Nanomechanical characterization of thin FeXN (X=Ta, Ti) films deposited by cosputtering from Fe, Ta and Ti targets on a Si/SiO$_2$ substrate has been conducted using a nanoindenter. To fully understand the influence of the substrate on the measurement of film properties a continuous measure of the hardness and modulus as a function of depth was performed. The hardness of both FeTa and FeTi films was improved with the incorporation of nitrogen due an associated reduction in the grain size. However at increased flow rates of nitrogen a small softening effect was observed. For binary Fe$_{(100-x)}$Ta$_x$ a rapid increase in hardness was observed at $x > 17\%$ which was coincident with a structural transformation from the nanocrystalline to the amorphous state. In the binary Fe$_{(100-x)}$Ti$_x$ the addition of 3.2 at. $\%$ Ti increased the hardness by a solid solution strengthening mechanism. © 2000 American Institute of Physics. [S0021-8979(00)39608-6]

I. INTRODUCTION

The magnetic properties of nitrogenated Fe based thin films have been investigated extensively in recent years because of their potential application in the next generation inductive heads designed to write onto high coercivity media. The low fly heights at which the future heads are expected to work will place increased importance on the durability of these soft magnetic alloys. Measurement of the mechanical properties of materials at the nanometer scale and correlation with the microstructure are very important in understanding their tribological behavior.

Nanoindentation has become important for evaluating the mechanical properties of thin films. In the standard indentation experiment, a three-sided Berkovich-shaped diamond indenter is pushed into the sample and then is withdrawn under very fine depth and load control. The force required during both insertion and extraction is recorded as a function of depth. For a single indentation, the elastic modulus $E$ and hardness $H$ are extracted from the unloading data using the analysis method of Oliver and Pharr. Unfortunately, the underlying substrate properties strongly influence the indentation response and it is difficult to obtain meaningful results. The derived values of $E$ and $H$ are due to the combined mechanical properties of the layer and the substrate. The relative contributions of the properties of the layer and the substrate depend on the depth. When the depth is small the measured parameters are dominated by the intrinsic properties of the layer alone. As the indentation depth increases the influence of the substrate increases.

In this work, we use a dynamic approach, termed continuous stiffness measurement (CSM) to continuously monitor the $E$ and $H$ values for all depths, rather than at the deepest penetration depth. This technique offers the possibility of progressively sensing the influence of the substrate on the measured mechanical parameters. The CSM approach was employed to characterize the mechanical properties of thin FeXN (X=Ta, Ti) films. A range of FeX and FeXN films was prepared by cosputtering from separate Fe, Ta and Ti targets to allow maximum control over the film composition. The hardness and Young’s modulus have been investigated as a function of both X and N content and correlated with their microstructure.

II. EXPERIMENT

Films were deposited by dc magnetron sputtering onto rotating oxidized Si substrates at room temperature. The deposition system had a base pressure of below $5 \times 10^{-8}$ Torr and deposition was carried out at an Ar pressure of 3 mTorr. A series of films composed of Fe$_{(100-x)}X_x$ were deposited with $x$ in the range of 0%–26%. The nitrogen content in the FeXN films was varied by changing the relative flow rate of $N_2$ to Ar. The deposited layer thicknesses were in the region of 55–90 nm. The exact thickness of each film was determined by stylus profilometry on etched steps. A detailed description of the structure and magnetic properties of FeXN films is given elsewhere.

All depth sensing indentation experiments were performed on a Nano Indenter XP using the CSM option. The indenter was a Berkovich pyramid with a nominal radius of 50 nm. For each sample a series of ten indents was performed, with each indent spaced 20 $\mu$m apart, and the results were averaged. The ac nanoindentations were performed under identical testing conditions, at maximum loads of 2000 and 5000 $\mu$N.

III. RESULTS AND DISCUSSION

Figure 1 shows the hardness and Young’s modulus response of the bare substrate and of FeTaN (Fe:Ta ratio =11:1) films prepared at various nitrogen flow rates as a function of indentation depth. Error bars represent the standard
deviation for the continuous stiffness data from all ten indents. For readability, only three representative flow rates have been included, and error bars are shown only on one sample, but scatter for the other samples was similar. These measurements were conducted at a maximum load of 5000 mN. Curves obtained at peak loads of 2000 and 5000 mN, were almost completely overlaid, verifying the reproducibility of the results. The samples were between 67 and 74 nm thick. Both the H and E values exhibit convergence, at large contact depths, to values representative of the substrate. The hardness follows a monotonic increase at the first 30 nm and then levels off at deeper levels as the influence of the substrate increases.

One approach for dealing with the substrate influence is to make the indentation small enough to avoid the substrate effect. In practice, this is accomplished by constraining the indentation depth to a small fraction of the film thickness, however, it should be large enough to reach full plasticity. A commonly accepted rule of thumb suggests that substrate independent measurements can be obtained if the indentation depth is kept to less than 1/10 the film thickness.\(^5\) In our case, according to the rule, nanoindentation characterization of a ~70 nm film would have to be made at a penetration depth of less than 7 nm. However, accurate measurements at this scale are difficult to obtain due to vibration, tip rounding effects and difficulties in precise determination of the location of the specimen surface. For purposes of comparison, in the following discussion, H and E at a contact depth of 50% of the coating thickness will be considered as representative of the composite film/substrate system.

Figure 1 shows that the oxidized Si substrate has a hardness value of ~10.7±0.2 GPa which is close to the SiO\(_2\) value (~11 GPa) reported in the literature. Since the films are deposited on the same substrate and they have similar thicknesses, it appears, without detailed analysis, that the hardness of pure FeTa films is improved with incorporation of nitrogen. The general behavior was consistent with that seen previously on FeTaN (Ref. 1) and FeN (Ref. 7) films. The increase in hardness is attributed to the grain refinement associated with the incorporation of nitrogen in the film.\(^5\) This dependence is in agreement with the Hall-Petch equation,\(^8\) which predicts increases in strength with grain refinement. The strengthening mechanism is based on dislocation pinning near the grain boundaries. The addition of nitrogen caused a dramatic decrease in coercivity to ~3 Oe at flow rates more than 9 sccm. The films exhibited a saturation magnetization greater than 16 kG for flow rates less than 8 sccm.

The substrate modulus shows linear indentation dependence. The E value is near 75 GPa at small depths and increases to 142 GPa at an indentation depth of 165 nm. The thermally oxidized layer has a thickness of ~400 nm. This linear behavior can be explained, based on the elastic constants of bulk SiO\(_2\) and Si. The modulus of bulk silica and silicon are 75 and 168 GPa, respectively. It is thus expected that the modulus will have values between those of SiO\(_2\) and Si as the indenter further penetrates the substrate.

The pure FeTa film shows a higher modulus than the nitrogenated FeTa films. One can obtain useful information for these materials from their hardness to modulus ratio H/E. This parameter can be used as a first order measure of the material’s ability to resist plastic deformation in a contact event.\(^9\) Resistance to contact damage depends not only on the hardness but also on the elastic modulus. Material with a low modulus can elastically deform and distribute the contact load over a large area, thereby reducing the contact pressure. Contact damage is then avoided in materials with high hardness and a low modulus. It is worth noticing in Table I that the nitrogenated FeTa films have H/E ratios approximately 23% larger than that of the pure FeTa and may thus be more resistant to plastic contact damage.

![FIG. 1. Hardness and Young's modulus vs contact depth for a series of FeTaN films deposited at various nitrogen flow rates.](image)

<table>
<thead>
<tr>
<th>Nitrogen flow (sccm)</th>
<th>Thickness (nm)</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
<th>H/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67</td>
<td>8.4</td>
<td>128.2</td>
<td>0.066</td>
</tr>
<tr>
<td>4</td>
<td>73</td>
<td>8.9</td>
<td>120.9</td>
<td>0.074</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>9.48</td>
<td>124.2</td>
<td>0.076</td>
</tr>
<tr>
<td>8</td>
<td>70</td>
<td>9.82</td>
<td>122</td>
<td>0.080</td>
</tr>
<tr>
<td>9</td>
<td>74</td>
<td>9.8</td>
<td>121.1</td>
<td>0.081</td>
</tr>
</tbody>
</table>
It should be mentioned that at flow rates of more than 9 sccm the hardness decreased slightly. The grain size in Fe-TaN films continuously decreases with an increase in nitrogen content. The decrease in strength as the grain size decreases is called the inverse Hall–Petch effect and has been observed in studies of nanocrystallines with very fine grain sizes (<8 nm). It appears that some nanocrystalline materials display a transition at a critical grain size, from a positive Hall–Petch slope at larger grain sizes to a negative slope at the smallest grain sizes. The reason for the softening effect is not completely clear, but it may be a result of the nature of the grain boundary material or a preferred crystallographic texture. At high nitrogen flow rates, the FeTaN material was no longer single phase body-centered cubic and a [111] TaN diffraction ring could be seen in the diffraction pattern, indicating precipitation of this phase.

The dependence of hardness on Ta content in binary FeTa films is shown in Fig. 2. The thicknesses of the films were in the region of 75–90 nm. The hardness curve of Fe₈₅Ta₁₇ shows a break in the slope at around 17 nm, presumably due to cracking of the layer. The Fe₇₄.₃Ta₂₅.₇ displayed an apparent increase in hardness compared to the lower Ta content films. The sudden increase in hardness is related to a rapid decrease in crystalline size, which is associated with a structural transformation from the nanocrystalline to the amorphous state upon increasing the Ta content above 17 at. %.

The amorphous structure of the Fe₇₄.₃Ta₂₅.₇ film was verified by transmission electron microscopy observations. Unfortunately, the rapid increase in hardness was followed by a significant drop in saturation magnetization to less than 5 KG, making these films not very interesting for soft magnetic applications. The behavior of the films in the amorphous regime was superparamagnetic.

An increase in the hardness with the incorporation of N has also been observed in FeTiN films. The Fe₉₀Ti₄ displayed an increase in $H$ from 8 to $8.5 \pm 0.3$ GPa when the flow rate was increased to 10 sccm.

Figure 3 depicts the dependence of the hardness on the Ti content in binary FeTi films. The samples were between 66 and 86 nm thick. The addition of 3.65% Ti on Fe increased the hardness by 15%. However a further increase of Ti brought the hardness to the original levels. It should be noted that, there was no significant variation in coercivity, being ~70 Oe, when the Ti content was increased from 1 to 3.7 at. %. This may indicate that the grain size of the films remained relatively the same. The hardening effect can thus be explained by a solid strengthening mechanism, since the grain size of Fe₉₀Ta₁ is similar to that of Fe₉₀.₃Ta₇.7

At 11 at. % of Ti the coercivity increased to 96 Oe, indicating grain growth according to the well-documented $D$¹⁰ dependence of coercivity for nanocrystalline alloys. The large grain size with increasing Ti content may have contributed to the substantial drop in the hardness data.

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