

[54] METHOD FOR SPUTTERING GARNET COMPOUND LAYER

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[22] Filed: Dec. 29, 1972

[21] Appl. No.: 319,589

[52] U.S. Cl. 204/192; 204/298

[51] Int. Cl. C23c 15/00

[58] Field of Search 204/192

[56] References Cited

UNITED STATES PATENTS

3,437,577	4/1969	Kay et al.	204/192
3,573,099	3/1971	Moore et al.	204/192
3,607,698	9/1971	Kay et al.	204/192

OTHER PUBLICATIONS

The Journal of Vacuum Science and Technology, 8, p. S12 (1971) by J. L. Vossen.

Vossen, "Control of Film Properties by RF Sputtering Techniques," The Journal of Vacuum Science and Technology, June, 1971, Vol. 8, No. 5, pp. S12-S30.

Titchmarsh, et al., "Bismuth-Based Glasses for Thin-Film Capacitors Deposited by rf Sputtering," J. of Vac. Sci. and Tech., Vol. 7, No. 1, Jan.-Feb., 1970, pp. 103-107.

Pratt, et al., "Fabrication of rf-Sputtered Barium Titanate Thin Films," J. of Vac. Sci. and Tech., Vol. 8, No. 1, Jan.-Feb. 1971, pp. 256-260.

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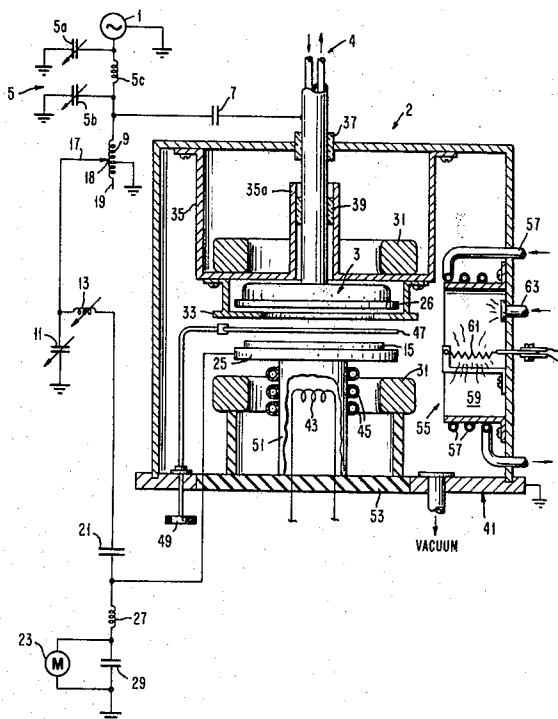
[57] ABSTRACT

A method is disclosed for sputtering epitaxially a layer of stoichiometric garnet composition from a single target wherein the target is composed of a mixture of the separate components of the sputtered layer.

Illustratively, both at a substrate temperature of approximately 450°C and at another substrate temperature between 800-850°C, there was obtained formation of a film of gallium substituted yttrium iron garnet (Ga:YIG). A target was made up of the desired stoichiometry with a mixture of the individual oxides pressed to 85% of the compound's theoretical density. Generally, the steps of the method are: (1) applying a radiofrequency bias to the substrate during sputtering to prevent the deposition of an easily resputtered component of the target; and (2) changing the power density to the target during deposition.

Specifically, a target was made up of a mixture of individual oxides $Y_2O_3 + Ga_2O_3 + Fe_2O_3$ which was pressed to 85% of its theoretical density. Exemplary films of stoichiometric composition were obtained with a radio-frequency bias on the substrate in the range approximately from ground to 100 volts and with power density to the target in the range of approximately 5 to 65 watts/in². The stoichiometric ratio for the composition was $Y_3Fe_{(5-x)}Ga_xO_{12}$, where $0 < X < 3$, whereas the ideal stoichiometric ratio of $[Fe_{(5-x)}Ga_x/Y_3]$ is 1.667. This procedure obtained stoichiometric ratios approximately in the range 1.4 to 1.6.

11 Claims, 7 Drawing Figures



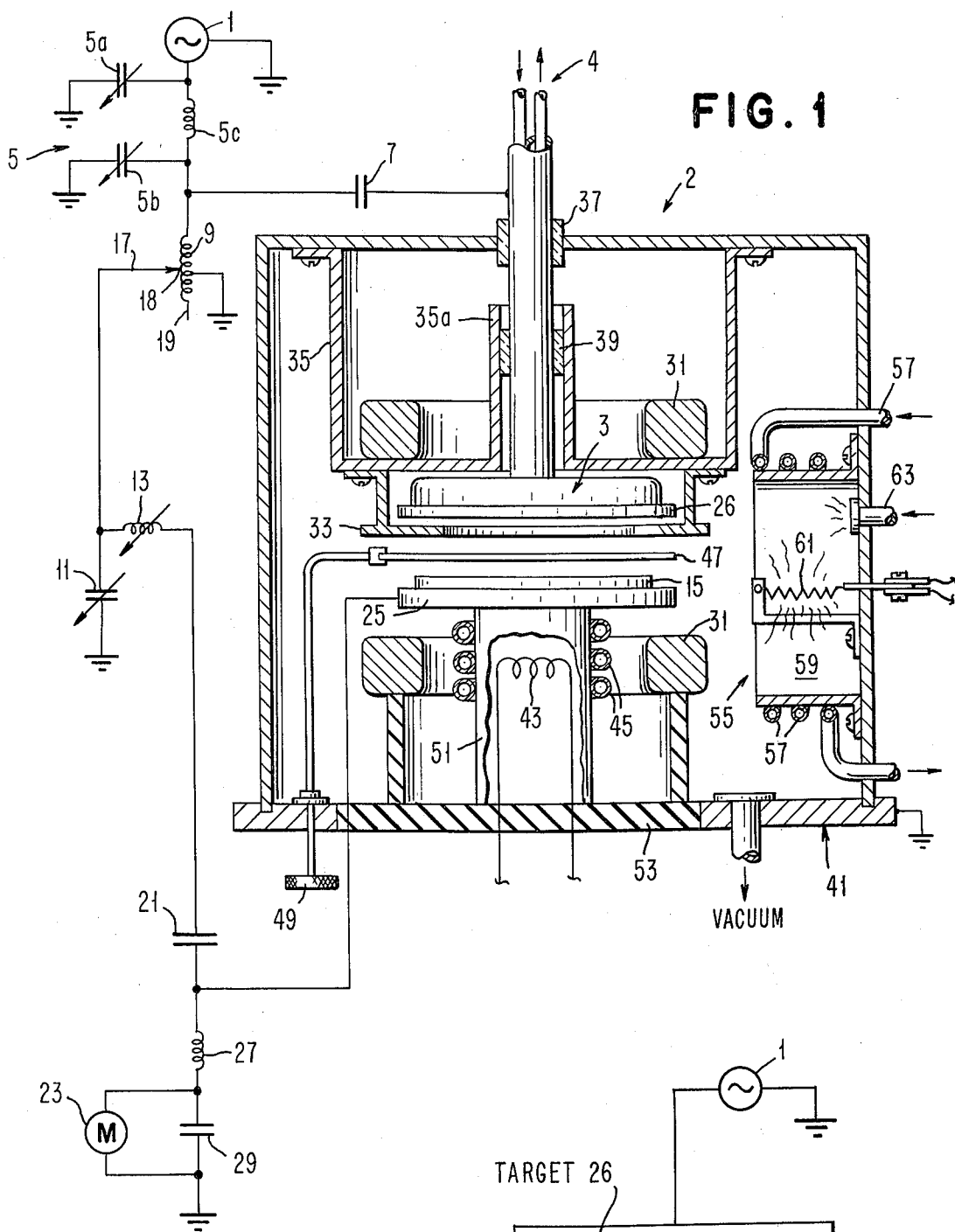
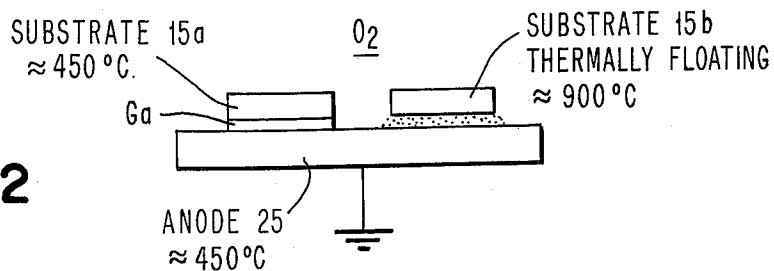


FIG. 2



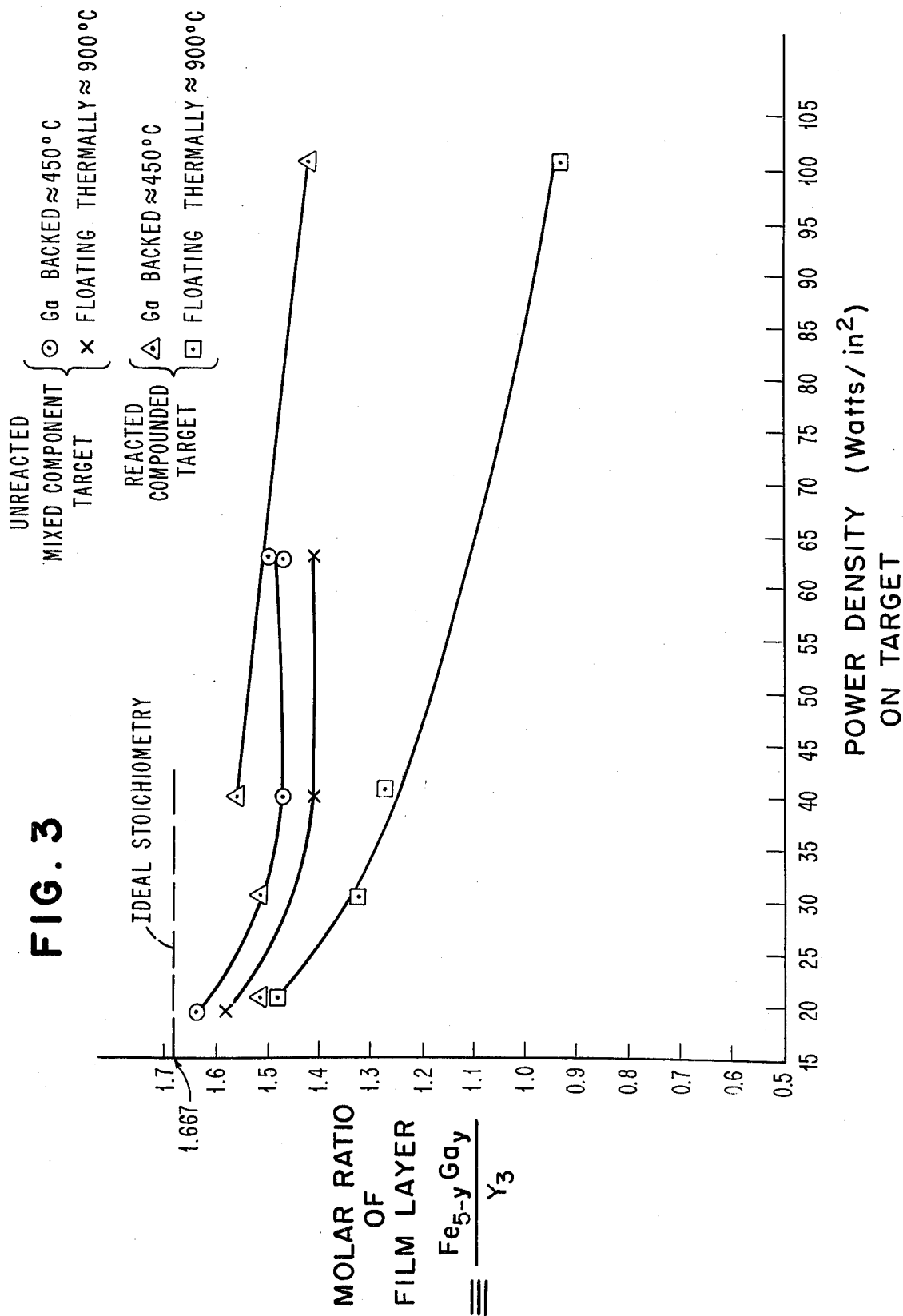


FIG. 4

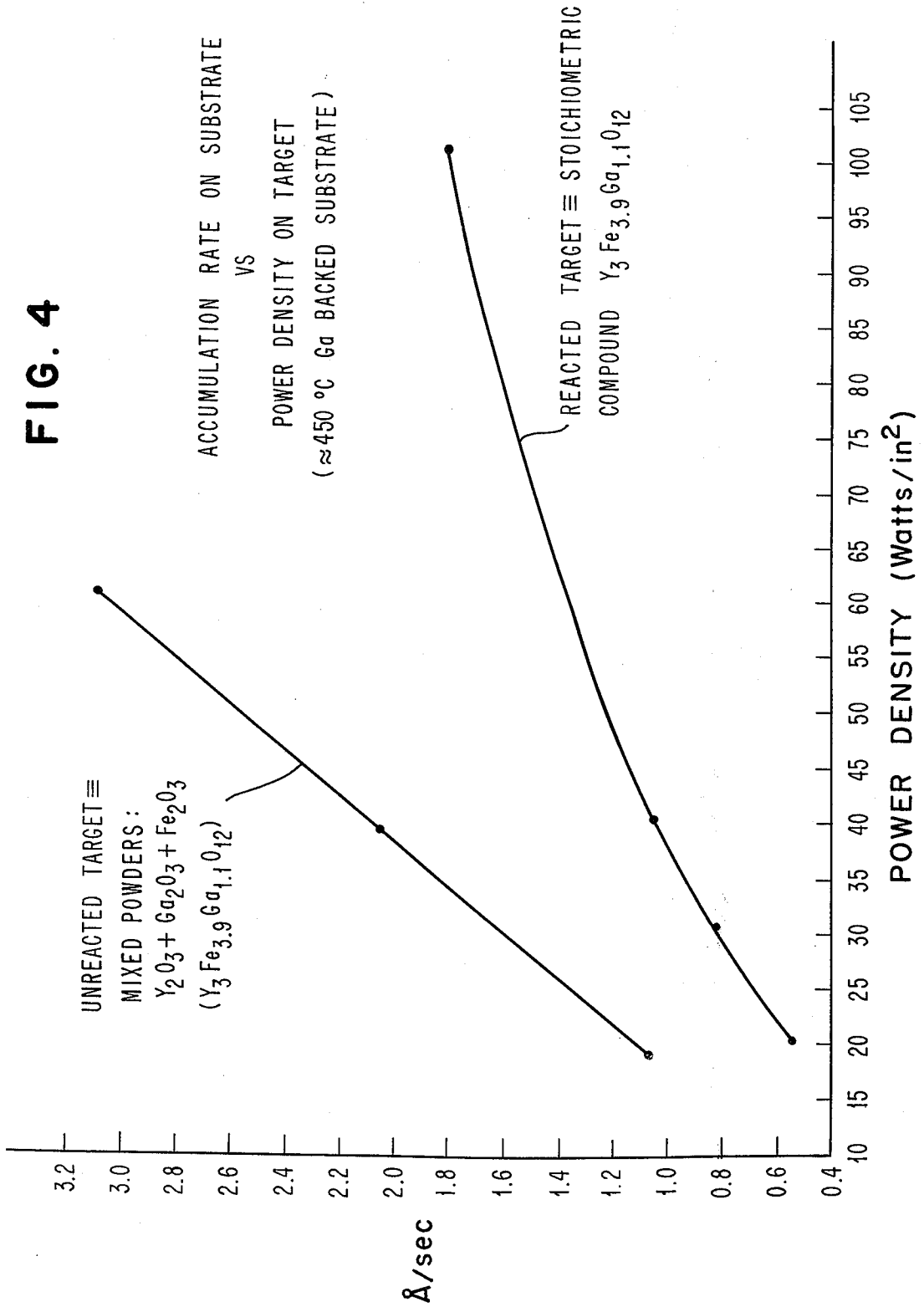


FIG. 5

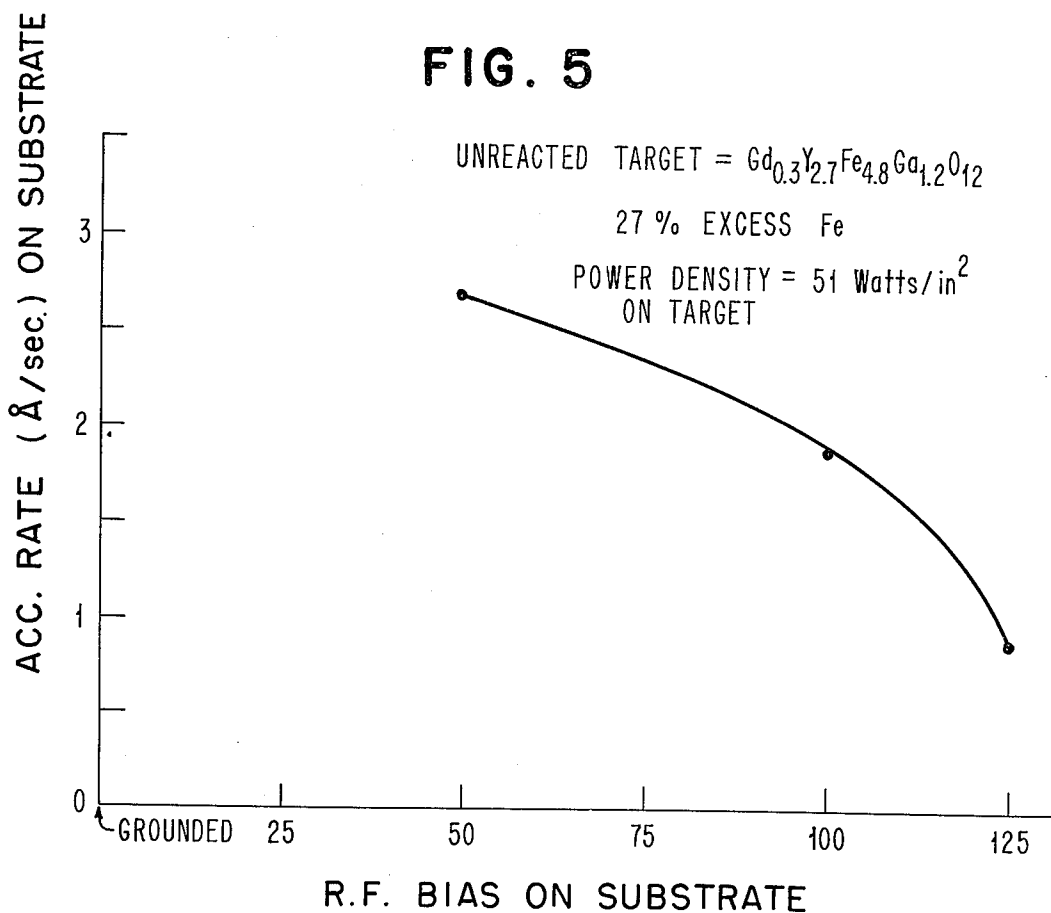


FIG. 7

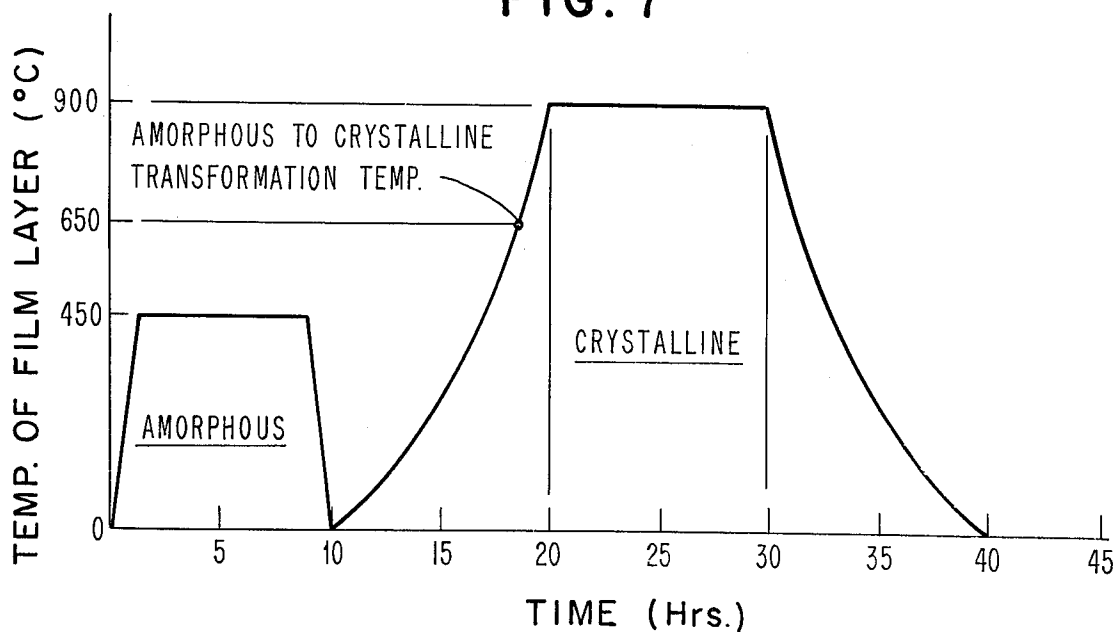
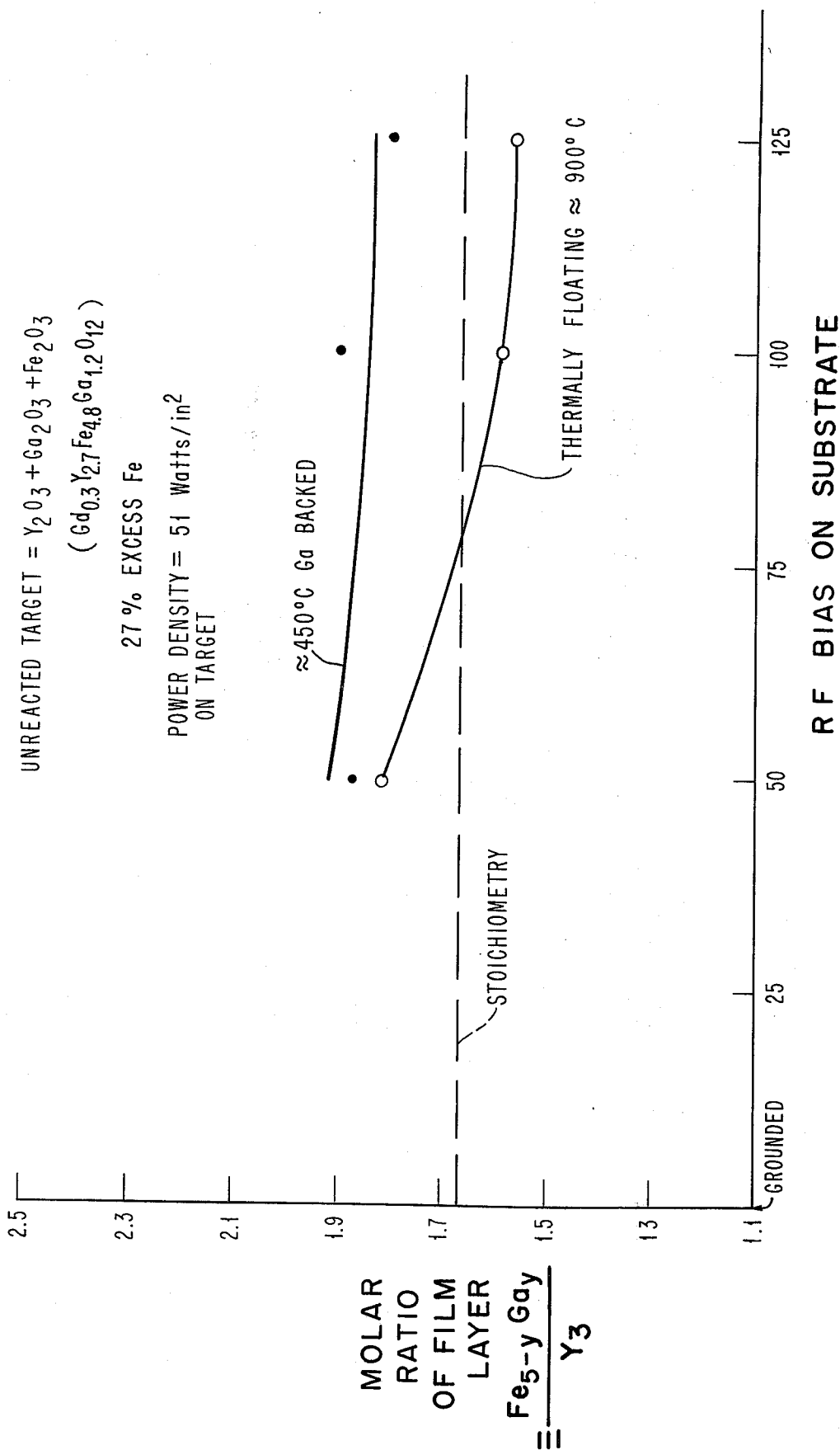


FIG. 6



METHOD FOR SPUTTERING GARNET COMPOUND LAYER

BACKGROUND OF THE INVENTION

Heretofore, fabrication of a multi-component compound film has been attempted predominantly by sputtering with the use of a target material in the same compound phase. Such film has had deficiencies in one or more of the components due to preferential resputtering, thermal removal, and transport losses. To offset the deficiency, the target was enriched with the component that was deficiently deposited. However, such supplemented targets could not deposit in a predictable manner so that the finally deposited film was not stoichiometric and the prior art accumulation rate was relatively poor. Target enrichment in the deficient material has been described at:

a. Applied Physics Letters, 15, 256 (1969), Takei, et al. The deficient material is added to the desired compounded material and mixed with it. They used mixed oxide targets rich in bismuth oxide for sputtering single crystal bismuth titanate film. The yield difference between the compound and the added deficient component is not predictable. Further, the added presence of the excess material shifts the target composition so that many phases are present.

b. IBM J. of Res. and Dev. 13, 696 (1969), by Sawatzky, et al., discloses cation deficiencies in garnet films, principally iron wherein the iron deficiencies are supplemented in the films with the use of an auxiliary independent target of iron. In greater detail, films of gadolinium iron garnet $Gd_3Fe_5O_{12}$ were prepared by radio-frequency sputtering but were found to have cation deficiencies, e.g., film deposited from a stoichiometric garnet target at substrate temperatures of 500°C had about a 25% iron deficiency while film deposited at 40°C had about a 7% iron deficiency. The loss in iron was compensated by the auxiliary iron target so that stoichiometric composition garnet films were prepared. However, a composition gradient was naturally introduced along the film surface. The latter method has problems of nonuniformity. Since the addition of the deficient iron is across the film surface, it is somewhat difficult by this latter technique to produce stoichiometric film with large area.

c. U.S. Pat. No. 3,607,698 by Kay, et al., discloses and claims the method of making single phase, rare earth garnet thin films in a sputtering apparatus comprising the steps of: maintaining a garnet substrate having a (111) orientation directed toward the sputtering flux at a temperature less than 500°C ; maintaining an atmosphere in said apparatus of at least 10 percent pressure oxygen; sputtering material from a source containing said rare earth iron garnet in bulk form to said substrate; crystallizing the deposited film which simultaneously maintaining said oxygen-containing atmosphere at a controlled reduced pressure to prevent said film from cracking.

d. Czech. J. Phys. B21, 351 (1971) by R. M. Josephs discloses mixed oxide targets for garnet film preparation and where it is stated that such targets are easier to fabricate and are more easily doped than compound targets.

e. Adjusting of the film composition by radio-frequency bias sputtering has been discussed at J. Vac. Sci. and Tech. 8, 512 (1971) by J. L. Vossen.

Although both mixed oxide targets and biasing of a growing film during sputtering have been discussed in the prior art literature, illustratively, the use of a target of an enriched mixture of oxides with power density on the target, radio-frequency bias on the substrate, and substrate temperature being controlled interdependently for a given accumulation rate has not been previously accomplished.

OBJECTS OF THE INVENTION

It is an object of this invention to produce garnet compositions by sputtering.

It is another object of this invention to produce garnet compositions in an amorphous form by radio-frequency sputtering on Gadolinium Gallium Garnet (GGG) substrates in a variety of orientations.

It is yet another object to convert the amorphous garnet composition of the preceding object to epitaxial single crystal films by heating.

It is an object of this invention to produce amorphous garnet films at substrate temperatures less than 675°C .

It is yet another object to prepare garnet compositions in amorphous form and in crystalline form from targets with compositions with excess of the resputtered species by adjusting the substrate temperature and radio-frequency bias on the substrate to produce stoichiometric garnet composition.

It is another object of this invention to practice the preceding object by a method which includes starting with a target compound of a mixture of materials, transporting these materials to an appropriate substrate where they are reacted to produce a garnet structure rapidly.

It is an object of this invention to provide a method for growing an epitaxial layer of garnet by sputtering of the components thereof from a target to a substrate controllably by setting interdependently the operational parameters: level of radio-frequency power at the target, radio frequency bias level at the substrate, and the temperature of the substrate.

It is another object of this invention to practice the foregoing object thereof by utilizing an unreacted target having concentrations of the components of the desired layer according to the stoichiometry thereof varying interdependently the recited operational parameters of the preceding object.

It is another object of this invention to practice the preceding object by establishing the levels of the recited operational parameters for a given accumulation rate of the layer at the substrate.

It is another object of this invention to produce garnet films with suitable properties for bubble domain applications.

It is another object of this invention to provide the crystalline garnet film of the preceding object epitaxially in single crystalline form.

It is another object of this invention to produce garnet film for magnetic bubble device by sputtering from a single target where the film is produced initially in amorphous form and is then converted to crystalline form.

It is another object of this invention to provide a method for producing a layer with a given composition by radio-frequency sputtering said layer onto a substrate wherein there is included varying interdependently the operational parameters of substrate temperature, radio-frequency power to said target, and radio-

frequency bias on said substrate, to establish said given composition of said layer on said substrate.

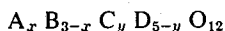
SUMMARY OF THE INVENTION

It has been discovered for the practice of this invention that yield, stoichiometry and accumulation rate of a sputtered garnet film can be controlled by interdependently varying magnitudes of radio-frequency power at the target, and both temperature and radio-frequency bias on the substrate. In general, it has been determined for practice of this invention that garnet structure so produced is suitable for bubble domain device.

In the practice of one aspect of this invention, a mixed oxide target is utilized. In the practice of another aspect of this invention, a stoichiometric compound garnet target may be utilized, but the accumulation rate is less than for comparable growth conditions for an unreacted target. Practice of another aspect of this invention utilizes an enriched mixed oxide target wherein the component normally deficient in the produced film is an enriched species. The enriched target is readily fabricated and the yield of the enriched species is predictable. The radio-frequency bias on the substrate removes the easily resputtered species from the growing film in a predictable way thereby producing the resultant stoichiometric garnet film.

Through the practice of this invention with mixed oxide component targets, desirable accumulation rate and stoichiometry of garnet film are obtained. Therefore, use of an unreacted mixture of the oxides as a target in radio-frequency sputtering obtains a substantial improvement in the rate of accumulation of the film compared to use of a reacted target of stoichiometric composition with time to grow garnet film thicknesses less by approximately one-third.

By a practice of this invention there is a method of producing stoichiometric garnet structure film



where A is a rare earth element of the lanthanide series, e.g., Gd, Eu, Tb, Er; B is Y, La or Sc; C is Al or Ga; and D is Fe, Ni or Co, through the steps of: establishing a single source target; establishing radio-frequency power at target in the range of approximately 5 watts/sq.in. to 100 watts/sq.in.; and establishing substrate temperature in the range approximately 0°C to 1,000°C. In greater detail, it is beneficial to utilize a target for practice of this invention which is a mixture of the components of said film and radio-frequency power at the target in the range of 2 watts/sq.in. to 23 watts/sq.in. with a substrate temperature in the range of approximately 500°C to 650°C.

Specifically, for a grown garnet film of composition $Y_3 Ga_y Fe_{5-y} O_{12}$, where $0 < y < 3$, the target is preferably a composite mixture of the oxides $Y_2 O_3$, $Ga_2 O_3$, and $Fe_2 O_3$, and is grown with radio-frequency bias on the substrate of less than approximately 200 volts d.c. level peak-to-peak, e.g., in the range of 20 watts/sq. in. to 100 watts/sq. in. However, for some operational circumstance, the target may be of garnet structure.

In an illustrative example of the practice of this invention for obtaining a stoichiometric composition of $A_x B_{3-x} C_y D_{5-y} O_{12}$, where $0 < x < 3$ and $0 < y < 3$, in a garnet film, the following are exemplary operational parameters: temperature of the substrate is approximately in the range 500°C to 1,000°C; radio-frequency

power to the target is approximately in the range 35 watts/sq. in. to 60 watts/sq.in; and the radio-frequency bias on the substrate is desirably in the range of 200 volts d.c. level to 25 volts d.c. level, e.g., 75 volts d.c. level, where the lower voltage may suitably be below 25 volts.

It has been demonstrated that D may be Fe in excess up to 27% of the target by weight composition. For an example of an excess of Fe in said target of approximately 27% Fe, the power density in the target is approximately 51 watts/sq. in. and the radio-frequency bias on the substrate is approximately in the range of 125 volts d.c. level to 25 volts d.c. level. For another example, the film may be deposited in crystalline form when the temperature on the substrate is greater than approximately 650°C. For another example, the film may be deposited in amorphous form when the excess Fe is up to approximately 40% Fe and the temperature is less than approximately 650°C. It has also been demonstrated that a variable substrate bias may be utilized while substrate temperature is kept fixed.

Generally, in accordance with the objects of this invention, there is provided a method for producing a layer with a given composition comprising the steps of: establishing a target which includes the components of said layer and a substrate; radio-frequency sputtering said layer onto said substrate; establishing operational parameters such that said substrate is at a given temperature, radio-frequency power to said target is at a given power density thereat, and radio-frequency bias on said substrate is at a given d.c. level; and varying interdependently said operational parameters to establish said given composition of said layer on said substrate. The target may be an unreacted mixture of different compounds of at least two components of said layer, e.g., oxides of said components. Additionally, by varying interdependently said operational parameters, there may be obtained a given accumulation rate of thickness of said layer on said substrate.

More particularly, in accordance with the objects of this invention, there is provided a method for producing a layer with garnet stoichiometry comprising the steps of: establishing a target which includes the components of said layer and a substrate with garnet composition; radio-frequency sputtering said film onto said substrate including, establishing operational parameters such that said substrate is at a given temperature, radio-frequency power to said target is at a given power density thereat, and radio-frequency bias on said substrate is at a given d.c. level; and varying interdependently said operational parameters to establish a given accumulation rate of thickness of said layer on said substrate. Illustratively, when said temperature is established approximately in the range of 650°C to 1,000°C, said power density on said target is approximately in the range of 35 watts/sq. in. to 60 watts/sq. in., and said radio-frequency bias on said substrate is approximately in the range of 200 volts d.c. level to 25 volts d.c. level; and said accumulation rate of thickness of said layer is approximately in the range of 1 Angstrom/sec. to 3 Angstroms/sec.

DRAWINGS FOR THE INVENTION

FIG. 1 is a schematic drawing partially in section and partially in circuit diagram of apparatus suitable for radio-frequency sputtering of material compositions according to the principles of this invention.

FIG. 2 is a schematic drawing illustrating the use of the apparatus of FIG. 1 wherein alternatively a substrate is in thermal contact with the anode electrode and wherein a substrate is thermally floating relative to the anode electrode.

FIG. 3 is a chart showing data in graphical form of the stoichiometric or molar ratio ($\text{Fe}_{5-x}\text{Ga}_x/\text{Y}_3$) plotted versus power density on the target for several growth conditions in the practice of this invention.

FIG. 4 is a chart showing data in graphical form of accumulation rate on the substrate versus power density on the target for radio-frequency sputtering according to the principles of this invention for targets of (a) powders of mixed oxides, $\text{Y}_2\text{O}_3 + \text{Ga}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and (b) stoichiometric compound $\text{Y}_3\text{Fe}_{5-y}\text{Ga}_y\text{O}_{12}$, illustrating that the target of mixed oxides yields a faster accumulation rate on the substrate according to the principles of this invention.

FIG. 5 is a graph showing data on accumulation rate versus radio-frequency bias on the substrate for an unreacted garnet target with excess Fe and a particular power density on the target illustrating that the accumulation rate at the substrate decreases with increase of the radio-frequency bias.

FIG. 6 presents data in graphical form of molar ratio of the grown stoichiometric garnet film according to the principles of this invention illustrating that the molar ratio is higher for a gallium-backed substrate at $\approx 450^\circ\text{C}$ than for a substrate thermally floating at $\approx 900^\circ\text{C}$.

FIG. 7 is a line diagram showing an idealized plot of temperature versus time illustrating the amorphous to crystalline transformation of a garnet film according to the principles of this invention.

GENERAL DESCRIPTION OF APPARATUS FOR THE PRACTICE OF THE INVENTION

A schematic diagram of apparatus suitable for the radio-frequency sputtering of garnet materials according to the principles of this invention is shown in FIG. 1.

Generally, the cathode holder 3 and the anode 25 are arranged in a diode configuration. A shutter 47 is placed between the cathode and anode and axial and horizontal motion are provided thereto to cover the substrate during presputtering of the target and also to protect the target during sputter cleaning of the substrate prior to deposition. Heating of the substrate 15 is obtained by resistance heaters 43 embedded in the anode assembly. The structure 41 is generally constructed of stainless steel. The molybdenum substrate holder 25 is precoated with garnet of approximately the target composition to prevent resputtering of molybdenum on the substrate 15. The radio-frequency power is split between the target 26 and the substrate 15 by the network 5 which provides independent radio-frequency bias control on the substrate.

The target is made of oxides pre-reacted to form the garnet compound which are ground, mixed and fired several times and then formed and fired into a disc. The preferable type of target is unreacted and comprised of the metal oxides which are mixed and pressed at high pressure and temperature and are only slightly sintered.

Generally, both reacted and unreacted targets have stoichiometric composition $\text{Y}_3\text{Fe}_{3.5}\text{Ga}_{1.5}\text{O}_{12}$. Additionally, a suitable target may also be unreacted Gd:Ga:YIG with excess Fe of up to approximately 40% compensation, e.g., 27% Fe. Illustratively, the sub-

strates are Gadolinium Gallium Garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$) (GGG) grown by Czochralski technique.

After polishing of the substrate, it is annealed at $1,250^\circ\text{C}$ for about 4 hours and chemically polished in hot phosphoric sulphuric acid and then rinsed in deionized water for about 10 minutes, then rinsed with ethyl alcohol and finally treated in freon vapor. The substrate showed single crystal electron diffraction patterns with Kikuchi lines, indicating a surface nearly free from lattice distortion. Surfaces with the [111], [110], [100] orientations were found suitable for growth of epitaxial single crystal films of garnet stoichiometric composition.

SPECIAL DESCRIPTION OF APPARATUS FOR PRACTICE OF THE INVENTION

FIG. 1 depicts an exemplary radio-frequency sputtering system, suitable for producing garnet film in accordance with the principles of this invention. As shown in the figure, an RF source 1 is coupled to target holder assembly 3, via the impedance matching network 5 and coupling capacitor 7. Impedance matching network 5 comprises variable capacitors 5a and 5b and inductor 5c and is employed to match the impedance of the sputtering system 2 to the impedance of RF source 1. During RF sputtering, it is possible to control to some extent the properties of the deposited films by applying a radio-frequency bias voltage to the substrate 15. For that purpose, there is provided a network comprising AC impedance elements 9, 11, and 13 which ensure that an appropriate bias is on substrate 15.

Inductor 9 is coupled at one end point to the node between impedance matching network 5 and coupling capacitor 7, and at another point to movable wiper arm 17 with contact 18. The center of inductor 9 is grounded and lower end 19 is floating, with the wiper arm 17 contact 18 on inductor 9 acting to provide a complete path. The wiper arm 17 is coupled to variable capacitor 11 and variable inductor 13 which is coupled to capacitor 21. Meter 23 is coupled to the junction between capacitor 21 and anodic substrate holder 25 via inductor 27 and is employed to measure the peak-to-peak radio-frequency voltage bias on the anodic substrate holder. Inductor 27 and capacitor 29 are employed to isolate the meter 23 from the radio-frequency bias on the substrate.

The grounded center tap inductor 9 inverts the RF voltage so that when the RF signal from source 1 is positive, the voltage between the grounded center tap and the floating end of inductor 9 is negative and vice versa. When wiper arm 17 is moved on inductor 9, the amplitude of the inverted voltage is varied. Variable capacitor 11 and variable inductor 13 are employed to tune the phase shift network, which may be varied over 360°C . Thus, both the amplitude of the RF substrate bias and the phase thereof may be adjusted. Therefore, the RF load, i.e., the impedance of the sputtering system, varies in accordance with the sputtering system parameters. Thus, where it is desirable to obtain a maximum peak-to-peak voltage on the substrate 15, for a particular wiper arm 17 setting, the entire radio-frequency circuit is adjusted to resonance.

Substrate 15 is mounted on substrate holder 25. Target 26 is mounted in conductive relationship with target holder assembly 3. Cathode target holder assembly 3 is water cooled, with water entering and exiting via pipes 4 in accordance with the arrows shown at the top

of the assembly. Respective Helmholtz coils 31 which are energized by a direct voltage source, not shown, surround the cathode target holder assembly 3 and pedestal portion 51 of anode substrate holder 25. Coils 31 provide a magnetic field of intensity approximately 30 to 80 gauss perpendicular to the plane of target 26 and substrate 15. This magnetic field increases the concentration of electrons in the sputtering environment to increase sputtering efficiency. Additionally, the magnetic field acts to increase the bias on the substrate 15. Ground shield 33 around target 26 limits and focuses the sputtering to the control portion of target 26. Shield 33 is removably affixed to mount 35 to permit changing of targets 26.

Ceramic sleeves 37 and 39 insulate the cathode target holder assembly 3 from the metal sputtering chamber 41 and the housing portion 35a of mount 35, respectively. Heating assembly 43 maintains the substrate 15 at the desired temperature. Cooling coils 45 cool the anode structure and therefor the substrate 15. Shutter arrangement 47 is movably positionable between substrate 15 and target 26. Turning knob assembly 49 which is external to chamber 41 permits movement of the shutter 47 from the region between substrate 15 and target 26. Pedestal portion 51 of the anode substrate holder is mounted upon insulation 53 to isolate electrically the substrate holder assembly from metal chamber 41.

The sputtering chamber incorporates a titanium sublimation pump 55 surrounded by liquid nitrogen container 57. Before the sputtering is initiated, the sublimation pump getters active species, such as carbon and carbon-bearing compounds, from within the chamber onto the surface of the cryogenically cooled drum 59 of the pump. Titanium filament 61 is energized via an electrical source, not shown. High purity oxygen enters at port 63 and is passed through the titanium pump into the sputtering chamber. The high purity oxygen becomes further purified in the titanium pump and is used to sputter-clean the surface of substrate 15.

Sputtering chamber 41 is pre-pumped down to a pressure of from 2.0 to 8.0×10^{-8} Torr while substrate 15 is maintained at the desired temperature for sputtering. This pre-pumping is achieved via the port at lower right of chamber 41. Illustratively, a freon-cooled diffusion pump may be used to achieve the desired vacuum in the system. The system is then backfilled with high purity oxygen until a pressure of approximately 2×10^{-2} Torr is reached. The oxygen is "scrubbed" in the titanium sublimation pump and the sputtering system is further readied for sputtering.

Next, the shutter 47 is positioned between the target 26 and substrate 15 by knob 49 and the circuitry power is turned on. Oxygen is established in chamber 41 via port 63. Oxygen plasma is generated and components of the target are sputtered upon shutter 47. Usually a pre-sputtering period of from 5 to 30 minutes is adequate, and it has been found that the average time for effective pre-sputtering is about 15 minutes.

Then, the substrate 15 is sputter cleaned in an oxygen environment. The system is first pumped down again to the base pressure of 2×10^{-8} Torr and is backfilled with oxygen. Simultaneously, radio-frequency voltage 18 is applied to produce a dc level bias on the substrate of approximately 150 volts. With shutter 47 in conductive contact with shield 33, which is grounded via the walls of mount 35 and chamber 41, there is sputter cleaning

of the substrates for about 5 to 10 minutes. A typical system sputtering pressure of 2×10^{-2} Torr is established and shutter 47 is removed thereby exposing substrate 15 to the atom flux from target 26. Conveniently, a mixture of argon and oxygen may be used for the sputtering and sputtering pressures from 10 to 10^{-3} Torr may be employed.

PRACTICE OF THE INVENTION

FIG. 2 is a schematic diagram illustrating functionally a portion of the apparatus to indicate two ways that a substrate 15 may be mounted on anode 25 for the practice of this invention. Substrate 15a is shown supported via a layer of gallium, i.e., it is gallium-backed, by molybdenum block 25; and substrate 15b is shown as thermally floating, i.e., it is placed on block 25 and is somewhat insulated therefrom by the lack of effective thermal control thereto. Consequently, substrate 15a is at the same temperature $\approx 450^\circ\text{C}$ as the block 25, whereas substrate 15b reaches a higher temperature $\approx 900^\circ\text{C}$, i.e., it is thermally floating.

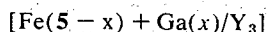
Thus, the $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrate wafers 15 were either gallium-backed to the molybdenum substrate holder or allowed to float thermally as illustrated in FIG. 2. The gallium backed substrate 15a is within a few degrees of the temperature of the molybdenum holder. The temperature of a substrate 15b as measured by optical pyrometry reached 900°C and greater depending on the power input to the target. Identical atom flux from the target impinged on the higher temperature floating substrate 15b and on the lower temperature gallium backed substrate 15a.

For an exemplary film growth procedure, with reference to FIGS. 1 and 2, the system is pumped to below 10^{-7} Torr, and pure oxygen is admitted into the system to about 2.5×10^{-2} Torr, which is maintained by pumping. With target 26 and substrate 15 shielded and the anode 25 grounded, the system is pre-sputtered for about 30 minutes. Then, the shield 47 is moved from target region to allow sputter cleaning of the substrates for about 10 minutes. The shutter shield 47 is then opened thereby permitting atom flux from the target to reach the substrates 15a and 15b. The radio-frequency bias on the substrate 15 is adjusted to a predetermined level and deposition occurs over a period, e.g., up to approximately 38 hours.

After deposition, the grown films are annealed in flowing oxygen in an open tube furnace. Desirable results were obtained when the grown films were maintained from 900°C to $1,100^\circ\text{C}$ for 24 hours, and then slowly cooled, e.g., 50°C/hr . Circular eruptions occurred in the film when rapidly heated to annealing temperature, whereas film slowly heated to annealing temperature showed tensile cracking. However, by selecting an intermediate rate of heating to annealing temperature, large nearly perfect films were obtained as regards such circular eruptions and tensile cracks. Proper lattice matching between the substrate and garnet film reduces the tendency for cracking to take place. Illustrative thicknesses of grown films, as measured by a Taylor-Hobson Tally Surf instrument, ranged from 0.01 to 15 microns, of which 1 to 5 micron films were typical. Optical absorption methods were also employed in determining film thickness and the results compared closely to the mechanical measurements.

EXEMPLARY DATA FOR THE INVENTION

Exemplary garnet films according to the principles of this invention were examined from various interdependent operational parameters of the sputtering of radio-frequency bias on the substrate, power density on the target, substrate temperature and accumulation rate of the film at the substrate. The film composition as determined by electron microprobe analysis, was normalized to 3 moles of Yttrium. The ratio of the sum of the normally occupied Fe^{3+} sites to the rare earth sites in a material with garnet composition



was considered as the stoichiometric or molar ratio. For comparison, the molar ratio for the ideal stoichiometric composition is 1.667. FIG. 3 is a plot of the molar ratio as a function of power density in watts/in² on the target showing results of reacted and unreacted targets either at $\approx 450^\circ\text{C}$ or $\approx 900^\circ\text{C}$.

Both types of targets for the data of FIG. 3 have the stoichiometric composition $\text{Y}_3\text{Fe}_{3.9}\text{Ga}_{1.1}\text{O}_{12}$. The substrates were gadolinium gallium garnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. Substrates that are gallium-backed and at $\approx 450^\circ\text{C}$ are compared to thermally floating examples which are at temperatures from 850°C to 980°C . For comparison purpose, films were deposited on both lower temperature substrate 15a and higher temperature substrate 15b of FIG. 2 simultaneously. The samples at $\approx 450^\circ\text{C}$ are amorphous and reddish while films deposited at $\approx 900^\circ\text{C}$ are crystalline and range in color from amber to greenish-yellow.

The difference in composition between films deposited on the high temperature $\approx 900^\circ\text{C}$ substrate films deposited on and the lower temperature $\approx 450^\circ\text{C}$ substrate is considerably smaller when produced from the unreacted target than when produced from the reacted target. The unreacted target produces an approximately constant differential in composition between the higher temperature substrate and the lower temperature substrate whereas the reacted compounded garnet target resulted in films that vary widely in composition. As the power density on the target is decreased, the composition of the grown film approaches more closely that of the target. Theoretically, the tendency for the convergence of compositions of the higher and lower temperature substrates at lower powers results because the heating of the thermally isolated substrates is decreased to a point where the films are deposited in amorphous form at approximately the temperature of the substrate holder. Sputtering at relatively low power density on the target produced more nearly ideal film stoichiometry. Films prepared from the unreacted, i.e., mixed component, target approach the target stoichiometry before the reacted, i.e., compounded garnet, target. Therefore, there is an improvement in the ratio of the species sputtered from the unreacted target compared to the species sputtered from the reacted target.

FIG. 4 shows the accumulation rate on the substrate as a function of power density for both the unreacted target and the reacted target. Illustratively, the accumulation rate from the unreacted target exceeds the accumulation rate for the reacted target by a factor of about 2 to 3. Illustratively, at 30 watts/in² on the target with substrates at $\approx 450^\circ\text{C}$, sputtered films were prepared from an unreacted target with an accumulation rate on the substrate of 1.5A/sec. Such films were

within 2% of the stoichiometric composition of the target, whereas for the reacted garnet target there was an accumulation rate of about 0.4A/sec with greater than 11% deviation from the target composition.

With reference to FIGS. 5 and 6, unreacted targets with 27% excess Fe ($\text{Gd}_{0.3}\text{Y}_{2.7}\text{Fe}_{4.8}\text{Ga}_{1.2}\text{O}_{12}$) were also fabricated. Since Fe is the preferentially resputtered ion from the growing film, its excess in the target allows the growth of stoichiometric crystalline garnet at relatively high temperature on the substrate and high power density on the target. Films were deposited on GGG substrates $\approx 450^\circ\text{C}$ and on GGG substrates thermally floating at temperature $\approx 900^\circ\text{C}$. FIG. 5 shows the accumulation rate on the substrate as a function of bias for the unreacted 27% excess Fe target. The decrease in accumulation rate as a function of radio-frequency bias on the substrate results from the large amount of resputtering which takes place at the relatively high radio-frequency bias levels on the substrate. The films on the Ga-backed $\approx 450^\circ\text{C}$ substrates are amorphous and nonmagnetic and upon crystallization become single crystalline garnet structures; occasionally small amounts of a second phase were found and were presumed to be perovskite. The films grown at $\approx 900^\circ\text{C}$ temperature were single crystal with the second phase appearing occasionally.

The data of FIGS. 5 and 6 show the trends of composition of the film produced and accumulation rate on the substrate with radio-frequency bias on the substrate and indicate a large influence of the bias on film composition, particularly at relatively high temperature. Therefore, it has been determined for practice of this invention that radio-frequency bias control of the substrate is advantageous for the fabrication of stoichiometric films of multi-component systems.

FIG. 6 presents plots of molar ratio versus radio-frequency bias on the substrate for both gallium-backed substrates $\approx 450^\circ\text{C}$ and thermally floating substrates $\approx 900^\circ\text{C}$. Generally, it is shown by FIG. 6 that unreacted targets with excess Fe can be used to prepare stoichiometric garnet compositions and structures by adjusting the power density to the target which can be generally greater than to a stoichiometric target and also by adjusting the temperature range at which stoichiometric films can be prepared as well as the bias that is applied to the substrate. It will therefore be understood from the foregoing discussion that the interrelationship among target composition, power density, substrate temperature and substrate bias can be selectively controlled to obtain stoichiometric garnet compositions and structures.

CONSIDERATIONS FOR THE INVENTION

It has been discovered for the practice of this invention that garnet films which will support movable bubble domains may be formed by radio-frequency sputtering. It has been demonstrated that composition control may be successfully achieved for single crystal garnet film at substrate temperatures higher than 500°C , which is the upper temperature limit given in the noted prior art U.S. Pat. No. 3,607,698 for the preparation of single crystal Gd:Ga:YIG films.

In the practice of this invention, a garnet structure is deposited as an amorphous layer on a GGG surface and then transformed to crystalline form by heating as illustrated by FIG. 7. The growth takes place outwardly from the interface between the film and the substrate

toward the surface of the film with resultant epitaxial single crystal garnet layer on the substrate. The epitaxial growth process via the amorphous to crystalline transformation is a relatively low temperature process for epitaxial growth of garnet films, when compared to the prior art practice. The typical thermal history of garnet films undergoing amorphous to crystalline transformation is shown in FIG. 7. For $Y_3Fe_{3.9}Ga_{1.1}O_{12}$ film on $Gd_3Ga_5O_{12}$ substrate, the amorphous to crystalline transformation temperature is between 650°C and 675°C for a film prepared at $\approx 450^\circ\text{C}$. Amorphous garnet films deposited on sapphire substrates showed an amorphous to crystalline transformation temperature higher than for GGG substrate, and the transformation temperature varied from 50°C to 100°C greater than the transformation temperature of film on GGG. Theoretically, these differences in crystallization temperatures are due to differences in the interfacial surface energy between the substrate and the film. The amorphous garnet films are a deep burgundy red in transmitted light and after crystallization range from a yellow-green to an amber-yellow depending on composition and thickness of the film.

Amorphous garnet films deposited in accordance with the principles of this invention have been found to be readily etched in dilute HCl, whereas the crystallized garnet deposited in accordance with the principles of this invention is only slightly soluble in dilute HCl. Patterns may readily be etched in the amorphous garnet, then recrystallized to form epitaxial garnet patterns.

Exemplary technology for providing special amorphous to crystalline transformation to obtain single crystal film is disclosed in copending application Ser. No. 319,125 filed Dec. 29, 1972 by P. Chaudari, et al., and commonly assigned.

We claim:

1. Method of producing film with garnet stoichiometric composition $A_xB_{3-x}C_yD_{5-y}O_{12}$, where $0 < x < 3$ and $0 < y < 3$, wherein
 - A is a rare earth element of the lanthanide series including Gd, Eu, Tb and Er;
 - B is Y, La or Sc;
 - C is Al or Ga; and
 - D is Fe, Ni or Co;
 comprising the steps of:
 - a. establishing a target with substantially non-garnet structure and with said stoichiometric composition and establishing a substrate with garnet composition;
 - b. sputtering said film onto said substrate from said target including establishing operational parameters by:
 1. establishing said substrate at a temperature approximately in the range of greater than 500°C to 1,000°C,
 2. establishing radio-frequency power to said target approximately in the range of 2 watts/sq. in. to 100 watt/sq. in;
 3. establishing radio-frequency bias on said substrate at a given d.c. level; and
 - c. varying interdependently said operational parameters to deposit onto said substrate a film having substantially said garnet stoichiometric composition and to establish a given accumulation rate of thick-

ness of said film on said substrate.

2. Method as set forth in claim 1 wherein

1. said temperature of said substrate is established approximately in the range of greater than 500°C to 650 °C, and

2. said radio-frequency power to said target is established in the range of 2 watts/sq. in. to 23 watts/sq. in.

3. Method as set forth in claim 2 including the step of establishing said radio-frequency bias on said substrate less than approximately 200 volts d.c. level peak-to-peak.

4. Method as set forth in claim 1 and wherein said radio-frequency power to said substrate is established approximately in the range of 35 watts/sq. in. to 60 watts/sq. in.

5. Method as set forth in claim 4 wherein said radio-frequency bias on said substrate is varied during production of said film thereon while said temperature of said substrate is maintained at an approximately fixed value.

6. Method as set forth in claim 1 wherein power density on said target is approximately in the range 20 watts/sq. in. to 100 watts/sq. in.

7. Method as set forth in claim 1 wherein said temperature of said substrate is greater than approximately 650°C, said radio-frequency bias on said substrate is approximately 75 volts d.c. level.

8. Method as set forth in claim 1 wherein said temperature of said substrate is less than approximately 650°C.

9. Method for producing a layer with garnet stoichiometry comprising the steps of

establishing a target which has substantially a garnet stoichiometric composition which is substantially nongarnet structure and establishing a substrate with garnet composition,

radio-frequency sputtering said film onto said substrate from said target including,

establishing operational parameters such that said substrate is at a given temperature approximately in the range of 650°C to 1,000°C, radio-frequency power to said target is at a given power density thereat approximately in the range of 35 watts/sq. in. to 60 watts/sq. in., and radio-frequency bias on said substrate is at a given d.c. level approximately in the range of 200 volts d.c. level to 25 volts d.c. level, and varying interdependently said operational parameters to deposit onto said substrate a layer having substantially said garnet stoichiometric composition and to establish a given accumulation rate of thickness of said layer on said substrate approximately in the range of 1 Angstrom/sec. to 3 Angstroms/sec.

10. Method as set forth in claim 9 wherein said target is comprised of a mixture of oxides

Y_2O_3 , Ga_2O_3 and Fe_2O_3 , and said film is produced with stoichiometric composition of

$Y_3Fe_{5-y}Ga_yO_{12}$, where $0 < y < 3$.

11. Method of claim 9 wherein said target is an unreacted mixture of different oxides of at least two components of said layer.

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