United States Patent

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[54] **SINGLE CRYSTAL FERRIMAGNETIC FILMS**
5 Claims, No Drawings

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[50] **Field of Search** 117/235, 237

[56] **References Cited**

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ABSTRACT: A process for preparing single crystal ferrimagnetic films having square hysteresis loops, a regulated coercivity, and a compensation temperature above 250° K. A film of gadolinium iron garnet wherein a carefully selected amount of terbium or dysprosium replaces part of the gadolinium is deposited on a tytrium or rare earth aluminum garnet substrate having [111] or [100] orientation and heated until crystallization occurs.

SINGLE CRYSTAL FERRIMAGNETIC FILMS

FIELD OF THE INVENTION

The present invention relates to a process for making single crystal films and more particularly to a process for making thin single crystal garnet films having ferrimagnetic properties and the advantage of simultaneously combining square hysteresis loops, controllable coercivity, and compensation temperatures near room temperature. The preparation of such films is very important, since the films are useful as modulators for light beams, as couplers or modulators in microwave systems, and as the active memory elements in beam addressable memory systems such as magnetothermal recording with magneto-optical readout.

PRIOR ART

Pending application Ser. No. 766,698, filed Oct. 11, 1968, by Eric Kay and Erich Sawatzky, and assigned to the assignee of the present application, discloses a process for forming single crystal garnet films. According to that application, gadolinium iron garnet is deposited on a substrate of yttrium aluminum garnet in the [111] orientation.

SUMMARY OF THE INVENTION

The present application differs from the prior one in that a portion of the gadolinium must be replaced by either terbium or dysprosium. The substrate, besides being yttrium aluminum garnet, may also be rare earth aluminum garnet. Furthermore, the substrate orientation may also be [100] as well as [111]. The substrate orientations are indicated according to standard crystallographic practice. See, for example, the textbook, STRUCTURE OF METALS, by Barrett, McGraw Hill Book Company, Inc., Second Edition, 1952, pages 8–9. According to the present invention, the garnet substrate has either [100] or [111] orientation, and the formula $R_3A1_5O_{12}$ wherein R is yttrium or a rare earth. The film has the composition $Gd_{31.x}M_x Fe_5O_{12}$ wherein M is terbium or dysprosium and x is within the range of about from 0.1 to 0.6 when M is terbium and the orientation is [111], within the range of about from 1 to 2.7 when M is terbium and the orientation is [100], within the range of about 0.1 to 1.7 when M is dysprosium and the orientation is [111], and within the range of about 0.27 to 1.7 when M is dysprosium and the orientation is [100].

In carrying out the process of the present invention, the deposition of the film on the substrate can be accomplished by any of several methods. Useful methods include spinning from an aqueous system of the proper composition and subsequent conversion to a crystalline state, and also include reactively sputtering the appropriate composition wherein the composition to be deposited constitutes the cathode of the sputtering system. The technique of sputtering with two cathodes can also be used, as described in copending application Ser. No. 818,588, filed Apr. 23, 1969, by Eric Kay and Erich Sawatzky.

The techniques employed for the steps of the present invention are the same as those which have been previously described in the literature. The chemical method of spinning is preferred because of the ease in changing composition and because the resulting films have particularly good optical quality. According to this technique, a concentrated stock solution containing gadolinium and iron ions and also those of either terbium or dysprosium (preferably all as nitrates) is first diluted with, for example, ethyl alcohol. A few drops of the diluted solution are applied to the prepared substrate held horizontally on a photoresist spinner. The solution is distributed into a uniform film by spinning. After 15–20 seconds of spinning, the film is sufficiently dry to remain quiescent on the substrate surface. Further drying on a hot plate at 300°–500° C. decomposes the nitrates to oxides and converts the film to a glassy state which makes the film insoluble in a spinning solution. The spin dry process may then be repeated to achieve the desired final thickness. Single coat thicknesses are about 1,000 A. The dry product is an amorphous solid which has the desired composition according to the formula $Gd_{31.x}M_xFe_5O_{12}$ given above, and wherein the amount of gadolinium, iron, terbium, or dysprosium is in accordance with the relative amounts present in the original solutions. The crystalline garnet is obtained by heating in the presence of oxygen, for example, in the ambient atmosphere. A temperature of about 650° C. to 800° C. is suitable for crystallization.

We have discovered that films having useful properties may be obtained by careful selection of the proper amount of terbium or dysprosium substituted for some of the gadolinium. It is essential that the proper amount of substituent be used. The proper amount is different for terbium from that for dysprosium, and it also depends upon the orientation of the substrate. When terbium is used and the substrate has the [111] orientation, the value of x in the formula $Gd_{31.x}M_xFe_5O_{12}$ is between 0.1 and 0.6. When the upper limit is exceeded, the hysteresis loop is no longer square. On the other hand, when the amount of terbium is below this limit, coercivity may be too high. When the substrate orientation is [100] the value of x is between 1 and 2.7. When the content is below this limit, the hysteresis loop is no longer square. On the other hand, when it is above the limit, the compensation temperature is too low. When the substituent is dysprosium the value of x should be between 0.1 and 1.7 when the orientation of the substrate is [111]. When the dysprosium content is too low, it does not exert sufficient influence on the coercivity. When the dysprosium content is too high, the compensation temperature becomes too low. When the orientation is [100] the value of x should be between 0.27 and 1.7. When the dysprosium level is below this limit, the hysteresis loop is no longer square and when the dysprosium content is above this limit, the compensation temperature drops too low.

The present invention provides a method of obtaining thin ferrimagnetic films having square hysteresis loops, compensation temperatures in the most desirable range near ambient temperatures, and also coercivities which may be regulated within a wide range of useful values. These three physical properties are simultaneously determined according to the present invention by the proper selection of the amount of terbium or dysprosium.

PREFERRED EMBODIMENTS

The general nature of the invention having been set forth, the following examples are now presented as to the specific preparation of preferred embodiments of the invention. The specific details presented are for purposes of illustration and not limitation.

Example I

$Gd_{2.75}Tb_{0.25}Fe_5O_{12}$ on [111] oriented yttrium aluminum garnet yields a coercivity of 250 oe at compensation temperature plus 30° C., and an Mr/Ms=1.0.

Example II

$Gd_{2.50}Tb_{0.50}Fe_5O_{12}$ on [111] oriented yttrium aluminum garnet yields a coercivity of 190 oe at compensation temperature plus 30° C. and an Mr/Ms=1.0.

Example III

$Gd_{1.6}Tb_{1.4}Fe_5O_{12}$ on [100] oriented yttrium aluminum garnet yields a coercivity of 520 oe at compensation temperature plus 30° C. and an Mr/Ms $\geq$ 0.95.

Example IV

$Gd_2Dy_1Fe_5O_{12}$ on [111] oriented yttrium aluminum garnet yields a coercivity of 1,140 oe at compensation temperature plus 30° C. and an Mr/Ms=1.0.

Example V

$Gd_{2.54}Dy_{0.46}Fe_5O_{12}$ on [100] oriented yttrium aluminum garnet would yield a coercivity of 520 at compensation temperature plus 30° C. and an Mr/Ms $\geq$ 0.95.

Example VI

In a manner like that shown in the above examples, in place of yttrium aluminum garnet substrate, rare earth aluminum garnet substrate may be employed and similar results obtained.

All of the above films were prepared at a thickness of $1.0\mu\pm0.2$.

While the invention has been shown and described with reference to preferred embodiments thereof, it will be appreciated by those skilled in the art that variations in form may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for preparing a single crystal ferrimagnetic film having a square hysteresis loop, a regulated coercivity, and a compensation temperature above 250° K., said process comprising:

a. depositing on a garnet substrate having [111] or [100] orientation, and having the formula $R_3Al_5O_{12}$ wherein R is yttrium or a rare earth, a film having the composition $Gd_{3-x}M_xFe_5O_{12}$ wherein M is terbium or dysprosium and x is within the range from 0.1 to 0.6 when M is terbium and the orientation is [111], within the range of 1 to 2.7 when M is terbium and the orientation is [100], within the range 0.1 to 1.7 when M is dysprosium and the orientation is [111], and within the range 0.27 to 1.7 when M is dysprosium and the orientation is [100]; and

b. heating in an oxygen-containing atmosphere until crystallization occurs.

2. A process as claimed in claim 1 wherein the substrate is yttrium aluminum garnet having [111] orientation and the film has the formula $Gd_{3-x}Tb_xFe_5O_{12}$ wherein x is within the range from 0.1 to 0.6.

3. A process as claimed in claim 1 wherein the substrate is yttrium aluminum garnet having [100] orientation and the film has the formula $Gd_{3-x}Tb_xFe_5O_{12}$ wherein x is within the range from 1 to 2.7.

4. A process as claimed in claim 1 wherein the substrate is yttrium aluminum garnet having [111] orientation and the film has the formula $Gd_{3-x}Dy_xFe_5O_{12}$ wherein x is within the range from 0.1 to 1.7.

5. A process as claimed in claim 1 wherein the substrate is yttrium aluminum garnet having [100] orientation and the film has the formula $Gd_{3-x}Dy_xFe_5O_{12}$ wherein x is within the range from 0.27 to 1.7.