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REPLY TO ATTN OF: GP

TO: NST-44
~~XXX~~/Scientific & Technical Information Division
Attn: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General
Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,837,908

Government or Corporate Employee : Caltech / JPL Pasadena, CA

Supplementary Corporate Source (if applicable) :

NASA Patent Case No. : NPO-11,336-1 w/ 13,247-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

YES [X] NO [ ]

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "...with respect to an invention of ..."

Bonnie L. Henderson

Bonnie L. Henderson

Enclosure

NPO-11,336-1 w/ 13,247-1

United States Patent [19]

Lewicki et al.

[11] **3,837,908**

[45] **Sept. 24, 1974**

[54] **MANGANESE BISMUTH FILMS WITH NARROW TRANSFER CHARACTERISTICS FOR CURIE-POINT SWITCHING**

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[73] Assignee: **California Institute of Technology**, Pasadena, Calif.

[22] Filed: **Nov. 1, 1972**

[21] Appl. No.: **302,913**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 57,439, July 23, 1970, abandoned.

[52] **U.S. Cl.** ..... **117/239**, 75/134 D, 117/107, 117/119, 117/234, 117/235, 117/237, 117/240, 148/6, 148/121

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

[58] **Field of Search** ..... 117/239, 240, 236, 237, 117/238, 107, 119; 148/6, 121; 75/134 D

[56] **References Cited**

UNITED STATES PATENTS

2,865,085 12/1958 Cornish ..... 75/134 X

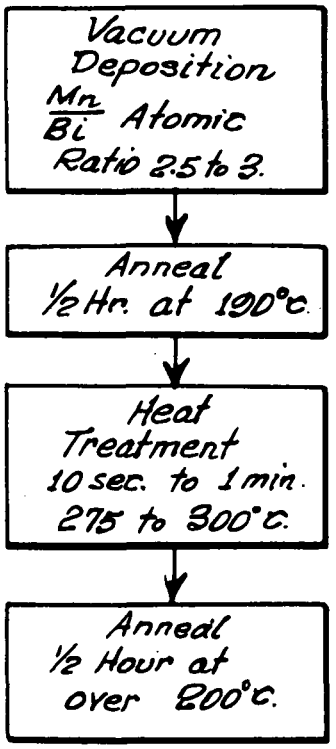
3,539,383 11/1970 Di Chen et al. ..... 117/240 X

Primary Examiner—William D. Martin
Assistant Examiner—Bernard D. Pianalto

[57] **ABSTRACT**

Manganese bismuth films having improved characteristics for recording information by Curie-point switching, and especially for Curie-point recording of information in analogue form, can be produced by a vacuum deposition of Bi and Mn with an atomic ratio of Mn to Bi between 2 and 3.5 or 1.4 and 1.6, followed by a specialized heat treatment which includes very brief exposure to a temperature between about 275° and 300°C. Similar MnBi films can be produced more reliably and reproducibly if the initial Bi layer is annealed prior to deposition of the Mn layer. Such an annealing step renders most other factors of the processing relatively non-critical. Deposition of both initial layers is preferably carried out in a vacuum approaching 10^{-8} Torr, but at least traces of oxygen are then made available to the reaction site prior to the subsequent reaction of the Mn and Bi layers to form ferromagnetic MnBi.

8 Claims, 7 Drawing Figures



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SHEET 1 OF 2

FIG. 1.

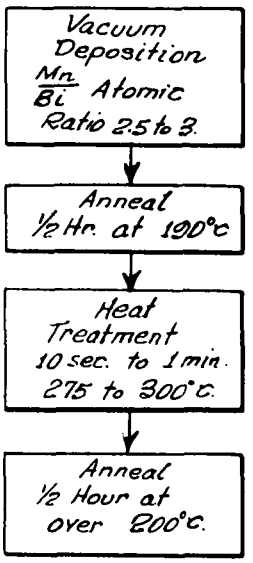


FIG. 2.

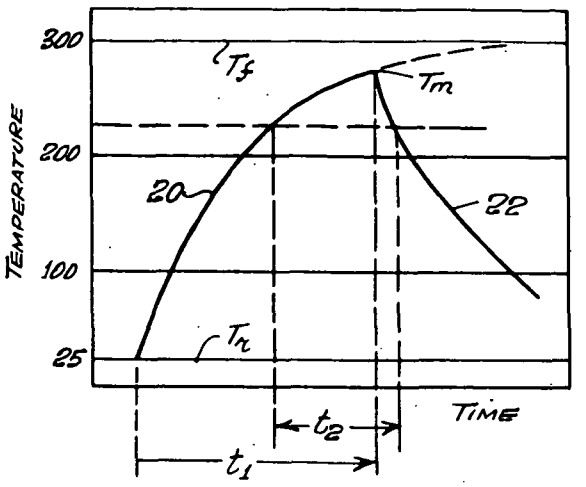


FIG. 3.

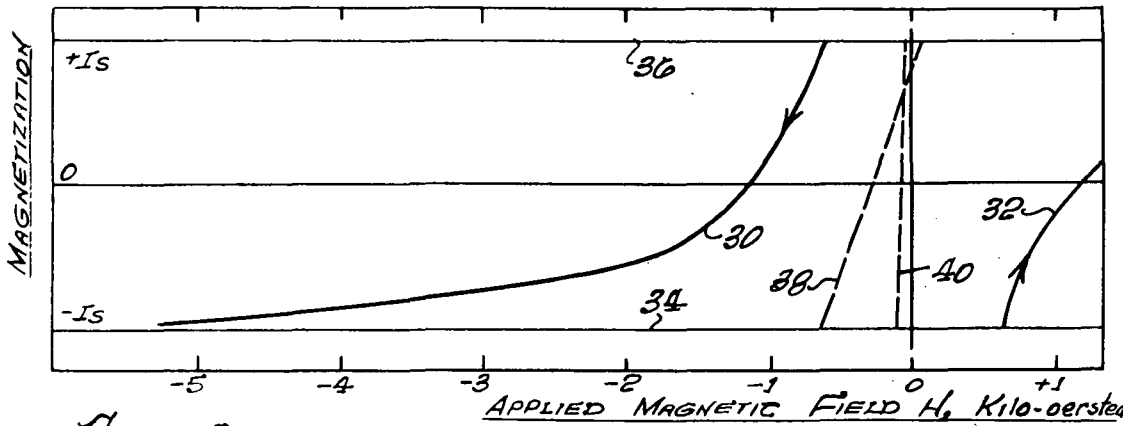
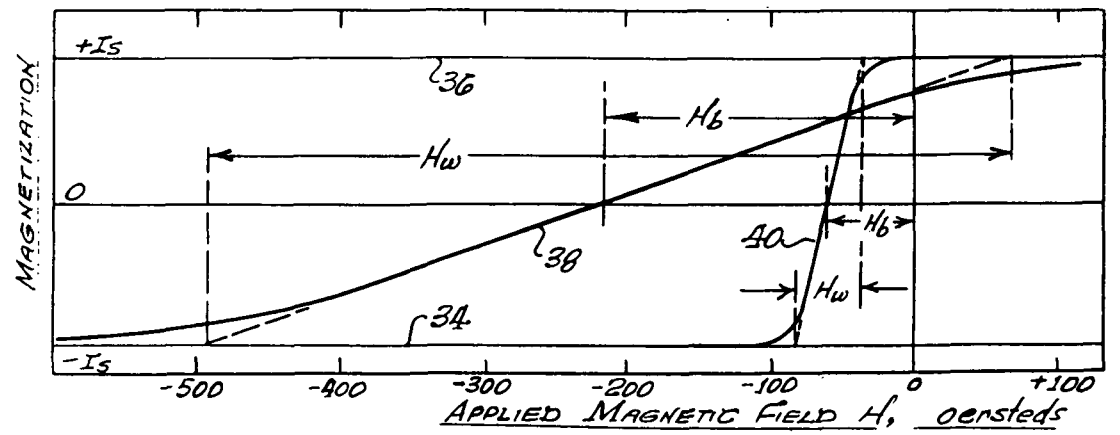


FIG. 4.



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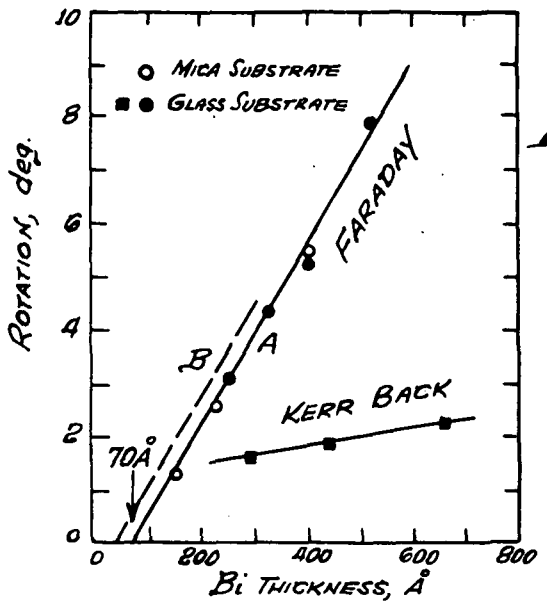

FIG. 5.

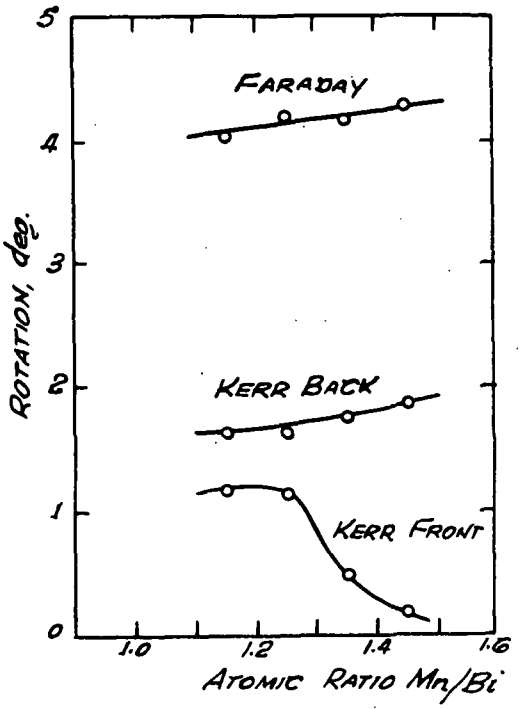

FIG. 6.

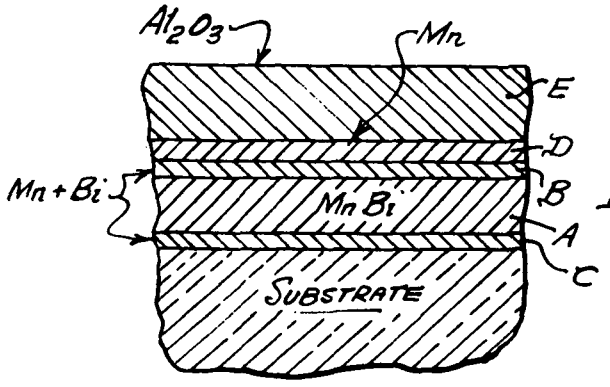

FIG. 7.

MANGANESE BISMUTH FILMS WITH NARROW TRANSFER CHARACTERISTICS FOR CURIE-POINT SWITCHING

RELATED APPLICATIONS

This application is a continuation-in-part of our copending application Ser. No. 57,439, filed on July 23, 1970 and now abandoned.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

This invention has to do with magnetizable thin films for recording information by Curie-point switching of the film magnetization.

The invention relates more particularly to methods for producing thin films of manganese bismuth alloy having improved characteristics for such data recording. The films of the invention are especially, but not exclusively, suitable for recording information in analogue rather than digital form.

It was suggested in 1957 that suitably prepared films of MnBi could receive information written by a strongly magnetized probe, and that such information could be rendered visible by the Kerr magneto-optical effect (H. L. Williams, et al., J. Applied Physics 28, 1181 (1957)).

That direct magnetic writing was soon supplanted by the so-called "Curiepoint" writing, whereby a small area of a magnetized MnBi film is rendered nonmagnetic by heating above the Curie temperature, using a sharply focussed beam of electrons or other intense radiation. As the area cools, it is subject to the field produced by the initial magnetization of the surrounding film areas. That imposed field is opposite to the initial magnetization, and is typically strong enough to magnetize the treated spot substantially to saturation. Readout may utilize the Kerr effect for reflected light or the Faraday effect for light transmitted through the film. See, for example, Ludwig Mayer, J. Appl. Phys. 29, 1454 (1958) and 31, 384 (1960) and U.S. Pat. No. 3,176,278; McGlauchlin and Ready U.S. Pat. No. 3,368,209; and Chen, et al., J. Appl. Phys. 39, 3916 (1968).

The present applicants discovered that thermal-magnetic recording is capable of recording analogue as well as digital information. For that purpose an external magnetic field is applied during cooling of a record area that has been heated above the Curie temperature, and that applied field is varied in accordance with the analogue signal to be recorded. That procedure is more fully described and is claimed in the copending patent application, Ser. No. 805,549, filed Mar. 10, 1969 by the present applicants, which issued on Dec. 7, 1971 as U.S. Pat. No. 3,626,114. Although such recording of analogue signals differs markedly from the digital action referred to by previous workers as "Curie-point switching," it will be convenient to apply that term to both types of recording.

A general purpose of the present invention is to provide films having a particularly favorable combination of properties for recording information by Curie-point switching, especially for recording information in analogue form. A more particular object of the invention is to provide films of manganese bismuth alloy capable of changing their magnetization progressively, when subjected to Curie-point switching, in essentially proportional response to relatively small variations of an impressed magnetic field.

Stated another way, the invention aims to produce a film of definite thickness combining satisfactory optical transmission, relatively high Faraday rotation of the plane of polarized light, and the steepest possible characteristic curve of film magnetization as a function of the magnetic field applied during Curie-point switching. The steeper that curve the lower the power that must be expended in producing the control field.

Further, the films of the invention are more uniform, and are believed to be more stable against heat and to have a higher ratio of Faraday rotation to optical absorption than films prepared in accordance with previous practice. The present films may also have a lower Curie temperature than previously reported manganese bismuth films.

SUMMARY OF THE INVENTION

Those and other objects and advantages of the invention have been attained by depositing films having an atomic ratio of manganese to bismuth in the range between about 2.5 and about 3, and by developing a conditioning process by which such films of intermediate composition can be given suitable magnetic characteristics.

In accordance with one aspect of the present invention, we have found that manganese bismuth films of such intermediate composition can be successfully prepared by suitable modification of the usual heat treatment, and that the resulting films are markedly superior to those containing a ratio of manganese to bismuth either approximating the stoichiometric ratio of MnBi or approximating four or more.

In the preparation of films of intermediate composition in accordance with that aspect of the invention, the initially superposed layers of manganese and bismuth are first annealed in vacuum, essentially as in the prior art, but preferably at a temperature of about 190°C. After annealing, the film is raised quickly, typically within a few seconds, to a selected transition temperature in the range from about 275° to about 300°C. The film is not held at that temperature, as in the prior art, but is returned quickly to a temperature which is at least 50° to 100° lower and may be room temperature. For a given film composition the total time at elevated temperature varies with the temperature selected; and both the preferred temperature and the time of treatment are found to increase somewhat with the ratio of manganese to bismuth in the film.

In accordance with a further aspect of the invention, we have found that MnBi films having conventional characteristics for Curie-point switching can also be produced over a wide range of atomic ratio of Mn to Bi in the initial dual layer, and without specialized heat treatment, provided the deposited Bi layer is annealed in vacuum prior to deposition of the Mn.

We have discovered also that the preparation of MnBi films can be made still more reliable and reproducible if the deposition is carried out under conditions of very high vacuum, such that oxygen is excluded

more rigorously than has been the practice in the prior art. More particularly, we prefer to employ a vacuum system all parts of which can be thoroughly baked, and to reduce the pressure in the system at least to 1 or 2 $\times 10^{-8}$ Torr prior to deposition of the films.

On the other hand, we have found that traces of oxygen should be present during the heat treatment by which the layers of Bi and Mn are reacted to form ferromagnetic MnBi, or during a subsequent heat treatment, to give superior characteristics for Curie-point switching. Moreover, that oxygen should be available to the portions of the dual layer which take part in the reaction. For example, if the initial Mn layer is so thick as to provide a great excess of Mn over the stoichiometric ratio, availability of oxygen only to the surface of that layer may not suffice to produce the most effective films.

In the prior art it has been common practice to apply a layer of SiO_2 as a protective coating on the surface of a MnBi film after it has been fully processed. We have found that far more effective protection is obtainable by coating the film with a layer of sapphire (Al_2O_3). Such a layer can form a completely tight seal against atmospheric oxygen, and is useful not only for preserving a completed film but for locking into a film a metered quantity of oxygen as a means of controlling the later heat treatment of the film.

A full understanding of the invention, and of its further objects and advantages, will be had from the following description of certain illustrative manners of carrying it out. The particulars of that description, and of the accompanying drawings which form a part of it, are intended only as illustration and not as a limitation upon the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow sheet representing an illustrative embodiment of the invention;

FIG. 2 is a schematic graph representing the general nature of the time course of the temperature during a typical heat treatment step in accordance with the invention;

FIG. 3 is a schematic graph representing magnetization of a typical prior art film in response to Curie-point switching with applied magnetic fields;

FIG. 4 is a schematic graph corresponding to FIG. 3, but for a typical film in accordance with the present invention;

FIG. 5 is a graph showing Faraday and Kerr rotations as functions of initial Bi thickness;

FIG. 6 is a graph showing Faraday and Kerr rotations as functions of initial atomic ratio of Mn to Bi; and

FIG. 7 is a schematic section illustrating typical film structure.

DESCRIPTION OF PREFERRED EMBODIMENTS

Special Heat Treatment

As schematically shown in FIG. 1, one aspect of the invention typically includes deposition in vacuum of a manganese bismuth film with atomic ratio of manganese to bismuth in the range between about 2.5 and about 3.0, a mild heat treatment of the film generally similar to the annealing step of the prior art, a heat treatment at more elevated temperature for a time period that is strictly limited to a period typically between 10 seconds and 1 minute, the duration and the maximum temperature depending upon each other and upon the film composition, and a further heat treatment at moderate temperature and for a time typical of conventional annealing operations.

The vacuum deposition of the film is typically carried out in conventional manner except for the distinctive ratio of the two ingredients, and the fact that the bismuth is preferably deposited as a first layer over which the manganese is applied. The desired atomic ratio of those ingredients is typically obtained by monitoring the thickness of each of the layers independently as it is deposited. Such monitoring may include optical absorption measurements made on the layer itself, or on a reference layer which may be arranged to have a thickness different from the actual layer by some predetermined factor. Such optical monitoring can be calibrated for a particular substance, as by weighing resulting films or by directly measuring their thickness by interferometry. Such prodedures are well known in and of themselves and do not require detailed description. The most desirable atomic ratio value of the manganese bismuth films for carrying out this aspect of the invention is believed to be approximately 2.75.

The initial annealing step is preferably carried out in vacuum at a temperature not exceeding about 200°C and preferably equal to about 190°C for a period that is not critical, being typically about one-half hour.

The characteristic heat treatment of the present invention is carried out in vacuum. A convenient method of obtaining the very rapid temperature rise that is required in this step is to utilize as a furnace two parallel plates mutually spaced by only a few millimeters. Those plates are preheated electrically to a definite temperature, typically from about 300° to about 350°C, which can be measured by a suitable thermocouple. After the furnace has attained uniform temperature the film to be treated is quickly inserted between the furnace plates, as by movement of a carrier consisting of a grid of fine wires. The film and its substrate are then heated primarily by radiant energy from the furnace plates. The film temperature thus increases asumptotically toward the furnace temperature T_f, as indicated schematically by the curve 20 in FIG. 2. The time constant of that temperature rise depends primarily upon the thickness of the substrate carrying the film. It is preferred to employ for that purpose freshly cleaved mica, especially since mica sheets can be made extremely thin and satisfactorily uniform. A substrate thickness of approximately 0.0005 inch is generally satisfactory and will be assumed in the following description. For other thicknesses of substrate the time and temperature conditions during the heat treatment are suitably adjusted.

After the film has remained between the oven plates for the desired time period t_1, it is removed to a cooler environment, which may be substantially room temperature, as represented in FIG. 2, or may be some higher temperature well below 200°C. The film then cools asymptotically toward that environmental temperature T_r as indicated by the curve 22. With heating techniques of that general type, the film reaches a maximum temperature T_m but is not maintained at that temperature for any appreciable time. The actual effective duration of the heat treatment depends upon the temperature range within which the change of condition of the film is assumed to occur. For example, for the schematic curves shown in FIG. 2, the treatment duration for a minimum effective temperature of 225°C is indicated as t_2. Although it may be difficult to define either

t_2 or T_m precisely, their approximate value is clear, and the essential nature of the treatment can be well portrayed by a definition of the furnace temperature T_f and the exposure time t_1. That time, like t_2, is typically of the order of 10 to 20 seconds, and is thus radically different from anything contemplated in the prior art.

SUPERIOR TRANSFER CHARACTERISTIC

The post-annealing temperature is typically at least 200°C, and is less by at least about 50° than the maximum temperature reached by the film during the primary heat treatment. A post-annealing time of about one-half hour is usually sufficient.

Films made in accordance with the above described aspect of the present invention are believed to differ from those of the prior art in numerous respects, of which perhaps the most important is the form of the transfer characteristic, as shown typically in FIGS. 3 and 4. As a reference standard, FIG. 3 shows somewhat schematically at 30 and 32 the negative and positive branches of a conventional hysteresis curve for an illustrative manganese bismuth film. For present purposes the same curve can serve both for films of the prior art and for those of the present invention. The applied field is plotted as abscissa and is given in FIG. 3 in kilo-oersteds. Plotted as ordinate is the resulting film magnetization when the applied field is varied progressively in the directions shown on each curve branch by the arrowheads. The saturation magnetization in the negative and positive directions normal to the plane of the film is shown in arbitrary units as $-I_s$ at the line 34 and as $+I_s$ at the line 36. When the film is saturated in the positive direction, for example, the negative magnetic field at which the magnetization abruptly starts to decline along line 30 is generally referred to as the critical field. The magnetic field required to bring the film to zero magnetization is the coercive force. Those two quantities are known to vary over a wide range with the detailed nature of the film and particularly with its thickness, the absolute values tending to decrease as the film thickness increases (DiChen, Flux Reversal in Single-Crystal MnBi Films, Journal of Applied Physics, Vol. 37, pages 1486–1488). The applied field needed to produce film saturation at room temperature is about 5 kilo-oersteds, as shown for curve 30, the corresponding region of curve 32 being beyond the range shown in FIG. 3. Thus a field of plus or minus 5 kilo-oersteds will erase all information that has been recorded on a film.

The curves 38 and 40, shown schematically as straight lines in FIG. 3, represent illustrative plots of the Curie-point transfer characteristic for conventional films and for the films of the present invention, respectively. For purposes of description, the Curie-point transfer characteristic is defined as the final average value of the magnetization that results when a small area of a film that has been uniformly magnetized to saturation in one direction is heated above the Curie temperature and is allowed to cool in a definite applied external magnetic field. The actual effective field at the spot is the sum of the applied field and the field produced at the spot by the initial magnetization of the surrounding film area. The present data are based on heating a round spot with a focussed beam of laser radiation; and determining the final average magnetization of the spot by measurement of the Faraday rotation of the plane of polarization of a plane polarized radiation beam that is optically identical but has been attenuated by a suitable filter. The Curie-point transfer characteristic is plotted as a function of the applied external magnetic field. Curves 38 and 40 are replotted in FIG. 4 with the scale of abscissae expanded by a factor of 10 for clarity of illustration. The curves were plotted from experimental points derived from direct measurements of the Faraday rotation after correction for the fact that the diameter of the area actually raised above the Curie temperature by the light beam is somewhat smaller than the illuminated area, whereas the entire area of the (attenuated) beam is involved in the measurement of the Faraday rotation.

Curve 38 was made with a film prepared with a manganese to bismuth atomic ratio of about unity and with essentially the heat treatment procedure specified by Williams in the above identified paper. That film had a thickness of about 500 Angstroms, an optical transmission of about 5 percent for helium-neon laser radiation at a wavelength of 6,328 Angstroms and a Faraday rotation of about 3.5° for the same wavelength when magentized to saturation. Curve 38 is also typical of films prepared with an atomic ratio of four or more and with conventional heat treatment.

Curve 40 was made with a film prepared with a manganese to bismuth atomic ratio of approximately 2.75. The superposed layers were consolidated by annealing at 190°C for half an hour, and the film was then inserted in a furnace heated to 300°C for only 15 sec. The resulting film was then treated at 200°C for half an hour. The film had a thickness of about 500 Angstroms, a measured optical transmission of 16 percent and a Faraday rotation of 4° under the same conditions mentioned above. The diameters of the spots actually subject to Curie-point switching were about 2.3μ for curve 38 and about 1.25μ for curve 40. We have found in general that the curve of the Curie-point transfer characteristic tends to be somewhat steeper with decreasing spot size and correspondingly increased temperature gradients during the heating step. However, that effect could contribute only slightly to the remarkable difference of slope between the two curves 38 and 40.

The characteristic curves 38 and 40 are well described by two parameters. H_w is the width of the characteristic and represents the range of the applied magnetic field that is required to produce Curie-point switching over the whole range of final magnetization from substantially $-I_s$ to $+I_s$. H_b is the applied field required to produce zero average magnetization within the switched area, and is a measure of the asymmetry of the characteristic with respect to zero applied field. Both parameters are typically expressed in oersteds. That asymmetry is undoubtedly associated with the demagnetizing field that is produced at the switched spot by the initial magnetization of the surrounding film. The asymmetry is of little practical importance, since it requires only a constant biasing magnetic field. The characteristic width H_w, on the other hand, is of fundamental practical importance as a measure of the power that must be supplied to a variable control field to record analogue signals with utilization of the entire available range of the medium.

As shown in FIGS. 3 and 4, the characteristic width H_w for manganese bismuth films made in accordance with the prior art is more than 500 oersteds. The corresponding width for films made in accordance with the

present invention is well below 100 oersteds and is typically less than 50 oersteds. That means a reduction of power requirements of substantially an order of magnitude.

ANNEALING BISMUTH LAYER

We have discovered, further, that many of the difficulties and apparent inconsistencies reported in the previous literature can be avoided, and MnBi films having uniform properties can be economically and reliably produced, by annealing the initial Bi film prior to deposition of the Mn. That annealing step is carried out in vacuum, preferably with vacuum conditions maintained continuously throughout the initial deposition of Bi, the annealing step and the subsequent deposition of Mn.

The Bi layer can be successfully annealed at temperatures above about 120°C and below a limiting maximum temperature at which pinholes may occur in the Bi film. That upper limit varies inversely with the thickness of the Bi film, being typically about 190°C for films 150 A thick and about 140°C for films 600 A thick, for example. For Bi films of the preferred thickness from 200 to 300 A and for temperatures in the range from 160° to 170°C, an annealing time of about 5 minutes is usually satisfactory.

After such an annealing step and the subsequent deposition of Mn, the reaction of the Bi and Mn layers to form ferromagnetic MnBi alloy occurs rapidly and reliably at temperatures from about 180° to about 250°C, typically requiring only 5 or 10 minutes. Further annealing at the latter temperature has substantially no effect on the films, and temperatures as high as 360°C produce only small changes in the films. The described annealing of the initial Bi layer thus transforms the subsequent Bi—Mn reaction from the relatively uncertain and critical operation of the prior art into a basically normal and quantitatively reproducible chemical reaction.

Moreover, that reaction is essentially independent of the substrate used, of the relative concentrations of Mn and Bi in the initial double layer, and of the overall thickness of the layers. Reaction of the dual layer is also found to be essentially independent of the rates of deposition of the individual layers, at least within the typical ranges of 2 to 10 A per sec for Bi and 0.3 to 2 A per sec for Mn. In particular, films deposited on glass behave in essentially the same way as films deposited on mica, suggesting that the step of annealing the Bi layer may enhance the uniformity and orientation of its crystal structure.

Over a wide range of atomic ratios of Mn to Bi in the initial dual layer, at least from about 0.9 to 3, the production of ferromagnetic MnBi alloy typically goes substantially to completion in a few minutes at temperatures of the order of 250°C when the Bi layer has been annealed as described above. However, uniform ferromagnetic properties throughout the area of the film are obtained only if the initial Mn layer is thick enough to provide at least a moderate excess of Mn over the stoichiometric atomic ratio for MnBi. That excess corresponds roughly to an additional Mn thickness of 50 to 100 A. In presence of less than that critical Mn excess the ferromagnetic MnBi reaction product occupies only random portions of the film area, the remainder apparently comprising mainly bismuth. As the Mn excess is increased above the defined critical value, optically uniform films are obtained.

FILM STRUCTURE

The structure of films produced as just described was studied by measuring the Faraday and Kerr magneto-optical rotations of the plane of polarized light, using radiation at 6,328 A from a helium neon laser. The Kerr rotations were measured for reflection both from the back surface of the film adjacent the substrate and from the front surface. FIG. 5 shows in curves A and B the Faraday rotation as a function of the initial bismuth thickness for various reacted double layers, the thickness of the manganese layer being always sufficient to provide an excess of Mn as compared to the stoichiometric atomic ratio for MnBi. The points shown for the curve A are for films that were reacted a few minutes at about 250°C and then further treated for some time at about 380°C. The agreement between the open circles for mica substrate and the solid circles for glass substrate is striking. Data obtained for films reacted only at 250°C gave a similar curve, but shifted uniformly to lower Bi concentrations, as indicated by curve B.

Curves A and B are consistent with the natural assumption that the thickness of the magneto-optically active layer of MnBi formed in presence of excess Mn is a linear function of the Bi available. However, the fact that extrapolation to zero Faraday rotation gives a finite value of Bi is unexpected. That fact indicates that a small but appreciable portion of the initial Bi layer combines with Mn to form a compound of unknown composition other than ferromagnetic MnBi. The possiblity that such Bi remains uncombined is believed excluded by the fact that the reacted films can be taken to temperatures as high as 380°C without forming pinholes. Prolonged treatment at the latter temperature does, however, appear to increase the thickness of the magneto-optically inactive layer at the expense of the active MnBi layer. Thus, a specific advantage of annealing the Bi layer before deposition of the Mn is the fact that reaction of the layers can then be carried out relatively rapidly and at temperatures not exceeding about 250°C. The specific Faraday rotation, or the rotation per unit thickness of the material, can be calculated from the slope of the curves in FIG. 5, which gives the rotation per increment of thickness of the Bi layer. Assuming that all of the bismuth in excess of 70 A goes into magneto-optically active MnBi, and that the density of the latter is the average of the densities of the initial Mn and Bi layers, we obtain a value of 120° per μm for the specific Faraday rotation. Combining that value with the measured absorption coefficient α for films made with atomic ratio of Mn to Bi equal to 1.2, we obtain a value of 4.7° for the so-called figure of merit, $2F/\alpha$. FIG. 5 also shows the Kerr rotation of the plane of polarization for light reflected from the back surface of reacted double layers, plotted as a function of the initial Bi thickness. That Kerr back rotation is not invariant, but increases slightly with increasing initial Bi thickness, indicating that there is a light absorbing layer between the substrate and the optically active layer of MnBi which decreases in thickness with increasing initial Bi thickness. Such a layer would reduce the observed Kerr rotation both by reflecting non-rotated light and by absorbing part of the rotated light.

FIG. 6 shows measurements of the front and back Kerr rotations and the Faraday rotation for reacted double layers which have the same initial Bi thickness of 290 A but different atomic ratios of Mn to Bi. Generally similar results are obtained with larger values of the initial Bi thickness. The Faraday rotation and the Kerr back rotation are seen to vary only slightly with relative concentration of Mn. The Kerr front rotation, however, decreases abruptly with increasing Mn concentration, indicating that the increasing excess of Mn in the initial double layer remains after reaction as a continuous layer of Mn on top of the MnBi layer. The fact that the front Kerr rotation is smaller than the back Kerr rotation for the smallest excess of Mn shown, at which presumably no free Mn remains on the surface, suggests that part of the Mn is regularly consumed in forming on top of the active MnBi layer a layer of light absorbing reaction product of Mn and Bi that is magneto-optically inactive. Such a layer is believed to lie between the ferromagnetic MnBi layer and the unreacted Mn.

FIG. 7 illustrates schematically the film structure just described, with addition of a sapphire sealing layer E, described below. The main layer A of magneto-optically active MnBi is sandwiched between the front and back layers B and C of light-absorbing but magneto-optically inactive material containing both Mn and Bi. Layers B and C are believed to contain more Mn than Bi on an atomic basis and to be typically of the order of 50 to 100 A thick. If more Mn is present than the above defined critical excess over Bi, which is consumed in layers B and C, the surplus Mn appears in uncombined form in the outermost layer D. That layer increases in thickness with the value of that surplus.

The data in FIGS. 5 and 6 were obtained for reacted Bi and Mn layers that had been originally deposited under conditions of substantially zero partial pressure of O_2. The vacuum system was based on a diffusion pump and provided with a liquid nitrogen trap. The system was thoroughly baked out at 275°C and the substrate itself was carefully cleaned and was baked out at 400°C for approximately one-half hour. Pressures measured on the bell jar were of the order of 10^{-8} Torr prior to evaporation and 10^{-7} Torr during evaporation. Those relatively high vacuum conditions, as compared to the reported prior art, were found to enhance reproducibility of the results, especially when combined with the step, already described, of annealing the deposited Bi layer prior to deposition of the Mn. That annealing step is preferably carried out without breaking or reducing the vacuum, but allowing the annealed Bi layer to cool to near room temperature before deposition of the Mn layer.

SAPPHIRE SEAL

The reaction of the Mn and Bi layers to form MnBi was then carried out either in a hard vacuum similar to that already described, or the double layer was first sealed by applying a layer of sapphire (Al_2O_3) by vacuum vaporization. Such a layer forms an effectively hermetic seal against atmospheric oxygen, so that partial release of the vacuum, or even temporary complete removal of the films from vacuum has no noticeable effect on the final product. Such a sealing layer is shown schematically at E in FIG. 7.

PRESENCE OF OXYGEN

The substantially complete exclusion of oxygen throughout the processing of the films leads to results that are more reproducible and self-consistent than have previously been obtained, and thus facilitates study of the magneto-optical behavior of the resulting films. However, we have found that the presence of at least traces of oxygen during reaction of the Mn and Bi is necessary in order to produce films having optimum characteristics for Curie-point switching, and particularly for producing films having the remarkably steep transfer characteristic that has been described.

Such oxygen can be made available by reacting the two layers in a vacuum of the order of 10^{-5} or 10^{-6} Torr, for example. Alternatively, the dual layer can be exposed with suitable heating to substantially any air pressure, the temperature and length of treatment being varied inversely with the pressure, and the reaction step can then be carried out in a hard vacuum such as has been described for the deposition process. Apparently oxygen is taken up by the Mn layer and remains available after evacuation. After such exposure to oxygen it is preferred to seal the film with a sapphire layer. The resulting reaction process is then rendered remarkably independent of such conditions as the degree of vacuum during reaction and the time and conditions of storage between oxygen treatment and reaction. It is noted, however, that double layers made in a hard vacuum and containing a large excess of Mn require relatively intensive oxygen treatment compared to those with only moderate excess of Mn. The oxygen is evidently taken up by the surface portion of the Mn layer. If that layer is too thick the oxygen may not become available at the site of the Mn—Bi reaction.

For producing MnBi films with optimum transfer characteristics of the type illustrated in FIG. 4, it is preferred to deposit the Bi and Mn in a hard vacuum, annealing the Bi layer as has been described before deposition of the Mn layer. The resulting dual layer is then treated with oxygen, typically by exposure to normal atmospheric air pressure at room temperature for 5 to 15 minutes. The oxygenated dual layer is then returned to vacuum and a sealing layer of Al_2O_3 of the order of 1,000 A thick is deposited by evaporation. The dual layer is then reacted by heating to a temperature in the range from about 200° to about 250°C to initiate reaction of the Mn and Bi. Useful films are obtainable by completing the reaction within that temperature range, typically requiring from 10 minutes to a half hour. However, we generally prefer, after a few minutes treatment at 200° to 250°C, to subject the film to a sharp increase of temperature to a range from about 275° to about 300°C for a time period of the order of 10 seconds and not exceeding about 1 minute, as has been described above.

An advantage of that overall preferred process is that the film thickness and the relative amounts of Mn and Bi in the films are less critical than is otherwise the case. However, it is preferred to employ an initial layer of the order of 300 A thick and to deposit the Mn layer to an atomic ratio of Mn to Bi of about 1.5 or between about 1.4 and about 1.6. That ratio insures an adequate excess of Mn, while holding the final layer of unreacted Mn to a thickness such that the applied oxygen is enabled to reach the reaction site and perform its re-

quired role in controlling the nature of the final layer of ferromagnetic MnBi.

We claim:

1. A magnetizable film capable of recording information by Curie-point switching of the film magnetization,

said film comprising a layer of ferromagnetic MnBi, produced using an excess of Mn over the stoichiometric atomic ratio for MnBi, having a transfer characteristic for Curie-point switching extending from substantial magnetic saturation in one direction normal to the plane of the film to substantial magnetic saturation in the opposite direction within a range of applied magnetic fields less than about 100 oersteds.

2. A magnetizable film according to claim **1** in which the overall atomic ratio of Mn to Bi in the film is between about 2.5 and about 3.

3. A magnetizable film according to claim **1** in which the overall atomic ratio of Mn to Bi in the film is between about 1.4 and about 1.6.

4. A magnetizable film according to claim **3**, said film being carried on a solid support and including a magneto-optically inactive layer between the support and said ferromagnetic layer and comprising Mn and Bi.

5. A magnetizable film according to claim **1**, said film being carried on a solid support and including a continuous layer of Al_2O_3 on its outer face.

6. A magnetizable film according to claim **1**, said film being carried on a solid support and including a magneto-optically inactive layer outward of said ferromagnetic layer and consisting essentially of Mn.

7. A magnetizable film according to claim **1**, said film being carried on a solid support and including a magneto-optically inactive layer outward of said ferromagnetic layer and comprising both Mn and Bi.

8. A magnetizable film according to claim **1**, said ferromagnetic layer being enclosed between magneto-optically inactive layers comprising both Mn and Bi.

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