

[54] **PROCESS FOR FORMING A METAL OXIDE PATTERN**

3,695,908 10/1972 Szupillo 117/106
 3,697,342 10/1972 Cuomo 156/13

[75] Inventors: **Alan R. Janus**, Pasadena; **Peter C. Fletcher**, Monrovia; **Michael H. Ridosh, Jr.**, Simi Valley; **Walter P. Freihube**, Sepulveda, all of Calif.

Primary Examiner—Douglas J. Drummond
Assistant Examiner—J. Massie
Attorney, Agent, or Firm—Nilsson, Robbins, Bissell, Dalgarn & Berliner

[73] Assignee: **Material Sciences Corporation**

[22] Filed: **Aug. 14, 1972**

[21] Appl. No.: **280,606**

[52] U.S. Cl. **156/7, 117/63, 117/106 R, 117/123 B, 117/138.8 R**

[51] Int. Cl. **C23c 11/08**

[58] Field of Search **117/106 R, 63, 62, 138.8 R, 117/236; 156/6, 7, 13, 16; 96/38.3**

[57] **ABSTRACT**

A process for forming a pattern of metal oxide on a substrate wherein a metal oxide is selectively formed or etched in accordance with a thermal pattern. In one embodiment, selected portions of a uniform layer of substantially amorphous metal oxide are converted to a more crystalline form by heat and remaining amorphous oxide portions are removed by chemical etching to form the pattern. In another embodiment, a metal-organic compound precursor of the metal oxide is thermally decomposed on the substrate in accordance with the pattern. A novel vapor etching process, and a novel sputtering process for forming amorphous metal oxide, are disclosed.

[56] **References Cited**

UNITED STATES PATENTS

2,919,207	12/1959	Scholzel.....	117/236
3,243,363	3/1956	Helwig.....	117/106
3,518,134	6/1970	Preist.....	156/13
3,615,953	10/1971	Hill.....	156/13

7 Claims, 10 Drawing Figures

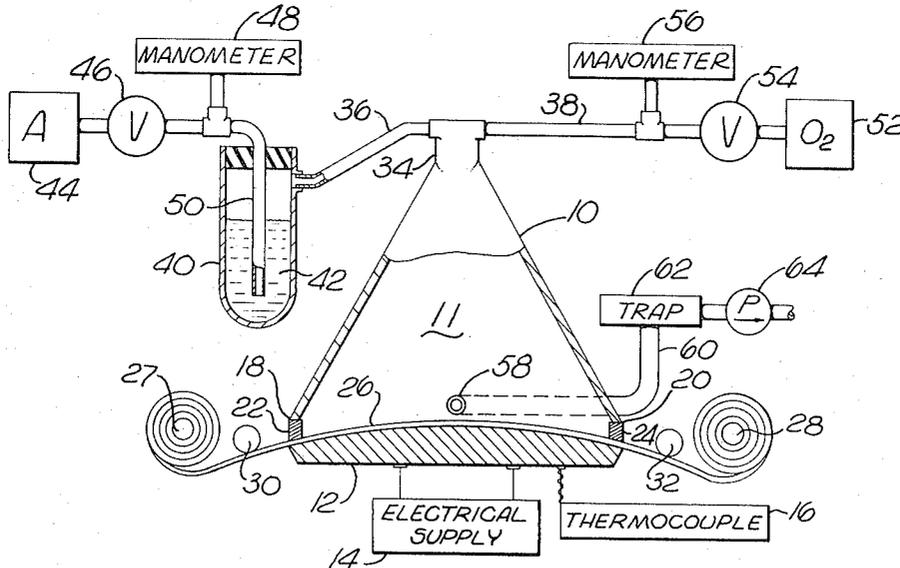


Fig. 1.

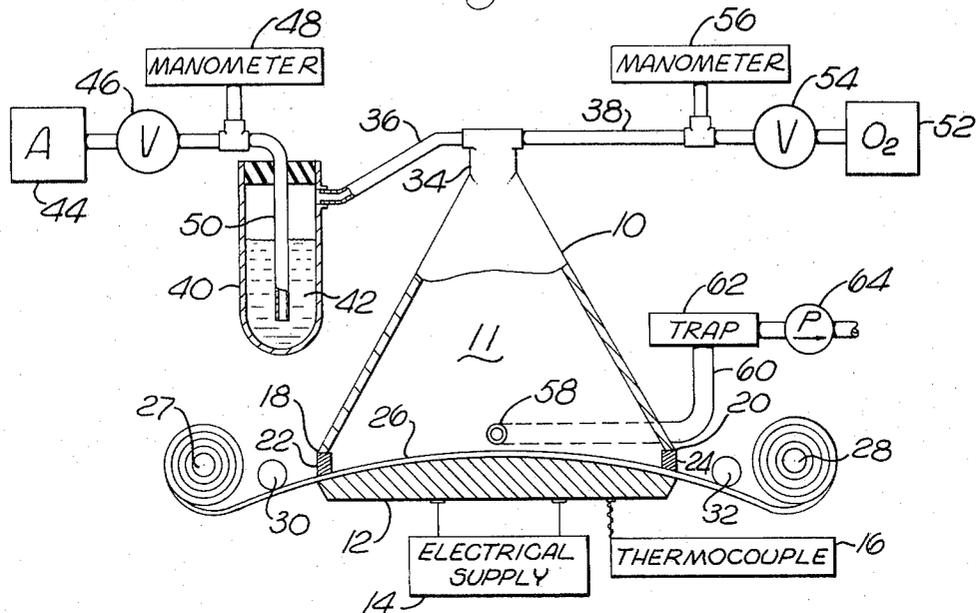


Fig. 2.

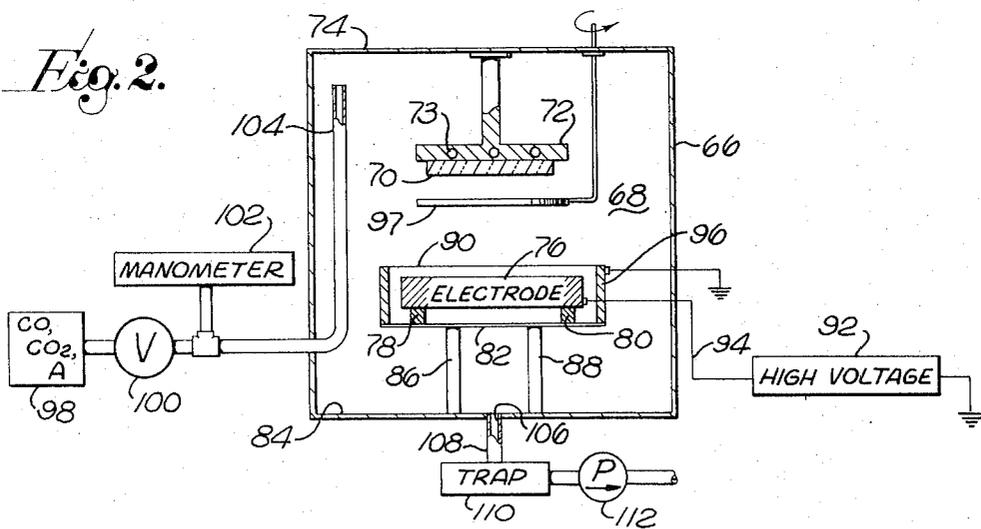
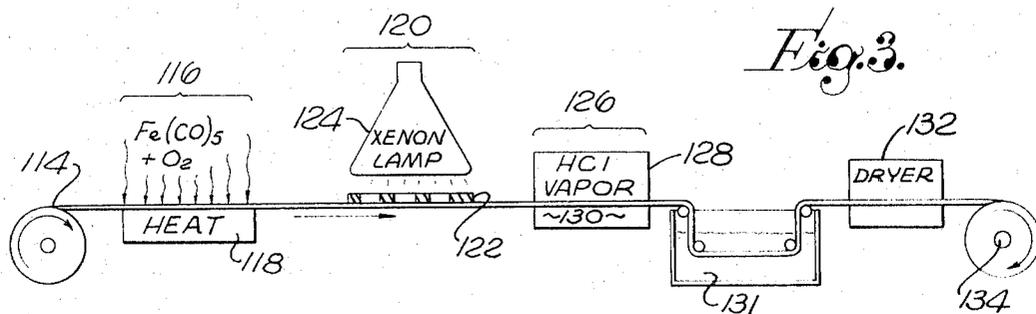


Fig. 3.



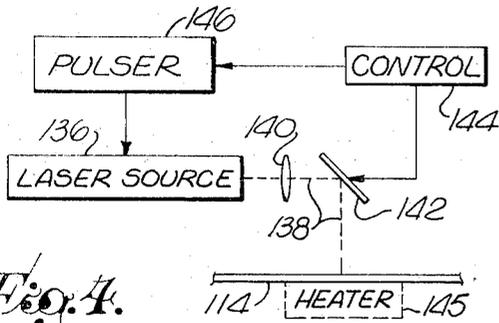


Fig. 4.

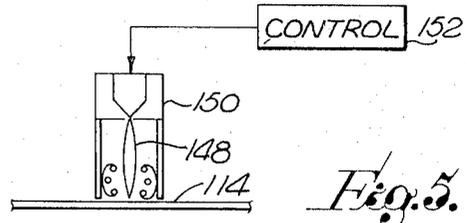


Fig. 5.

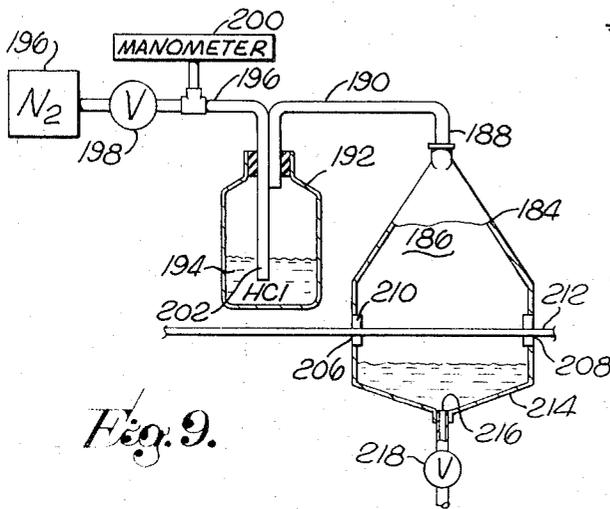


Fig. 9.

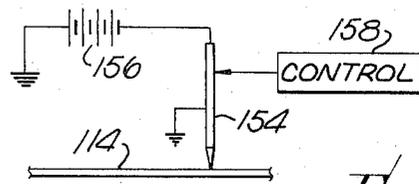


Fig. 6.

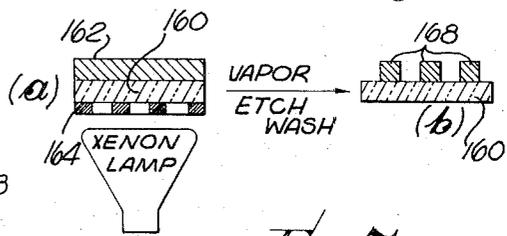


Fig. 7.

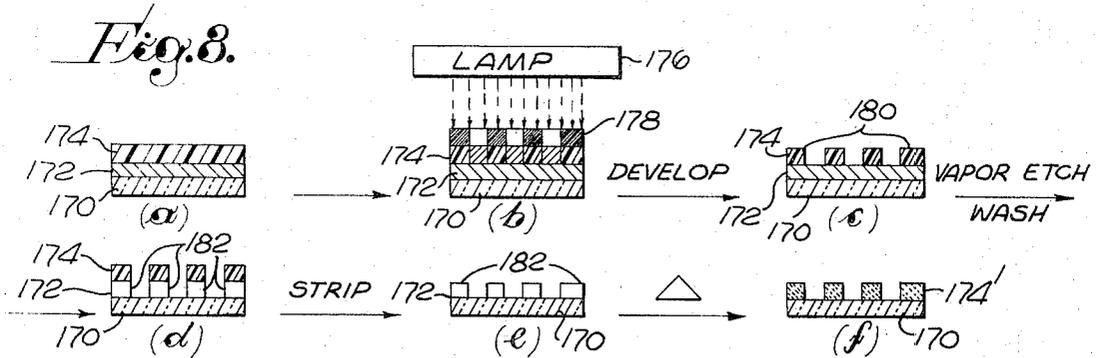


Fig. 8.

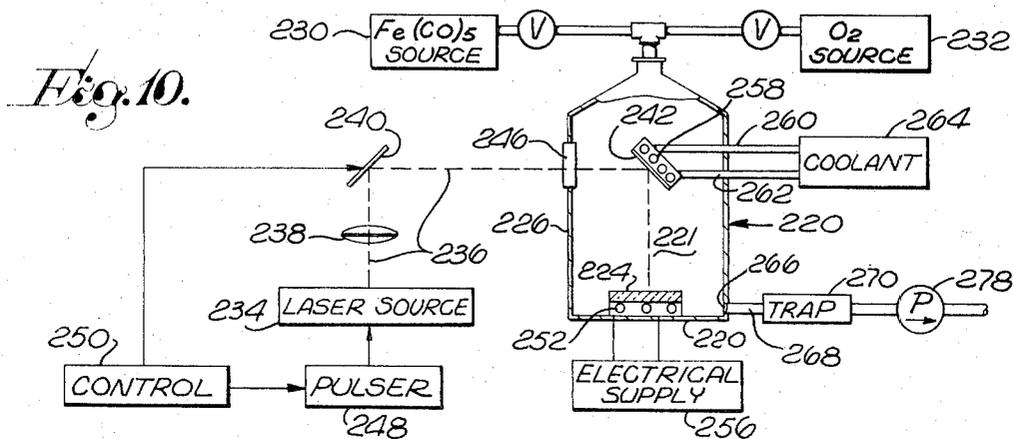


Fig. 10.

PROCESS FOR FORMING A METAL OXIDE PATTERN

FIELD OF THE INVENTION

The fields of art to which the invention pertains include the fields of metal oxide processes and treatment thereof, particularly involving chemical vapor deposition.

BACKGROUND AND SUMMARY OF THE INVENTION

In the manufacture of semiconductor devices and integrated circuits, extensive use is made of photomasks. The mask is applied to the photoresist coating on a semiconductor or integrated circuit substrate to absorb or reflect incident exposure light in desired areas and transmit light in other areas. In manufacturing complex semiconductor components, one may use three, four or more masks on one substrate. With silver grain or chromium film-on-glass masks, alignment is difficult and keys must be provided, increasing the manufacturing time and limiting accuracy of alignment. These difficulties have resulted in the development of partially transparent masks. Such masks should be strongly absorbing in the region of about 360-420 millimicrons and at least partially transmissive (about 30%) in the range of 575-595 millimicrons. The partial transparency characteristics of the plates allow them to be visually aligned yet they absorb that region of the spectrum which is reactive with common photoresist materials.

A number of materials have been suggested for such use including metal oxides such as iron oxide, vanadium oxide, nickel oxide, iron oxide-nickel oxide, and iron-oxide-vanadium oxide. See in this regard "Materials for Use in a Durable Selectively Semitransparent Photomask" by W. R. Sinclair, M. V. Sullivan and R. A. Fastnacht, *Journal of the Electrochemical Society*, Vol. 118, pages 341-344. Such masks have been made by sputtering techniques, as discussed in the Sinclair, et al., article, as well as by chemical vapor deposition. See in this regard "Chemical Vapor Deposition of Iron Oxide Films for Use as Semitransparent Masks" by J. B. MacChesney, P. B. O'Connor and M. V. Sullivan, *Journal of the Electrochemical Society*, Vol. 118, pages 776-781. Additional references which may be of interest to the present invention include "Vacuum Deposition of Thin Films" by L. Holland, Chapman and Hill, Ltd. (London), 1966, pages 474-480, "Reversible High-Speed High-Resolution Imaging in Amorphous Semiconductors" by S. R. Obshinsky and P. H. Klose, *International Symposium on Information Display*, 1971, pages 58-61, "Electron Beams Shine on IC Layouts," by L. Curran, *Electronics*, June 21, 1971, pages 83-84, Drummond U.S. Pat. No. 2,332,309, Chladitz U.S. Pat. No. 2,698,812, Gellar U.S. Pat. No. 3,108,014, Banks, et al., U.S. Pat. No. 3,148,079, Bakish, et al., U.S. Pat. No. 3,190,262, Burger U.S. Pat. No. 3,256,109, Toulmin, Jr., U.S. Pat. No. 2,847,330, Solomon, et al., U.S. Pat. No. 3,364,087, Hensler U.S. Pat. No. 2,923,624, Lepselter U.S. Pat. No. 3,442,701, Sinclair, et al., U.S. Pat. No. 3,388,053 and Sinclair, et al., U.S. Pat. No. 3,395,091.

To prepare photomasks from such materials, one can coat the partially transparent material with a photoresist, expose through a master mask and remove the soluble resist portions with an acid or alkali etchant. Accordingly, the metal oxide used for such masks must be

reactable with etchants compatible with the photoresist processing materials. As brought out in the aforementioned MacChesney, et al., article, sputtered iron oxide films have been found to be extremely resistant to normal etchants and certain films deposited by chemical vapor deposition techniques have also been found to be resistant. In particular, it was found that films which were chemically vapor deposited at temperatures of 160°C and higher consisted of $\alpha\text{Fe}_2\text{O}_3$, a crystalline iron oxide form and non-etchable. However, films chemically deposited below 160°C were amorphous and could be etched with normal etchants. It has recently been found that when iron oxide is obtained by sputtering in an atmosphere of carbon monoxide and carbon dioxide, amorphous oxide can be formed.

The present invention facilitates the preparation of photomasks and provides metal oxide images having exceptional resolution. Various of the embodiments presented can also be applied to the preparation of microfilm and microfiche and sufficient resolution is obtainable for producing ultrafiche copies having a resolution of 500 line pairs per millimeter or better. In particular, a process is provided wherein a metal oxide image is selectively formed or etched in accordance with a thermal pattern. In one embodiment a uniform layer of amorphous metal oxide is applied to a substrate surface and selectively heated to form a pattern of crystallized metal oxide. The remaining amorphous metal oxide portions are removed by etching. In another embodiment metal oxide is chemically deposited in a pattern by applying to the substrate a metal-organic compound precursor of metal oxide, in combination with an oxidant, while heating selected regions of the substrate at a temperature sufficient to thermally decompose the precursor to the metal oxide.

A novel sputtering process is provided to produce an amorphous layer of metal oxide with greater facility than heretofore obtainable. In this embodiment, a metal precursor of the metal oxide is sputtered onto a substrate in the presence of about 5 to about 40 volume percent carbon monoxide, about 20 to about 80 volume percent carbon dioxide and about 20 to about 70 volume percent inert gas, such as argon. Additionally, one can add up to 10 volume percent oxygen, but oxygen may be omitted. The use of argon or other inert diluant, to provide a temporary mixture, provides a higher throwing power during the sputtering operation, enabling a faster deposition rate.

In a further embodiment, a novel etching process is provided for removing the amorphous metal oxide portions and which is more rapid, more easily automated and results in less defects than prior art processes. In particular, the etchant is applied in the form of a vapor rather than as a liquid as heretofore practiced.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic view of apparatus for applying a layer of amorphous metal oxide to the surface of a flexible substrate, such as a plastic sheet, by chemical vapor deposition;

FIG. 2 is a diagrammatic view of apparatus for applying a layer of amorphous metal oxide to a substrate using sputtering techniques;

FIG. 3 diagrammatically shows a processing sequence for forming a metal oxide image on a flexible sheet;

FIG. 4 is a schematic representation of a mechanism utilizing a laser beam to provide a thermal pattern on a layer of amorphous metal oxide;

FIG. 5 is a schematic representation of a mechanism utilizing an electron beam to provide a thermal pattern on a layer of amorphous metal oxide;

FIG. 6 is a schematic representation of a mechanism utilizing a heated stylus to provide a thermal pattern on a layer of amorphous metal oxide;

FIGS. 7(a) and (b) are parts of a schematic flow diagram of processing steps for forming a metal oxide image from a uniform layer of amorphous metal oxide;

FIGS. 8(a) - (f) are parts of a schematic flow diagram of another process for forming a metal oxide image from a uniform layer of amorphous metal oxide;

FIG. 9 is a schematic representation of apparatus for applying an etchant in vapor phase to the surface of a metal oxide layer; and

FIG. 10 is a schematic representation of apparatus for depositing a layer of metal oxide on a substrate in accordance with a thermal pattern generated by a controlled laser source.

DETAILED DESCRIPTION

Referring to FIG. 1, there is illustrated the chemical vapor deposition of a layer of amorphous metal oxide, exemplified by iron oxide. The drawing is schematic and serves to illustrate the process steps; therefore, relative sizes and positions are not to be taken literally but are used for convenience and ease of illustration. In this regard, reference can be made to the aforementioned MacChesney, et al., article for process details and to various of the patent references, such as Galler U.S. Pat. No. 3,108,014 and Bakish, et al., U.S. Pat. No. 3,190,262 for other types of apparatus for accomplishing deposition. These patents relate to the deposition of a metal film, but can be modified for the introduction of oxygen for the deposition of a metal oxide film in accordance with the MacChesney, et al., article.

The apparatus includes a housing 10 enclosing a deposition chamber 11 and includes a convex wall 12 having implanted heating elements (not shown) connected to an electrical supply 14 and thermocouple 16 therefor. Opposite portions 18 and 20 at the bottom of the housing 10 are spaced from the bottom wall 12 and fitted with gaskets 22 and 24 which partially seal the chamber 11 from the exterior but allow the insertion and travel-through of a sheet of plastic 26 such as Mylar (a transparent polyethylene terephthalate), Kapton (a polyimide), polyethylene, or the like. The plastic sheet 26 is fed from a supply 27 through the chamber 11 and onto a takeup reel 28, the sheet being pressed against the heated bottom wall 12 by means of rollers 30 and 32.

The apparatus housing 10 is formed at its upper end with a neck 34 which continues as a T-junction forming two gas conduits 36 and 38. A side-arm tube 40 is connected to one of the conduits 36 and contains a supply 42 of liquid iron pentacarbonyl. A source 44 of inert gas, such as argon, is metered by a valve 46 past a manometer 48, via a tube 50 into the iron pentacarbonyl supply 42 to carry iron pentacarbonyl vapors through the conduit 36 into the T-junction. A supply 52 of oxygen is metered by a valve 54 past a manometer 56 into the T-junction to combine with the iron pentacarbonyl

and enter the deposition chamber 11. As the vapors contact the heated plastic sheet 26, the iron pentacarbonyl is thermally decomposed and, as a result of interaction with the oxygen, a layer of iron oxide is formed on the plastic sheet 27. The supply reel 28 is driven at a speed sufficient to deposit a uniform coating on the sheet 26 as desired, generally about 500-10,000 Å thickness. The chamber housing 10 is formed with an opening 58 at the bottom thereof connected via a conduit 60 to a trap 62 and from there to a pump 64 which exhausts the chamber at a rate adjusted to correspond with the metering action of the valves 46 and 54.

Importantly, the sheet 26 is heated at a temperature of about 60°C to less than 160°C to deposit the iron oxide as an amorphous layer. With deposition below 160°C, the layer of metal oxide is amorphous allowing its use in the image-forming processes hereinafter described. At temperatures of 160°C and higher, crystalline $\alpha\text{Fe}_2\text{O}_3$ oxide is deposited which is not etchable by normal etchants, i.e., by etchants which do not damage the plastic substrate or resists that may be applied to the oxide. Temperatures can be utilized which are somewhat below this range, but the deposition rate is very slow.

Referring to FIG. 2, there is illustrated another method for preparing a layer of amorphous metal oxide, using a sputtering technique and, in this regard, reference can be made to the aforementioned Sinclair, et al., article. The apparatus includes a housing 66 enclosing a sputtering chamber 68 in which a glass photomask plate 70 is secured to a support 72 dependent from the top wall 74 of the housing. A heating element 73 may be disposed in the support 72 and maintained at a suitable temperature, e.g., about 100°C, but below 160°C. A sputtering electrode 76 of metal precursor to the desired metal oxide, in this case, an iron disk, is supported in spaced opposed relationship to the plate 70 by insulative spacers, such as at 78 and 80, on a platform 82, which in turn, is supported spaced from the housing wall 84 by legs, such as 86 and 88. A grounded, annular conductive shield 90 is disposed spaced laterally around the electroplate 76. A source 92 of high voltage is connected by a lead 94 to the electroplate 76 through an aperture 96 in the shield 90. A rotatable cover mask 97 is disposed in the sputtering path to control the sputtering.

A source 98 of reactive gas mixture is fed via a metering valve 100, past a manometer 102, into the chamber 68 by means of a conduit tube 104. Exhaust gases are drawn through an opening 106 in the floor of the housing 66 via a conduit 108 through a trap 110 by means of a pump 112 adjusted with the metering valve 110 to maintain a low pressure atmosphere in the chamber 68, about 60 mTorr. The nature of the reactive atmosphere is very important in determining whether amorphous or crystalline metal oxide is formed. With an atmosphere of oxygen or oxygen-argon, only non-etchable crystalline iron oxide is formed, but with a mixture of carbon monoxide and carbon dioxide, the iron is sputtered onto the plate 70 as amorphous iron oxide. As will be detailed hereinafter, a particular novel mixture of carbon monoxide, carbon dioxide and argon is particularly advantageous. The electrode disk 76 can be sputtered at 2,500 volts and 100 milliamperes, sputtering time being controlled so as to deposit an oxide layer having a thickness of about 500-10,000 Å.

Referring to FIG. 3, a process is illustrated wherein a metal oxide image is formed on a plastic substrate. We have discovered that by post-heating the amorphous metal oxide at a temperature past its crystallization point, one can selectively crystallize the metal oxide in the heated areas without a corresponding change in the areas maintained below the crystallization temperature. Thus, we have found that when amorphous iron oxide is heated at 160°C or above, it is modified to the alpha, crystalline form. As previously noted, crystalline iron oxide is not readily etched by normal etchants whereas amorphous iron oxide is readily etched. By means of such differential etching, any desired pattern or image of iron oxide on substrate can be produced.

In the embodiment illustrated, a plastic sheet 114 is led from a supply thereof past a chemical vapor deposition station 116 where the plastic sheet 114 is heated, as at 118, while one surface of the plastic sheet is exposed to iron pentacarbonyl vapors and oxygen. The sheet is heated to a temperature below 160°C, but sufficient to thermally decompose the iron pentacarbonyl so as to deposit a layer of amorphous iron oxide on the plastic sheet surface. The apparatus of FIG. 1 can be utilized at the deposition station 116 in a continuous manner as shown, or the plastic sheet can be precoated with a layer of amorphous iron oxide, using the apparatus of FIG. 1 or any other apparatus suitably constructed for such deposition. In this regard, the sputtering apparatus of FIG. 2 can be modified to accommodate the processing of an elongate plastic sheet.

Alternatively, the plastic sheet 114 can be precoated with a layer of amorphous iron oxide.

The plastic sheet 114 is then conveyed to an exposure station 120 where it is thermally exposed through a terminal absorption or reflection mask 122 (e.g., of chromium metal or ferric oxide) to heat generated by a xenon lamp 124. Radiation from the lamp 124 heats the regions immediately below the openings in the mask 122 to a temperature of 160°C or higher, but is insufficient to heat the regions covered by the mask 122. Heating is conducted for a time sufficient to convert the amorphous iron oxide to crystalline $\alpha\text{Fe}_2\text{O}_3$, a mechanism (not shown) being provided to maintain the plastic sheet 114 at the exposure station 120 for a time sufficient to accomplish the conversion step. Generally, about 50 to about 250 microseconds at a temperature of about 160°-1,000°C is sufficient. Heating above 200°C may adversely affect the plastic substrate, but the higher temperature could be used with a sufficiently short flash exposure. If a refractory substrate is used, one could heat up to about the higher temperatures. The mask 122 can be in direct contact with the metal oxide layer to achieve high resolution, but with higher temperatures, the mask can be somewhat off-contact, decreasing heat distortion effects on the plastic albeit with some sacrifice in resolution.

The imaged film is next led through an etching station 126 where an etchant is applied to the layer of metal oxide. The etching station 126 is shown as a housing 128 enclosing a chamber 130 containing hydrogen chloride vapor, but any normal etchant can be used including acid solutions such as hydrochloric acid, hydroiodic acid, hydrobromic acid, phosphoric acid, or the like, such solutions being well known to the art. The use of a vapor phase etchant constitutes a specific embodiment of the present invention and will be discussed

in more detail hereinafter. The etchant is effective in regions of the metal oxide which are still amorphous but leave the crystallized regions virtually intact.

The film containing the metal oxide image is then led through a water bath 131, to dissolve the etch product and from there is led through a heater 132 (e.g., at 100°C, for drying) and then onto a takeup reel 134. The result is a crystalline iron oxide negative mode image of the mask 122 pattern. The image is extremely durable; the iron oxide is harder than chrome and can be used as an archival copy or as a microfilm or microfiche copy. In this regard, we have found that the process provides a very high degree of resolution, as low as 500 line pairs per millimeter, so that ultrafiche copies can be produced.

Referring to FIG. 4, an alternative thermal imaging station is shown. In this embodiment, a laser source 136 provides a laser beam 138 along an optical axis. The laser source 136 may be a gas laser or a solid state laser, such as a ruby rod that is energized by a flash tube, as is well known in the art. The laser beam 138 is directed through an optical lens 140 and reflected from a mirror surface 142 onto the layer of amorphous iron oxide carried by the sheet 114. The optical lens 140 focuses the laser beam 138 to a desired resolution and energy concentration so that the regions of the iron oxide layer exposed to the laser beam are raised above the crystallization temperature. A mechanism (not shown) is provided for pivoting the mirror surface 142 in accordance with a control 144 which also serves to actuate a pulser 146 for energizing the flash tube of the laser device 136 on or off in accordance with the pattern desired to be recorded. The control 144 may include an automated program or a prerecorded magnetic tape having pulses thereon in predetermined relationship, the pulses serving to actuate the pulser 146. If desired, a heater, as shown by the dashed lines 145, can be placed below the sheet 114 to thermally bias the layer of amorphous iron oxide to a predetermined temperature below the crystallization temperature. In such case, the laser beam 138 need only have sufficient energy content to raise the temperature of the iron oxide layer to above the crystallization threshold temperature. Rapidly raising the temperature to a high level is very desirable for high resolution and the laser beam is quite suitable in this regard.

Referring to FIG. 5, another thermal imaging station is illustrated utilizing an electron beam 148 to effect the desired local temperature changes. The electron beam 148 is generated by any mechanism 150 as known to the prior art and as determined by a control 152.

Referring to FIG. 6, there is illustrated a thermal imaging station wherein a hot wire stylus 154 is disposed in contact with the amorphous metal oxide layer carried by the sheet 114. The stylus is heated by an electrical source 156 as determined by a control 158.

Other thermal imaging stations can be utilized and a variety are known to the art. For example, the plastic sheet can be placed in contact with a heat absorbing mask and disposed around a drum in contact with the mask, heated to a level sufficient to crystallize the amorphous metal oxide in regions exposed through the mask, but insufficient to crystallize the covered regions.

Each of the foregoing mechanisms for thermal imaging is used to apply a thermal pattern directly to the

metal oxide surface. Thermal spread is thus minimized, producing high resolution images. However, the process has sufficiently high resolution capability that for many applications a thermal image can be applied through the substrate. Referring to FIGS. 7(a) and (b) there is illustrated the preparation of a photomask wherein the top surface of a thin glass substrate 160, about 60 mils thick, is coated with a layer 162 of amorphous iron oxide, about 2,200 Å thick. A chromium master mask image 164 is placed adjacent the bottom surface of the glass substrate 160, but may alternatively be placed directly on the iron oxide layer 162, and the assembly is exposed through the mask by means of a xenon lamp 166 with sufficient intensity to raise the temperature of the amorphous layer, in exposed regions only, to 160°C or higher, converting the exposed regions to crystalline $\alpha\text{Fe}_2\text{O}_3$. The substrate 160 and iron oxide layer 162 are then subjected to a vapor etch and wash as hereinbefore referred to, or to other etchant such as a concentrated hydrochloric acid solution. The remaining portions of amorphous iron oxide are removed to yield an image 168 in correspondence to the clear pattern of the mask 164. The iron oxide portions are opaque to those spectral regions which are actinic to normal resist materials but sufficiently transparent to yellow-red light to allow observation there-through for alignment purposes. An exemplary photomask can have an oxide thickness of about 2,100 Å, an optical density of about 2 at 420 millimicrons wavelength and an optical density of about 0.5 at 600 millimicrons wavelength.

Referring now to FIGS. 8(a)-(f), there is illustrated a process for preparing a photomask which does not involve the employment of a thermal image but utilizes light exposure of a resist coating and subsequent vapor etching and stripping to form the photomask. Referring initially to FIG. 8(a), a glass substrate 170 is provided with a layer of amorphous iron oxide 172, as referred to in FIG. 7(a). The layer of amorphous oxide 172 is overcoated with a layer 174 of resist material which in this example is a polymer formulation capable of depolymerization or dissolution on exposure to actinic light. Such resists operate in a positive mode but negative mode resists could also be utilized wherein light exposure effects polymerization to make the photoresist less soluble than unexposed regions. The composition of such resists are well known and do not constitute an aspect of the present invention. Examples include orthoquinonediazide such as sold by Shipley under the trade name AZ-1350 (positive mode) and polyvinylcinnamate such as sold by Kodak under the trade name KTRF (negative mode).

Referring to FIG. 8(b), the assembly of substrate 170, amorphous iron oxide layer 172 and resist 174 is next exposed to actinic light 176 through a mask 178 in contact with the resist 174. The assembly is then developed by applying a solvent, such as xylene to remove the dissociated resist areas yielding the structure shown in FIG. 8(c) in which the remaining resist portions constitute an image 180 of the mask 178 pattern.

Referring to FIG. 8(d), the assembly of substrate 170 amorphous iron oxide layer 172 and resist image 180 is subjected to a vapor etching step, as will be described hereinafter in more detail, and is then washed to remove ferric chloride reaction product, leaving a resin coated amorphous iron oxide image 182. The remaining resin 174 is then stripped by application of a deter-

gent or acetone to yield a photomask, as shown in FIG. 8(e) in which an image 182 of amorphous iron 172 is carried by the glass substrate 170. Optionally, the photomask then can be heated to a temperature of 160°C or higher to convert the amorphous iron oxide 174 to crystalline, $\alpha\text{Fe}_2\text{O}_3$ 174' so that the mask is more acid and alkali resistant, optically more dense and physically more durable. Thus, there is provided a novel high resolution mask (about 250 to about 750 line pairs/mm) having properties, as above described, not heretofore appreciated by the art.

Referring now to FIG. 9, there is illustrated apparatus for applying an etchant in vapor form to a layer of amorphous metal oxide. The apparatus includes a housing 184 enclosing a chamber 186 having conical side walls terminating in a neck 188. The neck 188 continues as a conduit 190 connected to receive vapors from a bubbler chamber 192 partially filled with a solution 194 of concentrated hydrochloric acid. An inert gas such as nitrogen is fed from a source 196 thereof through a metering valve 198 and past a manometer 200 into a bubble tube 202 in the chamber. Hydrogen chloride vapors are thus carried through the conduit 190 into the vapor etch chamber 186. Lower portions of the side walls of the chamber are formed cylindrically with opposed openings 206 and 208 and gaskets, such as at 210, to allow a sheet 212 carrying a layer of amorphous metal oxide to be conveyed through the chamber 186.

As the hydrogen chloride vapors contact the amorphous iron oxide, ferric chloride and water are produced, the water falling to the bottom wall 214 of the chamber which is provided with an opening 216 connected to a valve 218 for periodically removing the water. The metering valve 198 is adjusted in accordance with the consumption of the hydrogen chloride. A simplified form of apparatus can be used for batch processing. The apparatus can consist of simply a sealed chamber wherein the objects to be etched are rotatably supported above a concentrated solution of hydrochloric acid, the vaporous atmosphere of hydrogen chloride being sufficient to rapidly etch the amorphous metal oxide.

Vapor etching in accordance with the foregoing provides a very rapid room temperature process, dramatically more rapid than immersion processes in the same acid. Pattern reproduction is excellent and undercutting is minimal. Layers of about 250-10,000 Å can be readily etched by the foregoing process.

Referring now to FIG. 10, there is illustrated another embodiment of the invention wherein a pattern of metal oxide is formed on a separate substrate without requiring any etching step. In this embodiment, iron oxide is deposited on a substrate by means of chemical vapor deposition while the substrate is thermally imaged so as to selectively deposit the iron oxide in accordance with the thermal pattern. The apparatus includes a housing 220 enclosing a chemical vapor deposition chamber 221 and bottom wall 222 supporting a substrate 224 such as a glass plate. The housing 220 includes walls 226 which continue upwardly into a T connected on opposite sides, through metering valves and manometers (not shown), to a source 230 of thermally decomposable metal organic compound and to a source 232 of oxygen or other oxidant.

A metal-organic compound is used which is a precursor to the metal oxide desired to be formed; in this ex-

ample, the compound is iron pentacarbonyl. Other thermally decomposable compounds include iron dodecacarbonyl to produce the iron oxide, molybdenum carbonyl to produce molybdenum oxide, nickel carbonyl to produce nickel oxide, tungsten carbonyl to produce tungsten oxide, chromium carbonyl to produce a chromium oxide, and mixtures thereof to produce a mixed oxide such as iron-nickel oxide, iron oxide-chromium oxide, and the like.

A laser source 234 provides a laser beam 236 which is directed through an optical lens 238 and reflected by a mirror surface 240 into the chamber 221 where it is reflected by another mirror surface 242 onto the surface of the substrate 224. An optically inactive transparent window 246 is located in the wall 226 of the apparatus between the mirror surfaces 240 and 242 to allow the laser beam 236 to pass into the chamber 221 for reflection onto the substrate 224. The laser source 234 is energized by a pulser 248 which is regulated by a control 250. The mirror surface 240 can be pivoted by a mechanism, not shown, which is regulated by the control 250 so that the laser beam 236 can be directed onto the substrate 224 surface in accordance with any desired pattern. The substrate 224 is supported on a heater 252 connected to an electrical supply 256. The heater 252 can be maintained at any temperature which is below the thermal decomposition temperature of the iron pentacarbonyl. A practical lower temperature for the decomposition of iron pentacarbonyl is about 120°C and the heater can be maintained at a temperature below this level but sufficiently high so that the thermal affect of the laser beam in conjunction with the film temperature is sufficient to effect decomposition and deposition of amorphous iron oxide. Alternatively, a laser beam of sufficient intensity can be used so that the heater may be dispensed with. A mirror surface 242 is supported on a cooling unit 258 connected by conduits 260 and 262 to a coolant source 264. The mirror surface 242 is thus cooled to a point sufficient to prevent decomposition thereon of the iron pentacarbonyl, e.g., about 20°C.

One of the housing walls is provided with an aperture 266 connected via a conduit 268 through a trap 270 to an exhaust pump 278 which is adjusted in conjunction with metering of the gaseous components to provide an atmosphere within the chamber 221 of iron pentacarbonyl and oxygen. In operation, the iron pentacarbonyl and oxygen are metered into the chamber 221 forming an atmosphere therein while the laser is actuated in accordance with a desired pattern so that a thermal image is played onto the surface of the substrate 224 effecting decomposition of the vaporous materials to iron oxide directly onto the surface of the substrate in accordance with the thermal pattern.

As above indicated, the temperature of the thermal pattern is sufficient to cause decomposition of the iron pentacarbonyl to iron oxide. Since no etching step is required, this temperature may be above the crystallization temperature of the iron oxide. Accordingly, one can subject the substrate to a localized temperature above 160°C, as high as the substrate material will allow and governed only by questions of practicality. As above indicated, above 600°C, the metal oxide tends to spread; accordingly, a suitable range is about 120°-600°C. Thermal imaging sources other than a laser beam can be utilized, including the sources referred to in FIGS. 3, 5 and 6, with appropriate modifi-

cation to the apparatus. It is preferred that the heat source be disposed so that the thermal image is applied directly to the surface of the substrate onto which the iron oxide is intended to be deposited, enabling finer resolution.

Referring back to FIG. 2, as previously indicated, still another embodiment of this invention relates to an improved sputtering process for producing a layer of amorphous metal oxide. Specifically, the improvement involves the discovery that when sputtering is conducted in an atmosphere of carbon monoxide, carbon dioxide and inert gas, higher throwing power and a better deposition rate are obtained. In accordance herewith, the atmosphere consists, by volume of about 5-40 percent carbon monoxide, about 20-80 percent carbon dioxide, about 20-70 percent inert gas, and 0 to about 10 percent oxygen. Inert gases which can be used include argon, nitrogen, neon, krypton and helium, argon being preferred. Conducting sputtering at 6,000 volts and 1 kilowatt under a pressure of 7mTorr, and with 10 percent argon and 90 percent carbon dioxide, a layer of metal oxide was formed 700 A thick in 120 minutes. Using the same processing conditions but an atmosphere by volume of 50 percent carbon monoxide, 10 percent carbon dioxide and 40 percent argon, a film thickness of iron oxide of 2,600 A was obtained in 150 minutes.

The processes of the present invention as illustrated by FIGS. 3-7 can be applied to any metal oxide, such as the oxides of nickel, chromium and silicon, having both amorphous and crystalline phases.

Various modifications, changes, alterations and additions can be made in the present methods, their steps and parameters. All such modifications, changes, alterations and additions as are within the scope of the appended claims form part of the present invention.

We claim:

1. A process for forming an optical mask defined by a selected pattern of ferric oxide on a substrate, comprising:
 - depositing on said substrate, a uniform layer of amorphous ferric oxide;
 - heating selected regions only of said layer to a temperature of at least 160°C to convert said selected regions of ferric oxide to a crystalline form while leaving remaining regions in an amorphous form to obtain a desired pattern defined by said crystalline ferric oxide and amorphous ferric oxide regions; and
 - then selectively removing only said remaining regions of amorphous ferric oxide.
2. The process according to claim 1 in which said substrate is formed of glass.
3. The process according to claim 1 in which said substrate is a plastic sheet.
4. The process according to claim 1 in which said step of selectively removing only said remaining regions of amorphous ferric oxide comprises applying an etchant directly to both said selected regions and remaining regions for a time sufficient to convert said remaining regions of amorphous ferric oxide to a soluble product, while leaving said selected regions substantially intact, and removing said soluble product.
5. The process according to claim 4 in which said etchant is applied in the form of a vapor.
6. The process according to claim 5 in which said etchant is an inorganic acid vapor.

11

12

7. The process according to claim 1 in which said depositing step comprises applying a thermally decomposable iron-organic compound precursor of said ferric oxide in combination with an oxidant therefor to a surface of said substrate while heating said substrate at a

temperature less than 160° C but sufficient to thermally decompose said precursor to said amorphous ferric oxide.

* * * * *

5

10

15

20

25

30

35

40

45

50

55

60

65