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Calcium germanium substituted iron garnet films for magnetic bubble applications

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Mixed rare earth iron garnet films containing calcium and germanium have been grown on (111) oriented gadolinium gallium garnet (GGG) substrates. The effect of growth conditions on film composition and properties is discussed. The 5 μm diameter bubble films have good magnetic properties; however, temperature control during film growth is very critical.

1. Introduction

Garnet films, which have growth-induced uniaxial anisotropy, support cylindrical magnetic domains (bubbles) capable of storage densities of 10^6 bits in.$^{-2}$ and offer the feature of moving information at megahertz data rates.

In order for rare earth iron garnets to support stable 5 μm diameter bubble domains, their saturation magnetization, $4\pi M$, is lowered to a suitable value (150 to 200 G) by non-magnetic Ga or Al substitution in the tetrahedral iron sublattice. However, about 10% of the Ga or Al ions also substitute onto the octahedral iron sublattice, thereby counter-acting the tetrahedral iron dilution. For good temperature stability of the magnetic properties, the Curie temperature of the garnet and, consequently, its iron content, must be kept as high as possible. Geller *et al.* [1] have shown that both Si^{4+} and Ge^{4+} reside almost entirely on the tetrahedral iron sublattice. Therefore, substitution of either of these for Fe requires only ≈ 0.95 atoms per formula unit, as opposed to ≈ 1.2 for Ga substitution. Recently, Bonner *et al.* [2] and Nielsen *et al.* [3] have reported growth of films containing Si^{4+} and Ge^{4+}. Geusic *et al.* [4] have shown the feasibility of operating devices over a broad temperature range using these films. The garnet system $Sm_xY_{3-x-y}Ca_yFe_{5-y}Ge_yO_{12}$, studied by Smith *et al.* [5] and Lecraw *et al.* [6], looks promising where $x \approx 0.1$ and $y \approx 0.95$, since with this low concentration of Sm the domain wall mobility should be high and yet the films still have sufficient uniaxial anisotropy to support stable 5 μm bubbles.

2. Experimental

2.1. Film growth

Films were grown by the liquid phase epitaxy (LPE) isothermal dipping method employing axial rotation of the substrate in a horizontal plane as previously reported [7]. Growth temperatures between 970 and 1005° C were used. Substrates were (111) oriented $Gd_3Ga_5O_{12}$ (GGG) discs having a lattice parameter (a_0) of 12.383 Å. The melt compositions used, having varying Ca:Ge ratios, are given in Table I. Melts A and B were used for the growth of films supporting 5 μm bubbles whereas C was used for films supporting 1 μm bubbles. In addition, films were grown containing no Sm and also with Sm replaced by Eu.

TABLE I Melt compositions (g)

	A	B	C
Sm_2O_3	0.07	0.07	0.07
Y_2O_3	1.12	1.07	0.95
$CaCO_3$	3.83	3.05	2.10
GeO_2	4.26	3.18	1.76
Fe_2O_3	20.36	17.61	20.29
PbO	192.7	182.8	184.9
B_2O_3	4.09	3.82	3.66
T_{sat} (° C)	1015	1006	980

It was found that these melts, unlike their Ga-containing counterparts, had a pronounced tendency to creep up the sides and out of the crucible resulting in a significant lowering in the saturation temperature for consecutive growth runs and a lowering of both Ca and Ge in the film. This creeping was prevented by welding an annular platinum collar around the lip of the crucible.

2.2. Film properties

Film properties were measured as previously described by Giess *et al.* [8]. Film thickness (h) was determined by reflectance interference fringes in the $\lambda = 4500$ to 7000 Å range, using a 10° incidence angle and correcting for dispersion.

Domain strip widths were measured for the thermally demagnetized stripe domain patterns and the material characteristic length determined by the method of Fowlis and Copeland [9].

The unstrained lattice mismatches were determined from the X-ray peak separations between the (888) reflection of the film and the substrate measured simultaneously *in situ*, using a Young's modulus of 2×10^{12} dyn cm^{-2} and a Poisson's ratio of 0.29.

Film compositions were measured with an Applied Research Laboratories, California, EMX-SM electron microprobe. An accelerating voltage of 11 kV was used to reduce enhancement from secondary and continuum fluorescence. $Sm_3Ga_5O_{12}$, $Y_3Fe_5O_{12}$, $PbO.6Fe_2O_3$, CaF_2 and Ge single crystals were used as standards. The characteristic lines were Sm$L\alpha$, Y$L\alpha$, Ca$K\alpha$, Ge$L\alpha$, Fe$K\alpha$ and Pb$M\beta$. The less intense Pb$M\beta$ line was chosen in preference to the Pb$M\alpha$ which suffers interference from Y$L\gamma$. Intensities were corrected for absorption, electron scattering and retardation using a program developed in APL language (IBM Corporation, Armonk, N.Y.) by Reuter [10]. The absolute accuracy is $\pm$ 5% for all of the constituents except for the Pb which is $\pm$ 50%. The relative precision is $\pm$ 3% for all of the metals except Fe and Pb for which it is $\pm$ 1% and $\pm$ 50%, respectively, all values at the 95% confidence level.

3. Results and discussion

The properties of some of the films grown from melts are given in Table II. The most noticeable trend is that film composition is fairly sensitive to growth temperature; lower temperatures produce films containing more Ge. Although at these lower growth temperatures the films will contain more Pb [11] and this will charge compensate some of the extra Ge, the analyses indicate that the increase in the Pb content is too small to account fully for the effect. In addition, since Ge resides almost exclusively on the tetrahedral Fe sublattice, small changes in the Ge content produce significant changes in the magnetic properties of the film, as typified by the l values.

Films grown from melt A are clearly beyond the compensation point, having their net magnetization shifted onto the octahedral Fe sublattice. In addition, the analyses indicate that films grown from melts A, B and C all have a (Sm + Y + Ca):(Fe + Ge) ratio slightly in excess of 0.6 indicating that a small percentage of Ca or Y may reside on the octahedral Fe sublattice.

A series of films was grown from melt B at $\sim$ 988°C with growth rates changed by varying the substrate rotation rate. Rotation rates were varied in the order 16, 121, 81, 36, 100, 25 and 49 rpm to minimize the effects of melt composition drift. Growth rates varied from 0.74 μm min^{-1} at 16 rpm to 1.31 μm min^{-1} at 121 rpm. The data in Table II show no distinct trend in either film or composition or the l values with rotation rate.

The absence of a trend is not entirely unexpected. Using the normal definition of segregation coefficient (α) such that, for example

$$\alpha_{Ge} = \frac{\left(\dfrac{Ge}{Ge + Fe}\right)\text{film}}{\left(\dfrac{Ge}{Ge + Fe}\right)\text{melt}},$$

Ge has a segregation coefficient $\approx$ 1.8 whereas Ca, which resides on the dodecahedral sites has a segregation coefficient of only $\approx$ 0.15. It has been well established [12] that segregation coefficients tend to unity as the growth rate tends to infinity. On this basis, we would expect films to contain less Ge and more Ca at higher growth rates. However, for charge compensation, the concentrations of Ca^{2+} and Ge^{4+} in the film must be approximately equal as indicated by the analyses and this consideration helps cancel any trend in composition with growth rate.

In general Ca^{2+} seems to show the same segregation behaviour as does Pb^{2+}, and the Ge^{4+} concentration adjusts to compensate the Ca^{2+}. The scatter in the data of Table II, which is most noticeable in the l values, partly reflects the steep dependence of film properties on the growth temperature. In addition, a small amount of charge compensation for Ge^{4+} may be occurring in the form of Fe^{2+} which would affect the magnetic properties and also explain

TABLE II

Melt	Growth		Analysis			Properties	
	T_g (°C)	r (rpm)	Ca atoms	Ge atoms	Pb atoms	l (μm)	Δa (Å)
A	994.4	36	1.06	1.10	0.007	1.46	
A	982.8	36	1.11	1.16	0.011	0.51	
A	1003.5	100	1.00	1.07	0.008	≈ 30	
A	992.8	100	1.13	1.18	0.010		−0.0038
B	985.4	64	0.93	0.95	0.004	0.57	−0.0023
B	983.0	64	0.95	0.94	0.007	0.87	−0.0030
B	973.1	64	1.00	0.99	0.011	3.0	−0.0023
B	988.4	64				0.60	−0.0015
B	984.7	64				1.15	−0.0015
B	988.9	16	0.95	0.96	0.007	0.81	−0.0030
B	988.5	25	0.96	0.98	0.007	0.91	−0.0008
B	988.5	36				0.82	
B	988.3	49	0.97	0.99	0.007	0.98	
B	988.4	81	0.95	0.97	0.007	0.84	−0.0023
B	988.5	121	0.96	0.95	0.007	0.94	−0.0030
C	965.5	64	0.65	0.65	0.011	0.12	

why these films are substantially darker than comparable Ga-substituted films.

The growth kinetics of the rotation series of films was analysed according to the model of Ghez and Giess [13], correcting for the change in growth rate as a function of undercooling. Least squares fitting of the data gave a diffusion coefficient of 6×10^{-6} cm^2 sec^{-1} and a first order surface integration constant of 9×10^{-4} cm sec^{-1}. This value for diffusion coefficient is slightly lower than the one calculated for the $EuYb_2Fe_5O_{12}$ garnet system by Ghez and Giess. This low diffusivity may relate to the higher viscosity of these GeO_2-containing melts (Fig. 1).

Films grown from melts A and B have a number of desirable properties. Their relatively high Curie temperature (≈ 460 K) indicates good temperature stability of the magnetic properties. Collapse field values show only a 10% decrease in the range 25 to 122°C. In addition, they are highly amenable to ion-implantation for the high density storage devices. However, the films show a high coercivity of nearly one Oe. Also, for films supporting 5 μm bubbles both the $4\pi M_s$ (≈ 100 G) and the collapse fields (≈ 45 Oe) are low, indicating the Q value for this composition is low. Furthermore, films containing neither Sm nor Eu and films grown from melt C have insufficient anisotropy to support stable bubble domains, i.e. have too low a Q value. Although the growth induced K_u could be increased by simply increasing the Sm content to ≈ 0.2 this would also increase the film lattice parameter and consequently have an adverse effect on the strain-induced contribution to the anisotropy since Sm has a large negative λ_{111}. This problem could be overcome by the partial substitution of a smaller rare earth (Tm, Yb, Lu) for Y, resulting in a 6 component garnet film, or by replacing both Sm and Y by a different pair of rare earths.

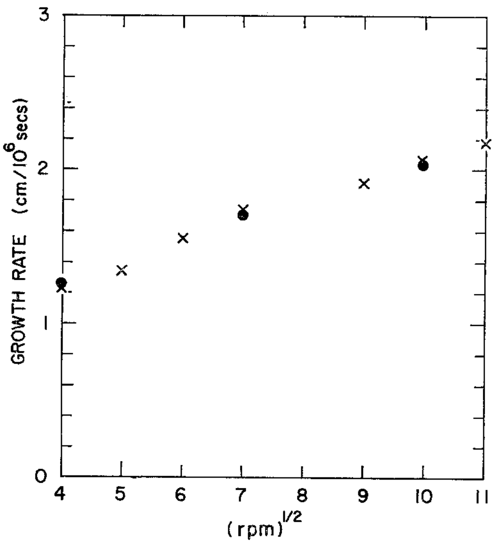

Figure 1 Film growth rate as a function of the square root of the substrate rotation rate. × measured growth rates, ● their values corrected to a growth temperature of 988.5°C, where necessary.

4. Conclusions

Garnet films containing both Ca and Ge are capable of supporting stable 5 μm bubbles and have been grown onto (111) oriented GGG substrates. These films have a higher Curie temperature than comparable Ga-substituted films and, therefore, have better temperature stability. Over the range of parameters studied, it appears that the effect of temperature is much more pronounced than the effect of substrate rotation rate on film composition. Thus, to produce films with highly reproducible properties, strict control of the growth temperature is essential.

The advantages of Ca and Ge substitution in films supporting 1 μm bubbles are fewer than for films supporting 5 μm bubbles since 1 μm films have ≈ 4.5 Fe atoms per formula unit and, therefore, already have a high Curie temperature (≈ 490 K).

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