Piezoelectric film electro-deposition for optical fiber sensor with ZnO coating

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The piezoelectric film electro-deposition for optical fiber sensor with ZnO coating is studied. The zinc oxide plating film is made on the copper surface directly by cathodic electro-deposition in the $Zn(NO_3)_2$ single salt aqueous solution systems. The influences of main experimental conditions on the properties of ZnO thin film in the electro-deposition processes are analyzed and a stable, practical and economic technique is obtained.

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Researches on fiber optic components made from fiber-coating have been the focus of many efforts in recent years as fiber optic systems have being found more and more applications in sensing, signal-collecting, data-transmission, and industrial processing.

The device structure consists of a silica fiber coated with a radically polarized piezoelectric jacket that is sandwiched between coaxial thin-film metallic electrodes. Application of an electric field between the metal electrodes induces strains in the piezoelectric jacket due to the converse piezoelectric effect. The strains in the jacket are directly transmitted to the glass core in the radial direction of the fiber, thus changing its refractive index. Therefore, if a light signal passes through this optical fiber with piezoelectric ZnO coating, the phase shifting of the signal will take place because of the changing refractive index inside the fiber. This is the basic working principle of the optical fiber acousto-optic sensor, or phase modulator, or rather an acoustic resonator[1,2]. The piezoelectric film electro-deposition method for optical fiber sensor with ZnO coating is studied in this letter.

Generally speaking, the following methods are commonly used presently for deposition of ZnO film such as ECR, MSIP, LP-MOCVD, MOCVD, MBE, PLD, Spray Pyrolysis, E-PVD and Sol-Gel[3−6].

There are advantages in electro-deposition methods over the other methods in the deposition of metal oxide film on metal substrate. Firstly, there will be no residual stress in the coated film since the processes of electro-deposition take place in low temperature bath. Secondly, since the electro-deposition particles' process is not a linear one, the uniformed coating films can be made on the substrate with varied and intricate shapes. Thirdly, many parameters of electro-deposition such as coating film thickness, chemical composition, microscopic structure and porosity can be adjusted through process conditions including deposition time, current density, temperature, concentration and pH value in solution. Thus higher deposition speed can be obtained. However, there are some influencing factors which are difficult to control when using electro-deposition methods. Therefore, the desired requirements of the micro-structure for the coated film sometimes are hard to achieve and more experiments are needed to get precise results.

Presently, the electro-deposition theories for metal oxide are cathode reduction and anode oxidation. According to the cathode reduction theory, the reducing matters such as H^+ or NO_3^- will revert on the cathode surface in the solution with pH value less than 7, thus the OH^- concentration will increase on the electrode surfaces. Then, the metallic ions in the solution will react with OH^- ions on the electrode surfaces, producing metal hydro-oxide which will dehydrate into oxide film under curtain conditions. The cathode reaction processes for ZnO film deposition will follow the equations below:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-, \qquad E^0 = 0.401 \text{ V}, \tag{1}$$

$$NO_3^- + H_2O + 2e \rightarrow 2OH^- + NO_2^-, \quad E^0 = 0.01 \text{ V}, \tag{2}$$

$$Cu + * + OH^- \rightarrow Cu - OH_{ad}^-, \tag{3}$$

$$Zn^{2+} + 2OH_{ad}^- \rightarrow Zn(OH)_{2(S)}, \tag{4}$$

$$Zn(OH)_{2(S)} \rightarrow ZnO + H_2O, \tag{5}$$

where E^0 is the electromotive force in hydrogen standard, "$*$" is the location of vacant base, "ad" means the capacity being adsorbed on a surface and "S" is the chemical intermediate.

According to the anode oxidation theory, the lower valence metallic ions on the anode surface will oxide into higher valence ions in the solution with higher pH value under certain conditions, and the higher valence metallic ions will react with OH^- ions on the anode surface, producing metal hydro-oxide which will dehydrate into oxide film under certain conditions. The anode reaction process for ZnO film deposition will follow the equation below:

$$4OH^- - 4e \rightarrow O_2 \uparrow + 2H_2O. \tag{6}$$

The following experiments are carried out in order to find the optimum process conditions for ZnO film deposition:

1) A crossed experiment of four elements plus four levels is designed to find the most suitable combination of

process conditions and affective parameters.

2) To determine the optimal ranges or values for the experimental parameters in the process and to find the every possible affective factors, the specific tests are done to assess the individual factors such as the deposition temperature, time, current density, concentration and pH value in solution.

3) Under the optimal process conditions obtained from the above experiments and using an electro-chemical working station, a three electrodes system is setup with copper sheets (99.99%) as the working electrodes, a Pt sheet as the anode, and a saturated calomel electrode as the reference electrode. By measuring the circulation volt-ampere curves, the mechanism of electro-deposition and electrodes reaction during the deposition process are examined.

4) After the deposition samples are made, they are sent to do further testing by a scanning electronic microscope (SEM), X-ray diffraction (XRD) and X-ray scan (XRS) to get the whole profile of the ZnO piezoelectric film structure on which the influences of deposition process conditions can be fully analyzed.

The influences of process conditions on deposition are studied. In order to eliminate the influence caused by shifting of the pH value and make sure the experimental condition remain steady, we use fresh solution in this experiment.

1) Current Density When the other conditions remains the same, we use a better point (D_k = 4.5 mA/cm^2) which get from the crossed experiment as a standard in order to study the upper and lower limit of current density. The purpose is to find out the rule of the current density affecting the ZnO deposition film, at the same time to find out the range of current density more suitable for deposition and the optimal current density point. The research shows that the optimal current density range is from 4.5 to 7.0 mA/cm^2. In this range, we can get the qualified films. The result of the experiment shows that $D_k = 6.0$ mA/cm^2 is the optimal current density. Under these conditions, the film made has better uniformity and color, its crystal tissue is also even and delicate. As a result, in the following experiment, the current density is chosen as 6.0 mA/cm^2.

2) Working temperature As shown in the experiment, the optimal range of temperature is between $50-60$ °C. The higher the temperature is, the faster the solution evaporates. Taking all factors into consideration, we choose 50 °C as the optimal temperate point. In the following experiment, we use 50 °C as the required temperature.

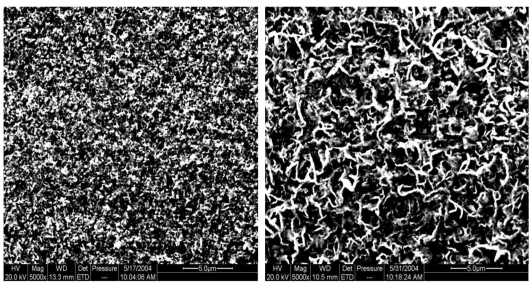
3) Deposition time The experiment is under the steady environments, that is, $D_k = 6.0$ mA/cm^2, $T = 50$ °C, $C_{\rm Zn}^{2+} = 0.15$ mol/L, and choosing deposition time of 10, 15, and 20 min. The experiment shows the range of optimal deposition time is between $10-20$ min, from which we make it 15 min.

4) $C_{\rm Zn}^{2+}$ of the solution From the crossed experiments, we know that the concentration value affects most to the film. In order to obtain how the concentration value affects deposition, we fix the environmental factors to $D_k = 6.0$ mA/cm^2, $T = 50$ °C, $t = 15$ min, and choose $C_{\rm Zn}^{2+}$ being 0.05, 0.10, 0.15, 0.20 and 0.25. When concentration value is over 0.20 mol/L, the film bleaches, and 0.10 mol/L concentration value blackens the film. While the value is below 0.10 mol/L, the film can no longer be seen. Figure 1 is the 5000 times enlargement SEM structure photos under different $Zn(NO_3)_2$ concentration values which are 0.15 and 0.25 mol/L. It shows that a higher concentration result in a larger crystalline structure. The experiment shows that the 0.15 mol/L concentration around makes better film. So the optimal concentration point $C_{\rm Zn}^{2+}$ is chosen as 0.15 mol/L.

5) Affections of the pH value The experiment shows that between the pH value $2.0-3.0$, the ZnO deposition film is even and of delicate uniformity.

Single ion deposition to get ZnO film is employed. By measurement of the circulation curve of Voltage-Current, the redox reaction of both cathode and anode in the deposition is examined. The process conditions of the experiment are: 1) the blank solution used as comparison is 0.05 mol/L KCl; 2) the target solution is 0.15 mol/L $Zn(NO_3)_2$ + 0.05 mol/L KCl (the purpose of adding 0.05 mol/L KCl to the solution is to make it easy when comparing with the blank solution); 3) the temperature $T = 50$ °C, pH = 4.43 (original value); 4) in the experiment, the first process is the cathode reduction, then circled to process the anode oxidation. The result is shown in Fig. 2.

In Fig. 2, it shows different peak values appearing in the same place, that is because during the first scan there are NO_3^- ions being reduced, which results fewer NO_3^- ions and leads to the dropping of the reduction peak value of NO_3^- ions in the second scan. However, during the second scan, the number of copper ions increased in the solution, resulting in the higher reduction peak value of copper at the second scan. The polarized curve experiments and the decreasing of pH value during the process show that the cathode reaction of the ZnO deposition



(a) 0.15 mol / L (b) 0.25 mol /L

Fig. 1. SEM structure photos of the films for different concentrations of $C_{\rm Zn}^{2+}$.

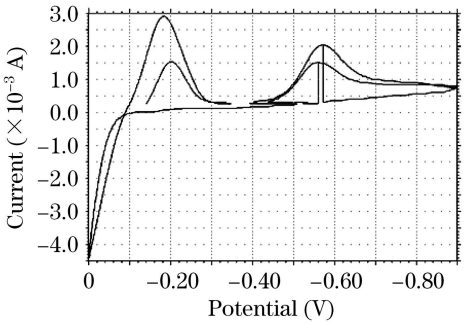


Fig. 2. Polarized curves of two scans.

film is accordant with reaction Eqs. (1)—(5), while the anode is with reaction Eq. (6).

To analyze the component of ZnO piezoelectric film, we use the energy spectrum analyzing method to compare the element contents of the film. In this way, we can get the quality of the film and process factors which influence the film indirectly.

The following results can be found from Fig. 3: 1) From the percentage of the element weight and the atom percentage, it shows that the deposition layer is ZnO film. 2) From the copper content of the energy spectrum, it also shows that the higher of the current density, the denser the film is. With $D_k = 1.5$ mA/cm^2, the copper atoms percentage reaches 1.59%, yet when $D_k \geq 4.5$ mA/cm^2, the percentage is less than 2%. Namely, the copper atoms is 1.59% when $D_k = 4.5$ mA/cm^2, 1.71% when $D_k = 6.0$ mA/cm^2, and 1.76% when $D_k = 7.0$ mA/cm^2, which means that the percentage of the copper atoms remains almost the same.

The formation analysis of the ZnO piezoelectric film is carried out. For samples under the process condition $D_k = 6.0$ mA/cm^2 , $t = 15$ min, $C = 0.15$ mol/L, $T = 50$ °C, we use a X-ray diffractometer in the experiment. The condition of the experiment is: voltage = 40 kV, current = 40 mA, page = 0.02° (scanning angle shifting step), scanning speed =1 s/p, beginning angle = 20°, ending angle = 80°, copper target, and $\lambda = 0.15406$ nm. The result is shown in Fig. 4.

It is found from the diffraction figure that, at the peak value where $2\theta = 36.25°$, the half-high-width $B = 0.275585$, Bragg diffraction angle $\theta_B = 18.125°$, and the

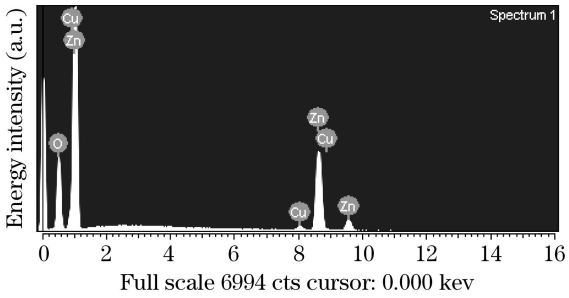


Fig. 3. Energy spectrum of the deposited film.

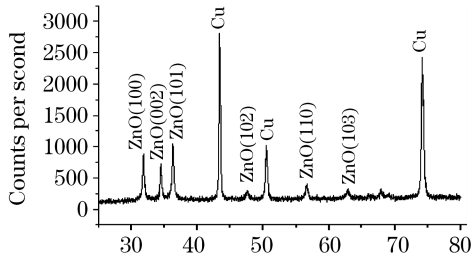


Fig. 4. Formation analyzing of the ZnO piezoelectric film by XRD.

X-ray wavelength $\lambda = 0.15406$ nm. Therefore, for Scherrer equation $t = 0.9\lambda/B\cos\theta_B$, the atom size of the ZnO film is about 0.52940 nm, which shows that the crystalline structure of the ZnO deposition film in the sample is very delicate, reaching the order of nanometers.

Finally, we use digital eddy thickness gauge to measure the thickness of the film at different position, and calculate the mean value. The mean value of the film $d = 2.8 - 3.2$ μm.

In summary, by studying the process factors, the relatively optimal ranges and points of the process are obtained: 1) the range of the current density is $4.5 - 7.0$ mA/cm^2, the optimal point $D_k = 6.0$ mA/cm^2; 2) the range of reacting temperature is $50 - 60$ °C, the optimal point is 50 °C; 3) the range of reacting time is $10 - 20$ min, the optimal point is 15 min; 4) the range of concentration is $0.10 - 0.20$ mol/L, the optimal point is 0.15 mol/L; 5) the range of pH value is $2.0 - 3.0$. Under the above conditions, the thickness of ZnO deposition film is $2.8 - 3.2$ μm, and the size of the film crystal is 0.52940 nm.

The study above is a part of the job involved to make the optical fiber acousto-optic sensor and the modulation sensitivity of the sensor[7]. When light signals pass through it, the maximum phase shifts $\Delta\phi_s$ are about tens of mil-radians in the vicinity of the fundamental modulating frequencies. If the series impedance connecting the sensor is negligible and a perfect quality ZnO film is fabricated, i.e., the piezoelectric coupling coefficient K_t could be greatly increased and the sensor's phase shift according to the theoretical calculation might be up to 250 mil-radians.

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