

EFFECTS OF DETERGENT-INDUCED ANTIFERROMAGNETIC CORROSION ON MAGNETIC PROPERTIES OF EXCHANGE-BIASED THIN FILMS

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Abstract

The corrosion behavior of $\text{Co}_{30}\text{Fe}_{70}/\text{Ni}_{81}\text{Fe}_{19}/\text{Ir}_{20}\text{Mn}_{80}$ thin films immersed in detergent solutions was investigated. X-ray diffraction revealed a clear (111) structure for IrMn and NiFe in the as-prepared thin films, whereas the crystal structure of Ru and CoFe underlayers remained undetected due to their limited thickness. Magnetic analysis showed minimal impact on the ferromagnetic underlayer, with a consistent saturation magnetic moment observed. Immersion in detergent solutions resulted in variations in the exchange bias field attributed to increased Mn corrosion within the antiferromagnetic layer. The electrical conductivity of the solution increases with rising detergent concentration, accelerating the corrosion rate of Mn. When the detergent concentration reaches a certain point, the surface-active inhibitor adsorbs onto the IrMn surface with greater surface coverage, leading to a decrease in the corrosion rate. Furthermore, temperature played a crucial role, increasing kinetic energy and accelerating corrosion processes. A comprehensive understanding of these factors is paramount for devising effective corrosion mitigation strategies in thin film manufacturing processes.

Keywords: Corrosion; Detergent; Exchange bias; Magnetic properties

Introduction

A Exchange-biased thin films are a class of magnetic materials that exhibit a unique phenomenon called exchange bias (EB). This occurs at the interface between two materials with different magnetic properties, typically a ferromagnetic (FM) layer and an antiferromagnetic (AFM) layer. The interaction at

this interface causes a unidirectional shift in the hysteresis loop of the ferromagnetic layer (Meiklejohn and Bean, 1956; Meiklejohn, 1962) denoted by the exchange bias field (H_{EB}), resulting in enhanced stability and control of magnetic properties. These thin films find applications in various technologies such as giant

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magnetoresistance (GMR) components for recording devices (Heim *et al.*, 1994; Fuke *et al.*, 1997; Samal and Anil Kumar, 2008) and sensors (Yu *et al.*, 2002) due to their improved performance and functionality. IrMn with 20 at.% Ir content exhibits the highest exchange field within the NiFe/IrMn exchange-biased bilayer (Hoshino *et al.*, 1996). A minimum IrMn thickness of 75 Å is necessary to induce a substantial exchange bias effect for a NiFe layer thickness of 250 Å (Devasahayam *et al.*, 1998). However, as the ferromagnetic layer thickness decreases, so does the critical thickness of the antiferromagnetic layer required for exchange bias occurrence (Mishra *et al.*, 2010).

In the thin films manufacturing process, a wafer is cut into individual die pieces, followed by etching and cleaning. Commercial detergent solution containing a mixture of linear alkylbenzene sulfonic acid (alkyl chain length from C10 to C14) and 2-aminoethanol is commonly used for cleaning various surfaces, including fabrics, dishes, and hard surfaces. The combination of the active ingredients is aimed at synergistically breaking down and lifting away impurities, resulting in effectively removing dirt, stains, and grease. Additionally, detergent solution may include additives such as fragrances or colorants to enhance its appeal.

In our previous work (Thongdee *et al.*, 2020), we investigated the effect of Mn corrosion by deionized (DI) water on the magnetic properties of NiFe/IrMn exchange-biased thin films. We found that Mn in the AFM layer was reduced to Mn^{2+} and dissolved into water, causing a loss of Mn in the AFM layer and a corresponding decrease in the sample's exchange bias field. In this work, we focus on studying the effect of Mn corrosion caused by the detergent solution, which represents an actual event in thin film cleaning process.

Materials and Methods

A thin-film wafer was fabricated by standard DC magnetron sputtering in an Ar atmosphere. Initially, a 10 Å thick Ru seed layer was deposited on a Si(100)/SiO₂ substrate. Then, a heterostructure thin film of Co₃₀Fe₇₀(10 Å)/Ni₈₁Fe₁₉(255 Å)/Ir₂₀Mn₈₀(200 Å) was deposited on the Si(100)/SiO₂/Ru surface. The IrMn AFM layer was sputtered as the top layer to ensure direct exposure to water and detergent solutions for corrosion testing. The exchange bias coupling was induced using a magnetic vacuum annealing oven (Futek Furnace, Inc.). The thin-film wafer was heated to 560 K in the Ar atmosphere to transform the IrMn into a paramagnetic state. A 50 kOe in-plane

external magnetic field was applied to align the magnetic moments at the NiFe/IrMn interface in the direction of the field. Subsequently, the system was cooled down to room temperature in the presence of the applied magnetic field. Finally, the exchange-biased thin-film wafer was coated with a protective photoresist layer to prevent oxidation.

The surface morphology and chemical composition of the sample were investigated using a scanning electron microscope (SEM; FEI Quanta 450) and energy-dispersive X-ray spectroscopy (EDS; X-Max, Oxford Instruments), respectively. An X-ray diffractometer (XRD; PANalytical Empyrean) was used to identify the structure and phase of the sample.

The thin-film wafer was cut into individual pieces with widths and lengths of about 3–4 mm, and then the photoresist layer was removed by wiping with acetone. The change in the in-plane magnetic moment (*m*) with respect to the applied magnetic field (*H*) was measured using a resonance-vibrating sample magnetometer (R-VSM). Once the *m*-*H* loop was completed, the sample was lifted from the measuring position and immersed in a 20 mL test solution with detergent concentrations ranging from 1% to 20% by volume in DI water for 60 to 360 s, without being removed from the holder. After the corrosion process, the sample was returned to the R-VSM measurement position, and a new *m*-*H* loop was recorded. The detergent solution temperature was controlled using a silicone oil bath.

Results and Discussion

The XRD pattern of the as-prepared sample at room temperature is presented in Figure 1. Distinct (111) peaks for IrMn and NiFe were observed at 2θ angles of 42.01° and 44.61°, respectively. However, no diffraction peaks for Ru or CoFe were detected, likely due to the thinness of both layers.

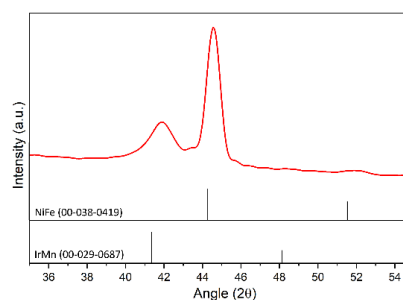


Figure 1. X-ray diffraction pattern of the as-prepared Ru/Co₃₀Fe₇₀/Ni₈₁Fe₁₉/Ir₂₀Mn₈₀ thin film after photoresist removal

To evaluate the effect of IrMn layer thickness on Mn corrosion and the magnetic properties of NiFe/IrMn exchange-biased thin films, the influence of immersion time on the magnetic properties was analyzed and compared with the findings of previous work. Figure 2 shows the m-H curves of the sample after immersion in 20 mL of DI water for durations ranging from 900 to 5400 s. The saturation magnetic moment of the sample after immersion in DI water remains unchanged compared to the as-prepared sample. As the magnetic moment in the exchange-biased system mainly comes from the FM layer, this suggests that the corrosion process does not affect the FM underlayer, as evidenced by the stable saturation magnetic moment. The m-H curves of the sample shifted toward the zero external field axis with increasing immersion time. The exchange bias field (H_{EB}) of the as-prepared sample decreased from 38.87 Oe to 23.83 Oe after immersion in DI water for 5400 s. The inset in Figure 2 shows the variation of H_{EB} as a function of the remagnetization cycle, which is known as the training effect. This effect refers to the shift in the hysteresis loop during the remagnetization process of a system in a biased state. It is related to the irreversible changes in the AFM domains at the AFM/FM interface (Radu *et al.*, 2003).

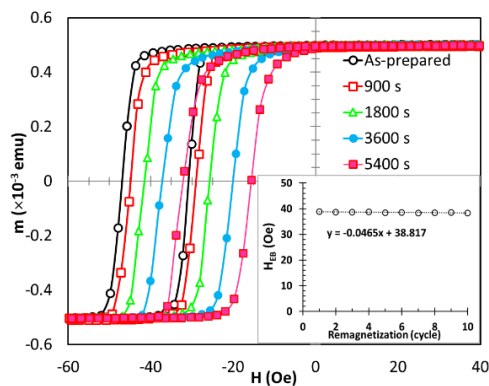


Figure 2. Hysteresis curves of as-prepared sample after immersion in 20 mL of DI water for 900-5400 s and variation of H_{EB} as a function of remagnetization cycle (inset)

The exchange bias field of the sample decreases from an initial value of 38.87 Oe to 38.38 Oe after the 10th remagnetization cycle. It is noted that the remagnetization process exhibited only a minor training effect, with a slight decrease in H_{EB} . Therefore, shifting of the m-H curve after immersion in the DI water is mainly due to

interaction of the sample with the DI water. However, corrosion in the exchange-biased thin films in this work reveals distinct effects on magnetic properties compared to those reported in thicker AFM layer exchange-bias thin films (Thongdee *et al.*, 2020). The step-like magnetization curve is absent in the exchange-biased thin films with the IrMn layer thickness of 200 Å.

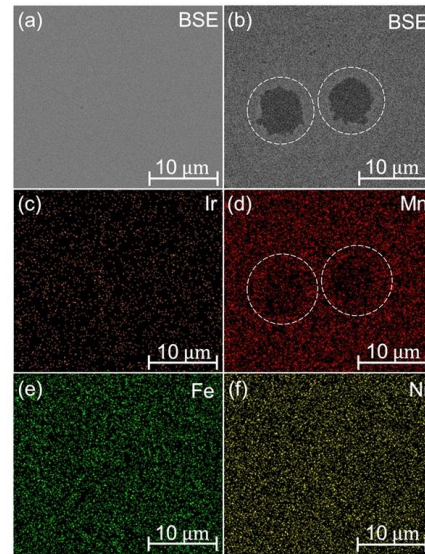


Figure 3. SEM images of the IrMn layer before immersion (a), after immersion in DI water for 5400 s (b) and the corresponding elemental mapping images of Ir (c), Mn (d), Fe (e), and Ni (f) of the immersed sample

The SEM images in Figure 3 illustrate how immersion in DI water affected the physical appearance of the IrMn surface. After immersion, the surface of the IrMn film exhibited signs of inhomogeneity. Additionally, elemental mapping of the sample was performed, with the SEM images of the mapping areas for both the as-prepared sample and the sample immersed in DI water for 5400 s displayed in Figure 3(a) and (b), respectively. The elemental color mapping of the corroded sample reveals a uniform distribution of Ir, Fe, and Ni particles, as shown in Figures 3(c), (e), and (f). In contrast, the atomic percentage (at.%) of Mn in the corroded area is significantly decreased, as depicted in Figure 3(d). EDS analysis revealed that the Mn atomic percentage (at.%) in the gray zone (outside the dashed circle) and the dark-gray zones (inside the dashed circles) of Figure 3(b) for the immersed sample decreased to approximately 86% and 34%

of that before immersion, respectively. This suggests that interactions occurred between the DI water and the IrMn layer. In the thinner IrMn exchange-biased thin films, corrosion manifests in small and scattered areas, whereas in the thicker IrMn layer, it is more aggressive in specific region, resulting in the formation of large strip-like corroded areas.

The m - H curves of the sample immersed in 20 mL of solutions containing detergent shifted toward the zero external field axis with increasing immersion time, but the saturation magnetic moment of the sample was not affected. Figure 4 shows the variation of the exchange bias field of the sample after immersion in solutions containing detergent concentrations ranging from 1% to 20% by volume in DI water for 60 to 360 s at room temperature (~ 300 K). A decrease in H_{EB} results from an increase in Mn corrosion within the AFM layer. Within the detergent concentration range of 1-5%, the corrosion rate increases with the concentration. However, as the concentration rises from 5% to 12% and 20%, the corrosion rate decreases and can be confirmed by SEM image in Figure 5. The smooth surface observed in the sample immersed in the solution with 12% detergent indicates the formation of an organic protective layer on the IrMn thin film exposed to the solution.

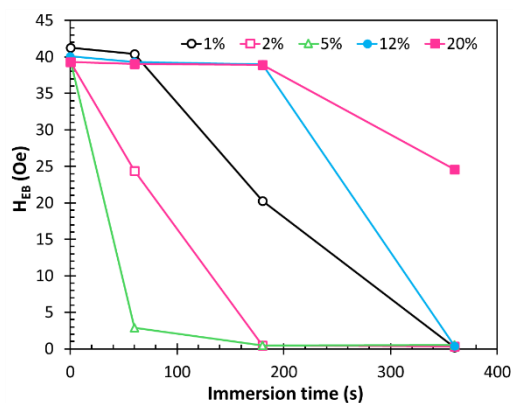


Figure 4. Variation of the exchange bias field with immersion time for the sample immersed in solutions containing detergent concentrations ranging from 1% to 20% by volume in DI water at room temperature

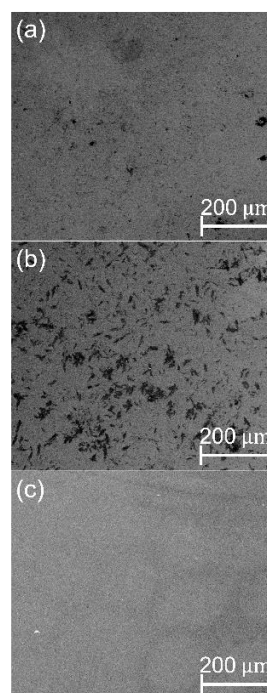


Figure 5. SEM images of the IrMn top layer after immersion in solutions with detergent concentration of 1% for 60 s (a), 180 s (b), and detergent concentration of 12% for 60 s (c)

The electric conductivity of the solutions, measured by conductivity meter (CM-21PW, DKK-TOA), increased from 0.530×10^{-3} S/m to 1.858×10^{-3} S/m as the detergent concentration increased from 1% to 5%, respectively. Electric conductivity can significantly influence the corrosion of materials, including metals like manganese. Higher conductivity solution can lead to faster corrosion rates due to increased ion mobility and more rapid electrochemical reactions. With a further increase in detergent concentration, the conductivity of the solution increases. The 2-aminoethanol molecules, acting as surface-active inhibitors, adsorb onto the IrMn surface with higher surface coverage, resulting in a decrease in the corrosion rate.

Variations of the exchange bias field as a function of temperature and immersion time for the sample immersed in a solution containing a detergent concentration of 1% by volume in DI water are compared in Figure 6. The H_{EB} of

the sample decreases with increasing temperature of the solutions. Significant reductions in H_{EB} with an increasing in immersion solution temperature indicate that temperature of the immersion solution is an important factor affecting corrosion rates.

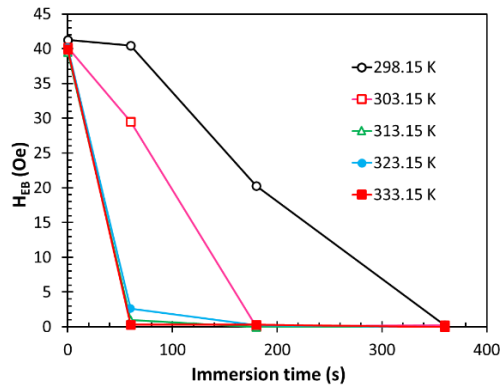


Figure 6. Variation of the exchange bias field with immersion time for the sample immersed in solutions containing a detergent concentration of 1% by volume in DI water, across temperature ranging from 298.15 K to 333.15 K

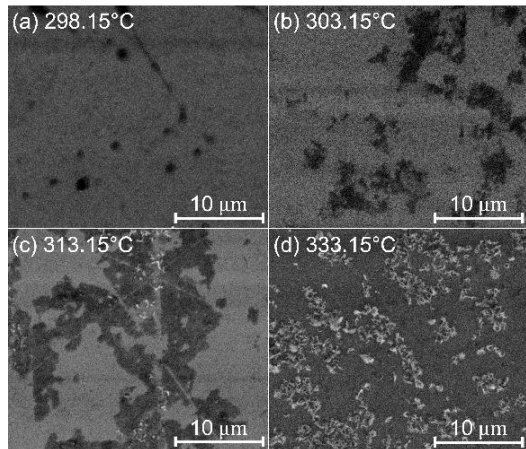


Figure 7. SEM images of the IrMn top layer after immersion in solutions containing 1% by volume of detergent in DI water, with temperature ranging from 298.15 K to 333.15 K

The effects of concentration and temperature on the corrosion rate can be explained using the Arrhenius equation (Laidler, 1984; Hamdy *et al.*, 2013; Ben Aoun, 2017).

$$C_R = Ae^{-E/RT}$$

Where C_R is the corrosion rate, A is the modified frequency factor (pre-exponential factor), E is the activation energy (J/mol), R is the gas constant (8.314 J/mol.K), and T is the absolute temperature. At a given temperature, solutions with higher conductivity exhibit lower activation energy. As a result, the corrosion rate tends to increase with rising conductivity. However, the presence of chemically stable surface-active inhibitors mitigates this effect by reducing the surface area vulnerable to corrosion and increasing the activation energy, thereby enhancing the solution's corrosion resistance.

According to the Arrhenius equation, the rate of a chemical reaction increases exponentially with temperature because higher thermal energy allows reactants to overcome activation energy barriers more easily. Furthermore, the decrease in inhibition efficiencies with increasing temperature in the presence of the inhibitor may be attributed to the weakening of physical adsorption at the metal/solution interface. This weakening causes the protective layer to lose its stability, thereby reducing the inhibition efficiency of the inhibitor, as depicted by the drastic corrosion observed on the surface of the sample when temperatures were raised, as shown in Figure 7. Therefore, temperature significantly increases the rate of metal electrochemical corrosion.

Conclusions

The investigation into the corrosion behavior of $\text{Co}_{30}\text{Fe}_{70}/\text{Ni}_{81}\text{Fe}_{19}/\text{Ir}_{20}\text{Mn}_{80}$ thin films immersed in DI water and detergent solutions provided valuable insights. Magnetic analysis showed minimal impact on the ferromagnetic underlayer, with a consistent saturation magnetic moment observed. Immersion in detergent solutions led to variations in the exchange bias field attributed to increased Mn corrosion within the AFM layer. Additionally, the study highlighted the significant influence of electric conductivity on corrosion rates, emphasizing the role of higher conductivity solutions in accelerating corrosion. Temperature also played a crucial role, increasing kinetic energy and accelerating corrosion processes. Understanding these factors is essential for effective corrosion mitigation in thin film manufacturing processes.

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