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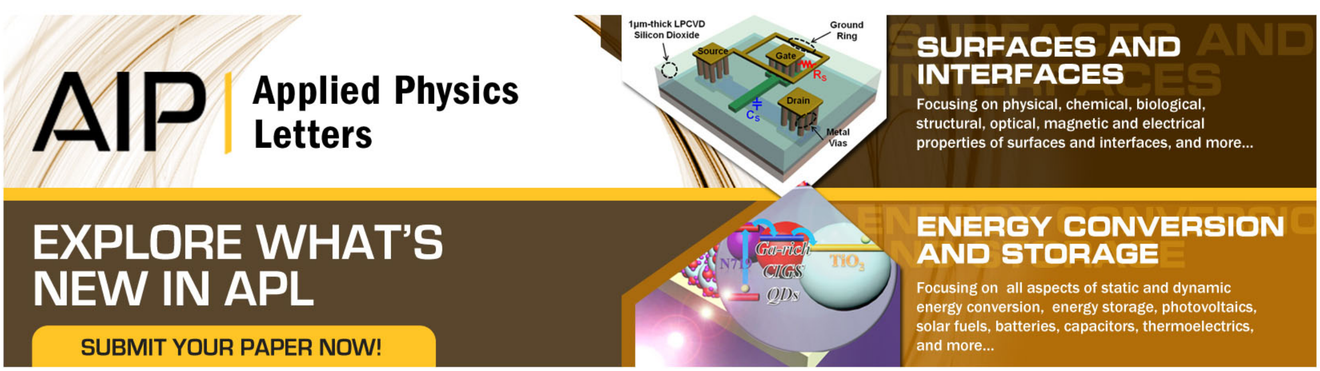

Synthesis of $Nd(FeTi)_{12}$ films by sputtering

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$Nd(FeTi)_{12}$ films have been synthesized by dc magnetron sputtering. The films have tetragonal $ThMn_{12}$ crystal structure as confirmed by XRD and magnetic measurements. The lattice parameters are $a=8.57$ and $c=4.801$ Å. The degree of the $ThMn_{12}$ phase formation and the texture of the films are found to be dependent on deposition parameters. The films can be aligned with the (001) basal plane in the film plane by suitable deposition conditions. Thus the films are textured so that the easy axis, which is the c-axis, is perpendicular to the film plane. After nitrogenation, the tetragonal $ThMn_{12}$ crystal structure is retained and the lattice parameters increase to $a=8.67$ and $c=4.862$ Å, corresponding to a volume expansion of 3.6%. The coercivity also increases upon nitrogenation.

R-Fe-based (R=rare earth) compounds are being investigated intensively at present because of their potential permanent-magnet application after nitrogenation. It is known that $R(FeTi)_{12}$ compounds with the tetragonal $ThMn_{12}$ crystal structure can absorb a moderate quantity of nitrogen when annealed in nitrogen atmosphere. The unit cell volume increases several percent with no change in symmetry and with improved magnetic properties.[1] In this class of materials $Nd(FeTi)_{12}N_x$ is the most promising candidate for permanent-magnet application because of its large anisotropy field, high Curie temperature, and high saturation magnetization.

One of the important characteristics necessary for the desired magnetic properties is a high degree of texture. Sputter deposition may offer great opportunity to achieve a high degree of texture because of the variety of adjustable parameters. The synthesis of $Sm(FeTi)_{12}$ films by sputtering in a controlled way has been previously reported,[3] but $Sm(FeTi)_{12}N_x$ is not a good candidate for permanent magnet for bulk or film because of its planar magnetic anisotropy so that a low coercivity is expected.

Here we present our study of the effect of the deposition parameters on the formation of the $ThMn_{12}$ phase and the texture of sputtered $Nd(FeTi)_{12}$ films. Results on the $Nd(FeTi)_{12}N_x$ films nitrogenated by annealing *in situ* in nitrogen atmosphere are also given.

$Nd(FeTi)_{12}$ films were prepared in a dc magnetron sputtering system on heated Ta substrates by using a single alloy target of nominal atomic composition $Nd_{9.5}Fe_{82.5}Ti_{8.0}$. The base pressure was better than 5×10^{-7} Torr. The argon gas pressure, applied dc power, and substrate temperature were varied in order to achieve the desired phase and a high degree of texture. The sputtering rates were from 6 to 16 Å/s. After the deposition nitrogen gas was introduced into the chamber with a pressure about 100 Torr at various sample temperatures for various lengths of time.

The crystal structure was determined by x-ray diffractometry (XRD) on a Rigaku DMAXB system with Cu K_α radiation. Film composition of $Nd_{9.4}Fe_{83.1}Ti_{7.5}$ in atomic percentage was determined by energy dispersive x-ray spectroscopy attached to a JEOL 840A SEM. A Quantum Design SQUID magnetometer with a maximum field of 55 kOe was used to measure the hysteresis loops at room temperature. Thermomagnetic measurements were made with the help of a Cahn electrobalance.

Figure 1 shows the XRD spectra for films with different thicknesses. The peaks are fitted to the (002), (202), (222), and (004) reflections of the tetragonal $ThMn_{12}$ structure. Attempts were made to fit to other phases which are related to the $ThMn_{12}$ phase by structural transformation, i.e., the rhombohedral Th_2Zn_{17} structure and the disordered $TbCu_7$ structure. For the Th_2Zn_{17} phase, the fitted result of c/a ratio is much larger than the reported value for bulk samples. This means that more dumbbell Fe pairs are occupying the Nd sites, indicating the $ThMn_{12}$ phase is more likely. The disordered $TbCu_7$ structure[4] is difficult to exclude only by XRD measurement because its lattice parameters, stoichiometry, and properties may change, depending on the precise composition and degree of disorder. It has been reported[5] that the binary $NdFe_{5+x}$ compound with an unknown x between 0 and 3.5 has the disordered $TbCu_7$ structure and has a Curie temperature of 97 °C. The experimental results given below suggest that our films do not have this structure as the main phase, but from the XRD data alone we cannot completely rule out a partial presence of the disordered phase.

Least-square fitting of XRD data to the tetragonal

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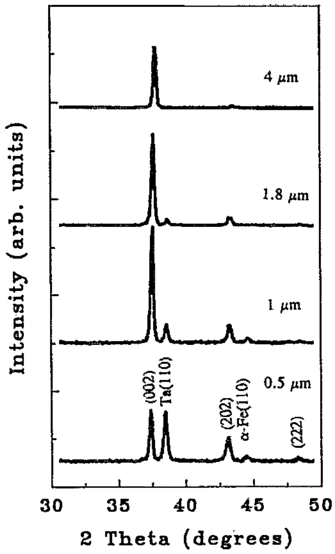

FIG. 1. X-ray diffraction patterns of $Nd(FeTi)_{12}$ films with different thicknesses on Ta substrates. The deposition conditions are an argon pressure of 1.5 mTorr, a power of 100 W, and a substrate temperature of 390 °C.

$ThMn_{12}$ unit cell gives $a=8.57\pm0.01$ Å and $c=4.801\pm0.001$ Å, where the uncertainties are determined from the iteration program[6] based on peak positions of the diffraction pattern. The greater error for a is due to the lack of enough (hkl) reflections which have nonzero h and k indices because of the film texture.

For the sputtering conditions used films are more or less c-axis preferentially aligned perpendicular to the film plane. Thus in the XRD patterns only (002), (004) peaks and a weak (202) peak appear; in a few cases for weakly textured films a weak (222) peak appears also. The ratio of the intensity of the (002) peak to that of the (202) gives a measure of the degree of texture. This is found to strongly depend on the film thickness and the sputtering conditions.

XRD patterns shown in Fig. 1 are examples for films sputtered under the same conditions (1.5 mTorr, 390 °C, 100 W) but with various final thicknesses from 0.5 to 4 μm. For thicker films the intensity of the (202) peak is almost negligible compared to that of the (002). The fact that texture is improved with thickness is understandable since the texture is controlled mostly through sputtering parameters rather than substrate epitaxy for the desired texture. It seems that the Ta substrate does not promote a complete (002) epitaxial growth.

Other substrates such as Cu, glass, and alumina have also been tried. In each case the films have an incorrect phase or have two phases including the $ThMn_{12}$ phase. More investigation is needed to search for a substrate which will enhance heteroepitaxial growth for this structure especially for thin films.

When films are annealed *in situ* at a temperature of 400 °C for 1 h in nitrogen atmosphere the unit-cell lattice parameters are increased. XRD spectra for both the nitrogenated and non-nitrogenated samples are shown in Fig. 2. The XRD peaks of the nitrogenated film are apparently displaced to the lower angle side due to the volume expansion caused by the nitrogen intake. The broadening in the XRD lines of the nitrogenated film spectrum might be attributed to stress effects (the substrates were curved slightly after nitrogenation) and the effect of incomplete nitrogenation. The unit cell lattice parameters of the nitrogenated samples are $a=8.67\pm0.01$ Å, $c=4.862\pm0.001$ Å. This means a volume expansion of 3.6% for the unit cell by nitrogenation.

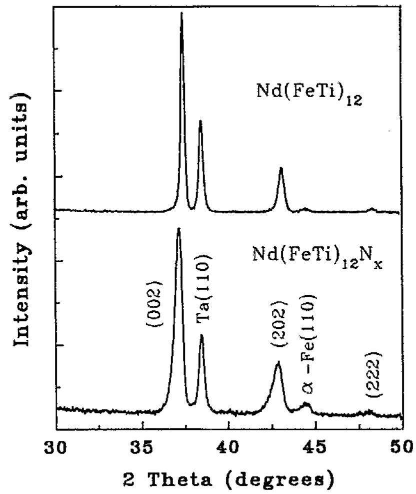

FIG. 2. X-ray diffraction patterns of a $Nd(FeTi)_{12}$ film and a $Nd(FeTi)_{12}N_x$ film of about 1 μm thick on Ta substrates.

Figure 3 shows typical hysteresis loops for a $Nd(FeTi)_{12}$ film of about 1 μm thick measured at room temperature with the applied field parallel and perpendicular to the film plane; for the latter case a demagnetization correction has been done. Figure 4 gives the hysteresis loops for a $Nd(FeTi)_{12}N_x$ film of about 1 μm thick measured at room temperature. It is noted that the films have perpendicular anisotropy and this anisotropy is greatly enhanced by nitrogenation. The coercivity for the nitride film is about ten times larger than the value of the $Nd(FeTi)_{12}$ film. It is noted that the maximum applied field of 55 kOe is below the saturation field for the nitride film when the field is perpendicular to the film plane.

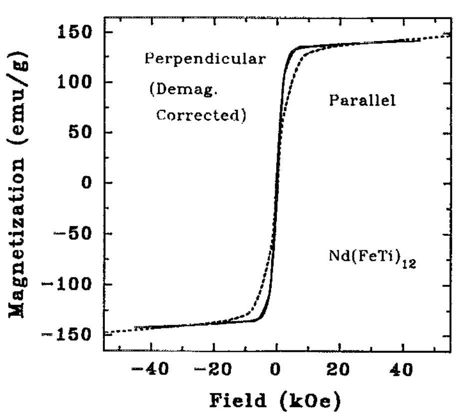

FIG. 3. Hysteresis loops of a $Nd(FeTi)_{12}$ film of about 1 μm thick measured at room temperature. The perpendicular loop has been corrected for demagnetization.

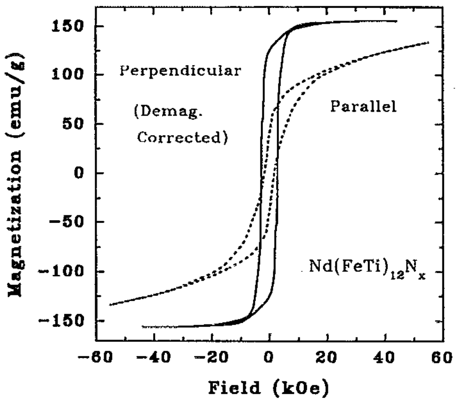

FIG. 4. Hysteresis loops of a $Nd(FeTi)_{12} N_x$ film of about 1 μm thick measured at room temperature. The perpendicular loop has been corrected for demagnetization.

Thermomagnetic measurements as shown in Fig. 5 indicate that the T_c of the $Nd(FeTi)_{12}$ film is about 250 °C, which is close to the reported value of 274 °C for bulk samples and much higher than the reported value of 52 °C for a sample with Th_2Zn_{17} structure[7] and 97 °C for the disordered $TbCu_7$ structure.[5] Similar measurements were tried for the nitride films but oxidation was found to be a severe problem from 425 °C and above, by which temperature the magnetization did not show any obvious decrease. We can only say that the Curie temperature is increased qualitatively upon nitrogenation.

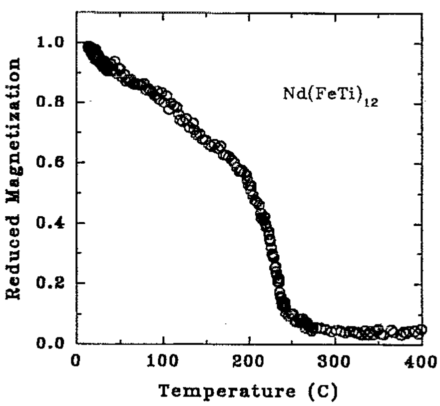

FIG. 5. Thermal-magnetization curve for a $Nd(FeTi)_{12}$ sample. The field was about 500 Oe and temperature changing rate was about 20° per minute.

Deposition conditions were varied to optimize the phase formation and the texture. The films sputtered at lower pressures show a better (002) texture down to 1.5 mTorr. Under various substrate temperatures and at sputtering gas pressures of 1.5 and 10 mTorr, the (002) texture is more favorable at higher temperatures (up to 430 °C), beyond which α-Fe starts to form and the degree of (002) texture starts to decrease. The existence of α-Fe is also seen at a lower temperature (310 °C) where the formation of the $ThMn_{12}$ phase is less favored. When the sputtering power is less than 50 W the $ThMn_{12}$ phase does not form but only α-Fe like peaks are seen. For power higher than 50 W, as long as the thickness is kept constant the film texture is not very sensitive to power variations.

In summary, $Nd(FeTi)_{12}$ films with $ThMn_{12}$ structure have been made by sputtering. The films can be oriented with the c-axis, which is the easy magnetic axis, perpendicular to the film plane. After nitrogenation, the lattice parameters increase from $a=8.57$ and $c=4.801$ Å to $a=8.67$, $c=4.862$ Å, corresponding to a unit cell volume expansion of about 3.6%. Both the coercivity and Curie temperature are increased by nitrogenation.

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