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Abstract.- Amorphous thin films of transition metal (TM)-metalloid and TM-rare earth (R) alloys have been prepared by sputtering and multiple-target, electron-beam vapor deposition. Application of these has been made in several technically important areas including continuously variable surface acoustic wave (SAW) delay lines or resonators and magneto-optic mirrors for biasing ring-laser-gyroscopes (RLG). This paper deals with preparation, characterization, and tailoring of these alloy films to meet the required performance parameters for each application. In most instances the magnetically soft TM-metalloid films such as Fe-B, Fe-Si-B, and Fe-Cr-P-C show the best performance characteristics for SAW devices and magnetically switchable mirrors. The magnetically hard R-TM alloy films such as Tb-Fe and Tb-Co are excellent candidates for use as polar magneto-optic mirrors.

INTRODUCTION

Thin film technology is a very important, and still developing, area of application for amorphous or metastable mixtures of metals. One of the earliest proposals for large-scale application of amorphous films was for magnetic bubble memories[1] using amorphous rare earth-transition metal (R-TM) alloys with R=Gd. Our own studies[2-5] of the amorphous Gd-Fe series have shown that they are very amenable to microwave and optical resonance and other basic research studies. For certain compositions[5] the amorphous Gd-Fe alloys have magnetic properties superior to permalloy, which has been the most widely used thin film for magnetic applications. For example, the ferromagnetic resonance linewidth[2] of $Gd_{.14}Fe_{.86}$ is the narrowest measured in metal films. Also, it is possible to transmit microwave signals through relatively thick films at very high frequencies (up to 1,000 GHz).

The amorphous R-TM alloys have been found to be stable over a wide range of compositions of the individual elements and the compositions are continuously variable. They can be prepared on virtually any substrate at room temperature or even higher which facilitates their adaptation to production line procedures. Some amorphous R-TM alloys have high magnetostrictions and magnetically induced sound velocity changes making them important for transducer, variable delay line, and tunable oscillator applications. Some have relatively large reflectivity-magnetic Kerr rotation combinations[6,7] which makes them excellent candidates for magnetic mirror applications. The large Kerr effect of these has also been promoted for thermomagnetic memory storage.[8]

A major breakthrough was achieved when it was discovered[9-11] that so-called metallic glass alloy films could be prepared using vacuum deposition techniques as opposed to the conventional bulk sample quenching of ribbons of material from the melt. This breakthrough opened a wide spectrum of application possibilities and allowed preparation of metallic glasses (e.g. Fe-B, Fe-Si-B, Fe-P-C-B, etc.) under more controlled conditions to investigate fundamental properties. Some of these metallic glass films have high magnetically induced sound velocity changes and require much smaller external magnetic switching fields than the R-TM alloys. Our own work[12,13] has shown that many of these are also excellent candidates for magnetic mirrors.

Work at NRL has thus far concentrated on utilizing the magnetostriction or magnetoacoustic properties and the magneto-optic properties of both amorphous R-TM and metallic glass alloy films. Applications pursued include transducer films for bulk acoustic wave (BAW) delay lines, magnetostrictive film overlays to allow magnetically variable surface acoustic wave (SAW) delay lines and resonators, magneto-optic mirrors for ring-laser-gyroscopes, and metal film/fiber optic devices. Some of these applications are discussed in detail below.

MATERIAL PREPARATION/CHARACTERIZATION

Although some films were made using conventional sputtering and ion-beam sputtering, most of our films were prepared using a specially designed 3-beam, electron beam vacuum deposition apparatus. Quartz crystal monitors were used to control the deposition rate from each individual metal target through a computer controlled feedback system. A fourth, resistively heated, evaporation boat was used to overcoat the films with Aℓ, Si, SiO, SiO_2 or others depending upon the requirements. Typical vacuum thresholds are in the 10^{-7} Torr range during evaporation but can be improved a factor of ten or more by using vacuum melted targets or by pre-melting a rare earth metal target to getter gases not pumped adequately by other means. Using a residual gas analyzer we find that even in the 10^{-6} Torr range, most of the pressure arises from hydrogen (from brakeup of H_2O by the e-beams) and helium (a residual picked up from background helium in the building containing the apparatus). The oxygen partial pressure seldom reaches the 10^{-9} Torr range.

High purity fused quarts (SiO_2) substrates are used for he magneto-optic samples. This allows laser light to be brought through the substrate with a special arrangement to avoid polarization changes[6] at the air-quartz interface and the magneto-optic properties of the inside surface of the film to be measured. This was done since most outside surfaces of the films were either overcoated or developed a thin oxide layer of unknown thickness and composition.

Films for BAW transducers were deposited on the end of a bulk delay line rod of single crystal sapphire or Mg-spinel. Films for SAW device applications were deposited on either single crystal ST-quartz or YZ-$LiNbO_3$. All other films were deposited either on glass cover slips or, when separation of the film from its substrate was desired (e.g. for electron diffraction), they were deposited on cleaved NaCℓ or collodian coated surfaces.

For a number of reasons, most of our films were deposited on stationary substrates. This allowed the flexibility of both heating (to 600°C) or cooling (to -190°C) and at least five different alloy compositions could be made on up to four substrates each in a single deposition cycle. A side effect of this procedure is that a weak, uniaxial, magnetic anisotropy is produced in the film plane because of growth conditions arising from the slightly different angles of incidence of material from different targets onto the substrates. Although it was necessary to be aware of this in-plane anisotropy and sometimes to account for it in analysis, it frequently was useful in that it defined a unique axis for magnetic switching purposes. This in-plane anistropy could be removed by rotating the substrates during deposition.

The degree of structural disorder of the alloy film was monitored by X-ray and electron diffraction and by Mossbauer spectroscopy. In the electron diffraction method, quite accurate radial distributions were measured. As a rapid and independent method, Mossbauer spectra gave definitive indications of micro-crystallinity when present, even though this frequently was not evident in the X-ray diffraction. The R-TM alloys were found to be amorphous even at elevated temperatures. In fact, it was difficult to crystallize these with the temperatures available in the deposition apparatus. The metallic glasses (all near 80 atomic percent of the transition metal) crystallized much more easily. For example, Fe-B films were amorphous if deposited at 25°C but were partly crystalline for $T > 150°C$. Fe-Si films deposited at 50°C were almost entirely crystalline.

MAGNETOSTRICTIVE APPLICATIONS

Magnetostrictive or magnetoelastic applications of these films may include either static situations, such as slowly varying magnetic fields, or dynamic situations, such as coupling to electromagnetic or elastic waves, or both. Theoretically[14,15] we have treated extensively both these situations.

The magnetostriction of the film plays an important role both through the magnetoelastic coupling constant in the free energy and through the "ΔE" effect which results in a magnetic field induced sound velocity change. Although not universally applicable, the following equation[16] is useful for estimating and comparing these sound velocity changes in different amorphous materials,

$$\Delta v/v \propto (\mu_o \lambda_s^2 E_s)/M_s^2 \qquad (1)$$

where μ_o is the initial permeability and E_s, λ_s and M_s are respectively Young's modulus, the magnetostriction and the magnetization at saturation. Since it was usually much more time consuming and expensive to test a film in a device configuration, it became important to develop an independent method of measuring the magnetostriction as well as magnetization. Both the sign and magnitude of the film magnetostrictions were measured using a cantilever-capacitance apparatus.[17] A representative selection of magnetostrictions and fields, H_s, required to saturate the as-deposited films of materials we have studied is given in Table I.

TABLE I

MATERIAL	$\lambda_s \times 10^6$	H_s (Oe)
Nickel	-33	1,000
Iron	-7	150
$Fe_{0.6}Tb_{0.4}$	285	5,000
$Dy_{.84}Tb_{.13}Fe_2$	100	1,000
$GdFe_2$	20	200
$Fe_{.85}B_{.15}$	30	20

Because of its prominence in Eq. (1) and its importance for magnetic shielding applications, we are currently studying the basic phenomena which control the magnitude of the initial permeability, μ_o. We have already shown[17] that crystalline or micro-crystalline inclusions in the amorphous structure can lead to wall pinning domination of domain wall motion whereas in purely amorphous structures this motion is generally nucleation dominated.

In the SAW delay line and resonator application, thin films of varying thickness were deposited between the input and output interdigital transducers which were designed for operation at different frequencies. A detailed description of the experimental techniques employed and analysis procedures is given in ref. 18. The magnetically soft TM-metalloid films show by far the best performance characteristics for this application with respect to required bias magnetic field. The continuously variable time delay with magnetic field depends on the magnetoelastic coupling in the metallic film, the "ΔE" effect which is approximately described by Eq. (1), the physical coupling of film to substrate, and the film thickness. The largest delay changes were measured[17,18] with the magnetic field in the film plane and perpendicular to the initial direction of M. Table II summarizes results of our delay-line measurements to date. Note that the Ni film was deposited on YZ-$LiNbO_3$ while all other films were deposited on ST-quartz. The Ni and Fe-B films were deposited by electron-beam evaporation and the more complex metallic glasses were deposited by conventional sputtering. MET1 is $Fe_{.80}B_{.20}$, MET2 is $Fe_{.77}Si_{.09}B_{.14}$, and MET3 is $Fe_{.74}Cr_{.06}P_{.13}C_{.07}$. Other terms in Table II are t (film thickness), f_o (center frequency), τ_m (maximum delay), α_F and α_o (film and device attenuation), P (required power), and H_B (required permanent magnet bias).

TABLE II
SAW DELAY LINE PARAMETERS

	Ni	MET1	MET2	MET3
t(μm)	0.85	0.8	1.6	1.4
f_o (MHz)	210	135	135	135
τ_m (nsec)	1.0	1.0	0.3	0.2
α_f (dB)	15	-	9	9
α_D (dB)	25	-	19	19
P (watts)	40	0.001	0.70	6
H_B (Oersted)	1,800	10	250	700

Since the SAW velocity can be changed only by 0.1% or less with our current technology, applications are restricted to those where only a small frequency or delay adjustment is required. Increases in delay or frequency adjustment can be obtained by using improved materials (e.g., with higher μ_o and λ_s) and thicker films allowing more of the surface wave to propagate in the magnetostrictive film.

MAGNETO-OPTIC APPLICATIONS

The primary magneto-optic (M-O) application of amorphous films which we have investigated thus far has been for mirrors in the ring-laser-gyroscope to provide a M-O solution to what is termed the "lock-in" problem inherent in these devices. A schematic diagram[13] of two possible ring laser gyroscopes is given in Fig. 1. In

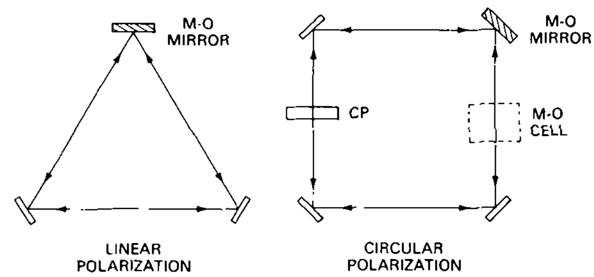

Fig. 1. Schematic diagram of possible ring laser gyroscopes operating in a linearly or a circularly polarized mode. CP is a required circular polarizer whereas the M-O cell is an optional approach not discussed in this text.

the linear polarization mode of operation, for example, there are two counterpropagating laser beams. Via the Sagnac effect, the two beams oscillate at slightly different frequencies and the difference frequency is proportional to the gyroscope rotation rate. The lock-in phenomenon occurs at low angular rotation rates of the gyro. The counterpropagating beams within a common cavity constitute two optical oscillators with a tendency to synchronize in frequency, analogous to coupled oscillators. M-O effects such as the Faraday, polar Kerr, and transverse Kerr effects are linear in the magnetization M and can be used to introduce a controllable differential phase shift ΔΦ and frequency difference or bias between properly chosen, similar counterpropagating beams[19] The frequency bias induced is given by

$$\Delta\nu_b = (\Delta\Phi/2\pi)\ c/L \qquad (2)$$

where c is the velocity of light and L is the optical length of the RLG. The minimum required bias[13] for a 40 cm perimeter RLG is $\Delta\nu_b$ = 50 kHz. For the He-Ne laser wavelengths λ = 1.15 μm and 0.63 μm commonly used in the RLG, bare metallic mirrors are poor reflectors. For this reason the bare M-O films must be overcoated with a multilayer dielectric (MLD) stack of films which is tuned to be highly reflecting at the wavelength and angle of incidence used.

Prior to our own work[6,7,12,13] there were no published measurements of the magneto-optical parameters of amorphous R-TM or metallic glass films. For this reason, we undertook a systematic investigation of several series of these and other alloys to determine the complex index of refraction N=n-ik and the complex magneto-optical coefficient $Q=Q_1-iQ_2$, both of which are needed to completely characterize the magneto-optical properties of the films. In addition, computer codes were developed[6,13] to design the optimum structure containing a M-O thin film and a reflection-enhancing multilayer dielectric film stack. Representative numbers obtained from this analysis for a particular design structure and our measured N and Q values are given in Table III, where $\Delta\Phi_T$ and $\Delta\Phi_p$ are the differential phase shifts for transverse and polar modes of operation. The numbers in parentheses are for λ=0.63 μm and the others are for λ=1.15 μm. The values for single crystal Mn-Bi are based on data from Ref. 20. The required values for successful RLG operation are noted at the bottom of the Table.

TABLE III
RLG Parameter Estimates Based on M-O Data at λ = 1.15 μm (0.63 μm) - all in mrad

Sample	$\Delta\Phi_T$	$\Delta\Phi_P$	$\Delta\Phi$/Loss
Fe	.5 (.12)	2.1 (.5)	10 (6)
Co	.42 (.10)	1.75 (.42)	8.5 (5.1)
$Ni_{.68}Fe_{.32}$	.25		4.9
$Fe_{.85}B_{.15}$	.34		6.8
$Fe_{.70}Tb_{.30}$		(.38)	(4.5)
Mn-Bi[20]		(1.7)	(85)
Required[13]	$\geq$ 0.4	$\geq$ 0.4	$\geq$ 8(>20)

The parameters in Table III clearly show that of the films we have studied to date only Fe and Co could be considered for use at 1.15 μm and none could be used at 0.63 μm. Both these materials have in-plane magnetizations, M, which is not easily switchable. To be a suitable M-O mirror M must either be in the film plane and be easily switchable (linearly polarization mode) or perpendicular to the film plane and be permanently magnetized (circularly polarized mode). $Ni_{.68}Fe_{.32}$ and $Fe_{.85}B_{.15}$ satisfy the switching requirements for LP operation and alloys such as Tb-Fe and Tb-Co near the compensation composition can be permanently magnetized perpendicular to the film plane for CP operation. However, in all cases, the addition of glass formers or rare earths reduced the parameters below those for pure Fe or Co. All evidence indicates that the transition elements govern the M-O effects. Recently[8] it has been shown that the addition of bismuth to amorphous Gd-Fe alloys near compensation enhances their Kerr rotation. However, this enhancement is still not enough to make these viable mirrors for the RLG.

From Table III we see that single-crystal Mn-Bi films are clearly the best metallic mirrors currently available for RLG applications. However, they suffer from fabrication and back-scatter problems. Our research is continuing in an effort to obtain about a factor of 2 improvement in $\Delta\Phi$/Loss and $\Delta\Phi$ for both the switchable and polar mirrors. Our main approaches are to (a) enhance $\Delta\Phi$ by alloying with elements which shift the electronic band structure controlling the M-O activity, (b) shift the compensation composition of R-TM alloys to higher TM concentrations by ternary additions, and (c) investigate totally new metastable structures.

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