

X-ray photoelectron spectroscopy study of the role of nitrogen in FeSiAl(N) reactive sputtered films

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Nitrogen has a profound effect on the stress, nanostructure, and magnetic properties of FeSiAl(N) reactive sputtered films. X-ray photoelectron spectroscopy is an excellent tool to investigate the role of N in these films, since it provides both compositional and chemical bonding information simultaneously. The N is observed to first combine with the Al in the films. For increasing amounts of N, increasing amounts of Al as nitride are observed. Then at the point that the Al is all nitride, the N starts to combine with Si. It is in this region that an abrupt change is observed in magnetic properties, stress, and nanostructure. For low N, the films consist of single phase 100-nm-diam bcc grains; after the transition, films consist of a two phase nanostructure of 10-nm-bcc grains in an amorphous matrix. The N content of the films also increases sharply at this point. The addition of N to the sputtering plasma also causes changes in the apparent relative sputtering yields at these higher N levels: Fe content of the films decreases considerably, while Al and Si percentages show modest increases. This can help explain why the saturation magnetization (M_s) has been observed to decrease with increasing N in the plasma, for these higher N levels. © 2002 American Institute of Physics. [DOI: 10.1063/1.1453949]

I. INTRODUCTION

There has been considerable recent research interest in the soft magnetic behavior of sputtered FeSiAl(N) films produced by reactive sputtering FeSiAl with Ar/N₂ plasma. Studies have shown that N can have a strong effect on the microstructure, stress, magnetic properties, and domain structure of the resulting films.¹⁻⁴ However, there are still some important questions concerning this materials system that are not well understood, in particular, the role of the N, how its addition to the sputtering gas affects the film composition, and where it goes and what it combines with in the resulting structure and micro/nanostructure. X-ray photoelectron spectroscopy (XPS) is an important characterization technique to investigate some of these issues, since it provides both chemical bonding and compositional information simultaneously.

II. EXPERIMENTAL DETAILS

A series of FeSiAl(N) films was deposited by reactive rf diode sputtering from a Sendust alloy target (nominal composition Fe 74; Si 17; Al 9 at.%) onto SiO₂/Si substrates. The target was a 6-in. diam disk, and the target-substrate distance was 2 in. Nitrogen partial pressure (pp) levels were varied for the series. Total gas pressure (9.6 mTorr) and forward power (1.43 W/cm²) were kept constant. This yielded a sputtering rate of 15.0 (±0.7) nm/min and film thicknesses of 1.7±0.1 μm.

The XPS data were obtained using a Physical Electronics (PHI™) 5500 Multitechnique ESCA system with monochromatic Al K α radiation. Energy calibration was done using the Au 4f_{7/2} and Cu 2p_{3/2} excitations at 84.0 and at 932.6 eV, respectively. The photoelectron take-off angle was 45°. Spectra were taken for the Fe 2p, Si 2p, Al 2p, N 1s, O 1s, and C 1s electron peaks for the series of samples after 20 min of ion etching using 4 kV argon ions at 3 μA target current. This corresponds to the removal of more than 20 nm of surface film. The removal of this amount of material provided stable Al/Fe/Si/N ratios in previous depth profile experiments. The atomic concentration calculations used the sensitivities provided with the PHI™ acquisition software.

Magnetic properties of the films were characterized by vibrating sample magnetometry and magnetic force microscopy. Film stress was determined by atomic-force microscopy measurements of the curvature of the film-substrate combination. Film structure and micro/nanostructure were determined from x-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) fracture cross sections. The micro/nanostructure, stress, and magnetic property relationships are discussed in greater detail in another publication.¹

III. RESULTS AND DISCUSSION

The Al (2p) binding energy results for the series of films with varying levels of N partial pressure are shown in Fig. 1, and the Si (2p) binding energy results for the series are shown in Fig. 2. The N (1s) and Fe (2p) binding energy results showed no discernable changes between films of the

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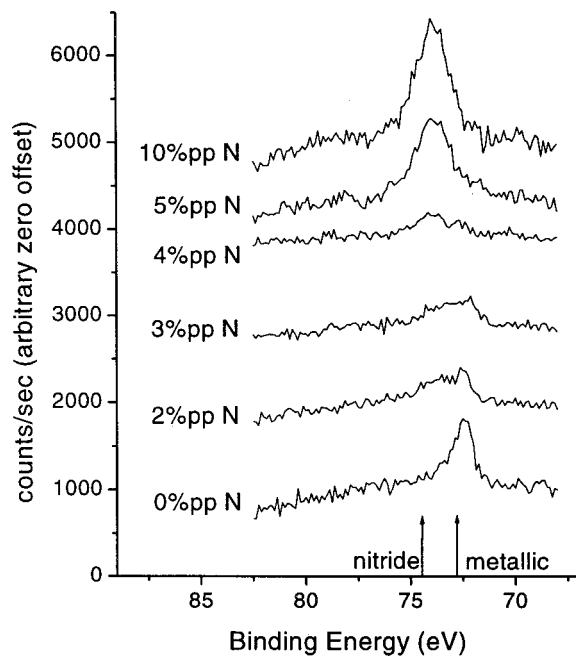


FIG. 1. XPS binding energy spectra of Al ($2p$) in FeSiAl(N) sputtered films, for varying levels of N partial pressure (pp) in the sputtering plasma. Arrows indicate expected positions of metallic and nitride binding energies (from Ref. 5).

series, so they are not shown here. The atomic concentrations of the elements are shown as a function of N% partial pressure (pp) in Table I.

The film sputtered with pure Ar shows metallic bonding for Al and Si, as might be expected (Figs. 1 and 2, respectively). The added N first shows up in the films associated

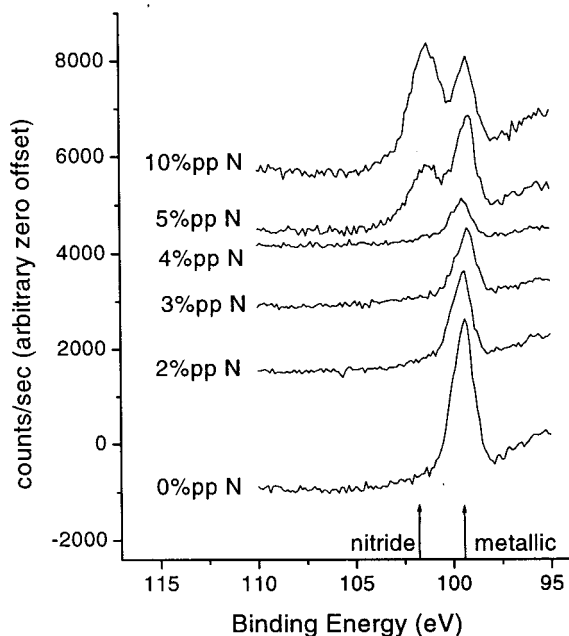


FIG. 2. XPS binding energy spectra of Si ($2p$) in FeSiAl(N) sputtered films, for varying levels of N partial pressure (pp) in the sputtering plasma. Arrows indicate expected positions of metallic and nitride binding energies (from Ref. 5).

TABLE I. Atomic concentrations of elements in the films.

N% pp in the plasma	N (at. %) in the films	Al (at. %)	Si (at. %)	Fe (at. %)	O (at. %)
0	0.0	3.41	8.30	86.90	1.39
2.1	3.22	4.93	6.76	83.90	1.20
3.1	3.82	3.93	6.61	85.23	0.42
4.2	5.15	4.39	5.98	82.36	2.12
5.1	13.62	6.52	9.20	68.41	2.43
10.4	18.18	7.69	9.95	61.42	2.76

with the Al. For the 2% pp N film, the Al ($2p$) spectrum shows a broad distribution that appears to be a combination of metallic Al and Al in AlN, while the Si ($2p$) spectrum shows a distinct sharp peak at the metallic position. This film has about 3 at. % N actually incorporated into the film, and 5 at. % Al and 7 at. % Si. Addition of further N causes the fraction of Al as nitride to increase (see 3% pp N film in Fig. 1), and the spectrum to appear as a more distinct bimodal AlN+Al distribution. Note that at 3% pp N, the N and Al contents of the film are essentially equal and the Si appears metallic, yet there is still a substantial amount of Al in the metallic state. This would appear to indicate that some of the N is in the bcc Fe(SiAl) lattice (by process of elimination, since in XRD and TEM, the material appears as single phase bcc). At 4% pp, the Al ($2p$) spectrum appears as a broad peak, with nitride predominating, but some metallic Al still appears as a lesser constituent. The Si peak shows predominantly metallic character, with no evidence of a nitride peak. Thus at this point, the Al is almost all nitride, but none of the Si is reacted yet. Again, the total amount of N in the film appears to be more than the amount of Al, so by process of elimination, it would appear to be associated with the Fe.

Between 4% and 5% pp N, abrupt changes have been observed in the micro (nano) structure, stress, and magnetic properties.¹ While the region from 0% to 4% ppN showed a microstructure of single phase bcc columnar grains about 100 nm diam, at 5% pp N and beyond, the films now consist of a two-phase nanostructure consisting of equiaxed bcc nanograins less than 10 nm diam, in an amorphous matrix. The compressive stress also decreases by about a factor of 6, and the coercivity shows an abrupt decrease as well.

The XPS results likewise show abrupt changes between 4% and 5% pp. There is a sharp increase in the amount of N content in the films, jumping from 5.1 to 13.6 at. %. The AlN peak becomes much more sharp and well defined, and a substantial amount of the Si now appears as nitride. The Si ($2p$) spectrum shows metallic and nitride peaks in the ratio of approximately 54%/45%, respectively. Allowing for the Si_3N_4 stoichiometry, there appears to be about 1.6 at. % N unaccounted for, and presumably associated with Fe in some way, although we do not know whether that is in the bcc nanograins, or the amorphous matrix. Further addition of N causes additional incorporation of N into the film, with the N content climbing to 18.2 at. %. The AlN XPS peak is sharp and distinct, and the Si spectrum shows metallic and nitride peaks, with Si_3N_4 now the predominant constituent, by a ratio of 34%/66%. Again, it appears that there is some N not accounted for (about 1.7 at. %). In the region of two-phase

nanostructure (5% pp N and greater) it is tempting to speculate that the bcc nanograins are predominantly Fe and incorporate the metallic Si (which is about 4.1 at. % for 5% pp N), while the amorphous matrix would consist of aluminum nitride, silicon nitride, and an unknown amount of Fe. However, the available TEM cannot make accurate composition measurements on such a fine scale.

The addition of N to the plasma also changes the apparent relative sputtering yields of Fe, Si, and Al from the alloy target. Fe decreases as N% pp increases, with an abrupt downward change between 4% and 5% pp N. In a previous publication, we reported that after the nanostructural and stress transition between 4% and 5% pp N, saturation magnetization (M_s) decreases with increasing N partial pressure.¹ It now appears that one of the major factors contributing to this is the decreasing Fe content of the films (see Table I). In addition, the Al and Si contents are both observed to increase modestly for 5% pp N and beyond. This could perhaps be an effect of sputtering ion mass. N is much lighter than Ar, and light ions would be expected to sputter lighter atoms (i.e., Al and Si) more efficiently than heavier atoms (Fe). Another possible explanation might be chemical reactions at the sputtering target surface for increased N partial pressure.

One previous study in the literature has reported XPS measurements of sputtered FeSiAl(N) films.³ Their films were thicker (3.0 μm) and were deposited by dc magnetron sputtering (generally a higher-rate, lower ion energy, lower substrate-temperature process than rf diode sputtering), at about 10 times higher rate (168 nm/min) onto AlTiC substrates. While their results and ours agree on the general picture of the N first reacting with the Al, then the Si, there are some major differences in our findings. They do not see the abrupt change in magnetic properties, N content, stress, and nanostructure that we observe. They observe a transition from 200 nm grains, to a mixture of 200 nm and 20 nm grains, to exclusively 20 nm grains as N content is increased. We see a transition from 100 nm grains to a two-phase nanostructure of 10 nm grains in an amorphous matrix. They find optimum magnetic properties (e.g., minimum coercivity) in the region where the Al is not entirely reacted, and the Si is

all metallic. In the present study, magnetic properties were observed to improve considerably after the transition to a two-phase nanostructure, when all the Al is nitride, and some of the Si is nitride and some metallic.

IV. CONCLUSIONS

N has a profound effect on the stress, nanostructure, and magnetic properties of FeSiAl(N) reactive sputtered films. The incorporation of N has been investigated by XPS. The N is observed to first combine with the Al. For increasing amounts of N, an increasing fraction of Al is nitride. Then at the point that the Al is all nitride, the N starts to combine with Si. It is in this region that an abrupt change is observed in magnetic properties, stress, and nanostructure. For low N, the films consist of single phase 100-nm-diam bcc grains. After the transition, the films consist of a two-phase nanostructure of 10 nm bcc grains in an amorphous matrix. The N content of the films also increases sharply at this point. The addition of N to the plasma causes changes in the apparent relative sputtering yields at the higher N levels; Fe content of the films decreases considerably, while Al and Si percentages show modest increases. This can help explain why for high N levels, the saturation magnetization has been observed to decrease with increasing N in the plasma.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82.

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