acidic solution is easily combined with oxygen in the AZO film, thereby increasing the number of oxygen vacancies and the carrier concentration to reduce the resistivity; Another reason is that AZO film as a cathode under the extra electrical action will generate activated hydrogen atoms to combine with the oxygen, which also increases the carrier concentration and thus the resistivity. When pH = 3, the resistivity suddenly rises because the AZO film is severely etched under high acidity, hindering the migration of carriers corresponding to low carrier mobility seen in Table 1.

Table 1 **Electrical properties of different samples**

		Resistivity / Ω·cm	Carrier concentration / cm^3	Mobility / $cm^2 \cdot v^{-1} \cdot s^{-1}$
As-prepared		7.10E-1	2.13E+18	4.13E+0
Electrical -voltage / V	2	4.49E-3	2.03E+21	6.80E-1
	5	2.57E-3	8.49E+20	2.87E+0
	8	1.76E-3	2.35E+21	1.50E+0
Chemical -pH	6	2.23E-2	8.52E+19	3.27E+0
	5	1.47E-2	4.96E+20	8.54E-1
	4	1.55E-2	4.01E+21	1.00E-1
	3	3.69E-1	1.69E+20	9.98E-2
Electro -chemical -pH	6	5.87E-3	5.71E+20	1.86E+0
	5	3.70E-3	4.08E+20	4.14E+0
	4	3.57E-3	4.72E+20	3.70E+0
	3	3.48E-1	3.69E+20	4.87E-2

Under the only Chemical action, when the pH of the solution is lowered to 4, the resistivity of the treated AZO film is only reduced to $1,55\times10^{-2}$ Ω·cm. It is easy to see the comparison between chemical-pH and electro- chemical-pH in Table 1. The electro- chemically treated samples have a lower resistivity under the same chemical conditions. This also suggests that the chemical and electrical synergy can more greatly adjust the resistivity of the AZO film compared to the chemical action.

XRD analysis

Figure 2 illustrates the XRD pattern of the electro-chemically treated samples, indicating that both the treated and as-prepared AZO films have a typical hexagonal wurtzite structure of ZnO. The peaks appeared around 34 °, 47 ° and 63 ° correspond to (002), (012) and (013) crystal planes of ZnO, respectively. All sample no new microstructure phase was formed in AZO

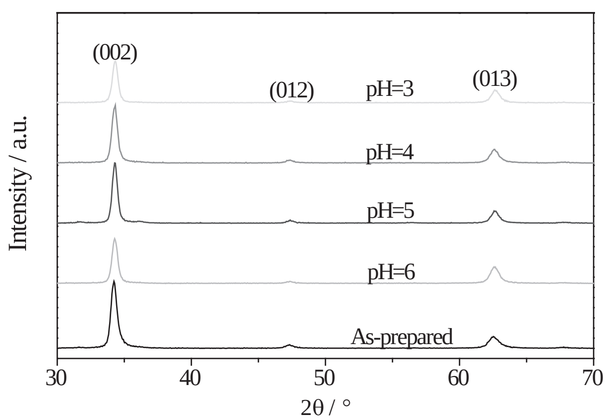


Figure 2 XRD pattern of AZO films treated by electro- chemical action

films, and there was no occurrence of zincadhesion on the surface of the AZO film despite immersed in Zn_2SO_4 acidic solution.

Raman spectroscopy

The optical phonon of the Brillouin zone of the wurtzite ZnO structure has the following irreducible representation:

$$\Gamma_{opt} = 1A1+2B1+1E1+2E2 \tag{4}$$

Among them, the optical vibration modes that can be activated by Raman are: A1 (LO), A1 (TO), E1 (LO), E1 (TO), E2 (high), and E2 (low). As shown in Figure 3, three phonon vibration peaks can be observed in the range of 100 - 1 000 wave-number. The peak at 450 cm^{-1} is a characteristic peak of zinc oxide wurtzite structure, which changes along with the structure of zinc oxide. A strong peak appears near 270 cm^{-1}, explained the Raman activity generated by the B2 mode caused by the built-in electric field in the depletion region. The peak at 580 cm^{-1} is related to oxygen vacancies, whose intensity of the treated samples increases significantly in comparison with the as-prepared sample. It indicates that the hydrogen produced through electrolysis combines with oxygen, increasing the oxygen vacancy-related defects.

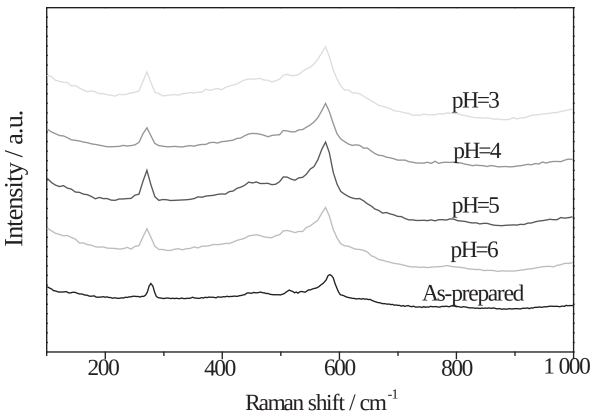


Figure 3 Raman spectra of AZO films treated by electrical action

CONCLUSION

This study investigated the effects of the chemical and electrical treatments on the properties of AZO films. Only under the electrical action, as the voltage increases from 2 V to 8 V, the transmittance of AZO film is reduced from 89,0 % to 85,0 %, and the resistivity is reduced from $4,5\times10^{-3}$ Ω·cm to $1,8\times10^{-3}$ Ω·cm. Only under the chemical action, the resistivity of AZO film treated in solution of pH = 4 decreases to $1,6\times10^{-2}$ Ω·cm from $7,1\times10^{-1}$ Ω·cm of the as-prepared AZO film. Under both the electrical and chemical interaction in the electrolyte of pH = 4, the resistivity of AZO film is lowered to $3,6\times10^{-3}$ Ω·cm. Compared with the only chemical action, the synergistic effect of the chemical and electrical action could tune the greater range of resistivity of AZO film at the cost of loss of light transmittance. The increasing amount of oxygen vacancy is responsible for that.

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Note: Y. X. Wang is responsible for English language, Anshan, China