

The effect of annealing on the structure and magnetic properties of FeCoN thin films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 989

(<http://iopscience.iop.org/0953-8984/11/4/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:45

Please note that [terms and conditions apply](#).

The effect of annealing on the structure and magnetic properties of FeCoN thin films

H Y Wang[†], E Y Jiang[‡], Z W Ma[§], Y J He[†] and H S Huang[†]

[†] Department of Physics, Tsinghua University, Beijing, 100084, People's Republic of China

[‡] Department of Applied Physics, Tianjin University, Tianjin, 300072, People's Republic of China

[§] Department of Material Science and Engineering, Tsinghua University, Beijing, 100084, Peoples's Republic of China

Received 6 July 1998, in final form 22 October 1998

Abstract. FeCoN films with 10 at.% Co content were prepared by the sputtering method. The effect of annealing on the structure and magnetic properties of FeCoN films was investigated. The as-deposited FeCoN films consist of α' -(Fe, Co) martensite. Annealing at 150–200 °C, α' -(Fe, Co) martensite transforms into the α'' -(Fe, Co)₁₆N₂ phase. The α'' -(Fe, Co)₁₆N₂ formed at 150–200 °C decomposes into α -(Fe, Co) and γ' -(Fe, Co)₄N at annealing temperature $T_a = 450$ °C, and it disappears in the FeCoN film annealed at $T_a = 500$ °C. The FeCoN films annealed at 150–400 °C show very high saturation magnetization $4\pi M_s = 25$ –27 kG, which confirms the high saturation magnetization of the α'' -(Fe, Co)₁₆N₂.

1. Introduction

Since the discovery of an abnormally high magnetization (2.83 T) in α'' -Fe₁₆N₂ by Kim and Takahashi [1], a lot of intensive work has been done to clarify the physical properties of α'' -Fe₁₆N₂. The reported values of the saturation magnetization range from about 3 T [2, 3] or 2.5–2.8 T [4–7] to almost the same as that of α -Fe [8]. Apart from the contradiction on the saturation magnetization of the α'' -Fe₁₆N₂ phase, the thermal stability of this phase reported in the literature was also quite different. According to the experiment by Jack [9], the α'' -Fe₁₆N₂ phase is metastable and it must decompose into $\alpha + \gamma'$ phases at about 200 °C. Most of the recent experiments have reconfirmed this fact [10, 11]. However, in studying the temperature dependence of saturation magnetization for α'' -Fe₁₆N₂ (001) films on InGaAs(001) or GaAs(001), Sugita *et al* [12, 13] have found that the saturation magnetization is changed reversibly with temperature up to around 400 °C.

In our previous work, we studied the structure and magnetic properties of FeCoN films [14]. Enhancement of the formation of α'' phase by Co addition was observed. The vibrating sample magnetometer (VSM) measurement shows that the FeCoN film with 10 at.% Co has saturation magnetization as large as 27 kG. This paper reports the effect of annealing on the structure and magnetic properties of the FeCoN films with 10 at.% Co content.

2. Experiment

The FeCoN films were prepared by facing targets sputtering on both Si and NaCl single crystal substrates. The sputtering targets are composite materials consisting of 30 mm × 15 mm

Co chips placed on 100 mm diameter \times 50 mm Fe (99.99%) targets. The sputtering gas and reactive gas were Ar (99.99%) and N₂ (99.99%) respectively. After the chamber was evacuated to a base pressure of 6×10^{-5} Pa, argon gas was introduced. During sputtering, the argon and the nitrogen gas pressures were kept at 0.3 and 0.04–0.06 Pa, respectively. The composition of the FeCoN films was adjusted by varying the number of Co chips mounted on iron targets. The deposition rate was about 0.2 nm s^{-1} . The substrate temperature was held at room temperature (RT). Annealing of the films was sequentially carried out from RT to 500 °C in vacuum (at least 10^{-4} Pa). The thickness of the film was 30–70 nm.

The crystal structures of the as-deposited and annealed FeCoN films were examined with a JEM-200CX transmission electron microscope capable of energy dispersive x-ray analysis. The saturation magnetization $4\pi M_s$ and coercivity H_c were measured with a vibrating sample magnetometer with a resolution of 2×10^{-6} emu in a magnetic field of 8 kOe which was applied parallel to the sample plane at room temperature. During annealing the specimen temperature was raised from room temperature to 500 °C in increments of 50 °C in vacuum. The sample was held at each temperature step for 30 minutes before the selected electron diffraction (SAD) patterns and bright field (BF) images were recorded. The cooling rate was about 10 °C min^{-1} . The thickness of the film was measured by the multi-beam interference technique. The composition was evaluated using electron probe analysis.

3. Results and discussion

To manifest the influence of the annealing behaviour on the structure and magnetic properties of FeCoN films, the concentration of Co was kept at 10 at.%. The effects of Co concentrations on the structural and magnetic properties of FeCoN films were reported in [14].

According to Jack [9, 15], in the α' -martensite phase, N atoms occupy randomly the octahedral interstices at the midpoints of the c edges of the bct cell (0, 0, 1/2), and the centres of the C faces, (1/2, 1/2, 0). As a result, the lattice constant c of the α' phase is elongated from 0.2866 to 0.3195 nm and the lattice constant a is shortened from 0.2866 to 0.2832 nm, respectively, depending on the N content. Under our conditions, the N content in the samples obtained by x-ray photoelectron spectroscopy was in the range of 9.5–11.1 at.%. According to [9], the lattice parameters are $a = b = 0.2837\text{--}0.2846$ nm and $c = 0.3118\text{--}0.3126$ nm.

The α'' phase has an ordered N site location of the octahedral interstices. The unit cell of the α'' phase contains eight of the expanded bct pseudo-unit cells and has dimensions $a' = 2a$ and $c' = 2c$, where a and c are the lattice constants of the pseudocell. In the larger true unit cell, the symmetry is also bct, since the α'' phase can be identified by observing reflections from this larger true unit cell for which $(h + k + l)$ is even. Based on this structural knowledge, phase identification is carried out in the present films.

Figure 1 shows the TEM selected area diffraction (SAD) patterns of the FeCoN film with 10 at.% Co content deposited onto NaCl(001) substrates at room temperature (RT) and TEM *in situ* annealed from 100 to 500 °C. The structural changes that occur with annealing temperature are observed clearly from the SAD patterns in figure 1. In the SAD of the as-deposited FeCoN film, only the α' (110) ring is observed. The SAD pattern shows a thick polycrystalline ring around the α' (110) ring. This is due to the distribution of lattice constants in addition to the tetragonal distortion of α -Fe by interstitial N atoms and the formation of the α' martensite phase. The sample shows no structural changes when heated below 150 °C; after annealing at 150 °C for 30 minutes, a new phase, α'' -(Fe, Co)₁₆N₂, starts to evolve and at $T_a = 150$ °C, the α' (110) thick ring, which had been observed in the as-deposited state, becomes sharpened. simultaneously, some single crystal diffraction spots of the α'' -phase, indexed as lying along the [001] direction in reciprocal space, come to be clearly observed. This

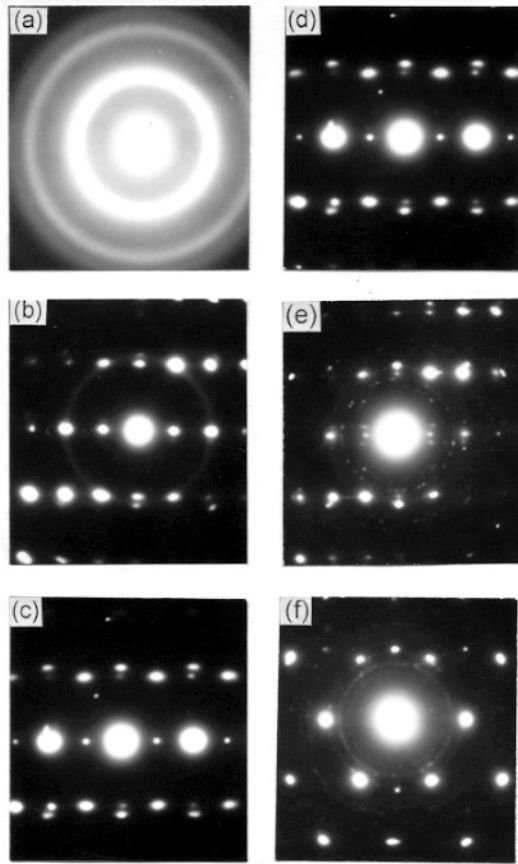


Figure 1. Changes in TEM selected area diffraction patterns of the FeCoN films with annealing temperature: (a) as-deposited; (b) $T_a = 150^\circ\text{C}$; (c) $T_a = 200^\circ\text{C}$; (d) $T_a = 400^\circ\text{C}$; (e) $T_a = 450^\circ\text{C}$; (f) $T_a = 500^\circ\text{C}$.

fact means that the N atoms become sufficiently mobile to redistribute over the interstitial sites and convert the N-martensite into α'' -phase at $T_a = 150^\circ\text{C}$. When $T_a = 200^\circ\text{C}$, the diffraction ring of α' -(Fe, Co) martensite disappears; the SAD only consists of single crystal diffraction spots of the α'' -phase, showing that α' - to α'' -phase transformation is completed at $T_a = 200^\circ\text{C}$. The SAD pattern shows no distinct change between 200 and 400°C . When $T_a = 450^\circ\text{C}$, some new phases, α -(Fe, Co) and γ' -(Fe, Co)₄N appear in the microstructure, which suggests that the α'' -phase decomposes into α' -(Fe, Co) and γ' -(Fe, Co)₄N phases at $T_a = 450^\circ\text{C}$. The intensity of α'' -spots decreases and that of α -(Fe, Co) spots and γ' -(Fe, Co)₄N rings increases distinctly. This reveals the decrease of α'' -phase and the increase of $\alpha + \gamma'$ -phases in the volume fraction. α -, γ' - and α'' -phases co-exist in the film at this annealing stage. When $T_a = 500^\circ\text{C}$, the α'' -spots disappear; only α [001]-spots and γ' -rings can be observed in the SAD pattern, indicating that the α'' -phase decomposes into $\alpha + \gamma'$ -phases entirely, and the sample is composed of α - and γ' -phases.

The structure evolves from the α' -martensite to the α'' -phase as the FeCoN film is annealed at 150 – 200°C . In the annealing process, collective reorientation of the martensitic $c_{\alpha'}$ -axes occurs, and finally, a full ordering ensues into the tetragonal α'' -phase. According to Jack

[9], in the α' -martensite phase, nitrogen atoms occupy randomly the octahedral interstices. The α'' -phase has an ordered nitrogen site location of the octahedral interstices. The crystal structure of α'' -Fe₁₆N₂ is bct ($a = 0.5728$ nm, $c = 0.629$ nm), so α'' -Fe₁₆N₂ can be described as a martensite with an ordered distribution of nitrogen atoms in the deformed octahedral interstices. The annealing treatment, needed to order the nitrogen atoms in the alloy, must be very gentle to prevent the stable compound forming. We found that a good annealing temperature was 150–180 °C.

For reliable phase identification in FeCoN films, a series of SAD patterns was obtained by means of double tilting. Figure 2 shows the selected area electron diffraction (SAD) patterns. Figure 2(a) is the SAD pattern with [001] incidence of the α'' single crystal. Figure 2(b) is the illustration of the SAD pattern with [001] incidence of the α'' -(Fe, Co)₁₆N₂ single crystal corresponding to figure 2(a). The representative indexing results are listed in table 1. Figure 2(c) shows the SAD pattern in the [011] direction at an angle of 42° to the [001] direction while figure 2(e) is the SAD pattern at an angle of 23° to [001] which is the incidence direction of $[\bar{1}13]$. The representative indexing results are also listed in table 1. Figures 2(d)

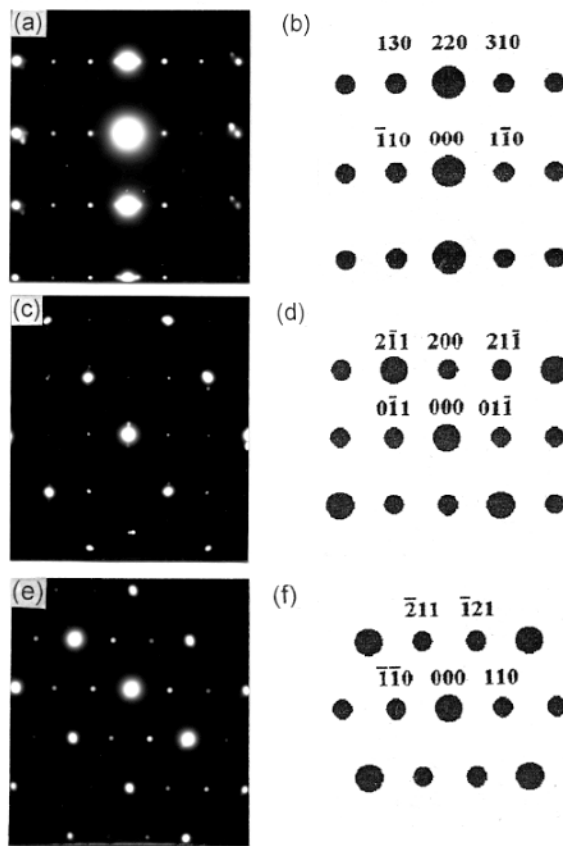


Figure 2. Selected area electron diffraction (SAD) patterns of α'' -(Fe, Co)₁₆N₂ (50 nm) films with 10 at.% Co content: (a) with the incidence of [001]; (b) schematic illustrations of SAD patterns corresponding to (a); (c) with the incidence of [011] by means of double tilting; (d) schematic illustrations of SAD patterns corresponding to (c); (e) with the incidence of $[\bar{1}13]$ by means of double tilting; (f) Schematic illustrations of SAD patterns corresponding to (e).

and 2(f) are the illustrations of SAD patterns with $[011]$ and $[\bar{1}13]$ incidence of the α'' single crystal corresponding to figure 2(c) and 2(e), respectively. One can see that the three patterns display a perfect symmetry. The superlattice reflections from (110), (011), (200), (202), (112), (211), (310), (031) and (004) of the α'' -phase are clearly observed. By using these superlattice reflections, the determined values of lattice constants $a = 0.5740 \pm 002$ nm and $c = 0.630 \pm 0.004$ nm of the α'' -phase are very close to the results obtained by Jack ($a = b = 0.572$ nm, $c = 0.629$ nm) [9]. This indicates that the Co containing α'' -alloy phase has the same structure as the α'' -Fe₁₆N₂ phase. EDX analysis was made of the same area of the SAD to determine the composition of the SAD area in the film. The composition of the area was determined to be 79 at.% Fe, 10 at.% Co and 11 at.% N. There are no diffraction spots or rings of Fe–Co or Co–N compounds in the SAD patterns. Therefore the phase corresponding to the single crystal spots in the SAD was determined to be a Co containing 16:2 nitride, which can be denoted by α'' -(Fe, Co)₁₆N₂.

Table 1. The interplanar spacing of the representative (hkl) in figure 2.

(hkl)	d_{exp} (Å)	d_{calc} (Å)
110	4.06	4.04
220	2.04	2.02
310	1.80	1.80
400	1.45	1.43
121	2.5	2.37
031	1.85	1.82
011	4.25	4.23
200	2.72	2.86

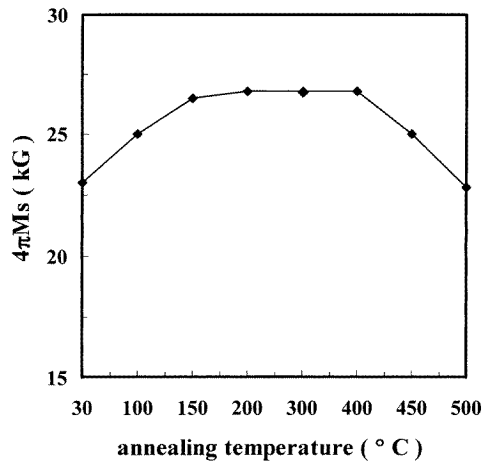


Figure 3. Dependence of $4\pi M_s$ for the FeCoN films on annealing temperature.

Figure 3 shows the dependence of $4\pi M_s$ on annealing temperatures in the FeCoN films. The value of $4\pi M_s$ gradually increases with the increase of annealing temperature. Around 200–400 °C, $4\pi M_s$ reaches the maximum of about 26–27 kG; with further increasing annealing temperature, $4\pi M_s$ decreases monotonically and reaches about 22 kG at 500 °C. This result is consistent with the structural changes in the FeCoN film. The increase of $4\pi M_s$ when $T_a < 200$ °C is ascribed to formation of α'' -(Fe, Co)₁₆N₂. The decrease in $4\pi M_s$ when

$T_a > 400^\circ\text{C}$ is considered to correspond to the phase change from α'' to $\alpha + \gamma'$. The FeCoN films annealed at 200–400 °C, in which the α'' -alloy phase gathered, have high values of $4\pi M_s = 26\text{--}27$ kG, which is larger than that of Fe–Co alloy with 30 at.% Co (24 kG). The saturation magnetization of the α'' -(Fe, Co)₁₆N₂ is as large as that of α'' -Fe₁₆N₂, indicating that appropriate Co addition does not induce notable changes in the giant magnetic moment of α'' -Fe₁₆N₂.

The temperature of phase transformation from α' to α'' in the FeCoN film is in good agreement with that of the α'' -Fe₁₆N₂ precipitates in bulk powder reported by Jack [9]. The temperature of α'' -phase decomposition in the FeCoN film is found to be quite different from that of Jack [9], but it is in agreement with the results reported by Sugita [12]. There is no observable change in the structure and saturation magnetization of the FeCoN film annealed up to 400 °C. The good thermal stability of the α'' -(Fe, Co)₁₆N₂ is discussed as follows. Due to a 10 at.% Co substitution, the lattice parameter of the bcc Fe–Co phase increased by 0.16% relative to that of the bcc pure Fe [16]. Assuming that the atomic volume of Co is the same as that of Fe, we presume that the interstitial sites are wider in the Fe–Co lattice than in the Fe lattice. This idea is supported by the fact that the solubility of nitrogen is increased by Co addition [17]. The α'' -phase is considered to be a nitrogen ordered form of the tetragonal Fe–N solid solution, which is derived without changing the basic arrangement of Fe atoms in the bcc structure. Therefore, it can be speculated that the Co containing 16:2 nitride also forms with less strain energy, leading to a higher stability.

In our previous work [18], we studied the role of alloying element Ti in the formation and stability of α'' -Fe₁₆N₂, and found that appropriate Ti addition can stabilize the α'' -phase to a temperature of 700 °C. The enhanced thermal stability of α'' in FeTiN films could be related to the presence and formation of TiN phase. Because Ti and TiN are non-magnetic materials, the saturation magnetization of FeTiN films with 15–18 at.% Ti is 23 kG, which is lower than that of FeCoN films.

4. Conclusion

The changes in the structure and magnetic properties of the FeCoN films with annealing temperatures were investigated. The FeCoN film deposited at RT, whose structure is bcc α' -martensite, possesses a saturation magnetization larger than that of α -Fe. Formation of α'' -(Fe, Co)₁₆N₂ was clearly observed in the films annealed at 150–200 °C. The magnetization of the annealed FeCoN films tends to increase with increasing volume fraction of α'' -(Fe, Co)₁₆N₂. This result indicates that the α'' -(Fe, Co)₁₆N₂ has a much larger magnetization. The α'' -(Fe, Co)₁₆N₂ phase is stable up to 400 °C, while beyond 400 °C it dissolves to α -(Fe, Co) and γ' -(Fe, Co)₄N. The $4\pi M_s$ value of the FeCoN films decreases rapidly once the annealing temperature exceeds 400 °C. The FeCoN films annealed at 150–400 °C show very high saturation magnetization $4\pi M_s = 25\text{--}27$ kG, which confirms the high saturation magnetization of the α'' -(Fe, Co)₁₆N₂.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No 59802005). The authors are grateful to Dr P Wu, H L Bai, Y Wang and others in the Thin Film Laboratory of Tianjin University.

References

- [1] Kim T K and Takahashi M 1972 *Appl. Phys. Lett.* **20** 492
- [2] Sugita Y, Takahashi H, Komuro M, Mitsuoka K and Sakuma A 1994 *J. Appl. Phys.* **76** 6637
- [3] Gao C and Doyle W D 1993 *J. Appl. Phys.* **73** 6579
- [4] Nakajima K, Okamoto S and Okada T 1989 *J. Appl. Phys.* **65** 4357
- [5] Ortiz C, Dumpich G and Morrish A H 1994 *Appl. Phys. Lett.* **65** 2737
- [6] Jiang H, Tao K and Li H 1994 *J. Phys.: Condens. Matter* **6** L279
- [7] Wallance W E and Huang M Q 1994 *J. Appl. Phys.* **76** 6648
- [8] Takahashi M, Shoji H, Nashi H, Wakiyama T, Doi M and Matsui M 1994 *J. Appl. Phys.* **76** 6642
- [9] Jack K H 1951 *Proc. R. Soc. A* **208** 216
- [10] Takahashi M, Shoji H, Takahashi H, Wakiyama T, Kinoshita M and Ohta W 1993 *IEEE Trans. Magn.* **29** 3040
- [11] Kopcewicz M, Jagielski J, Gawlik G and Turos A 1992 *Nucl. Instrum. Methods Phys. Res. B* **68** 417
- [12] Sugita Y, Mitsuoka K, Komuro M, Hoshiya H, Kozono Y and Hanazono M 1991 *J. Appl. Phys.* **70** 5977
- [13] Takahashi H, Komuro M, Mitsuoka K, Sugita Y, Kobayashi T and Kita E 1995 *J. Japan. Appl. Magn. Soc.* **19** 353
- [14] Wang H Y and Jiang E Y 1997 *Appl. Phys. A* **65** 203
- [15] Jack H K 1951 *Proc. R. Soc. A* **208** 200
- [16] Pearson W B 1958 *A Handbook of Lattice Spacing and Structures of Metals and Alloys*
- [17] Raghavan V 1987 *Phase Diagrams of Ternary Iron Alloys* part 1, p 167
- [18] Wang H Y, Jiang E Y and Wu P 1998 *J. Magn. Magn. Mater.* **177–181** 1285