United States Patent [19]

Lee et al.

[11] **3,850,690**

[45] **Nov. 26, 1974**

[54] **METHOD OF MAKING MnGaGe FILMS**

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[22] Filed: **Feb. 23, 1973**

[21] Appl. No.: **335,405**

[52] **U.S. Cl.** ..... **117/240,** 75/134 G, 75/134 M, 75/134 T, 117/235, 204/192, 340/174 QA, 340/174 NA

[51] **Int. Cl.** **H01f 10/02**

[58] **Field of Search** ..... 204/192; 117/235–240; 75/134 G, 134 M, 134 T; 340/174 QA, 174 NA

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[57] **ABSTRACT**

A method of making ferromagnetic films of MnGaGe upon a substrate, the films crystallizing in the tetragonal structure and having a grain size of less than one-half micron, made by the method of depositing a first layer of either manganese, or gallium and germanium upon a heated substrate, followed by the deposition of the remaining material upon the first layer, and annealing the deposited layers at a desired temperature until a homogeneous composition is achieved, and then cooling of the film-substrate combination. In this manner, with appropriately chosen temperatures, films having a grain size of less than one-half micron and being particularly usable for storage applications may be fabricated.

8 Claims, No Drawings

METHOD OF MAKING MnGaGe FILMS

FIELD OF THE INVENTION

This invention relates to methods of making ferromagnetic films in general and ferromagnetic films in particular characterized by having a fine grain structure.

PRIOR ART

The new ferromagnetic material MnGaGe crystallizing in the tetragonal structure has been disclosed in the copending patent application of Street and Sawatzky entitled "Ferromagnetic Material," filed Sept. 15, 1972, as application Ser. No. 289,512, which is a continuation-in-part of application Ser. No. 202,642, filed Nov. 26, 1971, now abandoned and assigned to the Assignee of this invention. Various compositions of the MnGaGe material are disclosed as well as the physical properties and particularly the magnetic properties of the material. This material finds particular application in magneto-optic data storage applications due to its low Curie point and high Faraday rotation. The application of Street and Sawatzky above, is incorporated into this application for its teachings of the particular material.

It is desirable for magneto-optic applications where readout of stored data is by the Kerr or Faraday effects, that the material has a high signal-to-noise ratio. This is most often achieved with a material having a very fine grain size. In the case of MnGaGe, a grain size of less than one-half micron is desirable to achieve signal-to-noise ratios for particular storage applications. Thus, it is an object of this invention to describe a method for providing a fine grain ferromagnetic film of MnGaGe crystallizing in the tetragonal structure.

Another object of this invention is to provide a range of working temperatures whereby this film may be deposited upon a substrate.

Another object of this invention is to provide alternative methods of depositing the film by vapor deposition and by sputtering techniques.

SUMMARY OF THE INVENTION

These and other objects are met by the method of this invention. Briefly stated, the method comprises depositing a first layer of either manganese, or gallium and germanium, in the desired compositional amount as desired in the finished film, upon a substrate maintained at a temperature of between 150° and 250°C in an evacuated environment, and then depositing a second layer chosen from the other of the manganese or gallium and germanium upon the first layer. The combination is then annealed at a temperature between 200°C to 475°C until a homogeneous composition is obtained, and the film-substrate combination is then cooled. This results in a fine grain manganese-gallium-germanium structure. Additional successive layers may also be deposited, and temperatures may be chosen as to achieve a simultaneous annealing-deposition situation.

The invention will thus be understood in relation to the following general description and claims.

GENERAL DESCRIPTION

Manganese gallium germanium as described in the aforementioned Street and Sawatzky application, crystallizes in the tetragonal structure and has a potential

range of Curie points as a function of the exact composition utilized. This film has proved valuable for magneto-optic storage applications. In attempting to achieve fine grain films which are most desirable in this type of application for high-density storage, we have found that films having a grain size of less than one-half micron may be obtained using the particular method described below. No other method has been found that consistently will produce grains of less than one-half micron in size. Before describing the method of our invention, it should be stated that the common technique of evaporating manganese, gallium and germanium, either simultaneously or each individually, and then annealing the film to achieve homogeneity, results in a grain size in excess of one-half micron, and is most typically approximately one micron or larger. These films also crystallize in the tetragonal structure and have their magnetization substantially perpendicular to the film plain. The tetragonal structure may be verified by the use of X-ray analysis, for example.

We have found that if a particular deposition method is carried out, we consistently prepare manganese-gallium-germanium films having a grain size of less than one-half micron. In this method, films are deposited upon a substrate either by sputtering or by vapor deposition. Where vapor deposition is utilized, it is preferred to have an atmosphere between 10^{-5} to 10^{-7} torr during deposition, although higher vacuums are acceptable. The substrate described may be rigid or flexible, magnetic or non-magnetic. Typically, a glass substrate, sapphire substrate, or molybdenum substrate may be utilized. It is important, of course, that the substrate not react with the film being deposited. In both the sputtering or vapor deposition systems, the substrate is maintained at a temperature of between 150°C to 350°C, as desired and as discussed below.

First, a layer of manganese, for example, may be deposited upon the substrate at a rate of at least 1 A per second, with a preferred rate of 2 A per second. An amount of manganese is deposited so that the film composition after annealing will contain the desired amount of manganese. Then, a combined film of gallium and germanium is deposited by the simultaneous evaporation from two separate sources of gallium and germanium, respectively. Separate crucibles are used as these materials have very different vapor pressures. Further, as different amounts of each is desired, while a minimum 1 A per second rate is also desired, and 2 A per second deposition rate is preferred, the surface areas or temperatures will have to be varied to achieve the simultaneous deposition of gallium and germanium in the desired amounts as desired in the final film in combination with the already deposited manganese. These amounts are easily calculated by those skilled in the art as a function of the desired final composition in conjunction with the known vapor pressures of the material. The composition may be measured by microprobe analysis.

After deposition of the film, the films are annealed while still in vacuum at between 200° and 475°C until a homogeneous composition is achieved, at which time the films are cooled. Measurement of the film grain size by optical or electron microscopic method shows films made in this manner have a grain size of less than one-half micron.

When the temperature of the substrate is between 200° and 250°, depending upon the particular composi-

tion desired, the annealing step occurs simultaneously with the evaporation of the second layer upon the first layer. Where an initial substrate temperature of less than substantially 200°C is utilized, a subsequent annealing step is desirable. The following table shows various compositions made by vapor deposition and by sputtering techniques, for various compositions of manganese, gallium and germanium showing also substrate temperature, the annealing temperature, the annealing time, the remanence, and the polar Faraday rotation, in degrees.

Vapor	(Atomic % . . .) Mn	Ga	Ge	Sub Temp°C	Anneal Temp°C	Anneal Time, hr.	Rem. %	PFR deg.
	.49	.23	.28	210	—	—	100	.20
	.50	.25	.25	150	210	1	70	.18
	.46	.29	.25	210	450	1 ½	50	.72
	.47	.22	.31	200	—	—	60	.57
	.46	.28	.26	210	475	1 ½	60	.34
	.47	.25	.28	200	—	—	70	.42
	.46	.29	.25	150	430	1 ½	60	.70
Sputt.	.45	.23	.32	200	425	1	30	.7

Each of the films in the table has its wavelength sensitivity and other magnetic properties such as the Curie temperature as described in the aforementioned Street and Sawatzky application, as a function of the particular composition. The structures are all tetragonal as noted by X-ray analysis, and the magnetization is sufficiently perpendicular to the film plane to yield the remanences listed above. As compared to the simultaneous evaporation technique of evaporating all three at once, mentioned previously, the signal-to-noise ratio may be improved to a factor of ten to one in comparison with a previous three to one signal-to-noise ratio. Further, the films made by the layered technique described above typically have 100 EMU/cc magnetization as a function of composition. Further, preferred films are in the 500 to 700 A thickness range.

While the invention has been particularly described where manganese is deposited first, followed by simultaneous deposition of gallium plus germanium, the layers may be deposited in the opposite manner. Thus, gallium and germanium may be simultaneously deposited, followed by deposition of manganese, followed by the annealing step. Further, alternative layers of the material may be deposited with the same result being achieved. Thus, alternating layers of manganese, gallium plus germanium, manganese, gallium plus germanium, etc., may be employed. As before, irrespective of which is the first layer, a substrate temperature may be chosen in relation to a particular composition so that the annealing step occurs simultaneously with the deposition of the second layer. The particular composition for which this is achievable and the particular temperatures are easily arrived at by analysis of the deposited film by techniques will known in the art, such as X-ray analysis.

In the above table is also shown a sputtering technique which illustrates again that the multilayer deposition may be utilized in sputtered films to produce a film having a grain size of less than one-half micron. Over 100 films have been made by the method of this invention, showing the small grain size to be reproducible over a variety of compositions by the technique of this invention. The preferred embodiments are shown in the above table.

While this invention has been shown in its preferred embodiments, variations therefrom will still remain within the scope and spirit of this invention and will be evident to those skilled in the art. Thus, a variety of substrates may be utilized, as well as the variety of deposition rates, and temperatures, within the teachings of this invention.

What is claimed is:

1. A method of making a fine grain ferromagnetic film of MnGaGe crystallizing in the tetragonal structure upon a substrate comprising the steps of:
   depositing a layer of Mn and a layer of (Ga + Ge) in the desired compositional amount based on the final desired composition in any desired order upon a substrate maintained at a temperature between substantially 150°C to 250°C as a first layer and a second layer upon said first layer;
   annealing the superimposed deposited layers at a temperature between substantially 200°C and 475°C until a homogeneous composition is achieved; and
   cooling the film-substrate combination, whereby a ferromagnetic film of MnGaGe crystallizing in the tetragonal structure and having a grain size of less than 0.5 micron is formed upon the substrate.

2. The method of claim 1 wherein the substrate temperature and MnGaGe compositional amounts are so chosen that the annealing step occurs simultaneously with the deposition of the second layer.

3. The method of claim 2 wherein the substrate temperature is chosen to be at least substantially 300°C.

4. The method of claim 1 including depositing additional sets of layers of Mn and (Ga and Ge) as desired while maintaining the desired compositional amount, prior to the annealing step.

5. The method of claim 1 wherein the layers are deposited by the method of vapor deposition.

6. The method of claim 1 wherein the Mn, Ga and Ge are each deposited from a separate source.

7. The method of claim 1 wherein the substrate is non-magnetic.

8. The method of claim 1 wherein the deposition rate of each layer is at least 1A/second.

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