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ARTICLE

Preparation and Analysis of Nanoporous Soft Magnetic Sensitive Film

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Abstract: The magnetic properties of the soft magnetic sensitive film are the key factors to determine the performance of the magnetic sensor. In order to ensure process compatibility, the sensitive film is usually fabricated by magnetron sputtering, and its performance is generally poor, which greatly restricts the development of magnetic sensors. Therefore, how to fabricate thin sensitive film on silicon substrate which meets the performance requirements of magnetic sensor and which is compatible with the process of (micro electro mechanical system, MEMS) is an urgent problem to be solved. The correlated research indicated that, change of microstructure is conducive to improving the magnetic performances of sensitive film. In this paper, nanoporous thin films were prepared by standard MEMS technology. The related characterization and testing of sensitive films with different apertures were carried out, and the influence of aperture size on the soft magnetic properties of thin films was analyzed. The porous structure with larger than 50 nm pore size can reduce the H_s and H_c of sensitive film, and the effect of 100 nm structures is the most obvious to improve the soft performance of sensitive film. The conclusion of the experimental analysis provides support for the determination of preparation scheme and the performances improvement of sensitive film.

Key words: nanoporous; sensitive film; performance; preparation technology

Magnetic sensors are widely used in geomagnetic research, space exploration, micro-satellite, micro-UAV, etc. [1]. With the advancement of micro-electro-mechanical systems technology, micro-magnetic devices have been developed continuously. Because of their small size, easy integration and other advantages, they have attracted wide attention. However, although the size of micro magnetic devices is effectively reduced, the performance index is also reduced. For better application, it is necessary to analyze the influencing factors and solve the problem of performance degradation [2-4].

The magnetic properties of soft magnetic sensitive films are the key factors to determine the performance of micro magnetic devices. In order to ensure process compatibility, soft magnetic sensitive films are usually prepared by magnetron sputtering method, and their performance is generally poor, which greatly restricts the development of micro magnetic devices. If the sensitive film can be prepared on silicon substrate which meets the performance requirements of micro magnetic devices and which is compatible with the process of MEMS, this will promote the micro magnetic devices [5-7].

Luo[8] prepared conical-shaped M-type ferrite magnetic nanodot arrays on alumina substrate. This unique structure impacts the distribution of demagnetizing field and reduces the intensity of demagnetizing field. Assaf [9]deposited three layers of Mn, Ge, and Co successively by magnetron sputtering on SiO_2 to form a 200 nm-thick Co/Ge/Mn stack, and annealed it. The obtained MnCoGe thin films are polycrystallined and show high porosity. Zhu[10] prepared CFO thin films with vertically aligned nanorod structures from the bottom to top on silicon substrates by high magnetic field assisted pulsed laser deposition. With increasing of mag-

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netic field in deposition, lateral size of nanorods decreases, while the coercivity and magnetization increase. Ramirez[11] presented a study on the relationship between the structure and magnetic properties of a $Fe_{0.89}Ga_{0.11}$(Fe-Ga) alloy deposited onto glass, Si and MgO substrates. Fe-Ga/Si films show a fibre-like texture. Test results show that the magnetic behavior is closely related to the structural observed textures. In summary, changing the microstructures of soft magnetic films is an effective way to improve their magnetic properties.

In this work, nanoporous soft magnetic sensitive film was fabricated. Porous alumina template was grown on silicon substrate by two-step anodization method, and nanoporous soft magnetic thin film was fabricated on the basis of template, which realized the compatibility between the fabrication process and the MEMS process. The main properties of the thin sensitive film were measured.

1 Experiment

The preparation steps started with 4-inch p-type <100> silicon wafers. First, Copper film was RF magnetron sputtered on silicon wafers with pure Ar gas[12]. The process was completed in high vacuum multifunctional magnetron sputtering instrument (JGP450, China). Experimental parameters are shown in Table 1.

Second, aluminum film was prepared on the copper layer by DC magnetron sputtering after the substrate temperature was reduced to 100 ºC and maintained for 10 min. Experimental parameters are shown in Table 2.

Third, the sputtered specimen was ultrasonic-cleaned in acetone for 10 min and a two-step anodizing process was adopted in 3 wt% oxalic solutions at 40 V and 10 ºC to achieve uniform pore distribution. The aluminum specimens acted as anode and a graphite plate as cathode. In the first one, the specimens were anodized for 2 min to obtain a thin porous alumina film and then immersed in a 5wt% H_3PO_4+ 2wt% CrO_3 solution at 90 ºC for 6 min to eliminate the anodic alumina films. In the second step the specimens were reanodized until the aluminum layer was completely transferred into the alumina. To remove the isolated barrier layer and expose the conductive Cu layer, the anodized specimen was immersed in 5wt% phosphoric acid solution at 30 ºC for 20 min.

Table 1 Experimental parameters of the first step

Parameter	Value
Background pressure/Pa	4.0×10^{-4}
Working pressure/Pa	2.6
Argon gas flow rate/mL·min^{-1}	50
Power/W	180
Self-bias voltage/V	40
Deposition time/min	30
Substrate temperature/ºC	200
Film thickness/nm	300

Table 2 Experimental parameters of the second step

Parameter	Value
Background pressure/Pa	4.5×10^{-4}
Working pressure/Pa	0.3
Argon gas flow rate/mL·min^{-1}	15
Power/W	280
Voltage/V	400
Deposition time/min	150
Substrate temperature/ºC	100
Film thickness/nm	3000

Fourth, the specimen was cleaned by ultrasonic for 20 min, then rinsed and dried by deionized water and nitrogen gas. It acted as the cathode and a copper plate as the anode. The Cu electroplateing deposition was carried out for 8 min in a mixture of $CuSO_4$ (200 g/L), H_2SO_4 (34 mL/L), HCl (60 mg/L) and $AuC_6H_5O_7$ (4 mL/L), with a current density of 3 A/dm^2 and air agitating. After electrodeposition, the alumina was removed by immersion in NaOH solution (1 mol/L) at 25 ºC for 30 min. Then, the samples were thoroughly rinsed with distilled water and subsequently dried in nitrogen. This step obtained a copper nanowires array. The nanowires are parallel to each other, with a diameter of about 100 nm and a height of about 3 μm.

Finally, the process of NiFe electroplating was carried out with a current density of 3 A/dm^2 at 57 ºC for 10 min. The copper nanowires array acted as the cathode and a nickel plate as the anode. The electroplateing solution is a mixture of $NiSO_4\cdot6H_2O$ (150 g/L), $FeSO_4\cdot7H_2O$ (15 g/L), $NiCl_2\cdot6H_2O$ (75 g/L), H_3BO_3 (45 g/L), $C_6H_{11}NaO_7$ (20 g/L), $C_{12}H_{25}SO_4Na$ (0.3 g/L), $C_6H_4SO_2NNaCO\cdot2H_2O$ (2.5 g/L). The pH value was adjusted to 3.3.

The process for the fabrication of the porous thin film is shown in Fig.1.

2 Results and Discussion

Two step anodizing method is employed to improve pore regularity of anodic alumina films[13]. Fig.2 displays the surface morphologies of alumina films after eliminating the barrier layers. The pore size and distribution of the anodic alumina films are uniform with average pore sizes of 90 nm. The zones of pore sizes ranging from 80 to 100 nm are very narrow. According to calculation, the porosities of these films are estimated to be 40%, which are fully applicable to the function as a template[14]. The pore sizes and intervals are proportional to the applied potential.

The thickness of the soft magnetic thin films has a direct effect on the magnetic properties, and hence needs to be controlled. The surface profiles and thickness of alumina film were investigated by DektakXT step profiler, as shown in Fig.3. The first anodizing step was performed to convert 300 nm thickness of aluminum into porous oxide. Then the nanoporous layer formed was removed from the residual

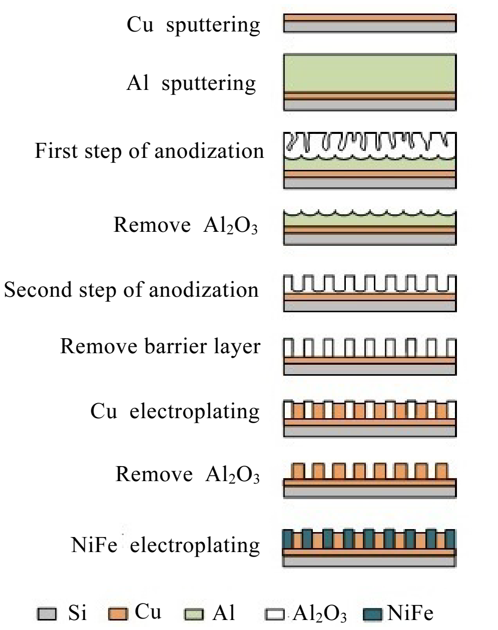

Fig.1 Fabrication process for the nanoporous magnetic film

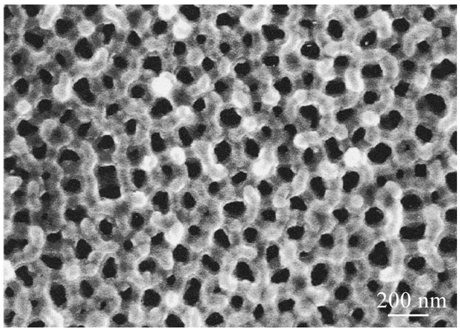

Fig.2 SEM image of the surface morphology of porous anodic alumina film

aluminum film (2700 nm). Following the second anodizing step the remanent aluminum layers were transferred to the anodic alumina films entirely. The thickness of alumina formed was anticipated to be about 3900 nm at the given anodizing conditions as the PBR (Pilling-Bedworth ratio) value for Al/Al_2O_3 was recorded to be 1.45.

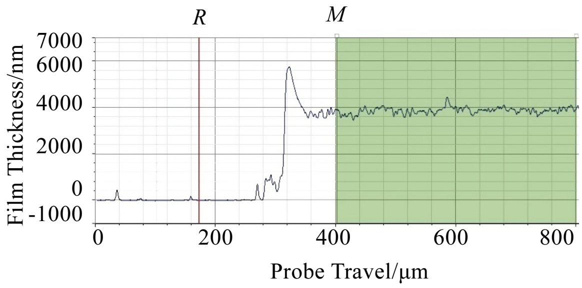

Fig.3 Thickness measurements for the specimen

The morphology of the sensitive film was investigated by SEM, as shown in Fig.4. The structure of nanoporous thin films has smaller crystalline particles, better shape size and uniformity, and regularly distribute in the substrate. The zones of pore sizes ranging from 80 nm to 100 nm is very narrow, which is consistent with the porous anodic alumina film.

The grains grow upward along the linear structure of copper nanowires array. When the plating time is 5 min, the gap in the middle of the nanowires is not filled. Over time, the grains grow gradually and occupy the gap part. At the same time, a large number of grains gradually agglomerate. When the plating time reaches 10 min, a dense NiFe film is formed, with regular distribution of nano-holes on the surface of thin film. Copper nanowires are retained in the middle of the holes. Because copper wire does not affect the magnetic properties of the films, it is not necessary to remove them.

The composition of thin film was tested by EDS. As shown in Fig.5, the characteristic peaks of EDS are relatively simple and the backs of each element characteristic peaks are relatively high. The results show that the mass content of Fe and Ni is 20.13% and 79.87%, respectively, which accords with the expected value.

In order to verify the enhancement of sensitive film magnetism by porous structure, and to study the influence

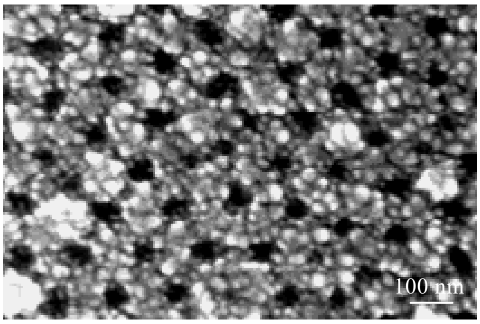

Fig.4 SEM image of the surface morphology of porous magnetic film

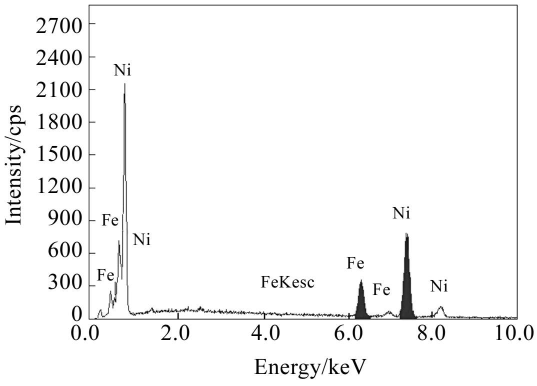

Fig.5 EDS analysis of porous magnetic film

of pore size on the soft magnetic properties of porous films, nonporous sensitive film and porous sensitive films with different pore sizes were prepared under the same experimental conditions, and their hysteresis loops were measured and compared. The hysteresis loops were measured by a vibrating sample magnetometer (JDJ9600). The maximum excitation field is 1500 A/m. The saturation magnetic field strength (H_s) and coercivity (H_c) are shown in Fig.6.

In Fig. 6, the blue line is the hysteresis loop of the nonporous sensitive film, while other lines are the hysteresis loop of the porous sensitive films prepared under the same conditions. Among them, the saturation magnetic field strength (H_s) and coercivity (H_c) of the nonporous sensitive film are 1200 and 190 A/m, respectively.

The saturated magnetic field strength and coercivity of porous sensitive film with 30 nm aperture are close to those of the nonporous sensitive film. The saturated magnetic field strength (H_s) and coercivity (H_c) of sensitive films with more than 50 nm aperture are significantly reduced. The corresponding values of sensitive films with various apertures are shown in Table 3.

By comparing the data in Table 3, it is shown that porous structure can reduce the H_s and H_c of sensitive films. Among the several porous structures tested, the 30 nm pore size structure has a very limited improvement on the magnetic properties of sensitive films. In addition, the porous structure with more than 50 nm pore size can reduce the H_s and H_c of the sensitive film to a certain extent, and improve the properties of sensitive films. Among them, the effect of 100 and 150 nm structures is the most obvious. The saturation magnetic field strength of the two structures is close, but the coercivity of 100 nm structures is slightly lower than that of 150 nm structures.

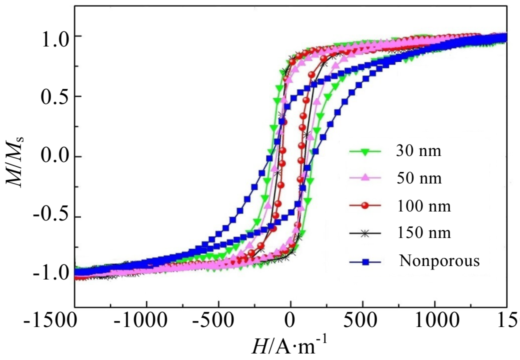

Fig.6 Comparison of hysteresis loops of the nonporous sensitive films

Table 3 Magnetism comparison of different sensitive films

Aperture/nm	H_c/A·m^{-1}	H_s/A·m^{-1}
Nonporous	180	1100
30	180	1000
50	132	750
100	81	500
150	103	500

The results show that the change of sensitive film microstructure can affect its magnetic properties. For magnetic thin films, grain refinement is helpful to improve their magnetism. Because of the existence of porous structure, the size and distribution of grains are more uniform. Therefore, the abnormal loss of materials are dramatically decreased, and the magnetization performance is improved obviously.

The decrease of H_s and H_c observed is also related to the change of additional stress in the sensitive film. The existence of additional stress can destroy the magnetic anisotropy of sensitive films, and lead to the increase of H_c and H_s. Additional stress is mainly composed of internal stress and thermal stress. Because the thermal stress of magnetic film is very small at room temperature, the additional stress involved in this paper is mainly composed of internal compressive stress. In porous structure, additional stress can be transferred evenly to nanowires, which can be buffered by the deformation of nanowires. At the same time, the existence of pores also contributes to the release of stress, which greatly reduces the impact of additional stress.

According to the above analysis, the decrease of H_c and H_s of nanoporous sensitive films can be attributed to the improvement of grain distribution and the release of additional stress in the film. The results of hysteresis loops show that porous Fe-Ni films have better soft magnetic properties than traditional nonporous sensitive films.

3 Conclusions

1) Porous anodic alumina templates are formed on silicon substrate through the anodization of sputter-deposited aluminum layer. The thickness of template, the pore sizes and interpore distance can be controlled by preparation conditions.

2) The nanoporous structure of the nanoporous thin sensitive films can reduce the H_s and H_c of sensitive films and improve the soft magnetic performance.

3) The porous structure with more than 50 nm pore size can reduce the H_s and H_c of sensitive films, and the effect of 100 nm structures is the most obvious in improving the soft performance of sensitive film.

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纳米孔软磁敏感膜的制备与分析

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摘 要：软磁敏感膜的磁性能是决定磁传感器性能的关键因素。为了保证加工工艺的兼容性，敏感膜通常采用磁控溅射法制备，其性能普遍较差，这严重制约了磁传感器的发展。因此，如何在硅基底上制备出符合磁传感器性能要求的敏感膜，同时加工过程与 MEMS 工艺兼容，是一个亟待解决的问题。相关研究表明，微观结构的变化有利于提高敏感膜的磁性能。本研究采用标准的 MEMS 技术制备了纳米多孔软磁敏感膜。对不同孔径的敏感膜进行了相关的表征和测试，分析了孔径大小对薄膜软磁性能的影响。结果表明，孔径大于 50 nm 的多孔结构可以降低敏感膜的 H_s 和 H_c，100 nm 多孔结构提高敏感膜的软磁性能效果最为明显。实验结论为制备方案的确定和敏感膜性能的改善提供了依据。

关键词：纳米孔；敏感膜；性能指标；制备工艺

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