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# Influence of nanostructure and nitrogen content on the optical and electrical properties of reactively sputtered FeSiAl(N) films

## Abstract

In this study, the optical properties and dc resistivity of a series of FeSiAl(N) films reactively sputtered with different partial pressures of N were investigated. Spectroscopic ellipsometry was used to measure the real and imaginary parts of the complex dielectric functions. There is a distinct micro/nanostructural transition from single-phase columnar body-centered-cubic (bcc) grains for partial pressure (pp) of nitrogen in sputtering gas  $\leq 4\%$  to a two-phase nanocomposite of equiaxed bcc nanograins in an amorphous matrix for films deposited with  $\geq 5\%$  pp N. To assess the effect of surface oxidation on the optical properties, optical measurements were repeated on the 2 and 5% pp N films (representative of the two different types of films with different structures) after they were sputter etched *in situ* while performing depth profiling of the chemical composition using x-ray photoelectron spectroscopy. The low-nitrogen films ( $\leq 4\%$  pp N) showed a dielectric function typical of a metal whose charge carrier contribution can be described by a classical free electron Drude model. The nanostructured films ( $\geq 5\%$  pp N) showed a positive real part of the dielectric function and no evidence of free-carrier plasmon excitation. The optical conductivity decreased and the dc resistivity increased by about a factor of 2.5 as the film structure changed from a single phase columnar structure to the two-phase material that consisted of nanograins in an amorphous matrix.

## Keywords

Ames Laboratory, Thin film structure, Sputter deposition, Dielectric function, Thin films, Dielectric thin films

## Comments

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# Influence of nanostructure and nitrogen content on the optical and electrical properties of reactively sputtered FeSiAl(N) films

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In this study, the optical properties and dc resistivity of a series of FeSiAl(N) films reactively sputtered with different partial pressures of N were investigated. Spectroscopic ellipsometry was used to measure the real and imaginary parts of the complex dielectric functions. There is a distinct micro/nanostructural transition from single-phase columnar body-centered-cubic (bcc) grains for partial pressure (pp) of nitrogen in sputtering gas  $\leq 4\%$  to a two-phase nanocomposite of equiaxed bcc nanograins in an amorphous matrix for films deposited with  $\geq 5\%$  pp N. To assess the effect of surface oxidation on the optical properties, optical measurements were repeated on the 2 and 5% pp N films (representative of the two different types of films with different structures) after they were sputter etched *in situ* while performing depth profiling of the chemical composition using x-ray photoelectron spectroscopy. The low-nitrogen films ( $\leq 4\%$  pp N) showed a dielectric function typical of a metal whose charge carrier contribution can be described by a classical free electron Drude model. The nanostructured films ( $\geq 5\%$  pp N) showed a positive real part of the dielectric function  $\epsilon_1$  and no evidence of free-carrier plasmon excitation. The optical conductivity decreased and the dc resistivity increased by about a factor of 2.5 as the film structure changed from a single phase columnar structure to the two-phase material that consisted of nanograins in an amorphous matrix. © 2003 American Institute of Physics. [DOI: 10.1063/1.1593802]

## I. INTRODUCTION

Recent investigations of FeSiAl(N) thin films, prepared by reactive sputtering of FeSiAl using an Ar/N<sub>2</sub> gas mixture with various partial pressures (pp) of N<sub>2</sub>, have shown that the structure, stress state, magnetic properties, and domain structure of the resulting films are strongly affected by the nitrogen content.<sup>1-3</sup> A distinct micro/nanostructural transition has been observed between films deposited with 4% pp N or less, which are single phase with 100 nm diam columnar grains and body-centered-cubic (bcc) crystal structure, and those deposited with 5% pp N or more, which consist of a two-phase nanostructure of 10 nm diameter bcc nanograins in an amorphous matrix.<sup>1</sup> It should be noted that the percentage of nitrogen in the films was not the same as the percentage of pp of nitrogen in the sputtering gas. The role of N in

FeSiAl(N) films was investigated using x-ray photoelectron spectroscopy (XPS) which provided information on both chemical bonding and the composition.<sup>4</sup> The N was observed to first combine with the Al in the low N films, whereas for N films with higher content, when all the Al is converted into nitride, N then combines with Si. This is the region where an abrupt change in micro/nanostructure, magnetic properties, and stress was observed. In a study of magnetization reversal in the FeSiAl(N) films using magnetic force microscopy, strong domain wall pinning was observed in 0–4% pp N films, while for 5 and 10% pp N films this strong domain wall pinning was not observed.<sup>3</sup>

The nature of the two-phase nanostructure observed in the FeSiAl(N) films deposited with  $\geq 5\%$  pp N is still not completely understood. In particular, the role of the amorphous matrix on the magnetic properties (e.g., its effects on exchange coupling between magnetic nanograins) and electrical properties of the films has yet to be determined. In this

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work we measured the complex dielectric functions, optical conductivities and dc resistivities for a series of FeSiAl(N) films sputtered with 0–10% pp N, with an eye towards obtaining a better understanding of the effects of the film structure on the optical and electrical properties. Optical properties of a material are sensitive to the surface of the material and can be strongly influenced by the micro/nanostructure. Therefore optical investigation of FeSiAl(N) films can provide information about the roles of different constituents (i.e., nanograins and the amorphous matrix) on the physical properties of nanocomposite films.

In this article, we report the results of extensive study using spectroscopic ellipsometry. It is a highly surface-sensitive, nondestructive technique which provides information on the complex dielectric function of materials. We also report four-point probe measurements of the dc resistivity.

## II. EXPERIMENTAL DETAILS

A series of FeSiAl(N) films was deposited by reactive rf diode sputtering using an Ar+N<sub>2</sub> gas mixture with different partial pressures of nitrogen. The target was a 6 in. diam Sendust alloy disk (nominal composition: Fe: 74; Si: 17; Al: 9 at. %) and the substrates were 3 in. Si(100) wafers with 300 nm of thermal SiO<sub>2</sub> on the surface. The target–substrate distance was fixed at 5 cm. During deposition, the nitrogen partial pressure was fixed at a preset value by controlling the nitrogen gas flow. The total gas pressure (9.6 mTorr) and forward power (1.43 W/cm<sup>2</sup>) were kept constant. The film thicknesses were measured to be 1.7±0.1 μm by cross-sectional scanning electron microscopy (SEM).

Complex dielectric functions,  $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$  where  $\omega$  is the angular frequency of the photons, and complex optical conductivity,  $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ , were obtained using rotating analyzer ellipsometry.<sup>5,6</sup> Optical measurements using spectroscopic ellipsometry between 1.5 and 5.0 eV at room temperature were carried out for 0, 1, 2, 3, 4, 5, and 10% pp N films. To investigate the effect of surface oxidation on the dielectric functions, the 2 and 5% pp N thin films were sputter etched to remove their surface oxide layer. The films were sputter etched *in situ* in an XPS system [Physical Electronics (PHI™) 5500 Multitechnique ESCA system] to allow determination of when sufficient material had been removed. The sample surface was etched using 4 kV Ar ions at 3 μA total target current, which gave an etching rate of approximately 1 nm/min. The total etching time for each sample was 20 min, and this gave stable Fe/Si/Al ratios and stable minimum oxygen contents, showing that surface oxide had been removed. This corresponded to removal of approximately 20 nm. The optical properties of the films were then measured again *ex situ* under the same experimental conditions.

The dc resistivity of the FeSiAl(N) thin films was measured using a four-point probe. The probes use a in-line geometry, and are spaced 1 mm apart. Each film sample was approximately 1 cm<sup>2</sup>. The resistance of each film sample was determined for currents of 0.1, 1, and 10 mA, and measured at five different locations on the film sample for each current level. The resistivity values  $\rho$  were obtained using the equa-

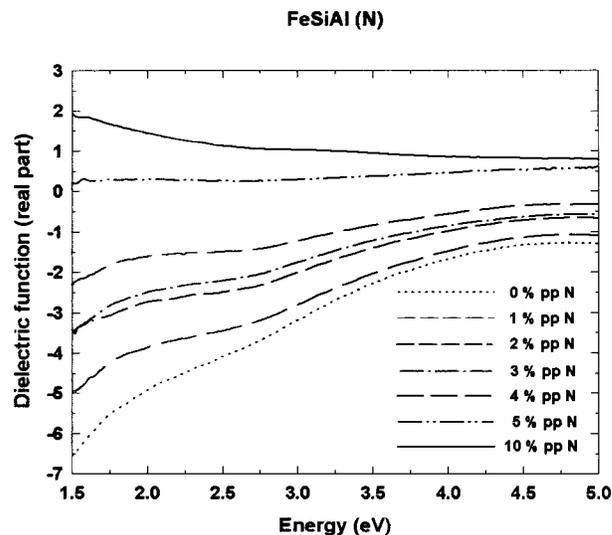


FIG. 1. Real part of complex dielectric function  $\epsilon_1$ , for a series of FeSiAl(N) thin films.

tion,  $\rho = (\pi/\ln 2)tR$ , where  $t$  is the film thickness and  $R$  is the resistance determined directly from the in-line four-point probe measurements.

## III. RESULTS AND DISCUSSION

Figure 1 shows the real part of the complex dielectric function ( $\epsilon_1$ ) for the 0, 1, 2, 3, 4, 5 and 10% pp N FeSiAl(N) films. As shown in Fig. 1, the sign of  $\epsilon_1$  was found to be different for the two types of films (0, 1, 2, 3, 4% and 5 and 10% pp N, respectively), which have different micro/nano structures. The 0% pp N film shows the largest negative values of  $\epsilon_1$ , thereafter  $\epsilon_1$  increases with an increase in N. It remains negative up to 4% pp N over the energy range measured. The 0–4% pp N films have microstructures similar to that in Fig. 2(a). They appear to be single phase, with a bcc crystal structure and grains about 100 nm in diameter.  $\epsilon_1$  crosses zero and becomes positive for the 5 and 10% pp N films, which have very different nanostructures [see Fig. 2(b)]. They consist of a two-phase nanocomposite of equiaxed bcc nanograins (10 nm diameter or less) embedded in an amorphous matrix.

The structural transition observed between the low-nitrogen and high-nitrogen films was accompanied by abrupt changes in magnetic properties.<sup>1</sup> As shown in Fig. 3, the coercivity increased with pp N, peaked for 3% pp N, and then decreased steeply for N>4% pp N where the transition to a two-phase nanocomposite structure occurred. The saturation magnetization was constant from 0 to 4% pp N, and then decreased with the addition of N as shown in Fig. 3. It dropped almost 50%, by 10% (pp) N, compared with the 0% pp N film. This indicates that one of the two phases (bcc nanograins or amorphous phase) has lower saturation magnetization.

Detailed comparisons of dielectric functions and optical conductivity between the 2% pp N film selected and the 5% pp N film, representative of the two different types of films, are shown in Figs. 4 and 5. The spectra of the real and imaginary parts of the complex dielectric function (i.e., both

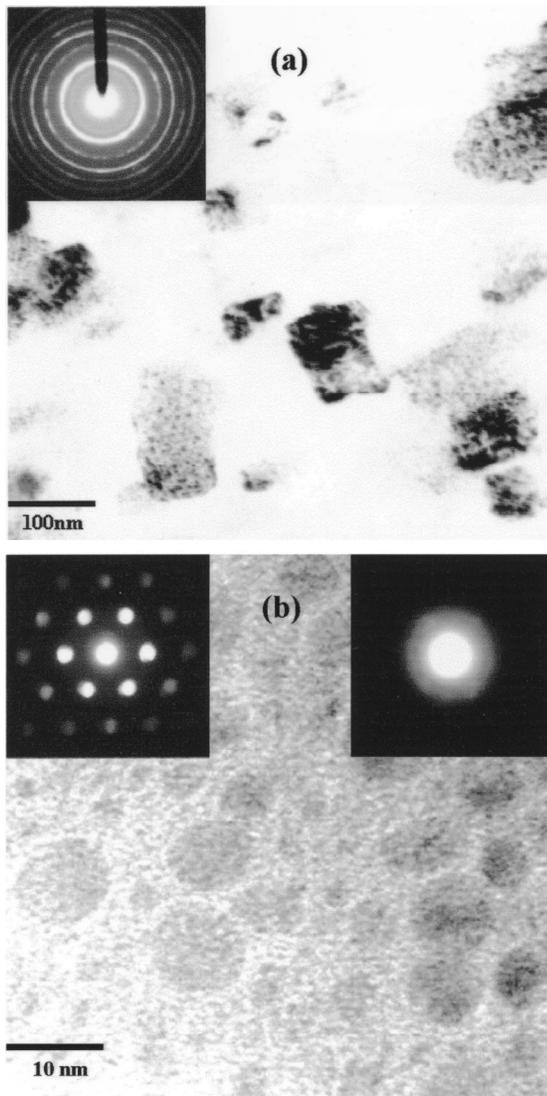


FIG. 2. Plan view TEM micrographs of the (a) 2% pp N film (negative of a dark field image) and (b) 5% pp N films (bright field image). The inset of (a) is the selected area diffraction pattern of the image. The inset at the top left-hand corner of (b) is a convergent beam electron diffraction (CBED) pattern that shows the bcc structure of the nanograins, and the one at the top-right hand corner is a CBED of the amorphous matrix. Note that magnification in (b) is 10× greater than (a).

$\epsilon_1$  and  $\epsilon_2$ , respectively) measured from the 2 and 5% pp N films before and after XPS sputter etching are shown in Fig. 4. The  $\epsilon_1$  spectrum for the 2% pp N film shows behavior similar to that of typical metallic materials which can be quantitatively described using a classical free electron Drude model.<sup>7</sup>

The small peak that appears at about 2.0 eV in the  $\epsilon_1$  spectrum of the 2% pp N film, which becomes evident after sputter etching of the oxidation layer, may originate from interband transitions. For the 5% pp N film, spectrum  $\epsilon_1$  is positive in the energy range measured. This excludes plasmon excitation, suggesting there is no free-carrier plasmon excitation in the 5% pp N film and that this material cannot be described by the Drude model. The magnitude of  $\epsilon_2$  for the 5% pp N film is noticeably smaller than that of the 2% pp

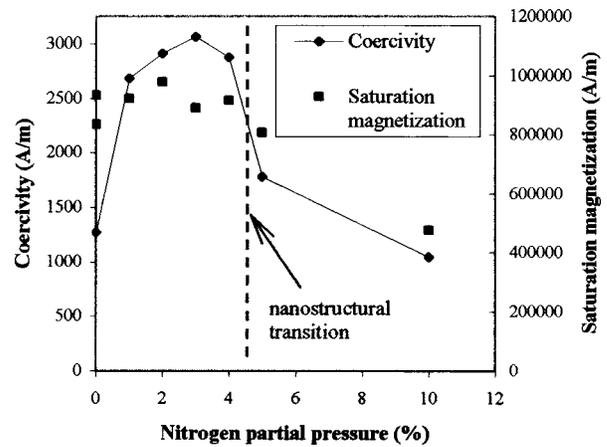


FIG. 3. Coercivity and saturation magnetization of the FeSiAl(N) films vs the percentage of nitrogen partial pressure.

N film. After sputter etching, the  $\epsilon_2$  spectra of both films show a slight enhancement in magnitude.

The real part of the complex optical conductivity  $\sigma_1$  is related to  $\epsilon_2$  by  $\sigma_1 = \omega \epsilon_2 / 4\pi$ .<sup>7</sup> As shown in Fig. 5, the  $\sigma_1$  spectrum for the 2% pp N film shows a feature at 2.4 eV that originates from interband transitions, whereas the 5% pp N film spectrum is monotonic. The wavelength of the incident light is an order of magnitude larger than the nanograins and

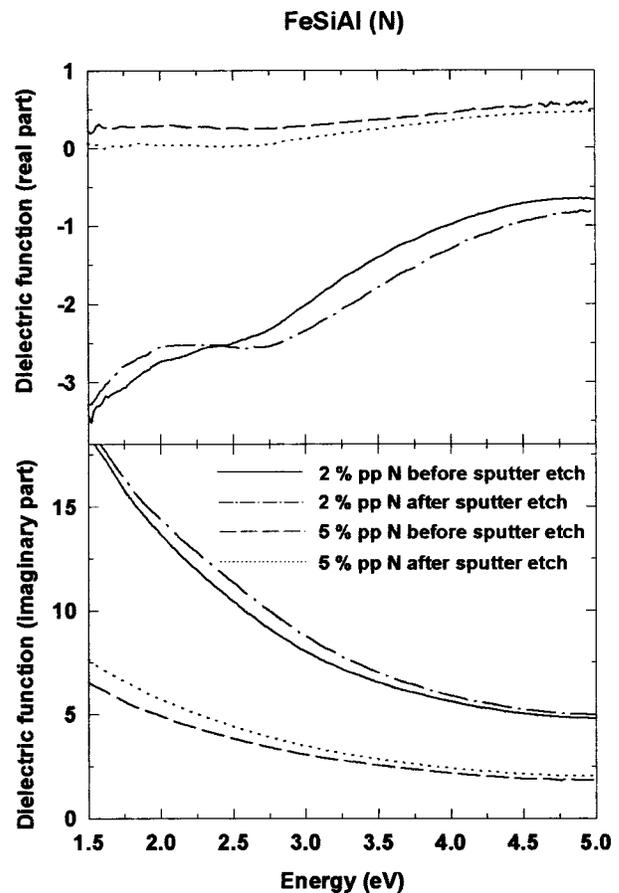


FIG. 4. Real and imaginary parts of complex dielectric function  $\epsilon_1$  and  $\epsilon_2$  for FeSiAl(N) thin films with nitrogen partial pressures of 2% and 5% before and after XPS sputter etch depth profiling.

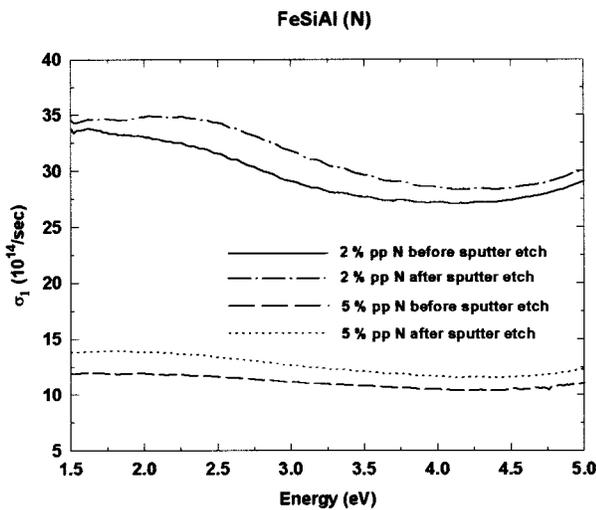


FIG. 5. Real part of complex optical conductivity  $\sigma_1$  for FeSiAl(N) films with nitrogen partial pressures of 2% and 5% before and after XPS sputter etch depth profiling.

therefore interacts with the material as a composite of nanograins and high-resistivity matrix material, rather than just a simple sum of two contributions. This causes the peak in the optical conductivity to disappear for 5% pp N film. The 5% pp N film has optical conductivity that is smaller than that of the 2% pp N film by a factor of about 2.5. The magnitude of the  $\sigma_1$  spectra increased slightly for both the 2 and 5% pp N films after sputter etching. Sputter etching removed the surface oxide layers and revealed a cleaner surface. It has been shown that as the thickness of the oxide layer is reduced, the magnitude of the optical conductivity increases and the features in the optical conductivity spectrum become more prominent.<sup>8</sup>

The dc resistivity results for all films in the series are shown in Fig. 6. For the low-nitrogen films (0–4% pp N),

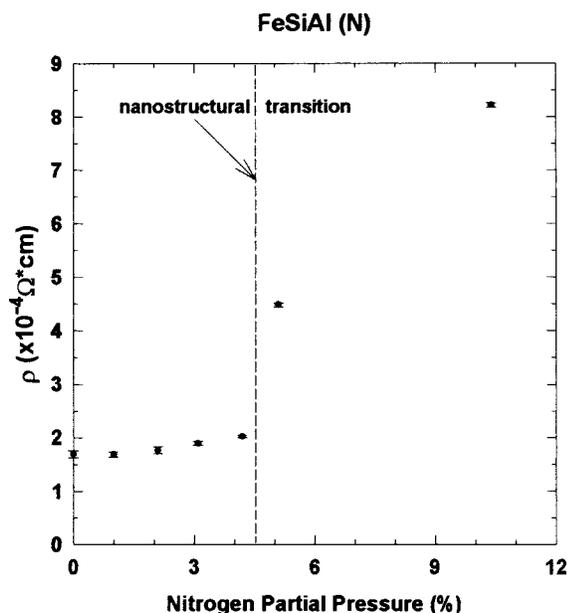


FIG. 6. Dc resistivity  $\rho$  of the FeSiAl(N) films vs the percentage of nitrogen partial pressure.

the resistivity showed a slight increase with an increase in N partial pressure, and reached  $2.02 \times 10^{-4} \Omega \text{ cm}$  for the 4% pp N film. XPS results have shown that they have increasing amounts of AlN compared with Al in the films.<sup>4</sup> Beyond 4% pp N, the micro/nanostructural transition occurs, and the dc resistivity increases by more than a factor of 2, to  $4.48 \times 10^{-4} \Omega \text{ cm}$  for the 5% pp N sample. Increasing the N partial pressure to 10% pp causes the dc resistivity to increase by yet another factor of 1.8, to  $8.22 \times 10^{-4} \Omega \text{ cm}$ . The dc resistivity of the 5% pp N film is a factor of 2.5 larger than that of the 2% pp N film. This is about the same factor by which the optical conductivity of the 5% pp N film is less than that of the 2% pp N film.

In the transmission electron microscopy (TEM) micrograph [Fig. 2(b)], it appears that for the nanostructured two-phase film, the bcc nanograins are separated from each other by the amorphous matrix material, and there are no connected paths that electrical current could traverse that would lie only in the metallic nanograins. Thus the amorphous material would appear to have higher resistivity. XPS results for the series have shown that for the two-phase nanostructured films, all of the Al is in the form of nitride, and also that a substantial amount of the Si is nitride (45% for the 5% pp N film, 66% for the 10% pp N film).<sup>4</sup> We speculate that the bcc nanograins are predominantly Fe and that they incorporate the Si that is in a metallic environment and perhaps a little of the N; however the amorphous matrix consists of aluminum nitride, silicon nitride, and an unknown amount of Fe. The dc resistivity and optical conductivity results are both consistent with this interpretation.

One previous study reported resistivity measurements of a series of sputtered FeSiAl(N) films.<sup>2</sup> Those films were deposited by dc magnetron rather than rf diode sputtering (the former is generally a higher-rate, lower ion energy, lower substrate-temperature process). Their deposition rate was about 10 times higher (168 nm/min), their films more than twice as thick ( $3.0 \mu\text{m}$ ), and their substrates were AlTiC rather than  $\text{SiO}_2/\text{Si}$ . They observed that the resistivity dropped slightly from about  $2.65$  to  $2.05 \times 10^{-4} \Omega \text{ cm}$  as the N partial pressure went from 0 to 2% pp, then the resistivity underwent a smooth, gradual increase to about  $3.35 \times 10^{-4} \Omega \text{ cm}$  as N was increased to 10% pp. This is considerably different from the current study, in which we observed a sharp increase in resistivity at the micro/nanostructural transition between 4 and 5% pp N, and resistivity values as high as  $4.5$  and  $8.2 \times 10^{-4} \Omega \text{ cm}$  for the nanostructured material. However, their series of films also showed a much different development of the micro/nanostructure with the addition of nitrogen. They did not see the abrupt change in nanostructure, magnetic properties, stress, optical constants  $n$  and  $k$ , reflectance  $R$ , and average N film content that we observed. Instead they observed a gradual transition from 200 nm grains to a mixture of 200 and 20 nm grains, to exclusively 20 nm grains as the N content was increased. Their high-N films did not show the two-phase nanostructure of nanograins in an amorphous matrix seen in Fig. 2(b) in the present work. We observed instead a sharp structural transition from 100 nm grains to a two-phase nanostructure of 10 nm grains in an amorphous matrix, accompanied by abrupt

changes in resistivity, magnetic properties, stress, and average N film content. Furthermore, they observed optimum magnetic properties for films that consisted of a mixture of the two grain sizes and had resistivity of about  $2.5 \times 10^{-4} \Omega \text{ cm}$ , whereas in the present study, magnetic properties were observed to improve considerably after the transition to the two-phase nanostructure,<sup>1</sup> where the resistivity was  $4.5\text{--}8.2 \times 10^{-4} \Omega \text{ cm}$ .

#### IV. CONCLUSIONS

It was found that the nitrogen partial pressure has a considerable effect on the optical and electrical properties of FeSiAl(N) reactively sputtered films due to its influence on the micro/nanostructure of the films. The sign of  $\epsilon_1$  in the measured spectrum range is negative for films deposited with  $\leq 4\%$  pp N (single-phase, bcc structure, 100 nm grain films), behavior typical of a metal whose charge carrier contribution can be quantitatively described using a classical free electron Drude model with an interband transition around 2.0 eV. The sign of  $\epsilon_1$  is positive for films deposited with 5 and 10% pp N (nanostructured films with 10 nm bcc grains in an amorphous matrix). In this case the free-carrier description of the dielectric function is no longer valid. FeSiAl(N) thin films with 2 and 5% pp N were sputter etched with *in situ* depth profiling to investigate the effect of surface oxidation on the optical properties of the samples. After sputter etching, the magnitude of  $\epsilon_2$  increased slightly for both samples while the sign of  $\epsilon_1$  remained the same. The dc resistivity values also showed a steep increase at the nano-

structural transition between 4 and 5% pp N, indicating that the metallic nanograins are indeed separated from each other by the high-resistivity matrix material. This is consistent with our understanding from TEM and XPS results. These results indicate that the change in nanostructure in FeSiAl(N) caused by the addition of N not only affects the stress and magnetic properties as was found in a previous study but also affects the optical and electronic properties of the films.

#### ACKNOWLEDGMENTS

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