

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in Methods of Forming Film Materials

We, FAIRCHILD CAMERA & INSTRUMENT CORPORATION of 300 Robbins Lane, Syosset, Long Island, New York, United States of America, a Corporation of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to forming a film of material into a predetermined configuration.

In many arts, such as the electronic art and the semiconductor art, a film of material is formed into a predetermined configuration on a selected surface. For example, after forming a monolithic semiconductor circuit, it is necessary to make electrical contact to the numerous elements and regions of the circuit. This is in some instances accomplished by forming a predetermined configuration of contacting material (e.g., aluminum) over the surface of the circuit. In other instances it is desired that a predetermined configuration in the form of a narrow cut in a passivating layer of material (e.g., silicon monoxide) be made or that a resistor having a predetermined configuration be formed from one of the high-resistivity film materials (e.g., nickel-chromium alloys, hereafter called NiCr).

Predetermined configurations of film material have been formed by etching and by lifting. Etching involves the selective chemical dissolution of undesired regions of the film material from the surface. However, certain materials are impractical (e.g., BaTiO₃) or very difficult (e.g., NiCr) to etch. In addition, during etching the etchant usually undercuts the film, reducing the accuracy of the process. For example, a one micron diameter opening in a deposited oxide film, or a 2×2 micron aluminum square cannot be

readily formed by etching. Also, the reliability of the etching process, in part, depends upon the adherence of a photo-resist layer to the film material being etched. This adherence cannot be readily checked so that application of the etchant to the photo-resist can be a hit-and-miss operation.

The lifting process on the other hand involves depositing the film, from which a portion is to be removed, partially upon the surface and partially upon the lifting material to be removed or lifted. This process in the past has employed organic lifting materials which decompose at elevated temperatures (e.g., greater than 300°C), or, alternatively thick metal film lifting materials which micro-alloy or diffuse into the film at temperatures greater than about 400°C. This alters the properties of the film. In addition, metal film lifting materials may affect a semiconductor junction when employed in close proximity therewith. The use of organic film lifting materials, such as photo-resist, has the short-coming of limiting the thickness of the layer to be lifted to several thousand angstroms. For these reasons the use of the lifting process has not been widespread and is only rarely employed in processes wherein elevated temperatures are employed.

This invention overcomes prior art shortcomings by employing as the lifting material in the lifting process an inorganic material which forms ionic crystallites. Briefly, the method of the invention comprises forming a pattern from a layer of Group II(A) halide upon a surface, leaving exposed a part of the surface, forming a film of material over said pattern, and removing the halide layer from the surface, whereby a predetermined configuration of film material is formed on the surface over the exposed part.

The lifting material of the invention, Group

[Price 4s. 6d.]

II(A) halides (alkaline earth metal halides), form porous ionic crystallites which may readily be deposited as a uniform integrally coherent layer. These inorganic materials have many desirable characteristics, as will be set forth in more detail later.

The invented method is illustrated in the single drawing, wherein:

FIGS. 1a to 1g show various steps in the performance of the method.

Referring to FIGS. 1a to 1g, in performance of the method, it is first necessary to form a pattern which is a layer of a Group II(A) halide (i.e., an alkaline earth metal halide) on a surface. Typically, the surface may be a surface 12 of substrate 10 (FIG. 1a). The substrate 10 may be a monolithic semiconductor integrated circuit with the components of the circuit formed therein and having a passivating layer thereon, or it may be a semiconductor (e.g., silicon) wafer, or a ceramic or glass wafer, to mention a few forms that the substrate 10 may take. In forming the halide mask, a layer of a conventional photo-resist material 14, such as AZ 1350 (Auto-Positive) marketed by the Shipley Corporation, is applied in the form of a continuous layer over surface 12 (FIG. 1b). The photo-resist is then exposed and developed according to well-known photoengraving techniques leaving an image 18 of photo-resist material such as shown in FIG. 1c.

The surface 12 and photo-resist image 18 are then covered with a layer of lifting material 20 formed from one of the alkaline earth metal halides. The halide lifting material 20 may be deposited by standard vacuum deposition techniques employing ordinary vacuum deposition chambers, having sources which operate at temperatures of about 1400°C. This is the temperature at which alkaline earth metal halide lifting materials, such as calcium fluoride, for example, are deposited. It should be noted that the alkaline earth metal halides, such as calcium fluoride, do not spatter. Granules of the halides, therefore, are not ejected and deposited on the substrate before the deposition process begins. This facilitates the forming of a uniform and regular layer of lifting material 20. In general, the alkaline earth metal halides form ionic crystallites having a relatively porous structure. These materials have the following advantageous properties: (1) They do not affect the electrical characteristics of semiconductor junctions; (2) They do not decompose at elevated temperatures (i.e., temperatures between approximately 300°—1000°C); (3) They do not readily alloy with metals commonly employed in the electrical and integrated circuit arts; (4) They may be lifted by dilute acids which do not affect the other components or materials associated with an integrated circuit or an electrical component such as the film being formed; (5) They

adhere to common substrate materials such as silicon, glass, ceramics and others; and (6) They are not affected by solutions commonly employed to remove photo-resist images. The alkaline earth metal halides have structural strength and reliability when formed in a thin film, and are available in a pure form or with such impurities that do not affect the electrical characteristics of semiconductor junctions. In this regard, sodium and potassium (deleterious to semiconductor junction stability) are commonly found as impurities in Group II(A) elements. This makes it necessary that the Group II(A) materials employed be readily subject to purification to eliminate such impurities. The Group II(A) elements most easily purified are calcium, barium and magnesium.

Of the alkaline earth metal halides, the calcium halides, in particular, calcium fluoride, is the preferred and most desirable compound to employ as the lifting material 20. Calcium fluoride is insoluble in acetone which may be employed as the solution for removing the photo-resist image 18. Yet, calcium fluoride is readily soluble in many common acids which do not alter the film materials, such as dilute sulfuric acid, dilute nitric acid, dilute hydrochloric acid, and other liquids, such as hot water and solutions of ammonium salts. The deposition of calcium fluoride can be carried out in standard vacuum deposition chambers with deposition occurring at about 1400°C, and with no tendency to spatter. The deposition of calcium fluoride occurs in a very uniform manner with the formed film being porous and of integral, coherent structure. The electrical characteristics of a semiconductor junction are not altered by calcium fluoride and the decomposition temperature is in excess of 1000°C with little or no tendency to alloy or diffuse into the substrate or associated metals. Some of the other halides which approach the performance of calcium fluoride are magnesium fluoride and barium fluoride.

The term "alkaline earth metal halides" as used above and herein is synonymous with Group II(A) halides. It is understood that this definition is for the purposes of this specification and may differ from the strict chemical definition of alkaline earth metal halides which may only include calcium, magnesium, strontium and barium halides. According to the Cherck Index published in 1952 by Cherck & Co., these four metals are included in Group II(A).

Following the deposition of the halide lifting material 20 (FIG. 1d), the photo-resist image 18 is removed by submerging the substrate 10 or submerging the portion of substrate having photo-resist image 18 and lifting material 20 thereon in a solvent, such as acetone. The application of the solvent removes the photo-resist image 18 and the por-

tion of the halide thereupon, leaving a mask or pattern 22 of halide lifting material 20 (FIG. 1d). This removal is possible notwithstanding the fact that the photo-resist image is covered with lifting material 22. The porous structure of the alkaline earth metal halides enables the solvent to penetrate lifting material 22 and thereby remove the undesired photo-resist and the halide covering it. The mask 22, while shown as a rectangle, may take on any of the more complex forms commonly employed in the integrated circuit masking art.

With the halide mask 22 formed, it is next necessary to form a film of material 26 over mask 22 (FIG. 1f). The film material may be any of those materials employed in the electronic or integrated circuit art, preferably a metal or metal oxide, for example, NiCr, BaTiO₃, Al or Ag. The film material 26 may be formed over the mask 22 by deposition methods such as vacuum deposition, vapor phase deposition, or pyrolytic deposition.

The final step of the invented method is the removal of the lifting material 20, along with the film material 26 deposited thereupon, whereby a predetermined configuration 28 of the desired film material is formed directly upon surface 12 (FIG. 1g). Mask 22 is removed by lifting with a dilute acid such as 10% HNO₃ or dilute sulfuric acid, dilute hydrochloric acid, hot water or a solution of an ammonium salt. These solutions readily remove mask 22 and the overlying film material 26, while leaving the predetermined configuration 28 of film material intact and unaffected. The predetermined configuration 28 takes the form determined by mask 22.

By employing the above-described method, it has been possible to form very small openings, such as 1 micron cuts, in deposited materials, such as silicon monoxide, and to form tiny 2×2 micron strips of materials, such as aluminum. The formation of such strips and cuts has heretofore not been possible by etching or lifting techniques. Further, materials such as NiCr, which have heretofore not been readily formed by such prior art techniques, are readily formed into predetermined configurations. The use of the Group II(A) halides as a lifting material enables high-temperature film materials to be deposited as these halides can withstand temperatures of up to 1000°C without affecting the desired film material being deposited

or the electrical characteristics of the semiconductor junction. In addition, these halides form a porous and structurally strong material which facilitates the forming of fine cuts and strips heretofore not attainable.

Although this invention has been disclosed and illustrated with reference to particular applications, the principles involved are susceptible of numerous other applications which will be apparent to persons skilled in the art. The invention is, therefore, to be limited only as indicated by the scope of the appended claims.

WHAT WE CLAIM IS:—

1. A process of forming a desired film material into a predetermined configuration upon a surface by forming a pattern from a layer of a first material upon the surface leaving exposed a part of the surface, by forming a film of a second material over said pattern and said exposed surface and by removing said layer of first material from the surface to form a predetermined configuration of said first material on the surface over said exposed part, wherein said first material consists of a Group II(A) halide.
2. A process as claimed in claim 1, wherein the removal of said halide layer is effected by lifting said halide layer and said film of second material formed over said pattern from said halide surface.
3. A process as claimed in claim 1, wherein said pattern consists of ionic crystallites of said Group II(A) halide.
4. A process as claimed in claim 1 or 3, wherein said Group II(A) halide is calcium fluoride.
5. A process as claimed in claim 1, wherein the halide layer and said film of second material formed over the pattern are removed by lifting them from said surface with a solution which readily attacks said layer but which does not substantially affect said film material.
6. A process of forming a desired film material into a predetermined configuration substantially as described with reference to the accompanying drawings.

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tion of the halide thereupon, leaving a mask or pattern 22 of halide lifting material 20 (FIG. 1d). This removal is possible notwithstanding the fact that the photo-resist image is covered with lifting material 22. The porous structure of the alkaline earth metal halides enables the solvent to penetrate lifting material 22 and thereby remove the undesired photo-resist and the halide covering it. The mask 22, while shown as a rectangle, may take on any of the more complex forms commonly employed in the integrated circuit masking art.

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By employing the above-described method, it has been possible to form very small openings, such as 1 micron cuts, in deposited materials, such as silicon monoxide, and to form tiny 2×2 micron strips of materials, such as aluminum. The formation of such strips and cuts has heretofore not been possible by etching or lifting techniques. Further, materials such as NiCr, which have heretofore not been readily formed by such prior art techniques, are readily formed into predetermined configurations. The use of the Group II(A) halides as a lifting material enables high-temperature film materials to be deposited as these halides can withstand temperatures of up to 1000°C without affecting the desired film material being deposited

or the electrical characteristics of the semiconductor junction. In addition, these halides form a porous and structurally strong material which facilitates the forming of fine cuts and strips heretofore not attainable.

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WHAT WE CLAIM IS:—

1. A process of forming a desired film material into a predetermined configuration upon a surface by forming a pattern from a layer of a first material upon the surface leaving exposed a part of the surface, by forming a film of a second material over said pattern and said exposed surface and by removing said layer of first material from the surface to form a predetermined configuration of said first material on the surface over said exposed part, wherein said first material consists of a Group II(A) halide.
2. A process as claimed in claim 1, wherein the removal of said halide layer is effected by lifting said halide layer and said film of second material formed over said pattern from said halide surface.
3. A process as claimed in claim 1, wherein said pattern consists of ionic crystallites of said Group II(A) halide.
4. A process as claimed in claim 1 or 3, wherein said Group II(A) halide is calcium fluoride.
5. A process as claimed in claim 1, wherein the halide layer and said film of second material formed over the pattern are removed by lifting them from said surface with a solution which readily attacks said layer but which does not substantially affect said film material.
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