Short Communication

Study on Preparation of NiFe Coating on Silicon by Pulse Electrodeposition and its Magnetic Property

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NiFe alloy coatings were prepared on silicon used for computer field by pulse electrodeposition. The effect of different pH values on the cyclic voltammetry, composition, structure, surface morphology and magnetic property of NiFe coatings was studied. NiFe electrodeposition is discovered to be a type of anomalous co-deposition. Appropriately increasing the pH value of the bath is beneficial to increase the overpotential and enhance the cathode polarization, which can accelerate the deposition rate and refine the surface grains. However, when the pH value of the plating solution is larger than 5, a large amount of ferrous ion in solution is converted into iron ions, resulting in a significant quantity of iron hydroxide precipitation, which inhibits the electrodeposition process and decrease the crystallinity of the NiFe coating. The NiFe alloy prepared from bath with pH equal to 5 has good crystallinity and excellent magnetic property. NiFe electrodeposited coating exhibits better perpendicular magnetic anisotropy because its magnetic property in the perpendicular direction is superior to that in the parallel direction.

1. INTRODUCTION

Magnetic materials are widely used in the computer fields. For example, computer speakers, optical disk drivers, disk drivers, magnetic storage media, fans and monitors all contain magnetic materials [1-4]. In recent years, with the rapid development of electronic computers and micro-motors, electronic components are increasingly becoming more miniaturized, integrated and intelligent. Because the size of traditional bulk magnetic materials is difficult to reach the micron level and nanometer level, it cannot fully meet the needs of micro-electronic components. With the development of thin coating technology, the use of chemical and physical methods to prepare micron or nanometer magnetic thin coating materials can well meet the needs of micro-electronic components in computer field. For example, many researchers prepare Co-based coating with optimal magnetic property by

electrodeposition [5-9]. Some people use electroless deposition technology to prepare CoP, CoNi and CoFe magnetic coating which can be used as the magnetic read-write head for computer [10-13]. Vapor deposition method is also reported to obtain Co-based alloy coating with optimal magnetic property [14-16].

It is known that there are numerous methods that can be utilized to manufacture magnetic thin coating in accordance with the results stated in the literature. Physical methods such as magnetron sputtering, vapor deposition and ion beam epitaxy can produce nano-scale and micro-scale magnetic coatings, but the cost is too high and the parameter setting is complicated. Compared with physical methods, chemical methods such as electrodeposition and electroless plating can produce thin coatings with optimal magnetic property more easily. Moreover, chemical methods have the advantages of simple equipment and lower cost. Electrodeposition is one of the most commonly used methods to prepare magnetic thin coating materials in the laboratory. It is very effective and efficient to prepare magnetic coating by controlling the proper temperature, pH value, current density, and other process factors during electrodeposition. However, the electrodeposition method also has some disadvantages, such as concentration polarization and hydrogen evolution, which will affect the electrodeposition efficiency and magnetic properties of the coating. It is found that pulse electrodeposition has many advantages, for example, pulse electrodeposition can suppress the concentration polarization phenomenon in the process of electrodeposition, so as to obtain the metal coating with better surface [17-19]. In addition, the pH value is a very important process parameter in the electrodeposition process. Hydrogen evolution is serious on the surface of cathode when pH value is small, which is not conducive to improve the efficiency of electrodeposition. However, higher pH value is easy to produce metal hydroxides that hinder the progress of the reaction. Therefore, in this paper, NiFe alloy magnetic coating was prepared on silicon by pulse electrodeposition technology, and the effect of pH value on cyclic voltammetry, deposition rate, morphology, structure and magnetic properties of NiFe alloy magnetic coating during the electrodeposition process was studied.

2. EXPERIMENTAL

2.1 Materials and technological parameter

The surface size of silicon is 2 cm×2 cm which is chosen as the substrate and the pure platinum sheet (3 cm×3 cm) is as the counter electrode. The chemical agents used to prepare 100 ml plating solution are as followings: $NiSO_4 \cdot 6H_2O$ 60 g/L, NaCl 30 g/L, $FeSO_4 \cdot 7H_2O$ 20 g/L, $C_6H_8O_7$ 100 g/L, H_3BO_3 30 g/L. Four cups of plating solution with 100 ml were prepared. The dilute hydrochloric acid or sodium hydroxide was used to adjust the pH value of plating solution to 3, 4, 5 and 6. Before the pulse plating, the silicon is immersed into the 100 ml acid solution for 5 minutes (10 ml 40%HF, 40 ml 68%HNO_3 and 50 ml pure water) to make pretreatment. After that, the silicon was cleaned and put into the plating solution to prepare NiFe coating on the silicon surface for 3600 s at the condition of 60 ℃ temperature, 0.5 duty ratio, 0.05 frequency and 2 A/dm^2 current density. After the pulse plating is finished, the samples are cleaned and dried to do the testing.

2.2. Testing methods

The electrochemical station (CHI760e) is used to test the cyclic voltammetry curves of silicon in the different plating solutions to investigate the electrodeposition process of Ni, Fe and NiFe. The size of silicon is 1 cm×1 cm as the cathode and the anode is the pure platinum sheet with size of 3 cm×3 cm. The saturated calomel electrode is as the reference electrode. The scan voltage is between -1.2 V~0.2 V at the scan rate of 10 mV/s. The high precision electronic balance (ATY124R) is used to calculate the electrodeposition rate of NiFe coating based on the weight gain. The composition of NiFe alloy coating on silicon is tested by energy dispersive X-ray detector (EDX4500) at the condition of 40 kV. The scanning electron microscopy is used to observe the surface morphology of NiFe coatings at 15 kV accelerating voltage while the structure of samples is characterized by X-Ray diffraction (PW3020) from 30° to 90° at the scan rate of 3°/s. Finally, the magnetic property of NiFe electrodeposited coating is evaluated by vibrating sample magnetometer (Lakeshore 7407) at the condition of -1.5 T~1.5 T applied magnetic field.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry curves of NiFe electrodeposition
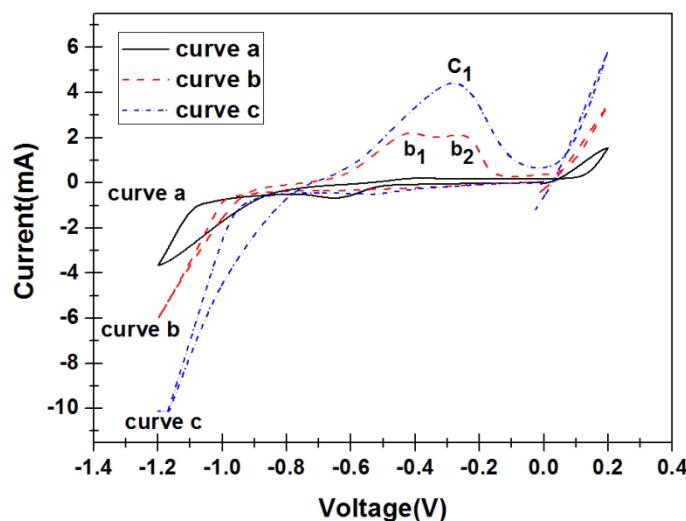
Figure 1. Cyclic voltammetry of silicon in different plating solutions: curve a. cyclic voltammetry of silicon in 0.01 mol/L $FeSO_4$ solution; curve b. cyclic voltammetry of silicon in 0.01 mol/L $NiSO_4$ solution; curve c. cyclic voltammetry of silicon in 0.01 mol/L $FeSO_4$ mixed with 0.01 mol/L $NiSO_4$ solution; The scan voltage is ranged from -1.4 V~0.2 V at the scan rate of 10 mV/s;

The cyclic voltammetry curves of Ni, Fe and NiFe electrodeposited on the surface of silicon are shown in Figure 1. According to curve a, the nickel electrodepsotion is predominate at the potential of -0.79 V where the cathode current begins to increase significantly. From the curve b, when the voltage

is moved to -0.97 V, the current on the silicon increases extremely that indicates the drastic reduction reaction of Fe. Moreover, two oxidation peaks (b_1 and b_2) can be observed at the position of -0.42 V and -0.28 V respectively which represent the oxidation of Fe. Regarding to the curve c, the cathode current of NiFe electrodeposition increases dramatically at the position of -0.85 V which is between that of Ni and Fe electrodeposition. The oxidation peak of NiFe is observed at the position (c_1) of -0.26 V which is more positive than Fe.

According to the study, the co-deposition of nickel and iron belongs to anomalous co-deposition [20-22]. It means that the Fe ions with more negative potential can be co-deposited together with nickel with more positive potential. Even if the concentration of Fe ions in the bath is very low, Fe ions can still precipitate together with nickel ions to form alloys, and the rate of Fe ion deposition is greater than that of nickel ion deposition. The anomalous co-deposition of NiFe alloy may be due to the reduction of hydrogen ions during the electrodeposition to increase the pH value near the cathode, resulting in the formation of ferrous hydroxide. The ferrous hydroxide adsorbed on the cathode surface inhibits the reduction and precipitation of nickel ions to a certain extent, thus increasing the electrodeposition rate of iron ions to form NiFe alloy.
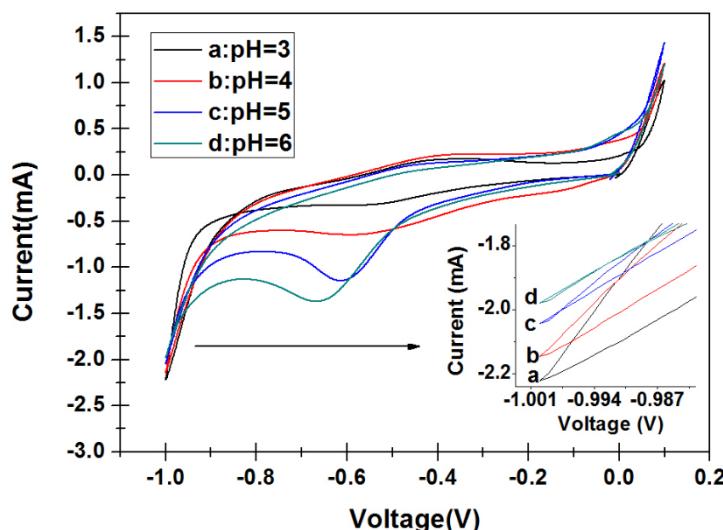
Figure 2. Cyclic voltammetry of NiFe electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6. The scan voltage ranges from -1.0 V~0.2 V at the scan rate of 10 mV/s in the plating solution with 0.01 mol/L FeSO4 and 0.01 mol/L NiSO4;

The electrodeposition of Ni and Fe can be explained by the Equations (1)~(4) below which is also reported by others [23-24]. Fe ions get electrons to be reduced to iron through ferrous hydroxide colloidal. The hydroxide of nickel gains electrons and is reduced to nickel.

$$Fe^{2+} + 2OH^- \Leftrightarrow Fe(OH)_2 \qquad (1)$$

$$Fe(OH)_2 + 2e \Leftrightarrow Fe + 2OH^- \qquad (2)$$

$$Ni^{2+} + H_2O \Leftrightarrow (NiOH)^+ + H^+ \qquad (3)$$

$$(NiOH)^+ + 2e + H^+ \Leftrightarrow Ni + H_2O \qquad (4)$$
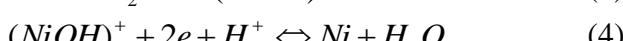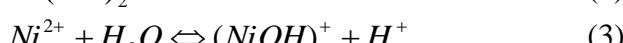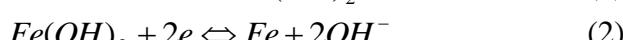
The effect of pH value on the cyclic voltammetry of NiFe electrodeposition can be seen in Figure 2. It is obvious that pH value has a significant influence on the cyclic voltammetry curve of

NiFe electrodeposition. The cathode current of NiFe electrodeposited from plating solution of pH value 3, 4, 5 and 6 is about -2.22 mA, -2.14 mA, -2.03 mA and -1.965 mA respectively. With the increase of pH, the cyclic voltammetry curve of NiF alloy electrodeposition shifts to the left direction, which leads to the gradual increase of the overpotential, so the polarization effect of cathode is enhanced. The increase of overpotential is beneficial to increase the nucleation rate and refine the grains, so as to obtain uniform and compact coating. This is because increasing the pH value of the bath contributes to the formation of a large amount of ferrous hydroxide on the cathode surface, which can increase the discharge rate of ferrous ion, but slow down the discharge rate of nickel ion, so as to improve the cathode polarization. The effect of pH value of plating bath on electrodeposition is investigated in some papers too [25-26].

3.2 Deposition rate and composition of NiFe electrodeposited coating

The relationship between pH value and deposition rate of NiFe coating is shown in Figure 3. It can be seen that, with the increase of pH value, the deposition rate of NiFe coating electrodeposition increases to a maximum value and then decreases gradually. When the pH value increases from 3 to 6, the deposition rate is ranged from approximate 19.83 mg/h to 39.12 mg/h. The NiFe coating prepared from plating solution of pH=5 has the maximum deposition rate equal to 39.12 mg/h. According to the analysis of cyclic voltammetry, increasing the pH value of solution is beneficial to increase overpotential to enhance cathode polarization, leading to the increase of deposition rate. The relationship between pH value and cathode polarization is studied in the published paper [27]. Moreover, the influence of pH value on the current efficiency during electrodeposition is studied by Srivastava [28]. However, when the pH reaches 6, too higher pH value can make the stability of the bath decrease, which is easy to produce a large number of metal hydroxides, so that the deposition efficiency and deposition rate decrease significantly.
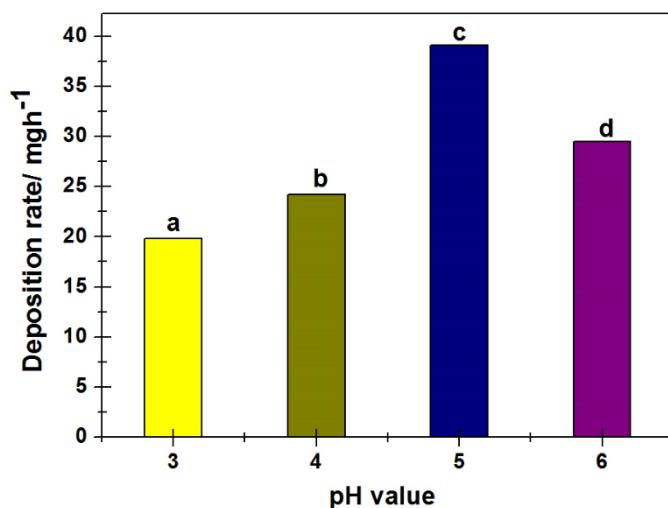
Figure 3. Deposition rate of NiFe coating electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6;

Figure 4 shows the influence of pH value on the chemical composition of NiFe electrodeposited coating. It can be seen that the composition of NiFe coating prepared from plating solution of different pH values is totally different. With the increase of pH value from 3 to 5, the amounts of nickel in NiFe coating decrease gradually while the content of iron increases to a maximum value. This is because the increase of pH value is in favor of the formation of ferrous hydroxide on the cathode surface, which can increase the discharge rate of ferrous ion, but slow down the discharge rate of nickel ion, so as to improve the amount of iron in the NiFe coating. However, when the pH value reaches 6, the iron content in the NiFe alloy coating decreases sharply. This is because if the pH value is too high, the ferrous ions in the bath will be converted into iron ions, resulting in a large amount of iron hydroxide precipitation, which is not conducive to the electrodeposition of iron, leading to a sharp decline of iron content in the NiFe coating. The relationship between pH value and iron content in the electrodeposited coating is researched by Winiarski [29].
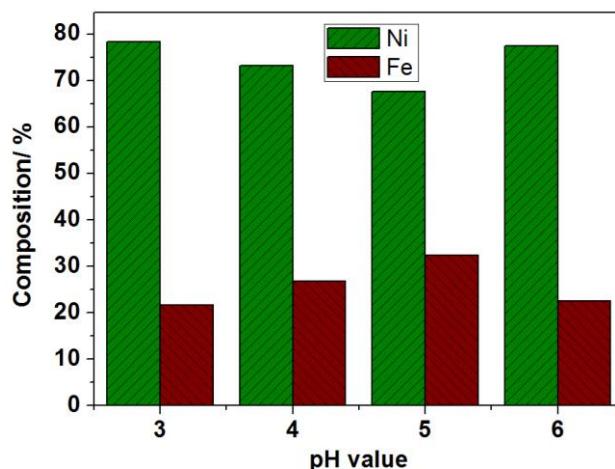
Figure 4. Composition of NiFe coating electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6;

3.3 Structure and surface morphology of NiFe electrodeposited coating

The XRD patterns of different NiFe coatings are shown in Figure 5. According to the XRD patterns, it is clear that all the prepared NiFe coatings are crystalline. Three strong diffraction peaks could be detected at the position of $2\theta=44.2°$, $2\theta=51.5°$ and $2\theta=74.8°$ respectively which represent the NiFe(111), NiFe(200) and NiFe(220). The intensity of diffraction peak is strong indicating better crystallinity. Similar structure of NiFe electrodeposited coating is reported in the literatures too [30-31]. Moreover, Xu also find that the amount of nickel in the NiFe coating can affect the structure of NiFe alloy [32]. With the increase of pH value, the diffraction intensity of all three peaks all increase gradually and then decrease. The NiFe alloy coating prepared from electroplating solution of pH=5 has the strongest diffraction intensity, which is mainly attributed to that the appropriate pH value is beneficial to increase the cathode polarization and the deposition rate, resulting in the improvement of phase content. When the pH value of solution is equal to 6, the deposition rate of NiFe alloy is greatly

reduced due to the large amount of iron hydroxide precipitated, which leads to a decrease in crystallinity.
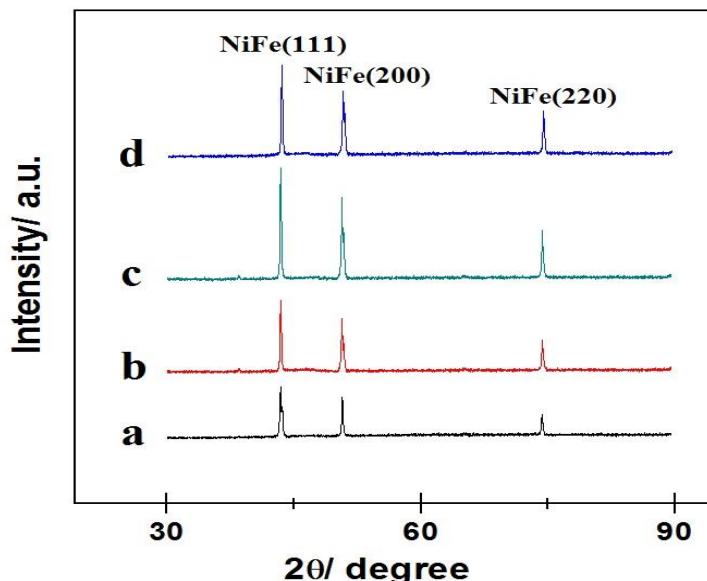
Figure 5. XRD pattern of NiFe coating electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6;
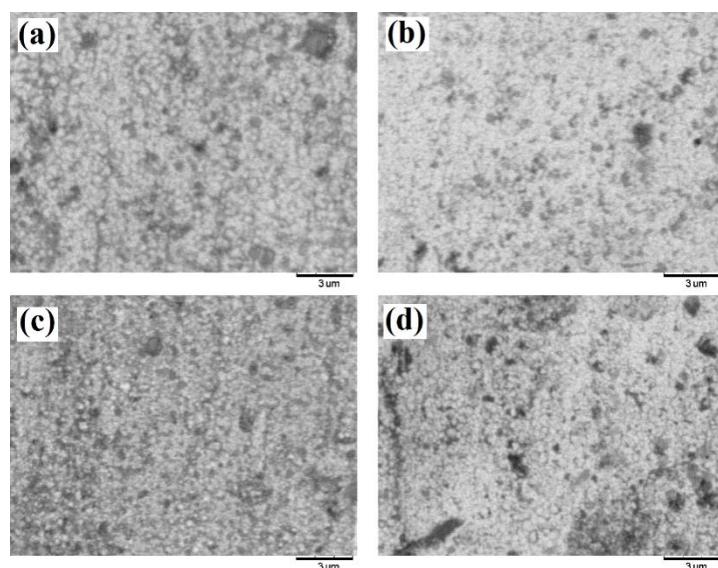
Figure 6. Surface morphology of NiFe coating electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6;

The electrodeposited NiFe alloy, as shown in Figure 6, is a typical granular coating. Due to the intensive hydrogen evolution, the surface particles on NiFe alloy coating formed at lower pH values are greater and the surface porosity is larger. With the increase of pH value, the overpotential is increased and the cathode polarization is enhanced to accelerate the nucleation rate, resulting in the uniform and dense surface morphology. The surface of NiFe alloy coating prepared from the solution

with pH value of 5 is uniform and compact, and the porosity is the lowest. However, when the pH is greater than 5, a large amount of ferrous ions are easily converted to iron ions, and a large amount of iron hydroxide is precipitated, which increases the surface roughness and decreases the compactness.

3.4 Magnetic property of NiFe electrodeposited coating
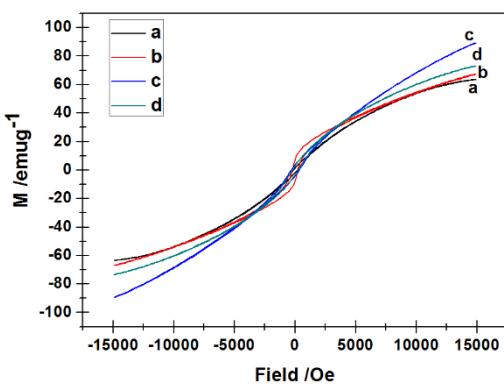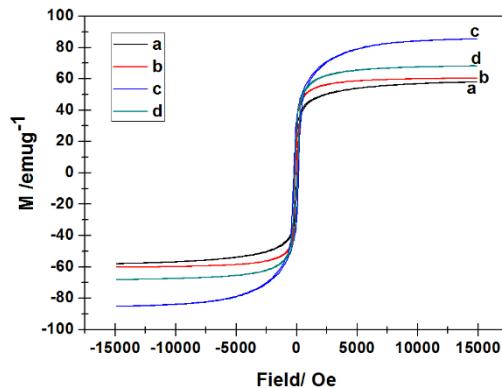
Figure 7(a)   Figure 7(b)

Figure 7. Hysteresis loop of NiFe coating electrodeposited from plating solutions of different pH values: a. pH=3; b. pH=4; c. pH=5; d. pH=6; Figure 7(a): Hysteresis loops perpendicular to the coating surface; Figure 7(b) Hysteresis loops parallel to the coating surface;

Table 1. Saturation magnetization and coercivity of different NiFe coatings

pH value	Perpendicular direction		Parallel direction	
	M_s /emug^{-1}	H_{ci} / Oe	M_s /emug^{-1}	H_{ci} / Oe
3	63.37	164.32	57.95	61.12
4	67.23	220.34	60.35	72.17
5	89.20	324.21	85.38	182.68
6	73.34	232.92	68.14	105.24

The NiFe coating hysteresis loops of perpendicular and parallel direction are tested by vibrating sample magnetometer to evaluate the magnetic property based on saturation magnetization and coercivity shown in Figure 7 and Table 1. Along with the increase of pH value, the saturation magnetization and coercivity of NiFe coating both increase extremely and then decrease. The NiFe coating obtained at the condition of pH=5 has the maximum saturation magnetization and the largest coercivity. According to the previous analysis, appropriate pH value can increase the overpotential which is beneficial to increase the nucleation rate and refine the grains, so as to obtain uniform and compact coating resulting in the increase of coercivity. The effect of grain size on the coercivity of materials is reported in some literatures [33-34]. The deposition rate is the largest at the condition of pH=5 that contributes to the increase of weight gain and saturation magnetization. Moreover, it is found out that the magnetic property of NiFe coating at the perpendicular direction is better than that

of at the parallel direction which means that the electrodeposited NiFe coating has better perpenticular magnetic anisotropy.

4. CONCLUSIONS

The NiFe alloy coating on the surface of silicon was prepared using the pulse electrodeposition technique. The pH value of the plating solution is changed to investigate its effects on the cyclic voltammetry, deposition rate, structure, surface morphology and magnetic property of NiFe coating. The co-deposition of nickel and iron belongs to anomalous co-deposition which may be due to the reduction of hydrogen ions during the electrodeposition to increase the pH value near the cathode, resulting in the formation of ferrous hydroxide. Appropriate bath pH can increase the overpotential to improve the nucleation rate and refine the grains, so as to obtain uniform and compact coating with better crystallinity and optimal magnetic property. With the pH value increases from 3 to 5, the deposition rate, crystallinity and magnetic property of NiFe coating all increases gradually. However, when the pH is greater than 5, a large amount of ferrous ions are easily converted to iron ions, and a large amount of iron hydroxide is precipitated, which decline the deposition rate and decrease the magnetic property and crystallinity. The NiFe coating electrodeposited from bath of pH=5 possesses the best crystallinity and excellent magnetic property.

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