

Cation Deficiencies in RF Sputtered Gadolinium Iron Garnet Films

Abstract: RF sputtering of stoichiometric, polycrystalline gadolinium iron garnet material results in films significantly deficient in iron content. The cation deficiency is shown to be quite sensitive to preparatory conditions and reflects itself markedly in the magnetic and structural properties of the resultant films. Temperature dependent sticking probabilities and selective resputtering at the growing film surface are thought to be the most likely causes for the observed deficiencies. A simultaneously operated rf-dc two-target sputtering system is described in some detail, which allows an expeditious study of and subsequent compensation for the observed cation deficiency. Films with essentially the bulk garnet composition and bulk structural and magnetic properties were prepared in this two target system.

Introduction

A number of film synthesis approaches have been reported for the preparation of ferrite films, particularly of the spinel crystal type.¹⁻⁶ This paper will be confined to a discussion of sputtering as a technique to prepare thin films of ferrimagnetic gadolinium iron garnet (GdIG — $\text{Gd}_3\text{Fe}_5\text{O}_{12}$). Correlations among various preparatory conditions and the resultant structural, compositional and magnetic properties of the films will be examined. We believe that most of the observations reported here can be generalized to thin film synthesis by sputtering of a large class of compound materials. Details of some of the structural properties of rf sputtered gadolinium iron garnet films have been presented in an earlier publication.⁷

From the literature^{8,9} it appears that the garnet structure of ferrimagnetic $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ exists only over a very narrow composition range, and the neighboring secondary phases, $\alpha\text{Fe}_2\text{O}_3$ and GdFeO_3 , can be expected to affect the properties of the garnet host material. Sputtering was chosen as having the best chance of incorporating a fixed and hopefully stoichiometric ratio of atoms into the garnet films.

Stoichiometric polycrystalline gadolinium iron garnet was used as the target source material in order to reduce the number of possible sources for non-stoichiometry. Since bulk GdIG has a resistivity of the order of $10^{11} \Omega\text{-cm}$, the rf

discharge mode of sputtering was used. By effectively cooling the source material, thermal vaporization and solid diffusion at or near the target surface were avoided. The sputtered material therefore had the same composition as the target. In the case of $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ this implies that once a steady-state sputtering process has been established, gadolinium, iron and oxygen will leave the target in the proportions 3:5:12, and most likely as atoms. Whether or not the stoichiometric compound can be resynthesized on the substrate will depend on both the *net* sticking probability of the various species arriving at the substrate and on the stability of the condensed compound in the particular plasma environment existing at the substrate. The *net* sticking probability of the various species depends on the temperature and morphology of the substrate and on the composition and kinetic energy of the species incident on the substrate during film growth. Previously reported work from our laboratory¹⁰ has shown that significant changes in film composition due to preferential resputtering can occur in situations where the film surface is subjected to high-energy particle bombardment during film deposition. This situation is commonly encountered in bias sputtering¹¹ and in rf sputtering and can only be minimized when the substrate surface potential is kept equal to the plasma potential near the substrate. Preferential thermal re-evaporation from the film surface during film growth due to the different binding energies of the various species at the surface must also be anticipated at elevated substrate temperatures.

The authors are located at the IBM Research Laboratory, San Jose, California.

Film structure vs. substrate temperature and morphology

One of the most striking observations of this work relates to the importance of the morphology as well as the temperature of the substrate with respect to the stability of the garnet-like crystal structure of the resultant film. Early in this work⁷ it was found that films deposited at substrate temperatures lower than 500°C are invariably amorphous, as judged by x-ray and electron diffraction independent of the substrate composition and morphology. Fused quartz, single-crystal quartz, sapphire and various single-crystal garnet substrates such as YAG, GdIG and GdGaG were used. A post-deposition heat treatment of at least 700°C was required to crystallize these films.

Films deposited below 500°C onto single-crystal garnet substrates would crystallize into single-phase gadolinium iron garnet *after* post-deposition annealing at 700°C, and assume an orientation equivalent to that of the substrate. Films deposited onto single-crystal garnet substrates at temperatures above 500°C would crystallize epitaxially as single phase garnet films *during* deposition, and further annealing had a negligible effect on their physical properties. Oriented films could therefore be deposited at will by either a one- or a two-step process. Films deposited onto fused quartz, single-crystal quartz, and sapphire at 500°C and under otherwise identical discharge conditions invariably crystallized upon post deposition annealing into polycrystalline films having primarily the perovskite structure GdFeO_3 together with small amounts of garnet.

Cation deficiency vs. substrate temperature and morphology

The relative cation concentrations in the films prepared under various conditions were determined by using standard microprobe techniques. The results from a representative set of samples deposited at various substrate temperatures are summarized in Table 1.

Substrate temperature was measured during deposition with a glass coated, 0.005-in.-diameter Pt-13% Rh/Pt thermocouple placed in a small pool of gallium on top of one of the substrates. Good thermal contact between the substrates and the heating stage was achieved with a thin layer of gallium placed between substrates and heating stages. The temperature of the top surface of the substrate, measured as described above, never differed by more than 2°C from the temperature of the heating platform.

Since we are interested primarily in changes in cation content, the Fe:Gd ratio in the film samples is considered rather than the proportion by weight of each cation. The values in the Fe:Gd count ratio column of Table 1 were obtained by normalizing the actual microprobe data to a value of 1.667 for the Fe:Gd ratio in a single-crystal sample of $\text{Gd}_3\text{Fe}_5\text{O}_{12}$. The thin film samples and the

Table 1 Microprobe analysis of GdIG films on different substrates prepared at deposition temperatures ranging from 40°C to 500°C.

Sample	Substrate	Deposition temperature, °C	Fe:Gd count ratio	%Fe loss	T_{comp} , °C
Single-crystal $\text{Gd}_3\text{Fe}_5\text{O}_{12}$	—	—	1.667	—	14
A	YAG	500	1.225	26.4	-92
B	Fused quartz	500	1.288	22.6	
C	YAG	320	1.337	19.7	-81
D	YAG	100	1.413	15.0	-54
E	YAG	40	1.528	8.3	-21
F	Fused quartz	40	1.551	6.9	-15

single-crystal reference sample were run under identical microprobe conditions. The percent loss of iron relative to stoichiometric gadolinium iron garnet, corresponding to the Fe:Gd count ratio for each sample, is shown in column 5 of Table 1. The observed iron loss is far outside the experimental error, which is at most $\pm 5\%$. The iron not incorporated into the film situated directly under the target will, of course, be deposited elsewhere in the room temperature metal vacuum chamber. All the samples in Table 1 were annealed at 900°C for two hours in a pure oxygen atmosphere.

From a comparison of the percent iron loss in the various samples it can be seen that the Fe deficiency is surprisingly large in the high temperature deposition runs (samples A and B). The efficiency with which Gd and Fe are incorporated into the growing film is very sensitive to substrate deposition temperatures, as indicated by samples C, D, E, and F of Table 1. A comparison of samples E and F shows a somewhat smaller iron deficiency on quartz than on YAG at the 40°C deposition temperature, as was also the case at 500°C. It should be noted that even at a 40°C deposition temperature both sets of films are iron deficient when compared with bulk material. However, after post-deposition crystallization at $\geq 700^\circ\text{C}$, both films show only the single-phase garnet structure.

This surprisingly high loss of iron during the deposition process cannot be explained on the basis of thermal re-evaporation, since the vapor pressures of any of the most likely species present on the film surface are quite low. Preferential cation diffusion¹² into the substrate must also be considered quite small at these temperatures. The preferential resputtering from the growing film surface during deposition in an rf discharge and its temperature dependence may, however, be quite significant, but the absolute magnitude of this effect is unknown at this time.

The above results on film structure and film composition would indicate that significant iron deficiencies relative to stoichiometric garnet material do not prevent the crystallization of the garnet-like structure on single-crystal garnet substrates but do prevent it on the other substrates. The variation in the iron deficiency, at equivalent deposition temperatures but on different substrate materials, reflects the dependence of the net iron sticking probability on the growing film surface, which in sample A was an epitaxially growing film and in sample B an amorphous film surface.

One of the most cation-concentration sensitive and readily measured magnetic properties in ferrimagnetic gadolinium iron garnet is the compensation temperature T_{comp} . At this temperature the net magnetization due to the antiferromagnetically coupled Gd and Fe sublattices vanishes. The values of T_{comp} for samples A through F are shown in column 6 of Table 1. T_{comp} decreases dramatically as a function of deposition temperature. The decrease qualitatively correlates with the observed increase in iron deficiency as reflected in the normalized Fe:Gd count ratio. From a more detailed consideration¹³ of T_{comp} and its relation to the sublattice moments in the $Gd_3Fe_5O_{12}$ structure one can in fact establish that if the decrease in T_{comp} is due primarily to a dilution of one of the magnetic sublattices, the observed iron deficiency must be primarily from octahedrally coordinated sites rather than tetrahedrally coordinated sites. Both of these sites are normally occupied by Fe^{3+} ions in the garnet structure. However, to account for the observed iron deficiency entirely in the form of unoccupied iron sites results in uncommonly large cation vacancy concentrations. For example, eight of the forty sites normally occupied by Fe^{3+} ions would have to be vacant in sample C of Table 1.

The decrease in T_{comp} could also be accounted for in part by the distribution of Gd^{3+} cations in sites normally occupied by Fe^{3+} and in dodecahedral sites usually occupied by the rare earth ions. Such a redistribution of Gd^{3+} ions avoids the need for the abnormally high iron vacancy densities. A considerable lattice dilation would be expected to accompany both the vacancy model and the Gd^{3+} redistribution model. We have, in fact, already reported observations of such lattice dilations in these films in an earlier communication.¹⁴

Optical data, also already reported,¹⁵⁻¹⁷ were not sufficiently sensitive to detect these structural and compositional changes but did verify that divalent cations such as Fe^{2+} were absent.

Two-target system for cation deficiency control studies

In an effort to verify and subsequently control cation deficiencies such as are encountered in the garnet films

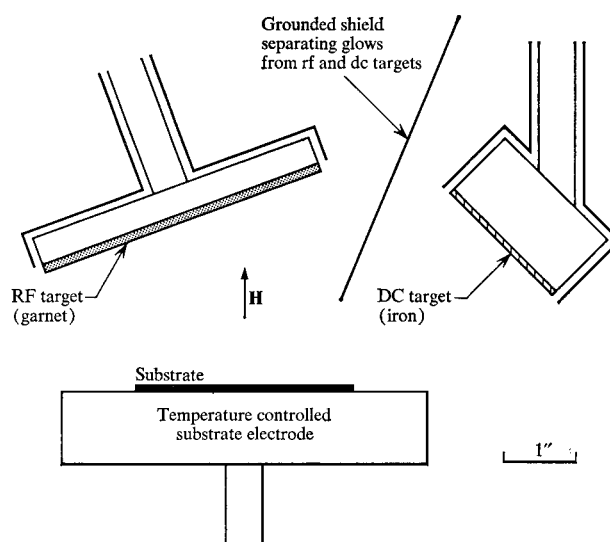


Figure 1 Electrode arrangement in the two-target sputtering system (to scale).

described in the last section, a two-target sputtering apparatus was constructed. This apparatus allows, in a single run, a particular cation to be incorporated in the condensing film in such a manner that its concentration varies continuously along the substrate surface. This approach avoids the necessity of producing a multitude of sputtering targets, each with a slightly different cation content (we remember that homogeneous compound targets such as garnets are often expensive and difficult to fabricate). Films with monotonically decreasing iron content along the length of fused quartz substrate slides were readily made in such a two-target system.

The main features of the system are shown to scale in Fig. 1. The vacuum system, substrate supporting electrode, and rf target electrode structure have been described in detail elsewhere.⁷ In the present configuration the 11-cm-diameter garnet target is mounted off-center and at an angle of 20° with respect to the substrate surface. A 5-cm-diameter iron target is mounted facing the garnet target and inclined 45° relative to the substrate. The two target regions are separated by a grounded stainless steel shield which serves to minimize the interaction between the two glows and largely prevents material sputtered from one target from reaching the other. The shield itself is not sputtered because it is grounded and well outside the Crook's dark space of either glow.

The iron target is sputtered in a dc mode in order to avoid the interaction between the power sources of the two targets that would occur if both were operated in rf modes at the same frequency. A magnetic field of about 30 gauss, oriented perpendicular to the plane of the substrate, has been used in most of the measurements. The magnetic field helps to increase the deposition rate and further decouples the two discharge regions.

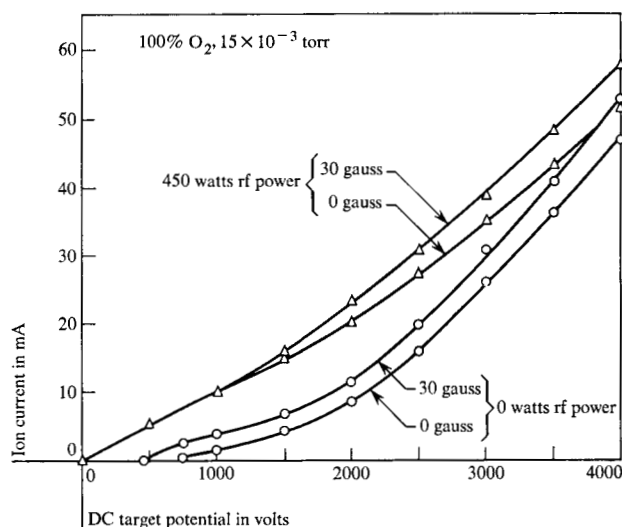


Figure 2 Ion current vs. applied voltage of the dc target with and without power applied to the rf target and with and without a magnetic field.

The characteristics of the dc target with and without rf power applied to the garnet target are summarized in Fig. 2. Since the dc target is situated essentially in the glow of the rf target, there is a sufficiently large number of ions in the vicinity of the dc target when the rf discharge is on, so that no threshold potential on the dc target is necessary in order to strike and sustain a dc glow. This situation has the very important consequence of allowing sputtering from the dc target at the lowest rates desired, and it alleviates the stringent pressure vs. operating voltage requirements normally encountered in dc sputtering. The ion current plotted in Fig. 2 was obtained by subtracting the leakage current to the iron target, measured under high vacuum conditions, from the total current flowing to the iron target when the discharge is on. The ionic species in the oxygen discharge were not identified.

The configuration with the targets inclined relative to the substrate plane necessarily results in deposition rate gradients in the plane bisecting the three electrodes as shown in Figs. 3 and 4 for deposition from the rf target and the dc target, respectively. Since the two targets face one another, the gradients are in opposite directions. In order to produce only relatively small changes in iron concentration relative to the garnet target composition, the iron target is sputtered at a much lower rate than the garnet target. When the two targets are sputtered simultaneously under these conditions, the thin end of the film has the highest iron content.

In order to isolate the effect of the varying iron concentration on magnetic properties, identical runs were made with and without any dc potential applied to the iron target. The substrates were 1.27×7.6 cm, fused

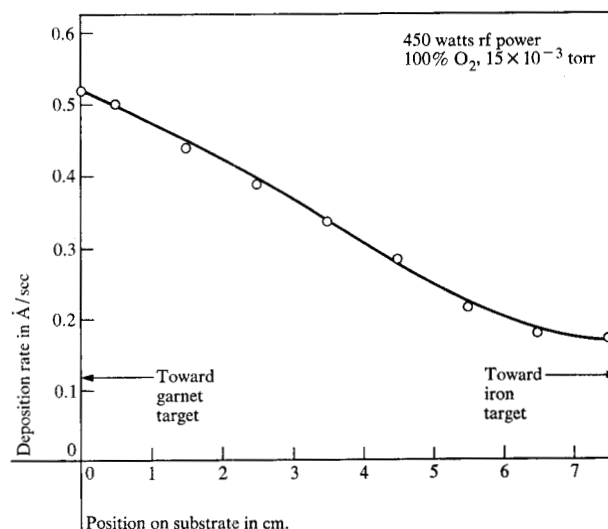
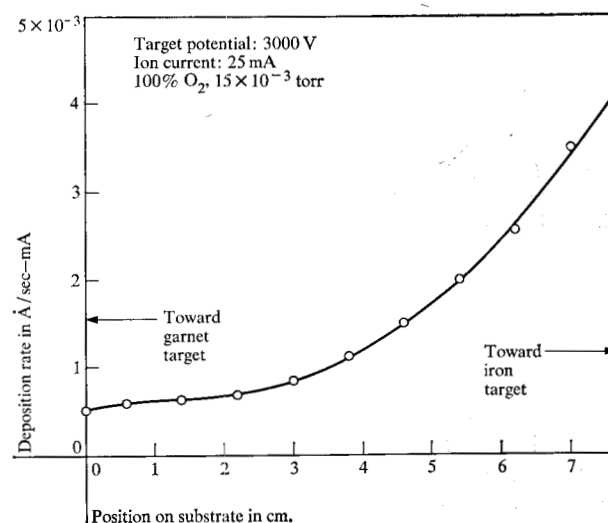


Figure 3 Deposition rate vs. substrate position from the rf target only. The substrate slide is centered on the substrate electrode with its long axis in the plane bisecting all three electrodes.

Figure 4 Deposition rate vs. substrate position from dc target only, normalized to unit ion current. Substrate position is the same as in Fig. 3.



quartz microscope slides placed symmetrically with the ends facing the two targets. In both cases the substrates were maintained at 60°C. The as-deposited films were amorphous and were annealed at 900°C for two hours in pure oxygen in order to crystallize the films. Standard multiple-beam interferometry techniques were used to measure the film thickness as a function of position along the slides.

The results for the rf-only run are shown in Fig. 5. The film thickness varies by about a factor of 2.5 over the length of the substrate, decreasing monotonically away

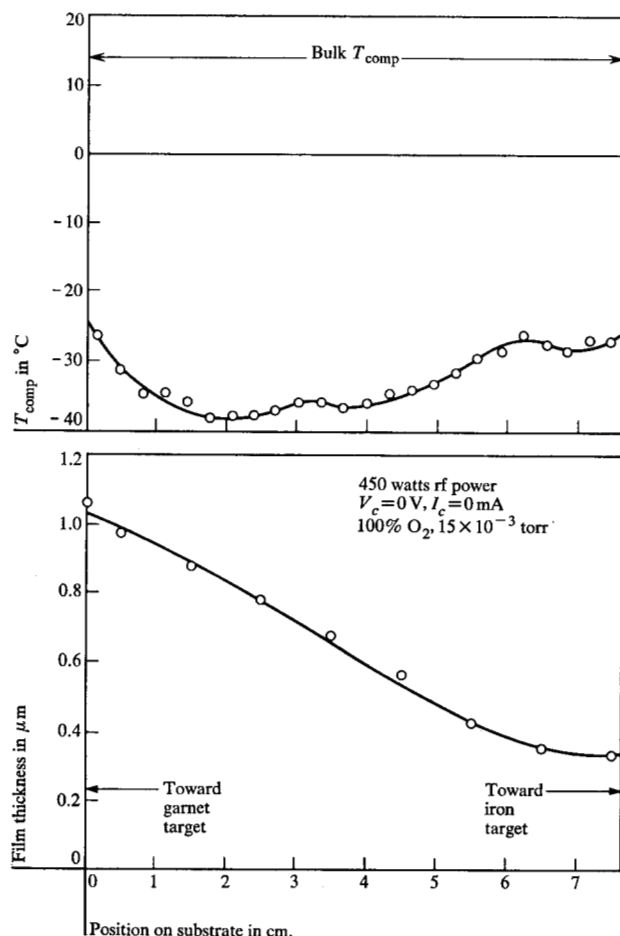


Figure 5 Film thickness and compensation temperature vs. substrate position for a film without any iron sputtered from the dc target.

from the rf target. The compensation temperature of this film was measured as a function of position along the slide with a Faraday-effect hysteresigraph¹⁸ and is also shown in Fig. 5. The variation of T_{comp} is interpreted as being connected with varying film growth conditions along the substrate, such as small changes in the ion concentration or oxidation conditions, which result in small variations in iron content. One should remember that in this case substrate and target are inclined to one another so that different areas of the substrate are situated in different regions of the glow relative to the target surface. Normally the substrate and target are coplanar, so that the plasma conditions surrounding the substrate can be expected to be completely symmetric and essentially uniform over the substrate area. Any possible sputtering from the iron target in the rf-only run was avoided by placing a grounded copper can over the iron target and in contact with the grounded shield surrounding it. The variation in T_{comp} for this run therefore cannot be due to any addition

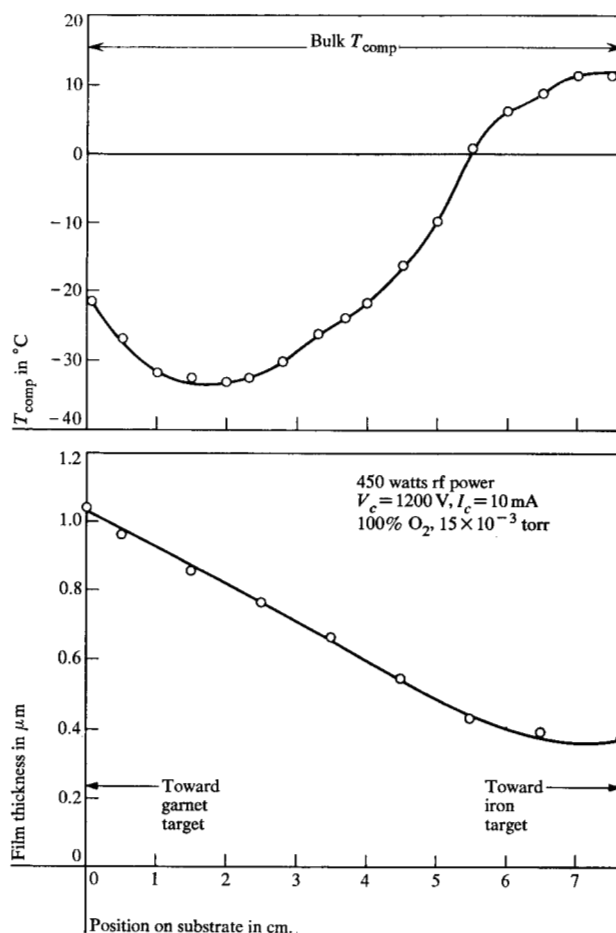


Figure 6 Film thickness and compensation temperature vs. substrate position for a film with iron content increasing toward end of slide nearest the dc target.

of iron from the dc target. The irregular variation in T_{comp} present in rf-only deposited films is found to be superimposed on the dependence of T_{comp} on substrate position when both the garnet target and iron target are being sputtered simultaneously.

The effects of iron doping on the compensation temperature of the rf sputtered garnet film are shown in Fig. 6, together with the variation of its film thickness. This film was prepared with -1200 V applied to the iron target (resulting in 10 mA of ion current), and with all other deposition parameters identical to those of Fig. 5. From the operating parameters of the dc target it is estimated that the iron doped film should be about 250 Å thicker than the undoped film at the end facing the iron target; this estimate is in good agreement with the measurements. As shown in Fig. 6, T_{comp} increases dramatically with iron content, rising to essentially the bulk value of T_{comp} for GdIG. This is in good agreement with the measurements of the Fe:Gd count ratio for this film, which are

shown in Fig. 7. The Fe:Gd count ratio also increases to almost the count ratio found for a single-crystal bulk sample (see Table 1). The observed Fe:Gd count ratio for a given set of experimental parameters varies from run to run by less than 5%.

The difference in compensation temperature ΔT_{comp} between the samples of Figs. 5 and 6 is also shown in Fig. 7. Note that ΔT_{comp} has none of the "wiggles" found in T_{comp} for the rf-only deposited film. The difference is a smoothly varying function of position.

Both the undoped and doped films of Figs. 5 and 6 were prepared under conditions similar to those discussed in the previous section, except that in the case of Fig. 6 iron was continually added to the growing film. As expected from the data presented in the earlier section, careful x-ray diffraction analysis of the undoped and therefore iron deficient film shows it to contain a small amount of $GdFeO_3$ perovskite in addition to the predominant garnet phase. The doped film also shows a slight amount of perovskite at its thick and least doped end, but only the garnet structure at the end where the Fe:Gd ratio is nearly that of bulk material.

Conclusions

One of the advantages of sputtering often cited is the contention that material may be transported from the target in whatever empirical composition it is present at the target surface. After steady-state conditions have been reached in a well defined system this contention will probably hold, in that the material leaving the target will be representative of the elemental composition of the target. This does not, however, insure that a film will grow which has the same composition as the target. In the compound case presented here we have seen what we believe to be a typical example of deviations from target composition that can be found in the condensing film for reasons already outlined in a previous section.

From the present work it is clear that some of the magnetic properties of gadolinium iron garnet films, particularly the compensation temperature, are very sensitive to iron concentration deviations, and that the iron content in the films is very sensitive to the deposition parameters, particularly substrate temperature. We believe that these effects at the growing film surface are largely responsible for reproducibility problems often encountered in compound sputtering. Even though the basic parameters, such as substrate temperature, deposition rate and sputtering gas pressure, are generally carefully controlled, the effective sticking coefficients of the arriving species will also depend on the details of the plasma such as ion and neutral concentrations, their energy distribution, self bias, gas throughput and slight configurational changes from run to run. Thus, the film properties can depend on the history of the apparatus with respect to configurational changes, what

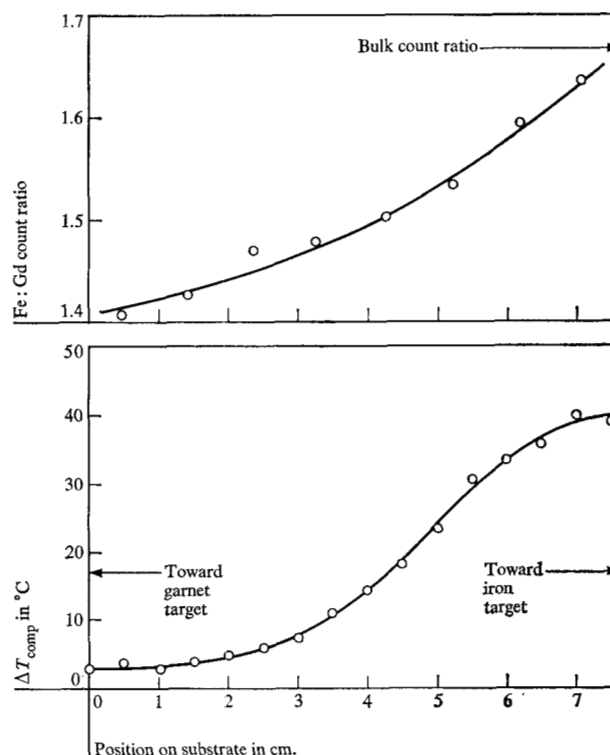


Figure 7 Fe:Gd count ratio of film in Fig. 6 and difference in compensation temperature between films of Figs. 5 and 6, vs. substrate position.

was sputtered in the preceding run, whether a trap was baked just prior to the run, and so on.

We have used the two-target system to study in an expeditious manner the effects of a cation deficiency in a magnetic insulator on some of its physical and magnetic properties. Once the effect and its magnitude of such a cation deficiency have been established, it is to be preferred in a practical system to adjust the composition of the target to counteract the loss of any species, because the two-target configuration described here inherently results in film thickness gradients. However, the substrate could be moved relative to the two targets under a narrow slit, which would result in practically uniform films limited in width only by the target dimensions.

The merits of the two-target system lie primarily in its usefulness in studying the effects of doping in compound sputtering. In a single run, films with a dopant concentration varying continuously over the length of a substrate slide can easily be produced with a single rf target. The range of dopant concentration can be shifted simply by adjusting the potential on the dc target.

Acknowledgments

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