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E. KAY ET AL
METHOD OF FABRICATING UNIFORM RARE EARTH IRON
GARNET THIN FILMS BY SPUTTERING
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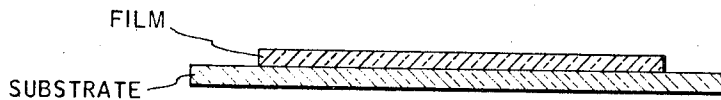


FIG. 1

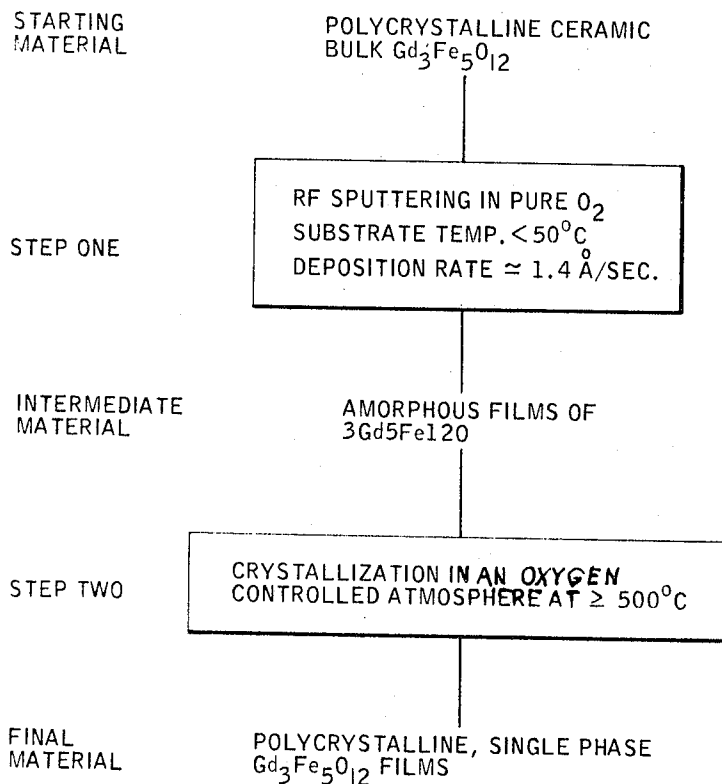


FIG. 2

INVENTOR.

ERIC KAY
ERIC SAWATZKY

Elmer Galli

ATTORNEY

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METHOD OF FABRICATING UNIFORM RARE EARTH IRON GARNET THIN FILMS BY SPUTTERING

Eric Kay, Campbell, and Erich Sawatzky, San Jose, Calif., assignors to International Business Machines Corporation, Armonk, N.Y., a corporation of New York

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7 Claims 10

ABSTRACT OF THE DISCLOSURE

The method of making single phase, polycrystal rare earth iron garnet thin films in a radio frequency sputtering apparatus. The film is sputtered from a source containing the rare earth garnet in bulk form. A substrate which has a thermal expansion coefficient in the range $80 \times 10^{-7}/^{\circ}\text{C.}$ to $130 \times 10^{-7}/^{\circ}\text{C.}$ is used. During the sputtering operation, the temperature at the surface of the source is maintained below the vaporization temperature of the rare earth garnet and the substrate is maintained at a temperature less than 50°C. The atmosphere in the apparatus includes at least 10% oxygen. After the film has been formed by sputtering, the film is crystallized at a temperature in the range of 700°C. to 1100°C. in a controlled atmosphere.

Cross references to related applications

The following copending applications which are assigned to the assignee of the subject invention are generally related to the subject invention: (1) application Ser. No. 593,387, by O. Voegeli et al., filed Nov. 10, 1966; (2) application Ser. No. 384,356, by A. P. Poenisch et al., filed July 22, 1964, now U.S. Patent 3,369,989.

Background of the invention

The present invention relates to a method of fabricating thin films and, more particularly, the present invention relates to a method for fabricating films which consist of rare earth iron garnet material and which are very thin, transparent, and uniform.

The preparation of rare earth iron garnet thin films with controlled physical properties has become of considerable importance in recent years. Such films have application as modulators for light beams, couplers or modulators in microwave systems, and as the active memory element in a beam addressable memory system. An example of a beam addressable memory system where such films can be used is shown in the previously referenced copending application Ser. No. 593,387.

There are several known techniques for fabricating rare earth iron garnet thin films. For example, a publication by Wade which appears in the Journal of Applied Physics, vol. 34, No. 4, April 1963 describes a chemical deposition technique for fabricating such films and a publication by Robert Linares which appears in the Journal of Applied Physics, September 1965, p. 2884, shows a technique for fabricating such films through chemical vapor reaction growth.

While the prior art does teach several techniques for fabricating such films, none of the known techniques are completely satisfactory with respect to the ability to repeatedly produce uniform, uncracked films with the desired physical characteristics. Furthermore, the prior art does not teach how to fabricate rare earth iron garnet films with controlled magnetic and magneto-optical properties.

The present invention provides an improved technique for fabricating rare earth iron garnet thin films. Using

the present invention, the parameters of the thin films can be more closely controlled than with the prior art. Furthermore, the present invention allows one to obtain controlled uniform properties over large areas. The uniformity of films fabricated in accordance with the present invention includes uniformity in both the structural and physical properties as a function of thickness and as a function of surface area. Thus, rare earth iron garnet films produced according to the present invention are thin, uncracked, transparent, and they are highly uniform.

Summary of the invention

The present invention utilizes conventional radio frequency sputtering apparatus. A substrate which has a thermal expansion coefficient in the range $80 \times 10^{-7}/^{\circ}\text{C.}$ to $130 \times 10^{-7}/^{\circ}\text{C.}$ is used. The substrate is maintained at a temperature less than 50°C. during the deposition operation and the atmosphere in the apparatus during the deposition includes at least 10% partial pressure of oxygen. Material is sputtered from a source containing rare earth iron garnet in bulk form and a thin amorphous film is formed. After the amorphous film is formed, it is removed from the apparatus and crystallized at a temperature of between 700° to 1100°C. , in a controlled atmosphere.

Brief description of the drawings

FIG. 1 shows a thin film of rare earth iron garnet deposited on a substrate.

FIG. 2 is a flow diagram which illustrates the method of the present invention.

Description of a preferred embodiment

The method of the present invention has two major steps. These are indicated in FIG. 1. The process begins with bulk rare earth iron garnet material. During the first step, the bulk material is transferred to a substrate in order to form a thin amorphous film. The transfer is by means of radio frequency sputtering. The conditions which must be maintained during the sputtering step in order to obtain satisfactory films are specified later. The second step in the process involves the crystallization of the amorphous film formed in the first step of the process. Again, in order to obtain films with the required characteristics, certain conditions, specified later, must be maintained during the crystallization step.

The present invention includes the discovery that in order to produce very thin uniform transparent uncracked films consisting of single phase, rare earth iron garnet by means of radio frequency sputtering, the following parameters are of primary importance: (1) the empirical composition at the surface of the cathode source during the sputtering operation; (2) the thermal expansion coefficient of the substrate whereon the films are deposited; (3) the temperature of the substrate during the sputtering process; (4) the atmosphere in the apparatus during the sputtering process; and (5) the temperature used to crystallize the amorphous film into a single phase film. The present invention includes the discovery that in order to obtain rare earth iron garnet thin films with the desired characteristics, a certain combination of the above specified parameters must be utilized. Each of the parameters will be discussed separately.

Rare earth iron garnet films can be described by the formula $\text{M}_3\text{Fe}_5\text{O}_{12}$ where M is one of the rare earths. An important aspect of rare earth iron garnet films is the fact that the ratio of the components is three to five to twelve. If the ratio of the components varies from the desired three to five to twelve ratio, the resulting film is not single phase and it has undesirable properties.

A very important aspect of the present invention is the fact that the surface of the cathode source material from

which the film is sputtered has the same empirical composition as the desired film during the entire sputtering process. To ensure that the three to five empirical composition at the surface of the cathode source remains constant through the sputtering process, thermal vaporization of the source material must be avoided. This can be done by keeping the surface of the cathode source relatively cold. The surface is maintained below the vaporization point by keeping the bulk temperature of the cathode source at approximately room temperature, which is far below the vaporization point of the material. However, keeping the bulk temperature at approximately room temperature ensures that the surface temperature of the cathode source remains below the vaporization temperature of the material. If vaporization takes place on the surface of the cathode source, the three to five ratio will not be maintained on the surface of the source and the composition of the film which is deposited will vary from the desired three to five ratio. While it might seem obvious that in order to make films with a particular stoichiometric composition, one would use a source having the same empirical composition as the desired film, it has been found that unless other parameters are maintained within the ranges specified later, the stoichiometric composition of the film will differ from the empirical composition of the source material. The present invention, therefore, includes the discovery of specific ranges of the various parameters which must be maintained so that one can use a source material which has the same empirical composition as the stoichiometric composition of the desired film.

The substrate on which the film is deposited must be selected very carefully. According to the present invention, a chemically inert substrate is selected and the desired chemical properties of the film are obtained without any interaction with the substrate. According to the present invention, a substrate with a high temperature resistance must be selected since, as will be explained later, the process includes a crystallization step at a relatively high temperature. Of paramount importance is the fact that a substrate must be selected which has a thermal expansion coefficient in the range between $80 \times 10^{-7}/^{\circ}\text{C}$. to $130 \times 10^{-7}/^{\circ}\text{C}$. If a substrate which has a thermal expansion outside of this range is used, the films will crack during the crystallization steps. Examples of substrates that can be used include magnesium oxide, X-cut single crystal quartz or a single crystal of the same rare earth iron garnet as that in the desired film.

It is noted that, considering films one micron thick, cracking of the films does not appear to have any effect on the macroscopic magnetic properties of the films down to the level of considering areas having a diameter of one millimeter. The same average values for the compensation temperature and the coercive force were obtained from similar films on various substrates inside and outside of the above defined thermal expansion range even though the films within the above defined range were uncracked, whereas the films outside of the above range were cracked. Elimination of any microscopic cracks within the film is particularly important in systems which utilize the films for optical purposes, such as the previously referenced beam addressable memory system.

The temperature of the substrate during the deposition process is the second highly important parameter. Considering the fact that one desires a crystalline film, conventional techniques would dictate the use of a relatively high substrate temperature, for example, above 500°C . However, if one attempts to utilize a substrate which is held at a relatively high temperature during the deposition process, and if one utilizes a source which has the same stoichiometric composition as the desired film, as is taught in accordance with the present invention, the film which results on the substrate will not have the desired stoichiometric composition. Instead the resulting film will be multiphased, i.e., it will include oxides which

have other stoichiometric ratios than the desired three-five-twelve ratio of the garnet.

The atmosphere in the deposition apparatus is another highly important parameter. Considering the fact that, in accordance with the present invention, one begins with a source material which has the same ratio of rare earth iron and oxide as that desired in the film, i.e., a three-five-twelve ratio, one might expect that an atmosphere of an inert gas, such as argon, should be used. However, if an inert sputtered gas is used, the resulting film does not have the desired three-five-twelve ratio. Instead, when an inert sputtering gas is used, one finds that the resulting film is oxygen deficient. Such films tend to gain oxygen during crystallization and they tend to crack and flake off the substrate during crystallization. If the sputtering gas includes at least 10% partial pressure of O_2 , the resulting films have the desired three-five-twelve ratio and there is no cracking or flaking during crystallization. It has been found that the composition of the film does not change significantly with increased amounts of oxygen and, hence, any amount of oxygen from 10% to pure oxygen can be used. A gas pressure in the range of 10×10^{-3} torr to 50×10^{-3} torr was found to result in uniform, uncracked single phase films. If less oxygen than 10% is used, the resulting films tend to crack during the crystallization step.

The final step in the process involves crystallizing the amorphous films which are produced during the first step in the process. Satisfactory results are obtained by crystallizing the films in an oxygen atmosphere at a temperature of 700° to 1100°C . for about one hour. Alternately, the films can be crystallized in a high vacuum of 10^{-7} torr for approximately one hour at a temperature range between 700° and 1100°C .

First Example: The following is one particular example of how the present invention was practiced. However, it should be clearly understood that the scope of the invention is indicated by the appended claims and not by the following specific example. The sputtering apparatus used was similar to that shown in a paper by P. D. Davidson, published in the Journal of Applied Physics, vol. 37, p. 574, 1966. However, commercially available radio frequency sputtering apparatus such as that produced by Materials Research Corporation, Model No. EVD850, could be used. One necessary feature of the apparatus used is the inclusion of a cooling mechanism in the sputtering cathode in order to avoid thermal vaporization of the cathode source. The sputtering apparatus was evacuated by commercially available vacuum equipment capable of producing background pressures of the order of 5×10^{-7} torr. The sputtering apparatus was activated with a conventional low power (50 watt) radio frequency oscillator and a standard radio frequency power amplifier capable of generating one thousand watts CW output. A frequency of 13.56 megacycles per second was used.

A "cathode" sputtering source which consisted of ceramic bulk, gadolinium iron garnet ($\text{Gd}_3\text{Fe}_5\text{O}_{12}$) was used. A single crystal of non-magneto-optically active garnet; namely, gadolinium gallium garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$) was used as a substrate. The substrate was gallium soldered to the temperature controlled counter-electrode in the sputtering apparatus in order to ensure a well-defined substrate temperature during film deposition. The substrate was maintained at $50^{\circ}\text{C} \pm 1^{\circ}\text{C}$. during the deposition operation. The temperature of the substrate was controlled using the mechanism shown in copending application Ser. No. 384,356 by A. Poensich et al., filed July 22, 1964, which is assigned to same assignee of the subject case. A set of Helmholtz coils was placed outside of the vacuum chamber in order to provide a magnetic field perpendicular to the dielectric target surface. The superposition of the magnetic field resulted in a significant increase in the deposition rate and it helped to stabilize and confine the glow in the space between the two electrodes

within the deposition apparatus. A field of 40 gauss was used throughout the work.

The apparatus was first evacuated to 10^{-7} torr and then oxygen was introduced in order to create a pressure of 20×10^{-3} torr. A spacing of 2.5 cm. between the source and the substrate was used. The deposition rate was $85^\circ \text{ A./minute}$. Films two microns thick were fabricated.

When first removed from the sputtering chamber, the films were completely amorphous. These amorphous films were converted to single phase polycrystalline GdIG films by heating them at 700° C. in an oxygen atmosphere. The heat treatment was performed in a 2 in. glow bar tube furnace. The tube furnace had a programmable power source, and generally, the heating and cooling rates were 600° C./hr. and 200° C./hr. respectively.

X-ray diffraction, electron diffraction, and X-ray fluorescence were used to determine the presence of crystallographic phases and to check the relative concentrations of Gd and Fe in the film. During the crystallization step, the weight of the films was accurately monitored to within 10^{-7} grams using an ultra-micro-balance. If the films had (1) a three to five gadolinium to iron ratio by X-ray fluorescence, (2) X-ray diffraction and electron diffraction, clearly indicated gadolinium iron garnet as the only phase, and (3) the films did not gain any weight during crystallization, it was then assumed that the oxygen content did not significantly deviate from the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ composition. By the above technique, it was clearly shown that the resulting gadolinium iron garnet films were single-phase films.

Several substrates were used covering an area of approximately 30 sq. cm. Measurements of the resulting films showed that the coercivity did not vary more than $\pm 5\%$ over the entire area and the compensation temperature did not vary by more than $\pm 1^\circ \text{ C.}$ over the entire area. The chemical and structural properties of the film did not vary over the thickness of the film and microscopic examination showed that the resulting film had no cracks.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that the foregoing and other changes in the form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of making single phase, rare earth iron garnet thin films in a sputtering apparatus comprising the steps of:

- (a) maintaining a substrate at a temperature less than 50° C. ;
- (b) maintaining an atmosphere in said apparatus of at least 10% partial pressure oxygen;
- (c) sputtering material from a source containing said rare earth iron garnet in bulk form to said substrate;

(d) crystallizing the deposited film while simultaneously maintaining said oxygen-containing atmosphere at a controlled reduced pressure to prevent said film from cracking.

2. The method recited in claim 1 wherein said surface of said source is cooled during sputtering so that it remains below its vaporization temperature and so that the empirical composition at the surface of said source remains the same as the desired empirical composition of said film.

3. The method recited in claim 1 wherein said crystallization is done at a temperature in the range of 700° C. to 1100° C.

4. The method recited in claim 3 wherein said crystallization is done in an oxygen atmosphere.

5. The method recited in claim 1 wherein said substrate has a thermal expansion coefficient in the range $80 \times 10^{-7}/^\circ \text{ C.}$ to $130 \times 10^{-7}/^\circ \text{ C.}$

6. The method recited in claim 1 wherein said sputtering is accomplished by a radio frequency field.

7. The method of making a single phase, gadolinium iron garnet thin film in a radio frequency sputtering apparatus comprising the steps of:

- (a) maintaining at a temperature less than 50° C. a substrate which has a thermal expansion coefficient in the range $80 \times 10^{-7}/^\circ \text{ C.}$ to $130 \times 10^{-7}/^\circ \text{ C.}$;
- (b) maintaining an atmosphere in said apparatus of at least 10% partial pressure oxygen;
- (c) sputtering material from a source containing gadolinium iron garnet in bulk form to said substrate by means of a radio frequency field;
- (d) cooling the surface of said source during the sputtering so that it remains below its vaporization temperature and so that the empirical composition at the surface of said source remains the same as the desired empirical composition of said film;
- (e) crystallizing the deposited film at a temperature in the range of 100° C. to 1100° C. in said oxygen atmosphere while simultaneously maintaining said oxygen-containing atmosphere at a controlled reduced pressure to prevent said film from cracking.

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ROBERT K. MIHALEK, *Primary Examiner.*

U.S. Cl. X.R.

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U.S. DEPARTMENT OF COMMERCE

PATENT OFFICE

Washington, D.C. 20231

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,437,577

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Eric Kay et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 38, "100°" should read -- 700° --.

Signed and sealed this 7th day of October 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents