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Cuttell et al.

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[54] **PROCESS FOR FORMING A MANGANESE BISMUTHIDE FILM**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** .... **117/71 R,** 117/106 R, 117/107, 118/49

[51] **Int. Cl.** **C23c 13/02**

[58] **Field of Search** .... 117/71 R, 107, 106 R

[56] **References Cited**

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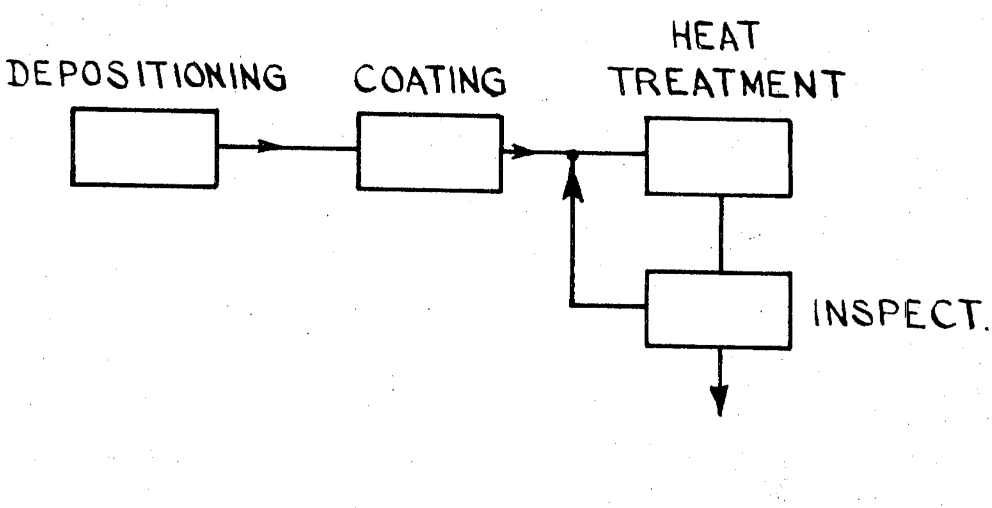
[57] **ABSTRACT**

A process for producing a manganese bismuthide layer on a substrate in which manganese and bismuth are vacuum deposited upon a substrate using high performance vacuum apparatus. The deposited materials are enclosed by an air impervious layer produced by a second vacuum depositioning stage using less sophisticated vacuum apparatus. The manganese and bismuth are then converted to manganese bismuthide by heat treatment which latter, because of the impervious layer, can be carried out in air.

7 Claims, 3 Drawing Figures



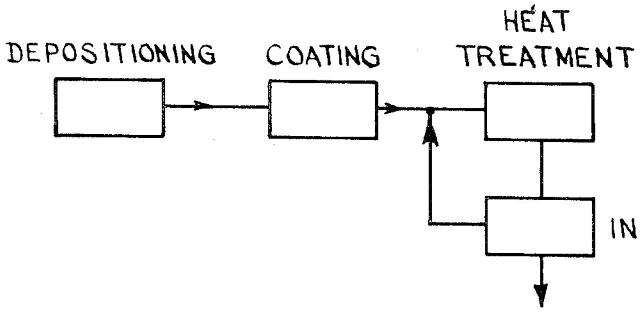


FIG. 1.

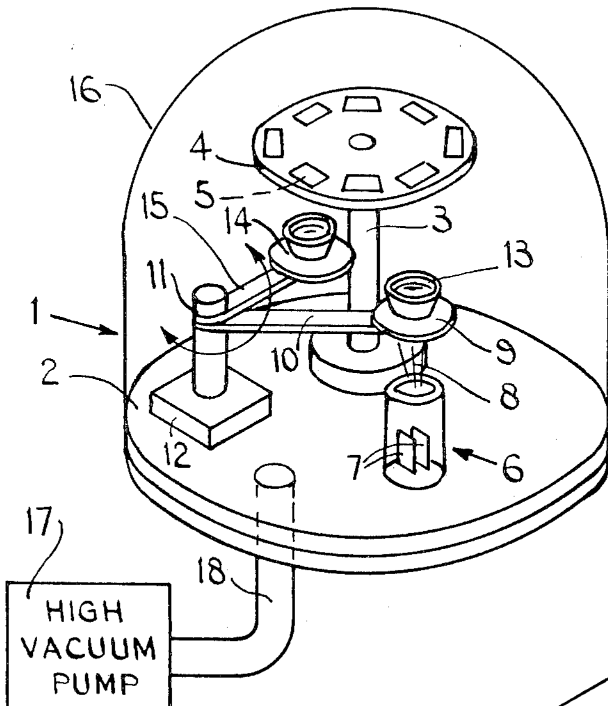


FIG. 2.

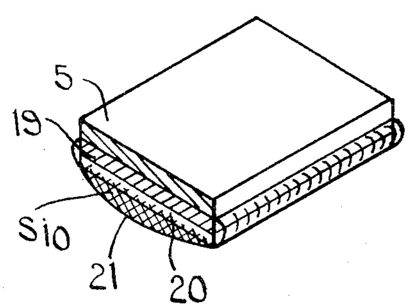


FIG. 3.

PROCESS FOR FORMING A MANGANESE BISMUTHIDE FILM

BACKGROUND OF THE INVENTION

The present invention relates to a process for forming manganese bismuthide film.

It has previously been proposed to form films of manganese bismuthide by the deposition of separate manganese and bismuth films on a substrate in a vacuum deposition apparatus and to apply a heating cycle to the newly deposited films while the substrate remains in the apparatus subjected to a high vacuum. Because the heating for the conversion takes a considerable time this process involves the allocation of a costly deposition apparatus for the heat treatment cycle during the whole of the conversion step thereby seriously reducing its productivity.

SUMMARY OF THE INVENTION

According to the present invention there is provided a process for the formation of a manganese bismuthide film including depositing bismuth and manganese in vacuo to form a layer upon a common substrate, depositing in vacuo material over the layer to form an air impervious coating and then subjecting, whilst in the presence air, the coated substrate to a temperature regime which converts the manganese and bismuth to a layer of manganese bismuthide.

BRIEF DESCRIPTION OF THE DRAWING

For a better understanding of the invention reference will be made to the accompanying drawing in which:

FIG. 1 schematically illustrates the principal stages of the process of the invention.

FIG. 2 is a diagrammatic representation of vacuum depositioning apparatus for performing the initial stages of the process and,

FIG. 3 illustrates a coated substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the process shown in FIG. **1** layers of manganese and bismuth are vacuum deposited on a substrate in a depositioning stage. The deposited layers are coated at a coating stage to form an air impervious layer thus producing a unit including a substrate, manganese and bismuth layers, and the coating. The manganese and bismuth layers are coverted to manganese bismuthide in a heat treatment stage. After heat treating the units are optically examined using polarized light at an inspection stage. Any units with incompletely converted manganese and bismuth are returned for further heat treatment at the heat treatment stage. Satisfactory units are removed from the process.

In FIG. **2** which illustrates in more detail the depositioning stage a first high vacuum unit **1** includes a base plate **2** carrying a column **3** supporting near the upper end thereof a rotatable support plate **4** for mounting substrates **5** which are to be coated with a manganese bismuthide film.

An electron beam unit **6** which includes an electron source (not shown) and suitable electrodes **7** is arranged to direct a beam **8** of electrons towards a target plate **9**, carried from an arm **10** mounted on a vertical shaft **11** for rotation about a vertical axis. A motor **12** is provided for rotating the shaft. The motor **12** is used

to swing the target plate **9** into and away from the line of the electron beam **8.** In addition means not shown are provided for rotating the plate **4** to bring the substrates successively into the depositioning position. It will be understood that suitable masking arrangements will be provided to prevent undesired coating of substrates. For example, a second plate with an aperture could be located below the plate **4** and substrate **5** such that rotating of the plate **4** brings succesive substrates into the coating position at the aperture. The rotation can be by means of an electric motor drive or hand drive system.

The target plate **9** carries a crucible **13** for receiving material to be melted.

To provide a facility of being able to melt two materials separately, a second target plate **14** likewise supported by an arm **15** is swingably mounted upon the shaft **11** for rotation by the motor **12.** Depending upon the facilities required the relative arrangement can be such that on moving a target into the line of the beam the other target is moved out from the line of the beam or alternatively the targets can be individually adjustable.

A transparent closure member **16** is hermetically sealable to the base plate **2.** The interior of the member **16** is connectable to a vacuum pump **17** by a suitable conduit **18.**

It will be clear that the above described apparatus is essentially a conventional high vacuum deposition apparatus having provision for the vapour deposition of two materials.

To use the apparatus a substrate **5** or a plurality thereof is or are mounted upon the plate **4.** The substrate **5** can comprise a glass such as Corning 7059 glass, or other transparent material such as a freshly cleaned optical ruby mica sheet of for example 2.54 × 1.28 mm in dimensions. An advantage of mica is that mica are readily cleaved and has a basal plane symmetry which is the same as an Mn Bi thereby encouraging expitaxial growth. A further suitable substrate was found to be a pyrex type glass disc some 10 centimeters diameter.

The coating process according to the invention is carried out as follows:

A measured quantity of bismuth is placed in the crucible **13,** and a measured quantity of manganese is placed in the crucible **14.** The chamber **1** is pumped down to a pressure of the order of 10^{-8} torr. The crucible containing the bismuth is brought into line with the electron beam and is vapourised to form a layer **19.** After which the other crucible is brought into line with the beam and the manganese is vapourised to form a layer **20.**

The quantities of bismuth and manganese vapourised are such that the films are deposited in the range 2.8–3:1, with a preferred range of 3:1. The thickness of the combined film lies within a range of 600 to 1000 Angstrom units.

Since a deposition pressure of 10^{-8} torr has been used it will be appreciated that the apparatus used is very high grade vacuum apparatus and preferably should be capable of being pumped down to 10^{-9} torr.

After the completion of the depositioning of the composite layer on the substrate it is necessary to heat treat the manganese and bismuth to convert the separate layers or films to an intermetallic layer of manganese bismuthide. It is however essential that the heat treatment be performed in the absence of air in order to prevent oxydation.

In practice the heat treatment is a relatively lengthy process as compared with the time required for vapour dispositioning the latter being aproximately 1 minute as compared with hours for the heat treatment.

The coated substrate could be heat treated in the deposition apparatus however this because of the time involved substantially reduces the productivity of the very high grade vacuum apparatus. To overcome this the coated substrate is, therefore, placed in a second vacuum deposition apparatus and the layers of bismuth and manganese are encapsulated, that is coated with a material which forms an air impervious layer **21** over the bismuth and manganese which does not chemically react with these materials. A convenient material is silicon monoxide. A layer **21** of this material is formed by vapour deposition over the layers of bismuth and manganese.

The second vacuum apparatus can be of the oil diffusion pumped system type capable of operating to produce pressures of the order of 10^{-5} or 10^{-6} torr, since the chamber pressures suitable for the production of the silicon monoxide films are less stringent than for the bismuth and manganese layers. The thickness of the silicon monoxide film is of the order of 6,000 Angstrom units thick.

The substrate together with its composite manganese and bismuth film and coated with silicon monoxide is then placed in an oven and is heated in air to a temperature of approximately 200°c for at least two hours. During this heating step the layer of silicon monoxide prevents the oxydation of the composite layer during its conversion to the intermediate manganese bismuthide. A preferred heating time period was five hours.

After the heating stage described is completed the substrate is cooled or is allowed to cool. The substrate is then examined in polarised light to ascertain whether or not the above mentioned conversion is completed. If the conversion is incomplete the substrate is returned to the oven for further heat treatment to complete the conversion stage.

With the above described process the formation of the silicon monoxide layer has two important advantages. Firstly, it avoids the necessity for the heating stage to be carried out in the deposition apparatus, with the result that this apparatus may now be used only for the initial formation of the composite layer, thereby greatly increasing its productivity.

Secondly, the process of conversion may also be improved and speeded up, since it is no longer imperative that the heat treated substrate be cooled in the absence of air before it can be examined. Furthermore, any further heat treatment that may be necessary may readily be applied simply by replacing the substrate in the oven without the need to clear and pump down a vacuum chamber.

The bismuth and manganese can be co-deposited. This can be effected by simultaneously vapourising measured quantities of bismuth and manganese thereby producing a film which comprises an intimate mixture of manganese and bismuth which is subsequently converted to the intermetallic compound Mn Bi during the above described heat treatment stage.

What is claimed is:

1. A process for the formation of a film of intermetallic manganese bismuthide on a substrate comprising the steps of; depositing under vacuum at a first pressure level manganese and bismuth on to the same region of the substrate; depositing under a vacuum at a second pressure higher than the first level an air impervious layer which is chemically inert to the manganese and bismuth to encapsulate the manganese and the bismuth; tranferring the substrate to a heating zone, and converting the manganese and bismuth into an intermetallic manganese bismuthide by heating the manganese and bismuth under ambient pressure conditions for at least 2 hours at a temperature of approximately 200°c.

2. A process for the formation of a manganese bismuthide film on a substrate comprising the steps of depositing under vacuum at a pressure of at least 10^{-8} torr manganese and bismuth on to the substrate; depositing an air impervious layer of silicon monoxide over the manganese and bismuth under vacuum at pressure of 10^{-5} torr to 10^{-8} torr; transferring the substrate into a heating zone and converting the manganese and bismuth to an intermetallic manganese bismuthide by heating the manganese and bismuth under ambient pressure conditions for at least two hours at approximately 200°c.

3. A process as claimed in claim **2**, in which the manganese and bismuth are applied as separate films with a combined thickness within the range 600 to 1,000 Angstrom units.

4. A process as claimed in claim **3**, in which the quantities of bismuth and manganese deposited are such that the relative thicknesses of the bismuth and manganese films are in the range 2.8–3:1.

5. A process as claimed in claim **2**, in which the manganese and bismuth are so deposited as to provide a single film having a thickness within the range 600 to 1,000 Angstrom Units.

6. A process as claimed in claim **2**, in which the air impervious layer has a thickness of the order of 600 Angstrom Units.

7. A process as claimed in claim **2**, in which after the heating stage the extent of conversion to manganese bismuthide is examined in polarised light and in the event of incomplete conversion the bismuth and manganese is subjected to a further heating stage.

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