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(54) METHOD FOR FABRICATING PHOTOMASKS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, 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 techniques for the fabrication of photomasks such as for use in photoresist or photolithographic processes.

The need for processing localized areas in microcircuit technology has generated a technology directed to the efficacious preparation and utilization of masks to define diffusion, evaporation and related operations. The use of well-known photomask processes for attaining this end has been universally applied in the microcircuit processing industry with varying degrees of success. Typically, such techniques involve the preparation of a suitable photomask defining the pattern of interest and the use of this mask to transfer an image to a photoresist pattern.

Until recently, it had been conventional to form the mask pattern in a photographic emulsion. In numerous applications, the masks so formed are used repetitively and due to the inherent softness of photographic emulsions deteriorate rapidly due to abrasion. Accordingly, workers in the art turned their attention toward the development of masks manifesting greater durability.

This end was attained by use of hard inorganic opaque materials, typically metal on glass. A popular mask falling within the scope of this class is prepared by evaporating chromium upon a glass substrate and thereafter forming the desired pattern in photoresist on this surface. Thereafter, the

pattern is etched into the chromium. These masks have been found to very durable and manifest a potentially higher resolution capability than photographic emulsion masks, such being attributed both to the thinness of the deposited metal and the lack of grain and thinness in the image defining photoresist. Although satisfactory from many standpoints, such photomasks are opaque and reflect a high percentage of incident radiation including the light normally used during alignment of the photomask with respect to patterns previously imposed on the substrate. Both the opacity and reflectivity contribute to the difficulty of carrying out this alignment, especially on equally reflective metallized substrates. These masks also reflect the light normally used to expose the photoresist after alignment, so creating a problem of fringing with the concomitant loss of resolution at the edges of the pattern due to multiple reflections between the substrate and the photomask.

Recently, these limitations were successfully overcome by reactively sputtering a hard inorganic compound upon a glass substrate and etching the deposited layer to form the desired pattern. A number of transition metal oxides were found satisfactory for this purpose, that is, transparent to the light used by the operator to align the photomask with the substrate and highly absorbing at the wavelength used to expose the photoresist on the substrate to be processed. Unfortunately, these masks have not proven to be completely acceptable in that rate of etching with reagents compatible with photolithographic processes is not readily controllable due to the crystallinity of the sputtered films, so prompting continued investigation.

In accordance with the present invention there is provided a method for the fabrication of a photomask comprising the steps of depositing a layer of iron oxide upon a sub-

strate and etching said layer to form the desired pattern, wherein the iron oxide layer is formed by vapour deposition by thermally decomposing an iron compound in an oxidizing ambient.

In accordance with the preferred embodiment of the present invention, the above prior art limitation is effectively obviated by controlling the morphology of the deposited film. Briefly, this end is attained by depositing a layer of iron oxide upon a heated substrate member by chemical vapour deposition techniques in a predominantly oxidizing ambient.

The resultant films are readily etched in solvents compatible with conventional photoresist processing material.

For a better understanding of the invention, reference is made to the accompanying drawing in which the single figure is a schematic representation of apparatus used in the preferred embodiment of the present invention.

In the figure there is shown a glove box 11 within which there is disposed a deposition chamber 12, positioned upon a hot plate 13, and connected by means of T conduit 14 to a chamber 15 capable of holding a source solution 16. Conduit 14 additionally includes an inlet 17 which may be used for the introduction of an oxidizing media thereto during the operation of the process. Chamber 15 also includes an inlet 18 for the introduction thereto of a carrier gas.

In the operation of the process, a suitable substrate, which may be ordinary glass or any well-known material which is transparent, over the range of 3000 to 6000 Å, is inserted within chamber 12 and an iron compound introduced into chamber 15. This may conveniently be iron pentacarbonyl, although other iron compounds manifesting a high vapour pressure at room temperature and a low temperature of thermal decomposition are considered suitable. Thereafter, a carrier gas is bubbled through the source solution, so resulting in the transport of the source material in vapour form to deposition chamber 12. The carrier gas employed may be selected from among any of the well-known inert gases such as argon, krypton, xenon, helium, carbon dioxide, nitrogen, et cetera. Deposition chamber 12 including the substrate member of interest is next heated to a temperature preferably within the range of 100 to 160°C and a quantity of oxygen sufficient to form iron oxide admitted to the chamber (either as an impurity in the inert gas or from an independent source), so resulting in the decomposition of the iron pentacarbonyl and deposition upon the surface of the substrate of a layer of iron oxide manifesting the botryoidal morphology. Studies have revealed that the use of temperatures less than the noted minimum of

100°C fail to result in satisfactory decomposition of the iron compound and hence result in inadequate deposition upon the surface of the substrate. Temperatures appreciably in excess of 160°C have been found to result in the formation of highly crystalline film typically obtained by sputtering in accordance with the prior art procedure alluded to hereinabove, such crystalline film being capable of being etched only with great difficulty.

As indicated, it is necessary for an oxidizing ambient to be employed. The term oxidizing ambient includes impurities in inert gases, or oxygen or a mixture of oxygen and water vapour mixed with the iron pentacarbonyl carrier gas mixture. It has been theorized that iron pentacarbonyl reacts with oxygen upon a reactive surface. Water and other molecular species which can be strongly absorbed on the reactive surface suppress the decomposition and consequent film formation. Nonetheless, increasing temperatures free the surface from absorbed water and lead to higher deposition rates. Accordingly, it is evident that the primary purpose of utilizing oxidizing media is to permit greater control of the deposition rate and to assure the formation of iron oxide.

The volume of carrier gas or carrier gas-oxidizing gas mixture is dictated by considerations relating to the desired rate of deposition. It has been found convenient to operate at flow rates of carrier gas within the range of 20 to 80 cubic centimeters per minute. However, it will be understood that such range is not absolute and variations may be made. Similarly, flow rates of comparable range may be used with respect to the oxidizing medium when employed. Deposition is continued for a time period calculated to produce the desired thickness for photomask purposes, typically within the range of 1000 to 2000 Å. The resultant iron oxide film is found to be selectively absorbing, typically exhibits less than one percent transmission at a wavelength of 4000 Å and exhibits more than 50 percent transmission at 5890 Å, the wavelength of a sodium lamp which is commonly used to facilitate alignment.

Examples of the present invention are set forth below:—

EXAMPLE I

A film of iron oxide approximately 1500 Å in thickness was deposited upon a 2×2 inch glass substrate member approximately 60 mils in thickness by the thermal decomposition of iron pentacarbonyl. The procedure involved adding 50 cubic centimeters of iron pentacarbonyl to source chamber 15 in an apparatus similar to that shown in the Figure. Thereafter, argon was introduced into the source chamber at a rate of 80 cubic

centimeters per minute and bubbled through the iron pentacarbonyl, thereby resulting in its transport to deposition chamber 12 within which was contained the substrate member. The substrate member was heated by means of a hot plate to a temperature of 125°C for a time period of three minutes, so resulting in the decomposition of the iron pentacarbonyl and the deposition upon the substrate of a layer of iron oxide.

Subsequent to the deposition of the iron oxide film, it was coated with a commercially available photoresist, exposed to a light pattern and developed by conventional commercial techniques. Next, an aqueous solution of hydrochloric acid (typically 5.8 molar at 50°C) was employed to etch the pattern in the iron oxide film. Etching was completed within 20 seconds.

EXAMPLE II

The procedure of Example I was repeated with the exception that deposition was effected at 105, 115, 130, 140 and 150°C. The time required to effect etching was an inverse function of deposition temperature and ranged from about 15 seconds at 105°C to 45 seconds at 150°C. It will be appreciated by those skilled in the art that variations in the temperature of the etchant will result in modification of etching rate.

For comparative purposes, an iron oxide photomask of comparable thickness to that described in the examples above obtained by reactive sputtering techniques was subjected to etching in the described manner and the rate of etching was found to be unreasonably long.

Studies of the resultant films reveal that, from the standpoint of scratch resistance, they are as good or better than the chromium masks. The described films were also found

to be superior to chromium films in that they are essentially pinhole free.

WHAT WE CLAIM IS:—

1. A method for the fabrication of a photomask comprising the steps of depositing a layer of iron oxide upon a substrate and etching said layer to form the desired pattern, wherein the iron oxide layer is formed by vapour deposition by thermally decomposing an iron compound in an oxidizing ambient.

2. A method in accordance with claim 1, wherein said iron compound is iron pentacarbonyl.

3. A method in accordance with claim 2, wherein said iron pentacarbonyl is decomposed in a mixture of an inert and oxidizing media.

4. A method in accordance with claim 2 or 3, wherein said substrate is heated to a temperature within the range of 100 to 160°C.

5. A method in accordance with claim 3, wherein said oxidizing media is oxygen.

6. A method in accordance with claim 3, wherein the inert medium is argon.

7. A method for the fabrication of a photomask, substantially as hereinbefore described with reference to the accompanying drawing.

8. A method for the fabrication of a photomask, substantially as hereinbefore described with reference to Example I or II.

9. A photomask prepared by the method according to any one of the preceding claims.

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