Fabrication of CuO Nanofilm preparation by Electrophoretic Deposition

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ABSTRACT

This paper uses electrophoretic deposition for coating a self-fabricated CuO nanofluid on a stainless steel substrate and measures the nature of this nanofilm. The pH value of the fabricated CuO nanofluid is 6.0, with a highly consistent mean particle size of 30nm. This paper investigates the effects of the CuO nanofluid's concentration, depositing time, voltage and sintering temperature on nanofilm, and also measures the micro-hardness of this CuO nanofilm and its UV-Vis absorption spectrum. The experimental results show that with voltage of 230V, depositing time of 5 minutes and sintering temperature of 200 ℃, we can acquire a CuO nanofilm of good compactness with micro-hardness higher then Hv110. Moreover, when the wavelength of illumination light is at the range of 400 nm ~ 700 nm, the CuO nanofilm has greater light absorbance, and the absorbance intensity grows stronger with the increase of depositing time.

Keywords: electrophoretic deposition, CuO, nanofilm, sintering, absorption

1 INTRODUCTION

Having the properties of extremely low infrared penetration rate, low resistance and high sensitivity to gas, CuO is a P-type semiconductor material with single-crystal structure that can be applied as a metal-oxide gas sensor. In addition, CuO thin film has been widely applied for solar energy batteries [1,2], mainly because of its high light absorption and low heat loss. Usually chemical or physical methods are used to conduct the film coating by CuO, and chemical methods can produce better thin films. However, chemical methods have the disadvantages of long growing time and expensive equipment. Abe of Japan previously used a solution method to develop a technique for ferrite plating in an aqueous solution, receiving much recognition for the solution method [3,4]. Electrophoretic Deposition (EPD) is a type of solution method, with the advantages of : (1) high coating speed, (2) simple fabrication, (3) ability for the coating to be applied on of all kinds of complicated inductive substrates, and (4) low equipment cost [5]. Its main disadvantage is that the edges of substrates could easily protrude when coating a ceramic film because of the congregation of current density therein, which further leads to difficulties in controlling the balance of coating, and also an unsatisfactor surface roughness [6,7]. There are many practical examples in producing ceramic thin and thick films by means of EPD [8-10], but we are aware of no reports on producing a CuO thin films by EPD.

This study has developed a Arc-Submerged Nanoparticle Synthesis System for preparing CuO nanofluids. The experimental device is comprised mainly of a heating system, an ultrasonic system, a pressure control system, and a temperature control system. Of these, the heating device can provide a stable electric arc to serve as the needed heat source for nanoparticle preparation.

The objective of this paper is to fabricate a nano CuO thin film by means of EPD. This study team has developed an Arc-Submerged Nanoparticle Synthesis System to prepare the CuO nanofluid. It provides good suspension with particle size distribution, which are the most necessary criteria for the EPD fabrication. This paper reports on an experimental investigation into how coating conditions such as deposited voltage, deposited current, deposited time, and distance between two electrodes can affect the formation of a nanofilm, and the product then undergoes sintering treatment after formation of the nanofilm. At the same time, micro-hardness of the nanofilm is measured and finally, the UV-Vis absorption spectrum of nanofilm is measured to confirm its nature.

2 EXPERIMENTAL

The Arc-Submerged Nanoparticle Synthesis System is an innovative and successful technology for manufacturing metal nanoparticles [11-13]. In this process, a bulk metal applied as the electrode is submerged in a dielectric liquid in a vacuum chamber. Applied electrical energy then produces heating source that generates an adequate arc with a high temperature ranging from 6000 ℃ to 12000 ℃. In the development process, a copper bar is melted and vaporized in distilled water, which is used as an insulating liquid. The vaporized metal powders are then rapidly quenched by the designed cooling system, thus nucleating and forming nanocrystalline powders. Nanoparticles can thus be successfully prepared and uniformly dispersed in dielectric liquid [14,15].

This paper uses self-manufactured CuO nanofluid to produce a CuO nanofilm by means of electrophoretic deposition. Different centrifugal filtering parameters and electrophoretic deposition parameters are set, in order to prepare a CuO nanofilm by electrophoretic deposition. The electrophoretic deposition fabrication equipment adopted in this study are shown in Figure 1. Mainly by adopting the

electrophoretic theory, the nanofluid, which was prepared beforehand and been processed by centrifugal filtering, is poured into the electrophoretic tank. The mirror-surfaced stainless steel substrate (20mm ×15mm ×1mm) waiting to be coated is regarded as anode and cathode, which are then soaked into the CuO nanofluid. After adjusting the distance between the two electrods, tens to hundreds of watts of DC voltage is connected. Affected by this high voltage current, electrophoretic motion of nanofluid occurs, and under the influence of the electric field, the particles carrying electricity in the fluid tend to move in the direction opposite to its electrical characterization, which is then adsorbed and congregates on the electrodes to form the nanofilm. Since there is no bonding force between nanofilm and substrate, and the also compactness is not good, it is necessary to undergo a sintering process towards the nanofilm, so as to increase the compactness and the hardness.

Before undergoing EPD, composition and concentration of the nanofluid has to be measured, which is then followed by the centrifugal filtering. A particle size analyzer is used to observe the sizes and distribution of the particles to acquire the centrifugal filtering parameter that is most suitable for EPD. This parameter is further used to sort out the best nanofluid for EPD. Upon completion, the composition of thin film is analyzed by XRD and EDAX, and FESEM is used to observe the surface structure and micro structure of the nanofilm. Then, AFM is used to measure the average thickness of the nanofilm. As to the EPD experiment, the influence of deposited current, deposited voltage, deposited time and the distance between two electrodes are investigated to find the best EPD parameters.

3 RESULTS AND DISCUSSION

The weight concentration of nanofluid prepared by the Arc-Submerged Nanoparticle Synthesis System is 0.2%. Moreover, the result of EDX measurement shows that its composition contains only the two elements of Cu and O. Also, by using XRD to measure its structure, it is confirmed that the prepared nanofluid is CuO. The properties of suspensions have a great impact upon the successful preparation of a CuO nanofilm having good properties. The suspensions suitable for EPD fabrication should have both good particle suspension and good nano particle distribution. Therefore, before proceeding with EPD, suspensions must undergo centrifugal filtering treatment, so as to acquire the centrifugal filtering parameters that are suitable for the application of filtering CuO nanofluid. After undergoing many experiments, a better quality CuO nanofluid can be acquired when the centrifugal speed is set at 6000 rpm, and centrifugal time at 5 minutes. Its secondary mean particle size is 30 nm and the standard deviation is 12 nm. Figure 2 is the TEM image of CuO nanoparticle after centrifugal treatment. In addition, the pH of the prepared CuO nanofluid is 6.

Next, we undergo EPD with the better CuO nanofluid acquired by the abovementioned process. Upon repetitive experiments, it is found that better EPD performance can be acquired when the parameter is set at a deposited voltage of 230V, deposited current of 100mA, deposited time of 5 min and the distance between two electrodes is 20mm. Its surface structure is shown in Figure 3, which is the FESEM image. During the EPD, since the position of the charged ion cannot be controlled, surface roughness of the nanofilm is not very satisfactory. Also, since there is no bonding force between nanofilm and the substrate, it is necessary to undergo sintering compactness treatment for the nanofilm, so as to increase its compactness and strength.

After acquiring the EPD parameters which are more suitable to apply on the preparation of CuO thin film, since many holes are observed on the surface of the nanofilm, the compactness of CuO film is not good. As a result, it is necessary to proceed with sintering compactness treatment. After using different sintering temperature treatments for the CuO nanofilm, by observing the surface of nanofilm through FESEM, it is found that with sintering temperatures of 100℃, 300℃ and 400℃, there is no obvious improvement for the compactness of the surface of CuO thin film, and also, the phenomena of intensive congregation of nanoparticles is observed. However, when the sintering temperature is 200℃, the FESEM image in Figure 4 shows that the compactness of CuO thin film is obviously improved, and the structure of CuO nanoparticles has not been damaged because of sintering. Therefore, a more satisfactory sintering temperature for the CuO nanofilm should be 200℃. Furthermore, when using the same sintering temperature of 200℃ to investigate into the influence of different speeds of increasing temperature towards CuO nanofilm, two sets of parameters are used for comparison, which is 5℃/min and 2℃/min respectively. It is shown in Figure 5 that, when the temperature increase is too fast, the original holes on the nanofilm cannot be improved by sintering treatment. Also, particle congregation can be observed. Clearly, the compactness of CuO nanofilm in Figure 5(b) is better than that in Figure 5(a). Therefore, adopting a slower increasing temperature for the sintering treatment helps to make the CuO nanofilm more compact.

In order to accurately measure the micro-hardness of the CuO nanofilm, different depositing times (5 min,10 min and 20 min) are used to match with the EPD parameters, so as to investigate the influence of depositing time on hardness of the nanofilm. The results of micro-hardness measurement are shown in Figure 6, indicating that when the deposited time increases, micro-hardness decreases. It can also be seen in this figure that, the average micro-hardness of CuO nanofilm is over Hv 110. When using AFM to measure the nanofilm thickness, results show that when the deposited time is one minute, thickness of the film is 200nm. When the time is 2 minutes, its thickness is 250nm, and when the time reaches 5 minutes, its thickness is around 350nm.

Figure 7 shows the nanofilms prepared with the depositing times of 1 and 5 minutes. The absorption spectra that are acquired after the illumination of UV/Vis Absorbance Spectrophotometer. It can be seen from the figure that there is an obvious absorption trend of the nanofilm between the Vis wavelength and UV wavelength. Also the absorbance intensity of UV by the CuO nanofilm is increased with increased depositing time. Figure 7(a) shows that when the deposited time is set at 1 minute, the CuO nanofilm has an obvious UV-Vis absorption spectrum when the light wavelength is larger than 400nm and its peak intensity is around 0.72. Figure 7(b) also shows that when the depositing time is set at 5 minutes, and the light wavelength between 400 ~ 450nm, the absorption peak intensity is increased to 1.2.

4 CONCLUSIONS

This paper uses a CuO nanofluid produced by an Arc-Submerged Nanoparticle Synthesis System to undergo experiments, so as to search for better fabrication parameters such suitable and stable centrifugal filtering parameters, deposited voltage, deposited time, sintering temperature and increased speed for sintering temperature. It also investigates the nature and characteristics of CuO nanofilm. After many experiments and analyses, the following conclusions can be made:

1. When the centrifugal filtering parameters are set at 6000 rpm and deposited time at 5 min, a CuO nanofluid that is more suitable for application on the EPD fabrication can be obtained. Its secondary mean particle size is 30 nm, and standard deviation is 12 nm.

2. When the EPD parameters are set at a deposited voltage of 230V, deposited time of 5 min, deposited current of 100mA and the distance between two electrodes is 20 mm, a better CuO nanofilm can be acquired. Furthermore, when the sintering temperature is set at 200℃, and the speed of temperature increase is 2℃/min, a CuO nanofilm with better compactness and average micro-hardness of Hv100 can be obtained.

3. By measuring the CuO nanofilm fabricated in this study with an UV-Vis Absorbance Spectrophotometer, when the wavelength of illumination light lies within the range of 400 ~ 700nm of Vis, an obvious absorption phenomena can be observed.

REFERENCES

[1] T. Maruyama, Sol. Energ. Mater. & Sol. Cell. 56, 85, 1998.

[2] M. Frietsch, F. Zudock, J. Goschnick and M. Bruns, Sens. & Actu. 65, 379, 2000.

[3] M. Abe, and Y. Tamaura, J. Appl. Phys. 55, 2614, 1984.

[4] M. Abe, T. Itoh and Y. tamaura, Thin Solid Films. 216, 155, 1992.

[5] A. A. Foissy, and G. Robert, Ceram. Bull. 6, 251, 1982.

[6] R. W. Powers, Ceram. Bull. 65, 1270, 1982.

[7] D. U. K. Roa and E. C. Subbarao, Ceram. Bulle. 58, 467, 1979.

[8] F. Hosseinbabaei and B. Raissidehkordi, J. Euro. Ceram. Soc. 20, 2165, 2000.

[9] M. Nagai, K. Yamashita, T. Umegaki and Y. Takuma, J. Am. Ceram, 76, 253, 1993.

[10] R. Thomas R, D. C. Dube, M. N. Kamalasanan and S. Chandra, Thin Solid Films. 346, 212, 1999.

[11] T. T. Tsung, H. Chang, L. C. Chen, L. L. Han, C. H. Lo and M. K. Liu, Mater. Transact. The Japan Institute of Metals, 44, 1138, 2003.

[12] H. Chang, C. Su, C. H. Lo, L. C. Chen, T. T. Tsung and C. S. Jwo, Mater. Transact. The Japan Institute of Metals, 45, 3334, 2004.

[13] L. C. Chen, T. T. Tsung, H. Chang and J. Y. Sun, Mater.s Transac. The Japan Institute of Metals, 45, 3011, 2004.

[14] H. Chang, C. S. Jwo, C. H. Lo, T. T. Tsung, M. J. Kao and H. M. Lin, Review. Advanc. Mater. Sci. 10, 128, 2005.

[15] H. Chang, T. T. Tsung, C.H. Lo, H. M. Lin, C. K. Lin, L. C. Chen and C. S. Jwo, J. Mate. Sci. 40, 1005, 2005.

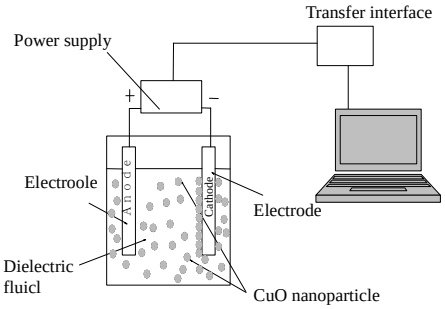


Figure 1: Schematic diagram of EPD fabrication equipment.

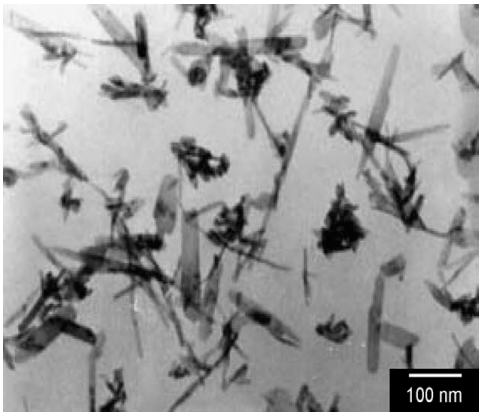


Figure 2: TEM image of CuO nanoparticles after centrifugal treatment.

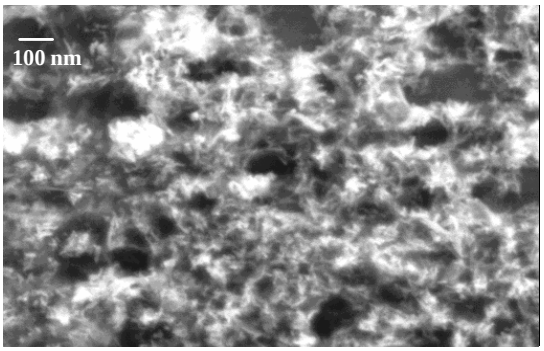


Figure 3: FESEM image of the surface structure of nanofilm.

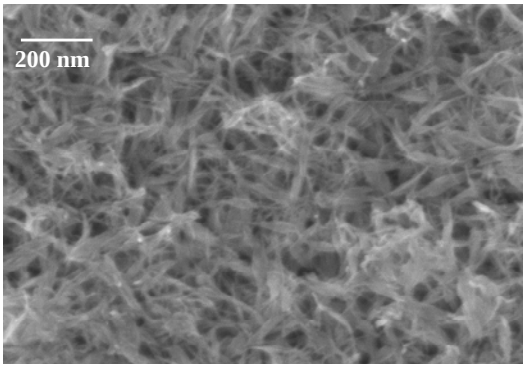
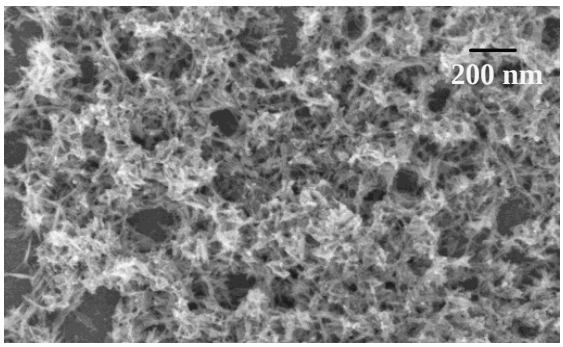
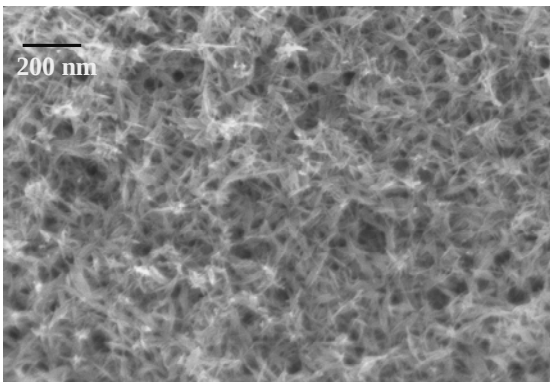


Figure 4: FESEM image of the surface structure of CuO sintering to 200℃.



(a)



(b)

Figure 5: FESEM image of CuO nanofilm with speeds of temperature increase of (a) 5℃/min (b) 2℃/min.

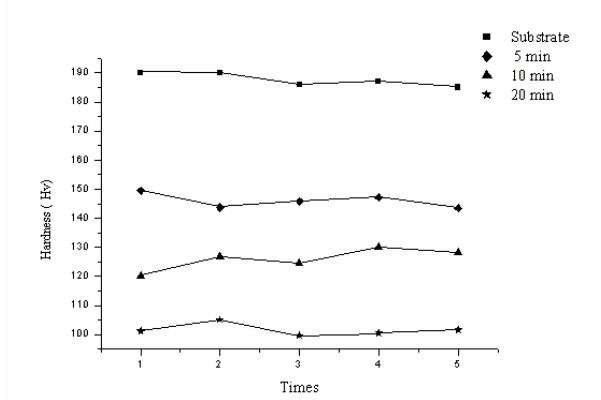
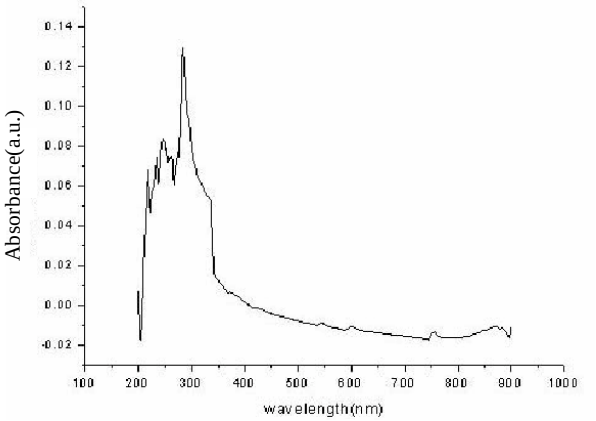
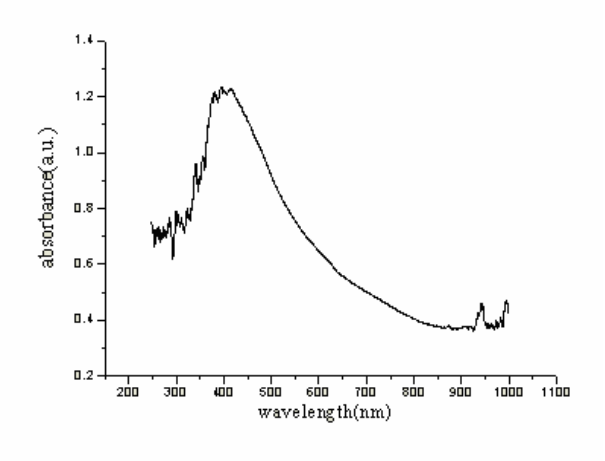


Figure 6: Micro-hardness of CuO nanofilms under different depositing times.



(a)



(b)

Figure 7: UV-Vis absorption spectra of CuO nanofilms with a depositing time of (a) 1 minute and (b) 5 minutes.