

## Magnetic Properties of Cobalt-coated Silicon Steels Prepared by Electrodeposition

Somkane PIROMRAK<sup>1</sup>, Pongsakorn JANTARATANA<sup>2</sup>  
and Chitnarong SIRISATHITKUL<sup>1</sup>

<sup>1</sup>*Magnet Laboratory, School of Science, Walailak University,  
Nakhon Si Thammarat 80161, Thailand*

<sup>2</sup>*Department of Physics, Faculty of Science, Kasetsart University,  
Bangkok 10900, Thailand*

### ABSTRACT

Magnetic properties of silicon steels (1.26 % silicon) coated by cobalt of varying thickness were studied. Cobalt ranging from 11 to 68  $\mu\text{m}$  in thickness was deposited on silicon steel substrates (0.5 mm thick, 0.4 mm wide and 55.0 mm long) cut from sheets of recycled transformer cores. By electrodeposition in  $\text{CoSO}_4$  electrolyte with 90 mA applied current at pH 1.86, the deposition rate was 1.11  $\mu\text{m}/\text{min}$ . Although deposition of cobalt increased saturation induction of silicon steels, it also increased hysteresis loss signified by wider hysteresis loops with larger remanent induction and coercive field. Since the magnetoimpedance (MI) is related to the magnetic softness of materials, the MI ratio decreased with increasing thickness of the cobalt layer. Although the cobalt coating did not enhance the MI ratio of silicon steels, it expanded the peak of frequency-dependent MI curves. Therefore, the frequency range with large MI ratio in silicon steels can be extended by the deposition of a cobalt layer. From microscopic images, grains and magnetic domains of the silicon steel were of the order of 10  $\mu\text{m}$  whereas smaller domain size was observed in the cobalt layer.

**Keywords:** Silicon steel, electrodeposition, magnetic properties, cobalt

## INTRODUCTION

Silicon steel, also called electrical steel or transformer steel, is a special type of iron that has 1 - 4 % silicon. The addition of silicon increases electrical resistivity and grain size but decreases the Curie temperature and anisotropy of the iron. When the silicon content is higher than 4 %, the steel becomes very brittle [1]. Silicon steel is a very important soft magnetic material that is easily magnetized and demagnetized whose most common application is as transformer cores. The desirable core has low energy loss. The core loss arises from (1) eddy current loss by the change in magnetic flux, (2) hysteresis loss from the domain wall movement and (3) acoustic loss due to magnetostrictive deformation of the core. These losses can be minimized by decreasing thickness, domain size and magnetostriction as well as increasing the resistivity of the core [2].

Besides its use in transformers, silicon steel can also be used as a sensor because of its demonstration of the magnetoimpedance (MI) effect. The MI is a reduction of electrical impedance of soft ferromagnetic conductors under the application of a magnetic field [3]. The applied magnetic field modifies the permeability which, in turn, influences the skin depth ( $\delta$ ) according to Eq. (1).

$$\delta = \sqrt{\rho / \pi f \mu} \quad (1)$$

where  $f$  is the frequency of the AC driving current,  $\rho$  is the electrical resistivity,  $\mu$  is the relative permeability of the conductor. Since the skin depth is the depth at which the current density reduces to 37 % of the value at the surface, it regulates the impedance of the materials. The high sensitivity of MI to the applied field and frequency of driving current makes MI materials especially convenient for sensor applications. Carara and co-workers reported a maximum of 150 % MI in silicon steels measured at 100 kHz and 4 mA driving current [4]. In our previous work, the MI ratio was studied as a function of the width of silicon steels. A maximum of 300 % MI was observed at a frequency of about 200 kHz for a  $0.5 \times 1.064 \times 35.0$  mm<sup>3</sup> sample [5]. Silicon steels were then implemented as sensing elements in a slot key switch, a position sensor, a current sensor and an angular velocity sensor [6].

Due to its vast commercial applications, there have been several attempts to improve the magnetic properties of silicon steel. Recently, Sheiko and co-workers increased the permeability and reduced energy loss of silicon steels by coating them with a layer of 1 - 10  $\mu\text{m}$  iron-silicon by the sputtering technique [7]. In this paper, we study the effect of cobalt coating on silicon

steels by the electrodeposition technique. By applying electrical current between electrodes, metal ions can be deposited onto substrates of various sizes and appearances at the cathode. This technique offers several advantages including its simplicity. In particular, it does not require a vacuum system or other high-cost equipment. Cobalt is chosen because, when added to iron, it is the only element which increases its saturation induction [8]. After the deposition, the effect of cobalt thickness on magnetic properties is studied.

## MATERIALS AND METHODS

### Preparation of cobalt-coated silicon steel

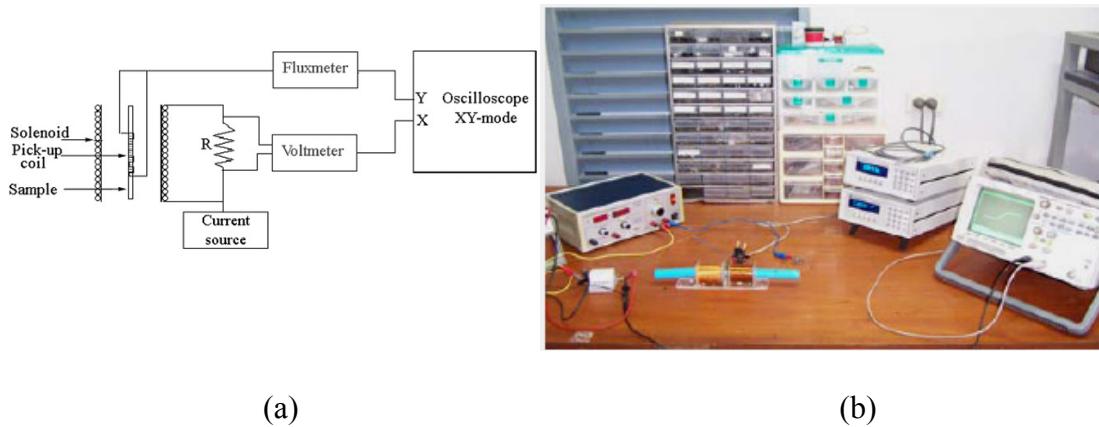
Silicon steel samples were cut from sheets of recycled transformer core by a linear precision saw (Buehler Isomet 4000) into  $0.5 \times 0.4 \times 55.0 \text{ mm}^3$  pieces. A laminated layer was removed by acetone in an ultrasonic bath (Kerry KC3) and the silicon steel samples were then polished by a grinder/polisher (Buehler Phoenix Beta). Cobalt was electrodeposited onto the sample in an electrodeposition system shown in **Figure 1**. The anode was a 5 mm-diameter cobalt rod (Sigma Aldrich, 99.95 %) and a piece of silicon steel was used as a cathode. Both electrodes were immersed in a jar of  $\text{CoSO}_4$  electrolyte prepared from  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in distilled water. During the deposition, the cathode was rotated at 8 rpm by a motor in order to achieve a uniform cobalt deposition on a silicon substrate. To study the effect of applied current, three values of constant current (80, 90 and 100 mA) supplied by a programmable current source (Kithley 220) were tested at the pH of 1.86 maintained by sulfuric acid. After the optimum current was obtained, samples with varying thickness (11 - 68  $\mu\text{m}$ ) were fabricated by varying time.



**Figure 1** Photographs of (a) electrodes and (b) an electrodeposition system.

### Characterization of cobalt-coated silicon steel

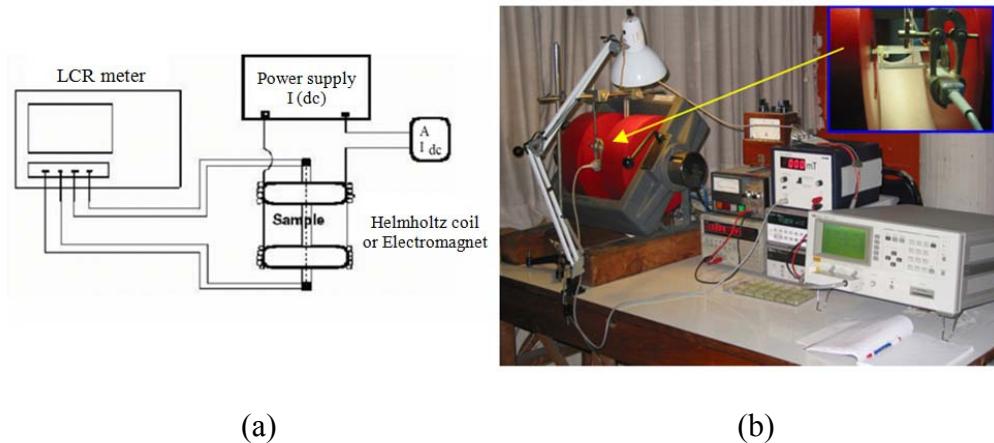
Silicon steels before and after the deposition were characterized by energy dispersive spectroscopy (EDS). Photographs of a sample in a block of resin were taken by an optical microscope (Nikon Eclipse ME600L) in two different planes. From the length-width plane, the thickness of a cobalt layer was averaged from measurements at 20 different points. For the grain inspection, the silicon steel was polished and etched with Natal solution. Arrangements of the magnetic domain in a demagnetized state were revealed by the Bitter pattern technique. Magnetic colloid (Sigma Hi-chemical A-07) was dropped on a polished surface and the resulting pattern was recorded by the microscope. Hysteresis loops were obtained by the fluxmetric induction method illustrated in **Figure 2**. The flux induced in a copper-wound sample was measured by a flux meter (Lakeshore 480) and plotted against an applied magnetic field in a digitizing oscilloscope (Agilent 54622A). From these loops, magnetic parameters such as saturation induction ( $B_s$ ), remanent induction ( $B_r$ ) and coercive field ( $H_c$ ) were evaluated.



**Figure 2** (a) Schematic diagram and (b) photograph of the fluxmetric induction magnetometer.

The auto balancing bridge method was implemented in room temperature to obtain MI measurements. Samples were placed in a variable magnetic field supplied by an electromagnet in a longitudinal direction. Its impedance as a function of the magnetic field was measured from 1 kHz to 1 MHz by an LCR meter (HP 4284A) with a four-terminal pair connection technique. The MI ratio was calculated by the formula  $100 \times (Z_0 - Z_{H\max})/Z_{H\max}$  where  $Z_0$  corresponds to the zero field and  $Z_{H\max}$  corresponds to the maximum

2 kOe-field. According to MI studies in silicon steels [4,5], a magnetic field of 2 kOe is enough to saturate the impedance.

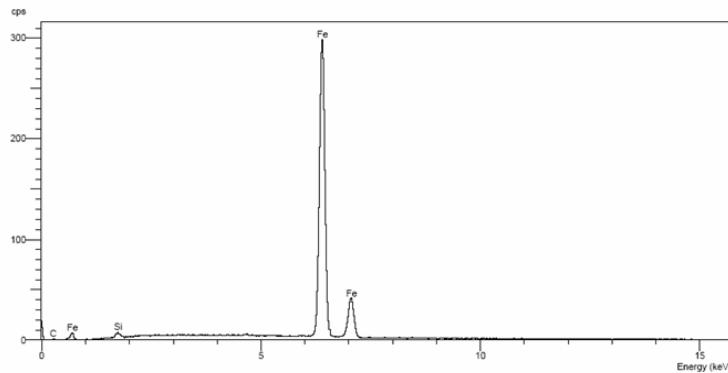


**Figure 3** (a) Schematic diagram and (b) photograph of the MI measurement system.

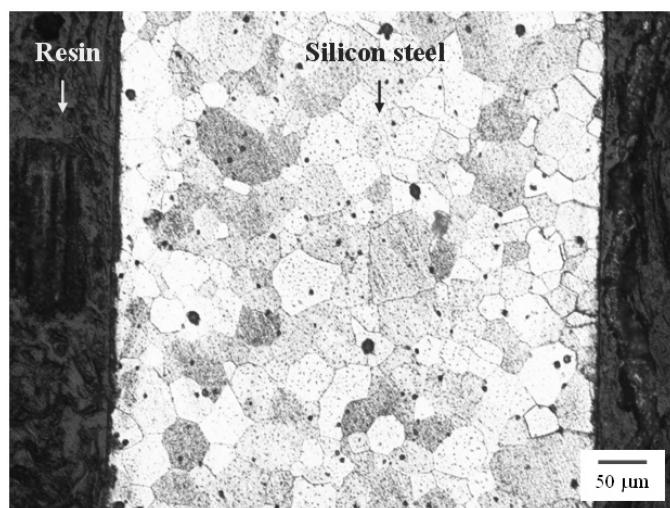
## RESULTS AND DISCUSSION

### Composition, surface imaging and thickness

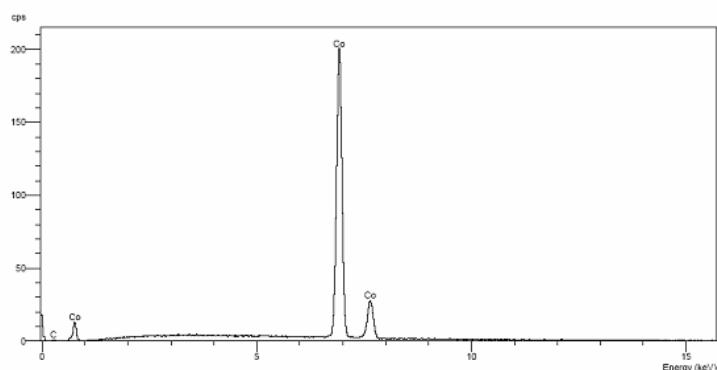
According to the EDS spectra in **Figure 4**, the silicon steel before coating is composed of 98.74 % iron and 1.26 % silicon. **Figure 5** shows a micrograph of a polished surface of silicon steel in a length-width plane. Varying sizes of these polygons of grains were averaged by drawing 15 lines along the width and the length of a picture. The number of grains along each line was counted and the average grain size was then calculated as 30  $\mu\text{m}$ .



**Figure 4** EDS spectra of silicon steel before deposition.

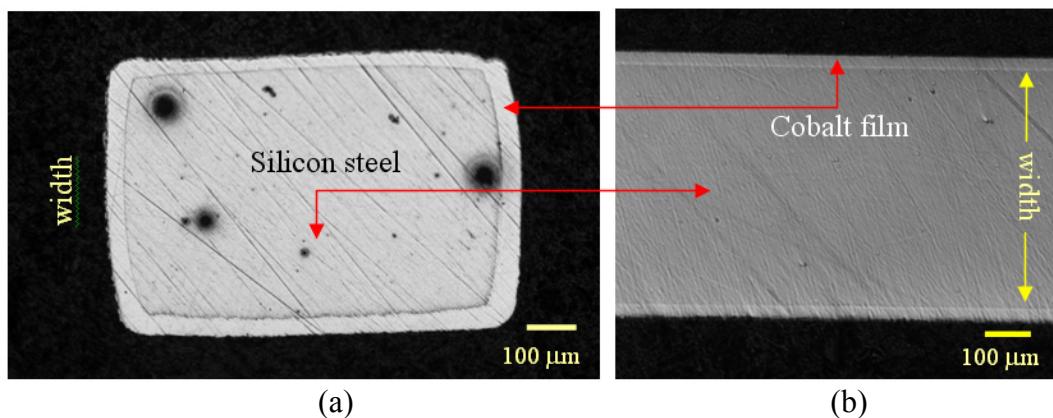


**Figure 5** Etched surface of a silicon steel sample before deposition obtained by an optical microscope.

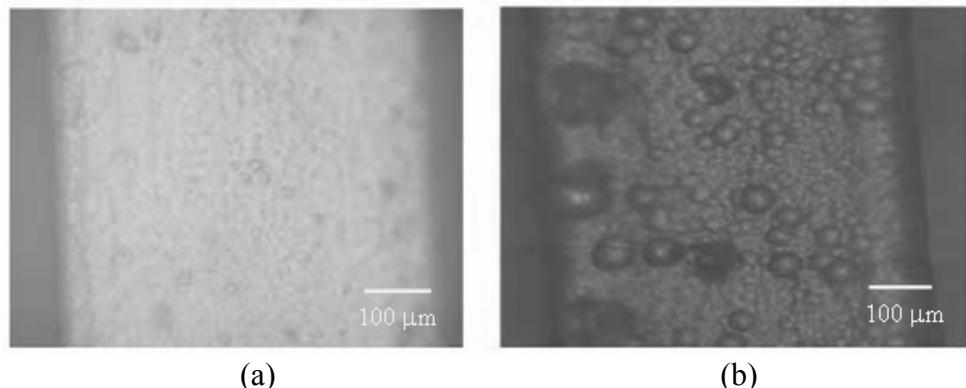


**Figure 6** EDS spectra of cobalt film on the silicon steel.

After the deposition, the composition analysis of the surface in **Figure 6** shows only cobalt and no other elements beyond a 0.1 % detection limit. **Figure 7** shows the micrographs of cobalt on silicon steels in two different planes. From these micrographs, the quality of the coating can also be inspected. Using 100 mA-applied current gave rise to the highest deposition rate but the quality of the coating was deteriorated due to a large amount of hydrogen gas during the deposition. **Figure 8** compares results between depositions with applied currents of 90 and 100 mA after 30 min. Judging from these figures, the optimum current of 90 mA was selected for the preparation of samples with different thickness.



**Figure 7** Micrographs in (a) a thickness-width plane and (b) a length-width plane of a cobalt- silicon steel sample.

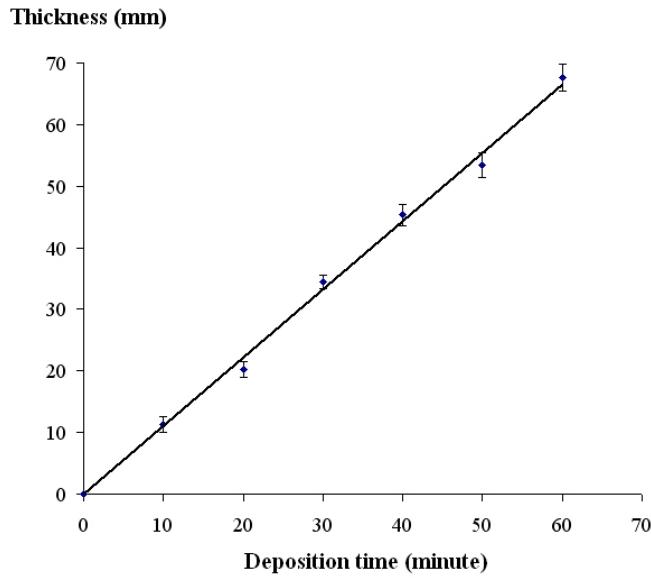


**Figure 8** Micrographs of (a) 90 mA-coated sample and (b) 100 mA-coated sample in a length-width plane.

The average thickness of cobalt layers is plotted against the deposition time in **Figure 9**. The slope of corresponds to the linear fitted graph gives a deposition rate of  $1.11 \mu\text{m}/\text{min}$ . This result agrees with the value predicted by Faraday's law of electrodeposition which states that the thickness of the deposit ( $T$ ) is linearly proportional to the deposition time ( $t$ ) as described in Eq. (2).

$$T = \frac{It\eta sM}{\rho AnF} \quad (2)$$

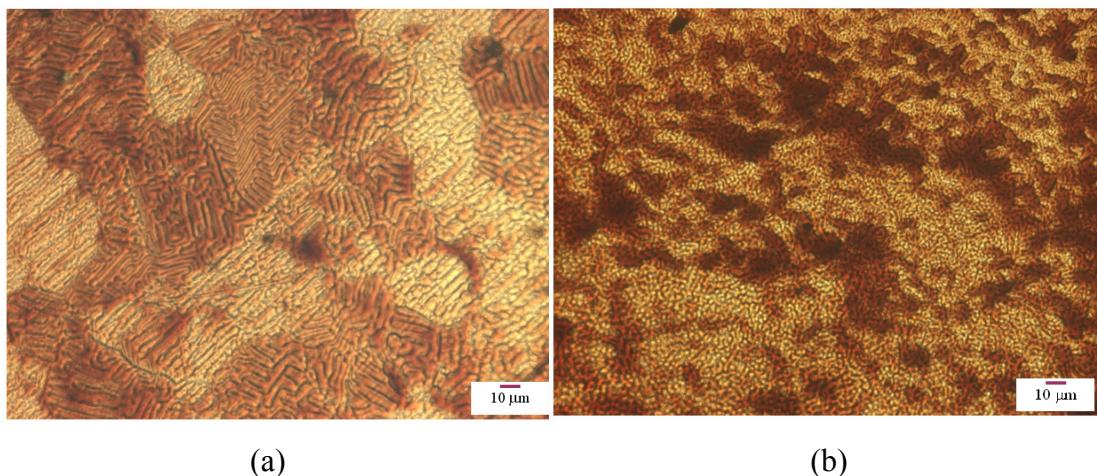
Here  $I$  is the applied current,  $\eta$  is the current efficiency defined as the ratio of current responsible for metal dissolution to total current,  $s$  is the stoichiometric coefficient,  $M$  is the molecular weight,  $\rho$  is the electrical resistivity,  $n$  is the number of transferred electrons,  $A$  is the area of deposit and  $F$  is Faraday's constant (96485 C/equiv) [9].



**Figure 9** Thickness of cobalt layer on silicon steels according to the deposition time with 90 mA-applied current at pH 1.86.

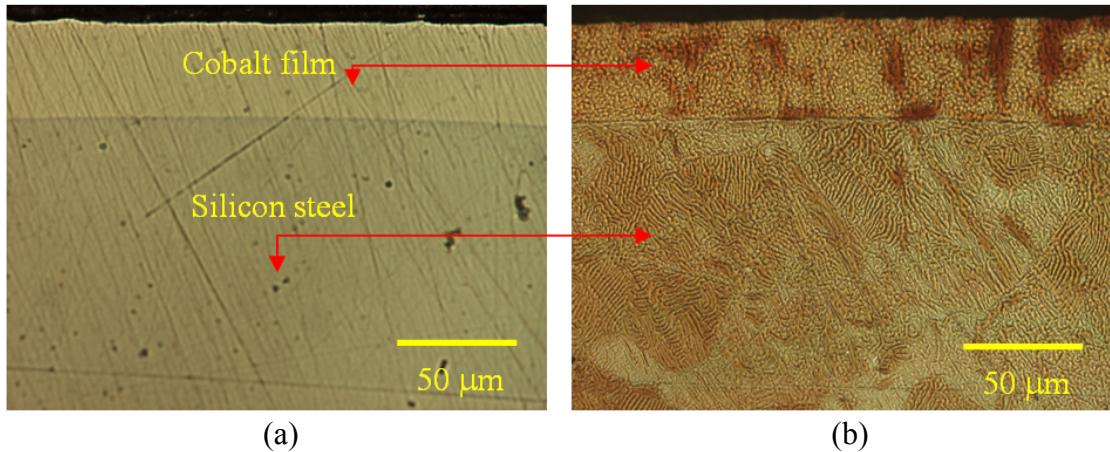
### Domain imaging

Microscopic images of magnetic domain patterns of silicon steel and cobalt before deposition are shown in **Figure 10**. Since ferromagnetic particles from the colloid are accumulated by stray fields from the domain walls, the magnetic domain pattern can be visualized. In the demagnetized state, both silicon steel (**Figure 10a**) and cobalt (**Figure 10b**) have maze patterns of randomly oriented domains. The domain size of silicon steel is of order of the 10  $\mu\text{m}$  whereas that of cobalt is much smaller.



**Figure 10** Bitter pattern showing magnetic domains of (a) silicon steel and (b) cobalt in a demagnetized state obtained by an optical microscope.

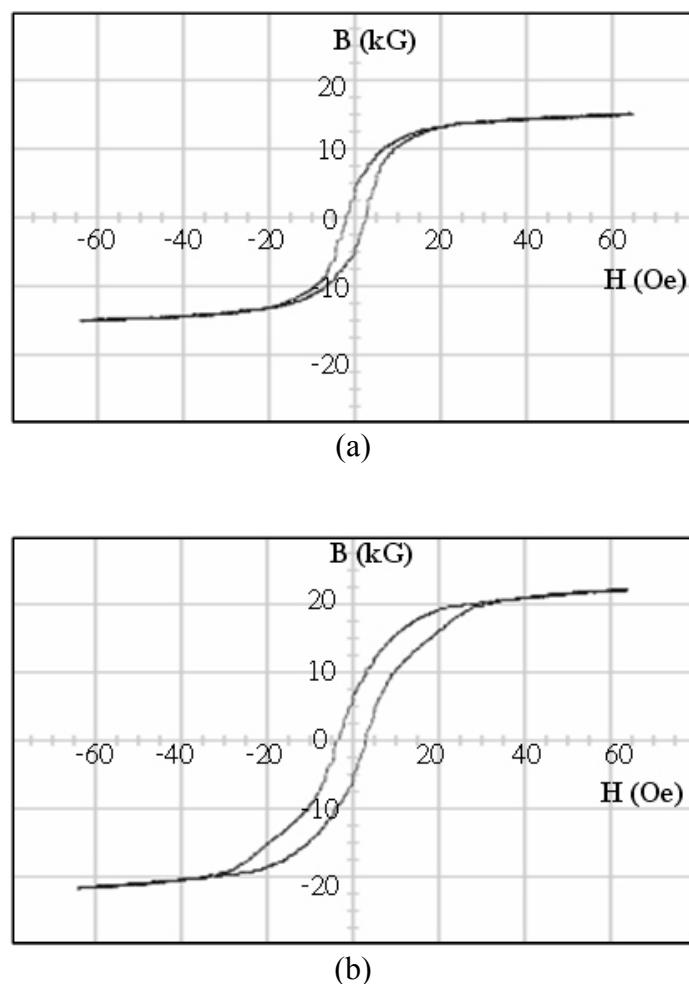
After the deposition, the Bitter pattern of a sample with 45  $\mu\text{m}$ -cobalt on silicon steel is shown with its corresponding surface image in **Figure 11**. In **Figure 11a**, the interface of silicon steel and cobalt is somewhat smooth but the surface of the cobalt film is rather rough. The Bitter pattern image in **Figure 11b** resembles those before the deposition by having large silicon steel domains and small cobalt domains. Such cobalt domains make the material hard to saturate in a magnetic field. Since this Bitter pattern technique does not separate the domain image from the surface topography, the roughness of the surface affects the domain imaging in some areas.



**Figure 11** Micrographs of (a) surface image and (b) Bitter pattern image from a cobalt layer on silicon steel substrate.

### Hysteresis loops

Examples of hysteresis loops of cobalt-coated silicon steel and uncoated silicon steel are shown in **Figure 12** and the following relevant parameters are summarized in **Table 1**; saturation induction ( $B_s$ ), remanent induction ( $B_r$ ) and coercive field increase ( $H_c$ ) with increasing cobalt thickness from 0 to 45 μm. It follows that hysteresis loss is also increased by cobalt coating. Although the permeability can not be precisely obtained from this setup, the shape of the hysteresis loops implies that the permeability of silicon steel is reduced after coating.



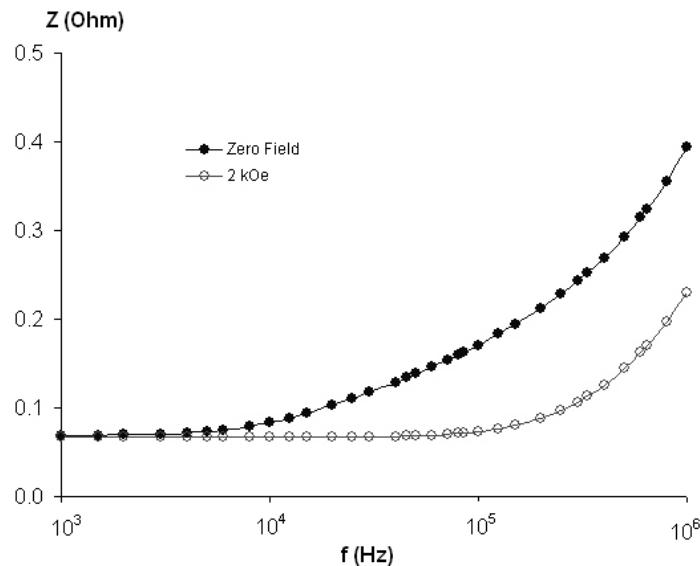
**Figure 12** Room temperature hysteresis loops of (a) uncoated sample and (b) 45  $\mu\text{m}$ -coated sample.

**Table 1** Saturation induction ( $B_s$ ), remanent induction ( $B_r$ ) and coercive field ( $H_c$ ) from samples of varying cobalt thickness.

Co thickness ( $\mu\text{m}$ )	$B_s$ (kG)	$B_r$ (kG)	$H_c$ (Oe)
0	15.2	4.7	2.4
11	18.9	5.0	2.5
20	20.0	5.9	2.8
34	21.5	6.0	3.1
45	22.4	6.9	3.3

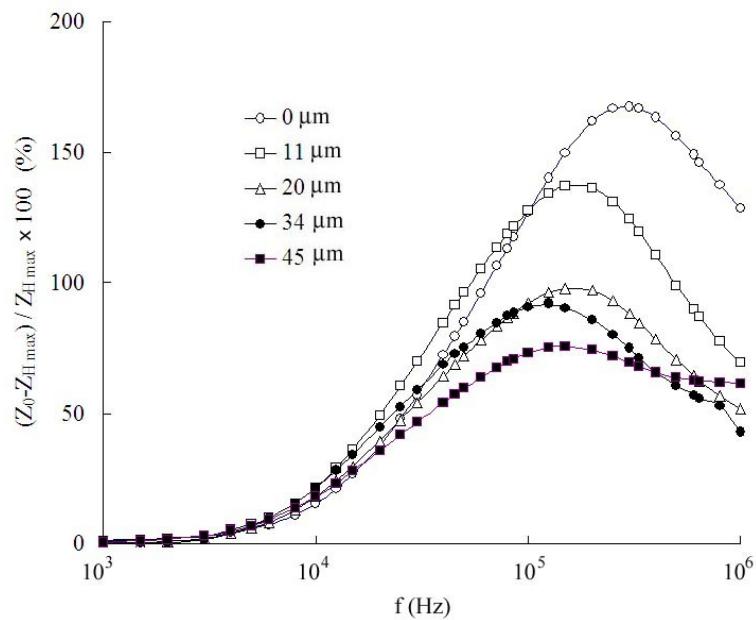
## Magnetoimpedance

**Figure 13** shows the dependence of electrical impedance for an 11  $\mu\text{m}$ -coated sample on the frequency of an AC driving current. Both in zero magnetic field and 2 kOe-field, the impedance is not sensitive to the change of frequency below a value called the critical frequency. Beyond the critical frequency, the impedance rapidly rises because the skin depth is reduced to a smaller value than half of the sample width. For the 11  $\mu\text{m}$ -coated sample in **Figure 13**, the critical frequency is 3 kHz in the case of zero field and becomes 100 kHz in the 2 kOe-field because the skin depth in Eq. (1) is not only dependent on the frequency but also on the magnetic permeability. The permeability is modified by the application of a magnetic field and the difference between the impedance with and without field is a demonstration of the MI effect.



**Figure 13** Frequency dependence of the impedance in a zero field (full symbols) and in 2 kOe-applied field (open symbols) for an 11  $\mu\text{m}$ -coated sample.

**Figure 14** shows frequency-dependent MI curves of samples with different cobalt thickness. Every graph has a peak of maximum MI ratio at a frequency called the characteristic frequency. According to our previous work in uncoated silicon steel [5], the width of samples influences the characteristic frequency and MI ratio. In this work, the characteristic frequency is also dependent on the size of samples. With increasing cobalt thickness, the characteristic frequency shifts to a smaller value because the skin depth is comparable to the width of sample at a lower frequency. The MI ratio is also reduced in the case of thick cobalt because of the reduction of the permeability by the coating confirmed by hysteresis loops. Modest permeability tends to be insensitive to the applied magnetic field and hence the MI ratio is diminished. Nevertheless, the coating of cobalt expands the peak of frequency-dependent MI curves and the range of frequency with large MI ratio is therefore extended. This broadening can be explained in terms of the difference between impedance of the cobalt layer and the silicon substrate. In the case of thick cobalt layer, its impedance is not much higher than that of silicon steel. The MI is therefore not very sensitive to the frequency change around the characteristic value.



**Figure 14** Frequency-dependent MI curves of cobalt-coated silicon steels of varying thickness.

## CONCLUSIONS

By electrodepositing in  $\text{CoSO}_4$  with 90 mA applied current at pH 1.86, the cobalt thickness is proportional to the time with a factor of 1.11  $\mu\text{m}/\text{min}$ . Grain and magnetic domain of the silicon steel were observed with average sizes in the order of 10  $\mu\text{m}$ . The cobalt layer also possesses randomly oriented domains in a demagnetized state with smaller size. Magnetic properties of cobalt-coated silicon steel are dependent on the thickness of cobalt layer ranging from 11 to 45  $\mu\text{m}$ . By increasing the thickness of cobalt on silicon steel, hysteresis loss is increased and the MI ratio is decreased. The cobalt coating also has advantages such as the increase of saturation induction and the extension of a frequency range with large MI ratio.

## ACKNOWLEDGEMENTS

This work was supported by Walailak University (Grant No. 8/2549). The authors would like to thank the Scientific Equipment Center at Prince of Songkla University for EDS spectra.

## REFERENCES

- [1] D Jiles. *Introduction to Magnetism and Magnetic Materials*, 2<sup>nd</sup> ed. Chapman & Hall, New York, 1998, p. 325-61.
- [2] RC O'Handley. *Modern Magnetic Materials: Principle and Applications*. John Wiley & Sons, New York, 1999, p. 357-8.
- [3] P Jantaratana and C Sirisathitkul. Giant magnetoimpedance in electrodeposited cobalt on silver wires. *Walailak J. Sci. & Tech.* 2006; **3**, 261-71.
- [4] M Carara, A Gundel, MN Baibich and RL Sommer. Magnetization process and magnetoimpedance in (110)[001] $\text{FeSi}_{3\%}$ . *J. Appl. Phys.* 1998; **84**, 3792-97.
- [5] P Jantaratana and C Sirisathitkul. Giant magnetoimpedance in silicon steels. *J. Magn. Magn. Mater.* 2004; **281**, 399-404.
- [6] P Jantaratana and C Sirisathitkul. Applications of silicon steel based on its giant magnetoimpedance effect. In: Proceedings of the Third Thailand Materials Science and Technology Conference: MSATIII, Bangkok, Thailand, 2004, p. 90-1.

- [7] L Sheiko, S Gaiduk and Y Troschenkov. Influence of thin ferromagnetic coating on magnetic properties of silicon steel sheets. In: Proceedings of the Joint European Magnetic Sympoia: JEMS, Dresden, Germany, 2004, p. 113.
- [8] Cobalt Development Institute: Cobalt Fact, Available at:  
<http://www.thecdi.com/cobaltnfacts.php>, accessed August 2006.
- [9] M Paunovic and M Schlesinger. *Fundamental of Electrochemical Deposition*, Wiley-Interscience, New York, 1998, p. 53-4.

## บทคัดย่อ

สมคบณ ภิรมย์รักษ์<sup>1</sup> พงศกร จันทรัตน์<sup>2</sup> และ ชิตตัครงค์ ศิริสกิตย์กุล<sup>1</sup>  
สมบัติเชิงแม่เหล็กของเหล็กซิลิกอนที่เคลือบโอบอลต์ด้วยเทคนิคไฟฟ้าเคมี

งานวิจัยนี้ได้ศึกษาสมบัติของเหล็กซิลิกอน ( $1.26\%$  ซิลิกอน) ที่เคลือบด้วยโอบอลต์ความหนาต่างๆ กัน โอบอลต์ความหนาดังนี้ 11 ถึง 68 ไมโครเมตร ถูกเกลือบนนวัตกรรมรับเหล็กซิลิกอน (หนา  $0.5$  มิลลิเมตร, ยาว  $55.0$  มิลลิเมตร และกว้าง  $0.4$  มิลลิเมตร) ที่ได้จากการตัดแผ่นแกนของแม่เหล็กไฟฟ้าที่เสียเหล้า การเคลือบใช้เทคนิคไฟฟ้าเคมีในสารอิเล็กโทรไลต์  $\text{CoSO}_4$  ด้วยกระแส  $90$  มิลลิแอมป์ร์ ที่  $\text{pH } 1.86$  ได้อัตราการเคลือบเป็น  $1.11$  ไมโครเมตร/นาที แม้ว่าการเคลือบโอบอลต์เพิ่มค่า saturation induction ของเหล็กซิลิกอน แต่ทำให้การสูญเสียจากฮิสเทอริซิสมากขึ้นด้วย ซึ่งสังเกตได้จากกราฟฮิสเทอริซิสที่กว้างขึ้นพร้อมกับการเพิ่มขึ้นของค่า remanent induction และ coercive field เนื่องจากแมgneto โอมพีแคนซ์ (MI) เกี่ยวข้องความเป็นแม่เหล็กอ่อนของวัสดุ ดังนั้น MI จึงลดลงเมื่อความหนาของฟิล์มโอบอลต์มากขึ้น แม้ว่าการเคลือบจะไม่เพิ่มขนาด MI แต่ส่งผลดีทำให้กราฟระหว่าง MI กับความถี่กว้างขึ้น ทำให้ช่วงความถี่ที่ MI มีค่าสูงสามารถขยายให้กว้างได้ด้วยการเคลือบโอบอลต์บนแกนแม่เหล็กไฟฟ้าเคมี จากภาพถ่ายด้วยกล้องจุลทรรศน์ ขนาดเฉลี่ยของกรนและโอดเมนแม่เหล็กของเหล็กซิลิกอนอยู่ในระดับขนาด  $10$  ไมโครเมตร ส่วนชั้นโอบอลต์มีโอดเมนขนาดเล็กกว่า

<sup>1</sup> ห้องวิจัยแม่เหล็ก สำนักวิชาวิทยาศาสตร์ มหาวิทยาลัยยกักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80161

<sup>2</sup> ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ วิทยาเขตบางเขน เขตจตุจักร กรุงเทพมหานคร 10900