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Original Research

# Preparation of CoP films by ultrasonic electroless deposition at low initial temperature

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**Abstract**

Electroless deposition technology has been considered as a kind of common ways to obtain cobalt alloy films. However, in order to get cobalt alloy films, high temperature (353 K) is necessary during the electroless deposition process which will increase costs and energy consumption. Ultrasonic was introduced during electroless plating process to obtain cobalt alloy films at lower initial temperature. It was found that the cobalt thin films could be prepared at lower initial temperature (323 K) with the introduction of ultrasonic. Therefore, different powers of ultrasonic were applied during the electroless deposition process to prepare CoP thin films on copper substrates from an alkaline bath in this investigation. The effects of different powers of ultrasonic on deposition rate, surface morphology, anticorrosion performance and magnetic property of films were studied. It was found that the deposition rate increased gradually with the rise in ultrasonic powers due to cavitation phenomenon. All the CoP films presented the typical spherical nodular structures with the impact of ultrasonic. Smaller and regular shaped structures could be observed when the films were deposited with higher power of ultrasonic which contributed directly to enhancement of anticorrosion performance. Saturation magnetization and coercivity of thin films increased gradually with the rise in ultrasonic powers during the electroless deposition process due to the higher amounts of cobalt.
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*Keywords:* Ultrasonic; Electroless deposition; Magnetic thin films; CoP films

## 1. Introduction

With the development of microelectronic devices, magnetic thin films are starting to attract attention. Cobalt is an element with great ferromagnetic and anticorrosion performance. It is found out that cobalt alloy thin films are potential materials in the field of electronics and magnetics industry and some kinds of cobalt alloys have been reported so far [1–6]. For example, CoW alloy films possess optimal magnetic performances which could be used in the field of magnetic storage system. Due to their great abrasion resistance, CoCr films have many applications in mechanical system. CoPt films are considered as a kind of hard magnetic films with higher coercivity. Meanwhile, CoP films not only possess great magnetic performances, but also have wonderful anticorrosion resistances which have potential applications in the field of integrated sensors and circuit systems. For instance, copper interconnections in microelectronic devices are very common in integrated circuits. However, oxidation and easy diffusion into $SiO_2$ layers are the major drawbacks of copper interconnections which may degrade the performance of microelectronic devices. It is essential to introduce barrier layers with dielectric or metallic materials to prevent copper from oxidation and diffusion. In this case, CoP layer has been found as a kind of promising material because of its better barrier capability and performance. Cobalt alloy films could be obtained by many approaches, such as electro-deposition, physical vapor deposition and so on. Meanwhile, the electroless deposition known as

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autocatalytic plating is an effective and efficient way to prepare thin films. [7–9] Consequently, some studies have been reported about preparing cobalt alloy films by electroless deposition. Electroless CoFeB films with good soft magnetic properties were fabricated by Liu [10]. Huang investigated performance of NiCoP alloy films obtained by electroless deposition [11]. A method of electroless plating was utilized to deposit CoFe films to test their electromagnetic properties by Yan [12]. Electrical property of electroless CoB films was studied by Anik [13]. Although high magnetic and electrical properties of Co alloy films could be obtained by electroless plating technology, electroless methods still possess some disadvantages. Higher temperature is necessary for the electroless deposition process. Generally speaking, operation temperature during the electroless deposition process of Co alloy films should be higher than 353 K which would increase costs and energy consumption. Moreover, films obtained with higher temperatures usually posses rough surface with agglomerate morphologies. Hence, it is necessary to find a method to obtain Co alloy films by electroless deposition at relative low initial temperature. Traditional energy input during electroless deposition is based on water bath heating. Ultrasonic is also a kind of energy input which is clean and safe. Ultrasonic with different powers were applied during the electroless deposition process to investigate their effects on deposition rate, surface morphology and properties of CoP films.

## 2. Experimental

Different powers of ultrasonic with the same frequency 40 KHz were introduced during the electroless deposition process to prepare CoP alloy films on a copper substrate. Influences of various ultrasonic powers on the deposition rate, surface morphology and magnetic properties of the films were investigated. The composition of the electroless deposition bath (100 ml) with 0.1 mol $L^{-1}$ $CoSO_4$, 0.2 mol $L^{-1}$ $NaH_2PO_2$ and 0.5 mol $L^{-1}$$C_4H_4KNaO_6$ is listed in Table 1. All the chemical agents are bought from Aladdin Industrial Corporation of Shanghai. The working temperature was kept at 323 K and the bath pH value was adjusted to 11 with NaOH at the start of ultrasonic electroless deposition. Finally, the copper substrate was put into 100 ml electrolyte to perform ultrasonic electroless deposition for one hour. Detailed information about experimental procedure is shown in Fig. 1.

Thickness and roughness of CoP thin films were measured with profile meter (Klatencor P-6). Scanning electron microscope (Hitachi S-4700) was used to observe the surface morphology of CoP films prepared with ultrasonic electroless deposition. Magnetic properties were tested by vibration sample magnetometer (Lakershore VSM7407).

Table 1
Composition of ultrasonic bath for CoP films.

| Component | Function | Concentration (mol $L^{-1}$) |
|---|---|---|
| $CoSO_4(7H_2O)$ | Source for Co ions | 0.1 |
| $NaH_2PO_2(H_2O)$ | Reducing agent | 0.2 |
| $C_4H_4KNaO_6$ | Complexing agent | 0.5 |

## 3. Result and discussion

### 3.1. Ultrasonic electroless deposition process

Sketch map of the ultrasonic electroless deposition process is shown in Fig. 2. According to the Fig. 2, the copper substrate was at the bottom of beaker which was full of 100 ml electrolyte. The beaker was put into the water bath system with initial temperature of 323 K. Ultrasonic waves were transmitted from the bottom up during the ultrasonic electroless

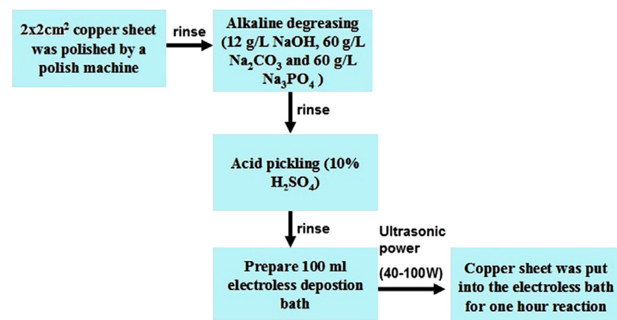


Fig. 1. Flow chart of the ultrasonic electroless deposition process.

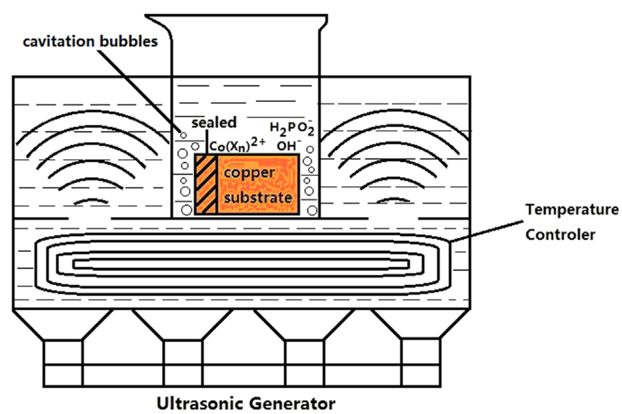


Fig. 2. Sketch map of the ultrasonic electroless deposition process.

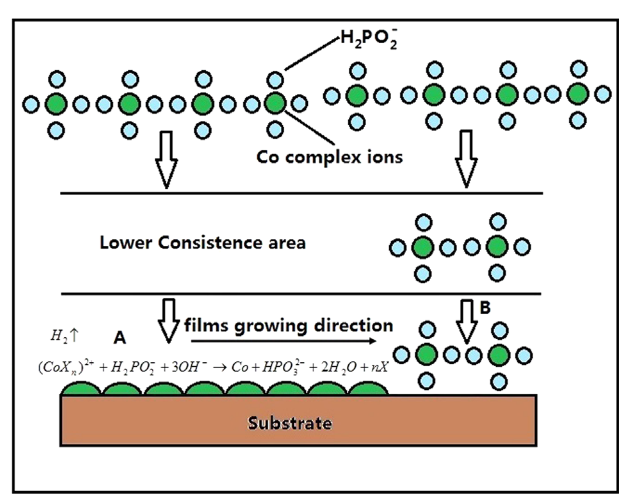


Fig. 3. The growth mechanism of electroless plating.

deposition process. Ultrasonic cavitation phenomenon is the main aspect that affects the chemistry reaction process during electroless deposition [14,15]. When the ultrasonic wave is introduced in the solution, medium molecules vibrate around the equilibrium position. If the intensity of ultrasonic wave is large enough, average distance of molecules will increase extremely to destroy structural integrity of the liquid which could result in formation of the cavitation bubbles. Collapse of some cavitation bubbles is accompanied by higher temperature and pressure with the impact of ultrasonic waves. It is found that the ultrasonic cavitation can produce 5000 K instantaneous high temperature and enhance the collision process between molecules which could affect the chemistry deposition process. With the interaction of cavitation, ultrasonic can effectively improve mass and heat transfer, change the phase equilibrium process and fasten chemistry reaction rate.

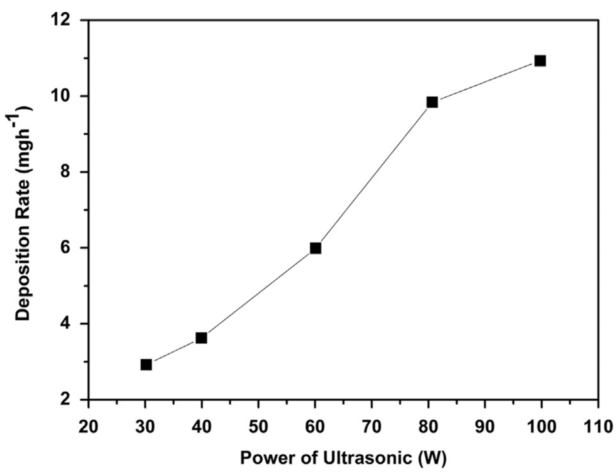


Fig. 4. Effects of ultrasonic powers on electroless deposition rates.

### 3.2. Deposition rate and thickness

Electroless plating known as autocatalytic plating is a kind of chemical process. Electroless CoP alloy films plating is based on the use of cobalt salt solution with the action of strong reducing agent—sodium hypophosphite to prepare cobalt and phosphorus on the surface of catalytic activity. Chemical reaction mechanism can be described as the

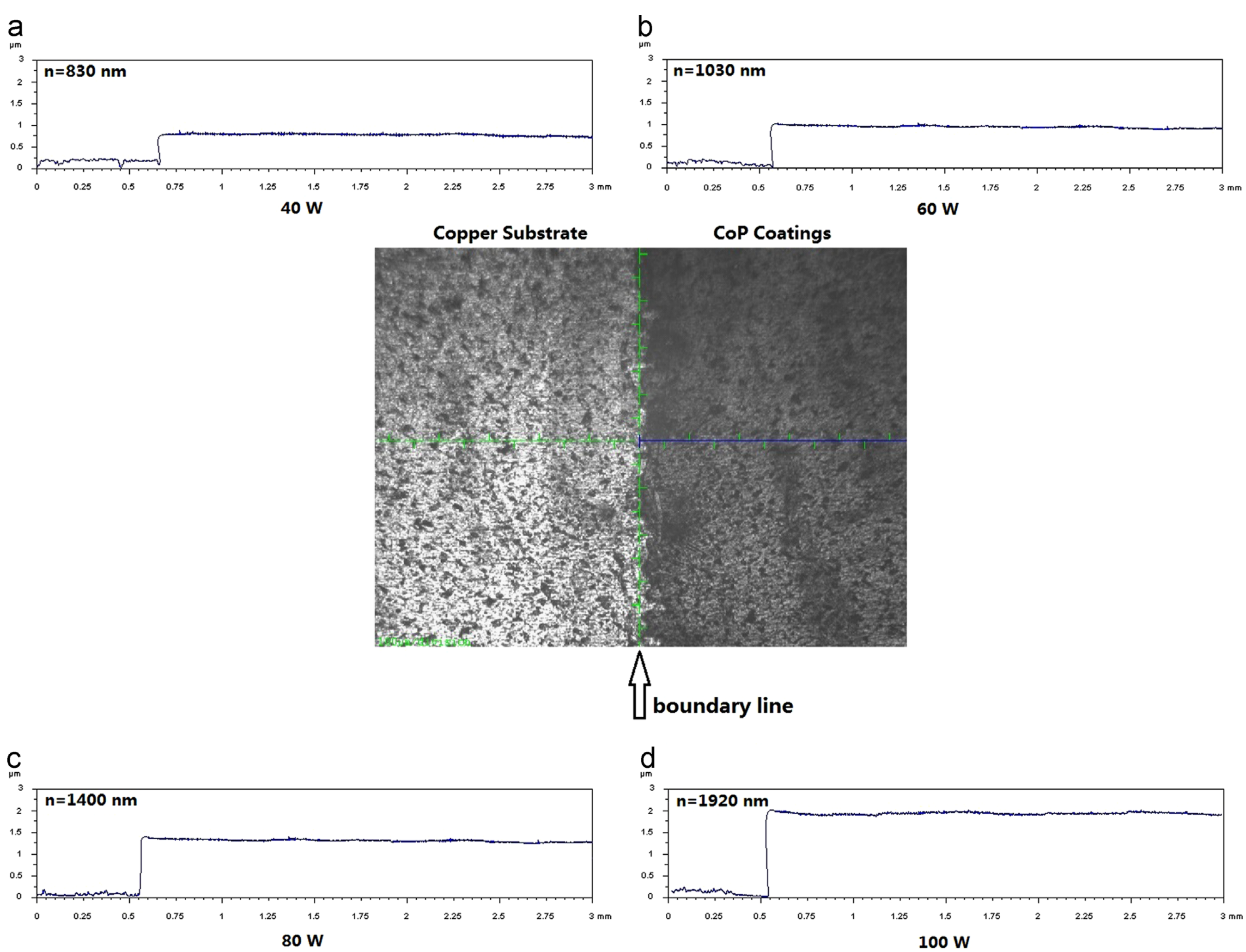


Fig. 5. Thickness of CoP films prepared with different ultrasonic powers.

following equations: [16,17]

$$(\mathrm{CoX}_n)^{2+} + \mathrm{H_2PO_2^-} + 3\mathrm{OH^-} \rightarrow \mathrm{Co} + \mathrm{HPO_3^{2-}} + 2\mathrm{H_2O} + n\mathrm{X} \quad (1)$$

$$3\mathrm{H_2PO_2^-} \overset{\text{catalysis}}{\Longrightarrow} \mathrm{H_2PO_3^-} + \mathrm{H_2O} + 2\mathrm{OH^-} + 2\mathrm{P} \quad (2)$$

$$\mathrm{H_2PO_2^-} + \mathrm{H_2O} \overset{\text{catalysis}}{\Longrightarrow} \mathrm{H_2PO_3^-} + \mathrm{H_2}\uparrow \quad (3)$$

Electroless deposition process consists of several steps: (a) cobalt-complex and hypophosphite ions are transported to the surface of substrate; (b) ions are absorbed on the surface of substrate as adatoms; (c) chemical reactions on the surface of catalytic activity; (d) desorption of products ($H^+$, $H_2$, $H_2PO_3^-$, etc.); and (e) products moving away from the surface;

The growth mechanism of electroless plating is shown in Fig. 3. The chemical reactions often occur on the surface of catalytic activity [18]. The reduction reactions start along the surface expansion and eventually the entire substrate is covered with a layer of film. However, the bath concentration near the films makes the reduction reactions hard to continue. In this case, the deposition rate is very slow in the perpendicular direction. In order to increase the deposition rate, it is necessary to use other means like agitation to unify the concentration near films. Introducing ultrasonic waves during electroless deposition can be considered as a function of agitation to affect deposition rate [19]. Therefore, influence of ultrasonic waves with different powers on deposition rate and thickness of CoP films were investigated in this investigation. The effects of ultrasonic powers on electroless deposition rates are shown in Fig. 4. It is conspicuous that the deposition rate increased gradually with the rise in ultrasonic powers. Higher deposition rate of the ultrasonic electroless depsotion process at relative low initial temperature is due to the phenomenon of ultrasonic cavitation and agitation mentioned above. On one hand, activation state of hydrogen with the impact of ultrasonic is helpful to improve reduction performance and deposition rate of cobalt. One the other hand,

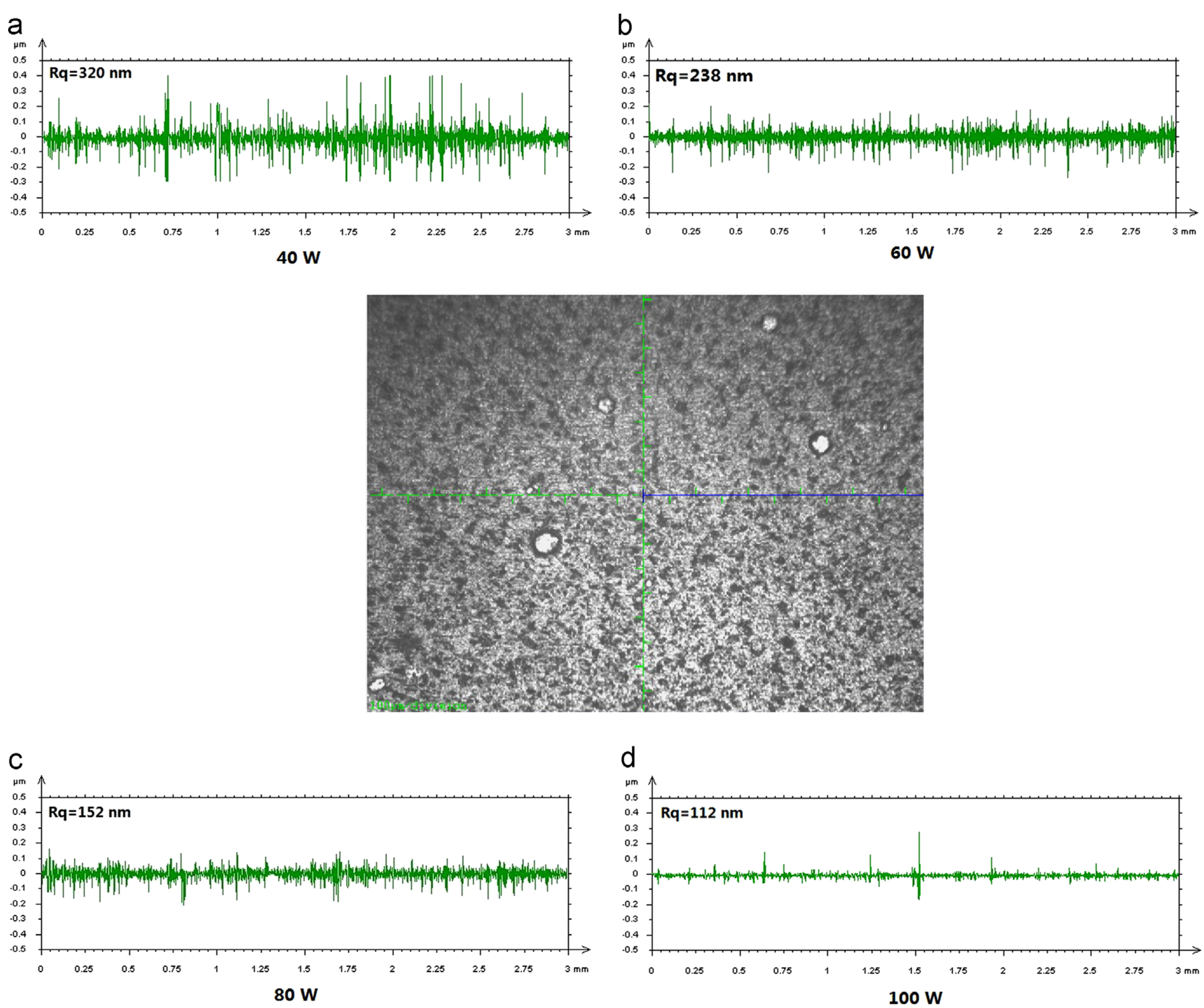


Fig. 6. Roughness of CoP films prepared with different ultrasonic powers.

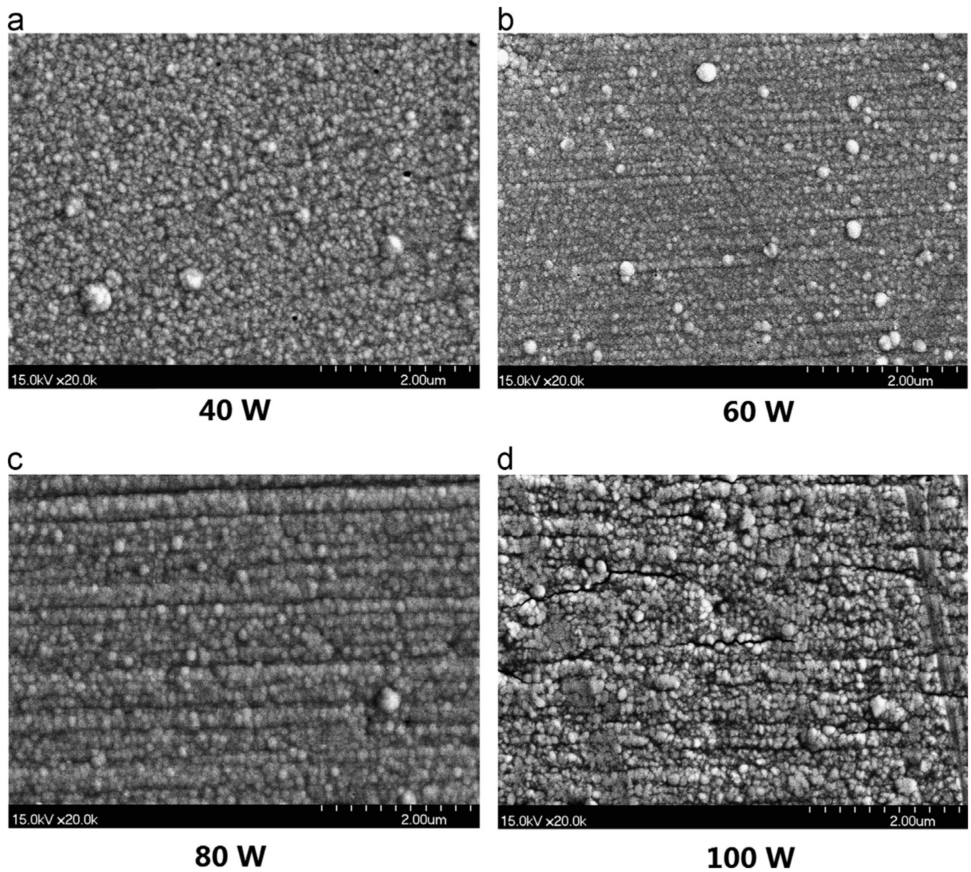


Fig. 7. Effects of ultrasonic powers on surface morphology of films.

Table 2
Hardness of CoP thin films obtained by different ultrasonic powers.

| Ultrasonic power (W) | Force (kg) | Diagonal $D_1$ (mm) | Diagonal $D_2$ (mm) | Hardness (HV) |
|---|---|---|---|---|
| 40 | 0.5 | 2.87 | 2.83 | 182.65 |
| 60 | 0.5 | 2.53 | 2.49 | 235.48 |
| 80 | 0.5 | 2.33 | 2.38 | 267.49 |
| 100 | 0.5 | 2.33 | 2.27 | 293.04 |

collapse of cavitation bubbles produced by ultrasonic could produce higher instantaneous temperature to enhance molecules collisions and accelerate cobalt deposition rate.

Thickness and roughness of CoP films prepared by different ultrasonic powers are shown in Figs. 5 and 6, respectively. In order to measure the thickness precisely, a small area of the substrate was sealed before the experiment. The boundary line between copper substrate and CoP coatings could be obtained after the ultrasonic electroless deposition process. Average step height from copper substrate to CoP coatings measured by profile meter is considered as the thickness of films. It has been found that thickness of films increased from 830 nm to 1920 nm with the rise in ultrasonic powers from 40 W to 100 W. Reduction reactions started on the catalytic activity surface of copper substrates during the electrodeposition process. When the substrate was covered with CoP films, deposition rate decreased due to lower metal ions concentration near the films. Ultrasonic waves with higher powers could agitate and increase molecules collisions near areas with lower metal ions concentration to extremely increase perpendicular deposition rate and thickness of films. Moreover, with the ultrasonic powers increase from 40 W to 100 W, roughness of CoP films ranges from 320 nm to 112 nm. It is clear that ultrasonic applied during the electroless deposition process could crash and agitate the surface of films to obtain films with compact and smooth morphology.

### *3.3. Surface morphology and hardness*

Surface morphologies of CoP thin films prepared with different powers of ultrasonic are shown in Fig. 7. All the CoP films presented the typical spherical nodular structures with the impact of ultrasonic. It has been found that the films fabricated with 40 W ultrasonic possess some agglomerate structures. Relatively smaller and regular shaped structures could be observed when the films are deposited with 80 W ultrasonic. Cavitation phenomenon of ultrasonic with higher powers could agitate and increase molecules collisions near films surface to smooth surface structures. However, some cracks on the surface of films could be observed when the ultrasonic power is up to 100 W. Therefore, although ultrasonic could help to prepare films with dense and compact structures, if the ultrasonic power is too larger, tiny cracks

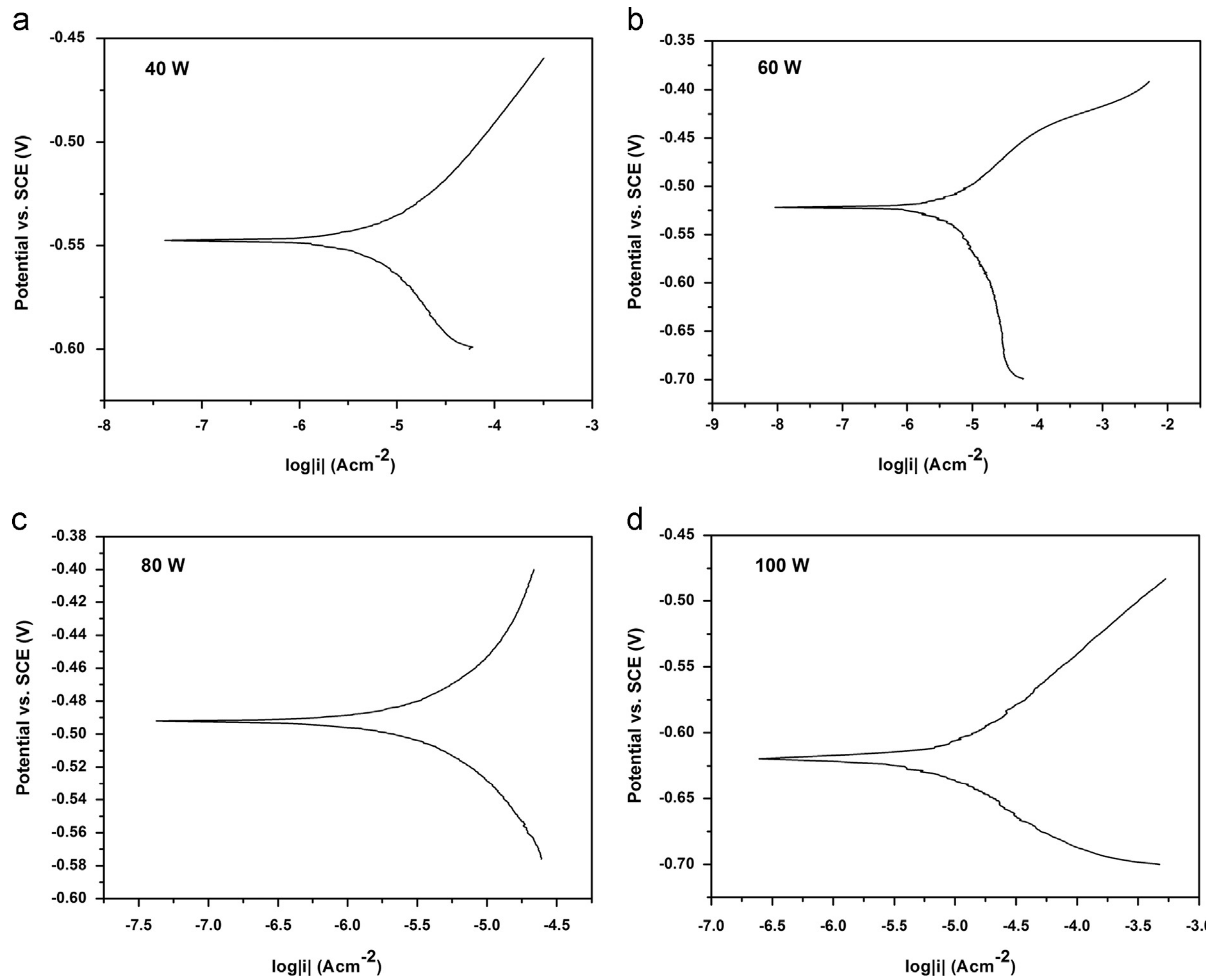


Fig. 8. Polarization curves of CoP alloy films.

Table 3
Corrosion potential and current of CoP films.

| Ultrasonic powers (W) | Corrosion potential (V) | Corrosion current (μA) |
|---|---|---|
| 40 | −0.547 | 12.59 |
| 60 | −0.521 | 5.01 |
| 80 | −0.492 | 1.99 |
| 100 | −0.618 | 19.7 |

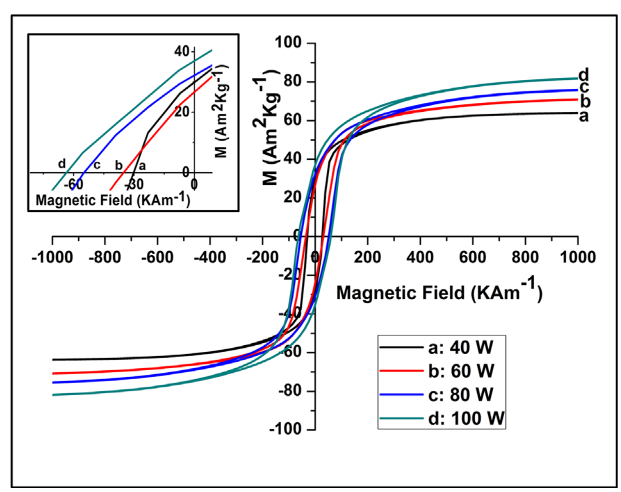


Fig. 9. Magnetic hysteresis loops of CoP alloy films.

would be easily formed on the surface of films due to drastic cavitation effects.

Vickers hardness tester was used to measure the hardness of films in Table 2. It has been found that CoP thin films prepared with higher powers of ultrasonic possess higher thickness and compact structures which contribute directly to the rise in hardness.

### 3.4. Anticorrosion performance

Electrochemistry polarization method was used to analyze the corrosion process of CoP thin films, and the results are shown in Fig. 8. The corrosion potential and current of CoP films are summarized in Table 3. According to Fig. 8, CoP films prepared with 80 W ultrasonic possess the most positive corrosion potential (−0.492 V) and lowest corrosion current (1.99 μA ). It means that CoP films obtained in the condition of 80 W ultrasonic have optimal anticorrosion performance. Moreover, with the increase of ultrasonic power from 40 W to 80 W, the corrosion current of CoP thin films decreased, which means that anticorrosion performance of the samples improved. However, compared with the other films, the films obtained with 100 W ultrasonic possess poor anticorrosion performance with the most negative corrosion potential (−0.618 V) and largest corrosion current (19.7 μA). Compact and dense films with smaller nodular structures could be formed with the rise in ultrasonic powers. Smaller nodular structures and dense surface may help to distribute corrosion currents during the polarization process to increase anticorrosion of films. Nevertheless, tiny cracks would be easily formed on the surface of films if higher power ultrasonic is introduced, which contribute directly to the decrease of anticorrosion performance.

#### 3.4.1. Magnetic performance

CoP thin films deposited with different ultrasonic powers show various magnetic properties. According to Fig. 9, with the increase of ultrasonic powers, saturation magnetization slightly increases from 64 $Am^2 Kg^{-1}$ to 82 $Am^2 Kg^{-1}$. Fast deposition rate could be obtained during electroless deposition with higher ultrasonic powers which contribute to larger amounts of cobalt in the films, resulting in the rise in saturation magnetization. Moreover, coercivity of films starts to increase from about 30 $kAm^{-1}$ to 62 $kAm^{-1}$ when the ultrasonic powers increase from 40 W to 100 W. Compact and dense films with smaller nodular structures could be formed with the rise in ultrasonic powers, which attribute to the increase of coercivity.

## 4. Conclusions

CoP thin films were prepared on copper substrates from an alkaline bath by ultrasonic electroless at lower initial temperature of 323 K. The influences of different ultrasonic powers on deposition rate, roughness, anticorrosion performance and magnetic property were investigated.

The deposition rate increased gradually with the rise in ultrasonic powers due to cavitation and agitation phenomenon. Ultrasonic waves with higher powers could agitate and increase molecules collisions near lower concentration areas to extremely increase perpendicular deposition rate and thickness of films.

All the CoP films present typical spherical nodular structures with the impact of ultrasonic. Ultrasonic applied during the electroless deposition process could crash and agitate the surface of films to obtain films with compact and smooth morphology. Smaller and regular shaped structures could be observed when the films were deposited with higher power of ultrasonic, which contributed directly to enhancement of anticorrosion performance.

CoP films prepared with 80 W ultrasonic possess the most positive corrosion potential (−0.492 V) and lowest corrosion current (1.99 μA), which indicates that the films have optimal anticorrosion performance. However, films with cracks could be obtained if the ultrasonic power was further increased, which is attributed to the decrease of anticorrosion performance. Saturation magnetization and coercivity of the thin films increase gradually with the rise in ultrasonic powers during the electroless deposition process which is due to the higher amounts of cobalt.

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