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THIN FILMS OF ALPHA Fe_2O_3 AND METHOD OF FORMING

Filed June 29, 1970

2 Sheets-Sheet 1

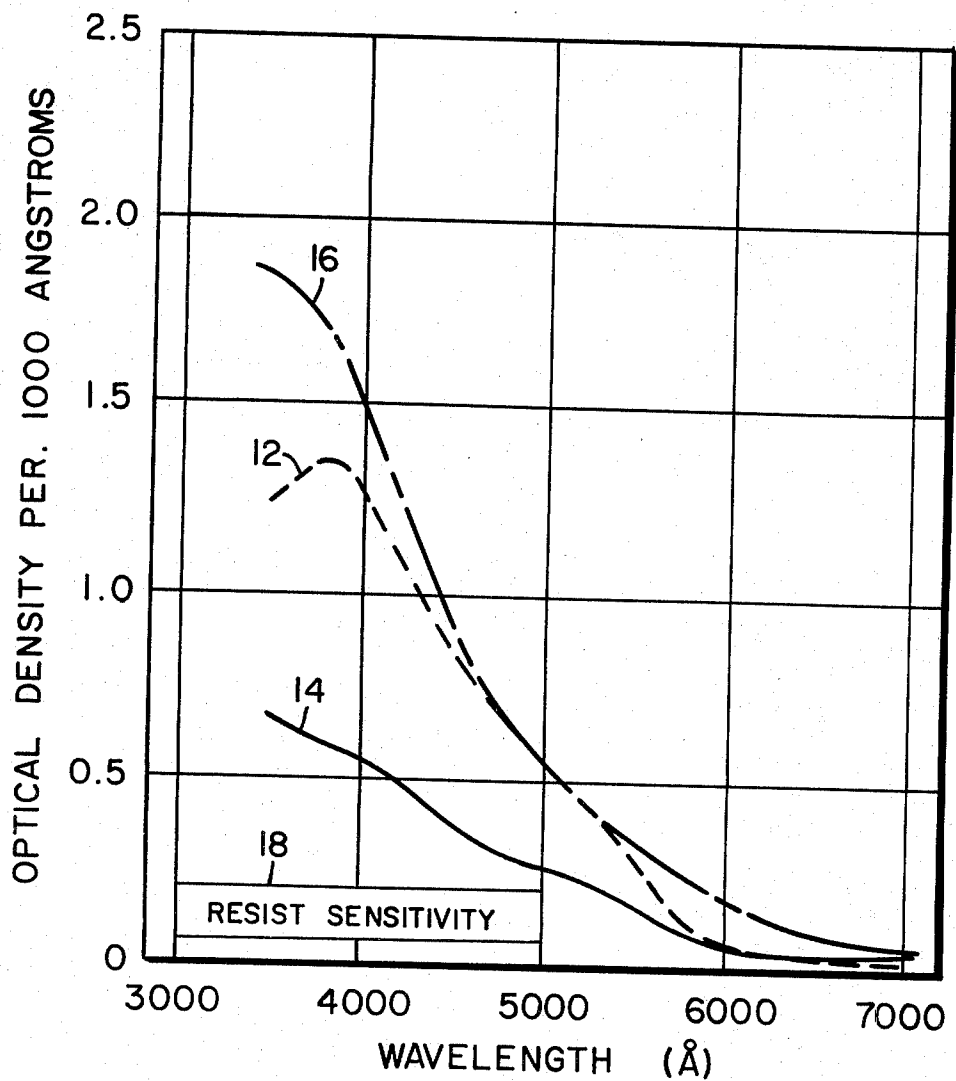


Fig. 1

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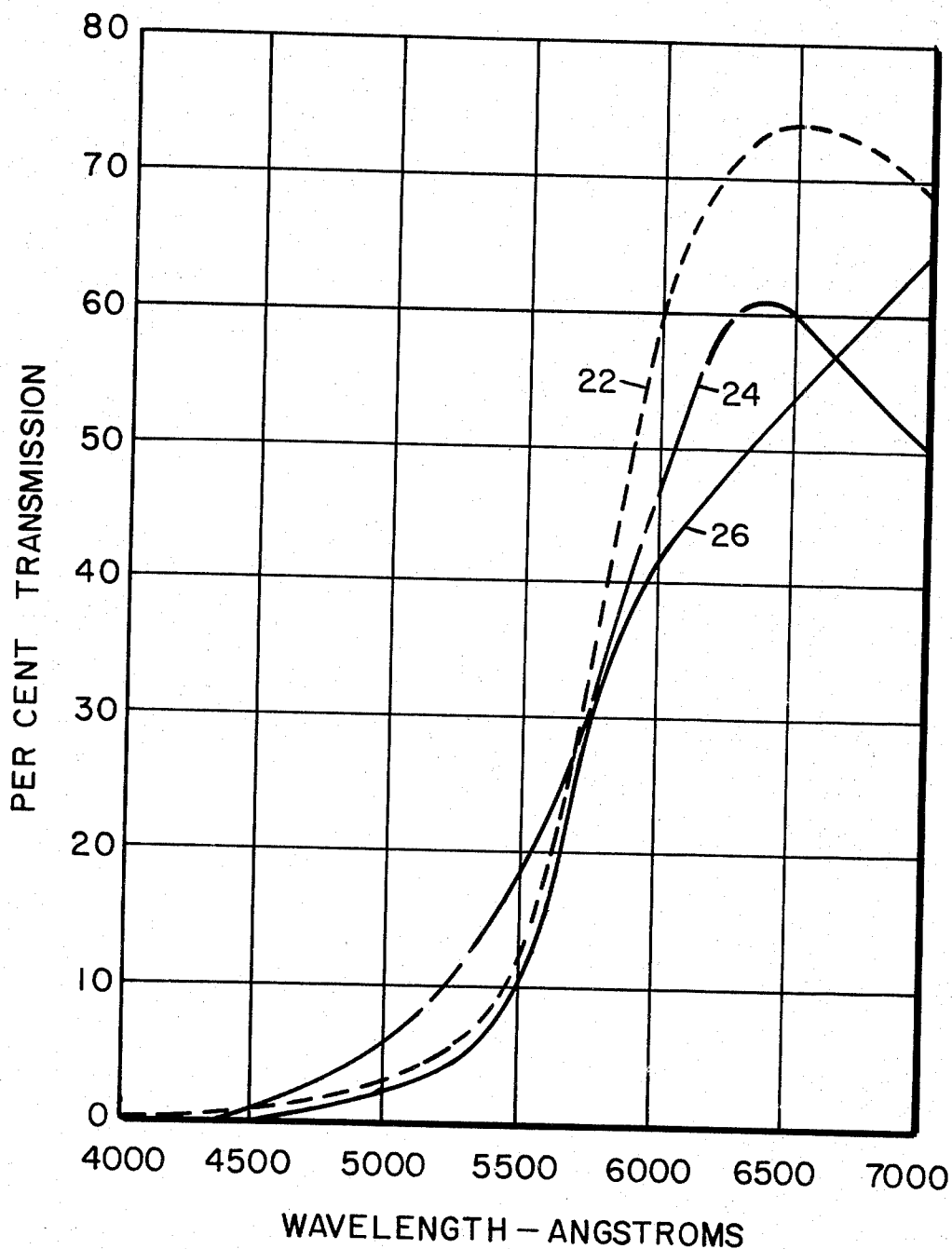


Fig. 2

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3,695,908 THIN FILMS OF ALPHA Fe_2O_3 AND METHOD OF FORMING

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10 Claims

ABSTRACT OF THE DISCLOSURE

A method of making thin films of alpha Fe_2O_3 by applying to an unheated substrate a film of a highly permeable non-crystalline form of iron oxide by subjecting the substrate to vapor produced by evaporating a source of iron oxide at a pressure less than 10^{-4} torr and thereafter heating the deposited film in an oxidizing atmosphere at a temperature of at least 425°C . for a period of time sufficient to convert it to a stable, crystalline film of hematite, alpha Fe_2O_3 . A film of hematite so formed having a thickness in the range of 1000 Å–3600 Å. on a substrate of transparent, alkali-free glass may be patterned to form a microcircuit mask having increased transmission in the visible portion of the spectrum.

BACKGROUND OF THE INVENTION

The invention relates to a method of making thin films of alpha Fe_2O_3 . The optical, electrical, magnetic properties of thin iron oxide films are a function of both the crystalline state and grain size thereof, these parameters being determined by the oxidation state and the method of film formation. These films are usually prepared by such methods as decomposition of an iron compound such as ferrocene or iron carbonyl at or near the surface of a hot substrate, reactive sputtering of an iron cathode in an oxygen-argon atmosphere or evaporating metallic films of iron in a vacuum followed by an oxidizing heat treatment of the film deposit. Usually, an attempt is made to obtain the desired oxide properties in the deposition operation. If that is not possible, the deposition operation is followed with a high temperature treatment in a reactive atmosphere. Since the above-described deposition operations produce a stable crystalline state in the oxide, the second operation must be relatively severe to be effective. Moreover, pure iron films formed by a vacuum deposition process require temperatures well in excess of 600°C . for complete oxidation to occur.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method of forming iron oxide, alpha Fe_2O_3 , using lower temperatures and/or shorter periods of heat treatment than those of the heretofore mentioned film formation techniques.

In accordance with the present invention, a thin film of iron oxide, alpha Fe_2O_3 , is formed by the following method. An unheated substrate is disposed in a vacuum chamber. A film of a black, highly permeable non-crystalline form of iron oxide is applied to the substrate by subjecting the same to vapor produced by evaporating a source of iron oxide at a pressure less than 10^{-4} torr. Thereafter, the film so formed is heated in an oxidizing atmosphere at a temperature of at least 425°C . for a period of time up to one hour which is sufficient to convert the initially deposited film to a stable, crystalline film of hematite, alpha Fe_2O_3 . Iron oxide films produced by the method of this invention possess unique optical transmission properties. These films exhibit greater optical transmission in the visible portion of the spectrum than that which is exhibited by iron oxide films pro-

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duced by other methods, the thickness of each film being such that all films exhibit a similar opacity to ultraviolet light. These optical transmission properties make iron oxide films produced by the method of this invention particularly useful for microcircuit masks which consist of thin patterned films of masking material disposed on transparent substrates.

In well known processes for forming patterns in photo-sensitive resists, microcircuit masks are disposed with the image side thereof in direct contact with a resist coated wafer. The use of such masks will be briefly described in connection with the exposure of negative resists; however it is obvious that positive resists may also be selectively exposed through the use of masks. Illumination of the proper spectral distribution is directed at the upper surface of the mask and passes through the clear areas thereof to impinge on the resist. The exposed areas of the resist become insoluble and remain behind on development, protecting the coated areas during etching. The final microcircuit product is produced by a succession of etching, diffusion and metallizing steps utilizing various patterned masks. Since device fabrication employs about 6–12 masks, each of which must register with the preceding pattern on a semiconductor wafer, and since defects in the final product are generally the sum of the flaws in the individual masks, it is obvious that the masks must be of high quality and that each mask be properly aligned in order to obtain economical yields of semiconductor devices. The alignment of the mask pattern with that on the semiconductor wafer is the most painstaking operation in the fabrication of a semiconductor wafer. This step becomes even more difficult with those masks having a large proportion of opaque area, i.e., masks having only small openings available for viewing the underlying structure. Orientation of such masks to the necessary close tolerance becomes a tedious, time-consuming task, especially when the masking film is a material such as chrome which is opaque to visible light. Since iron oxide films formed in accordance with the method of this invention exhibit the aforementioned optical transmission properties, microcircuit masks made therefrom are relatively simple to align.

Therefore, another object of the present invention is to provide a method of making iron oxide films having increased transparency in the visible portion of the spectrum. A more specific object is to provide a method of forming patterned iron oxide films for use as microcircuit masks.

Other objects and advantages of the present invention will become apparent upon consideration of the following description as read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of optical density per 1000 Å. of film thickness vs. wavelength for films of iron oxide, alpha Fe_2O_3 , formed by three different methods.

FIG. 2 is a graph of transmission vs. wavelength for iron oxide films formed by different methods, all films having 0.032% transmission at 4000 Å.

DETAILED DESCRIPTION

In accordance with the present invention iron oxide is evaporated from an iron oxide source, which may consist of Fe_2O_3 powder, Fe_3O_4 powder or mixtures thereof, onto an unheated or cooled substrate in a conventional vacuum evaporation apparatus at pressures lower than 10^{-4} torr. The source of heat for evaporating the iron oxide source material can be resistive filaments of refractory metals or electron-beam bombardment of the source material. Regardless of which of the above source powders is used, the resultant film is a reduced oxide,

which is black in appearance, gray in transmission and metallic in conductivity. This power-evaporated film oxidizes readily in air at temperatures as low as 425° C. For example, a one micron thick film will oxidize in one hour at 425° C. and will oxidize in five minutes at 550° C. Films thicker than about 10 microns would require much more severe heat treatment and are therefore not within the scope of the present invention. Also, if greater percentages of oxygen were added to the oxidizing atmosphere, a lower temperature would be required to completely oxidize the film in a given period of time. The as-deposited film, which X-ray analysis characterizes as being slightly indicative of gamma iron oxide, apparently has a very open structure which readily lends itself to adjustment to almost any oxidation state by heating in the proper environment.

The vacuum deposition operation is followed by treatment of the film at an elevated temperature in an atmosphere with controlled percentages of oxygen present. The film deposition method produces a film which is essentially a highly permeable and non-crystalline form of iron oxide having physical appearance characteristics similar to FeO, the lowest oxidation state of iron. The subsequent treatment of that film in a reactive atmosphere at elevated temperatures both adjusts and fixes the oxidation and crystalline states of the resultant film. Due to the nature of the deposited film, the heat treatment may be performed at lower temperatures and/or for shorter periods of time than has been heretofore possible. This feature is particularly advantageous when the film is to be formed on a substrate that should not be subjected to high temperatures. For example, a glass substrate, which is required in the formation of microcircuit mask blanks, may become soft and begin to react with the film at temperatures in excess of 600° C. Moreover due to differences in the thermal coefficients of expansion of the iron oxide film and the substrate, the film could begin to flake off during cooling if the heat treatment temperature were too high.

In accordance with one embodiment of the present invention, a film of Fe₂O₃ is formed on a glass substrate for use as a microcircuit mask blank. Substantially alkali-free glass is preferred since it permits the formation of a better film, the use of such glass preventing a high incidence of pinholes and other deformations of the film which especially occur during the heat treatment portion of the process. By the use of the term, "substantially alkali-free glass substrate," is mean those substrates of glass material typically containing no more than about 0.25% by weight of alkali compounds as compared with the total weight of the material. One of the commercially available glass compositions which meets the above requirements is made from a batch consisting of the following oxides: SiO₂—50%, BaO—25%, Al₂O₃—10% and B₂O₃—15%.

Also, numerous processes well known to those skilled in the art can be employed to remove quantities of alkali compounds from alkali containing glasses. Often, for example, it is possible to remove such compounds from surface portions of otherwise alkali containing glass substrates by using cleaning agents which leach alkali from surface layers. In such cases, alkali containing glasses are within the meaning of the term, "substantially alkali-free glass," as used in this disclosure, where the alkali compounds at or near the surface of the substrate are not greater than 0.25% by weight of the total weight of glass in that region. The region of criticality is that region near the iron oxide filmed surface of the substance in which the presence of substantial quantities of alkali compounds would produce material alkali contamination of the film as a result of the particular heat treatment temperature employed.

The surface of the substrate on which the film is to be deposited should be reasonably flat and smooth. Prior

to film formation, the substrate surface should be thoroughly cleaned. In accordance with a particular effective cleaning process, a glass substrate is first soaked in a common laboratory or household detergent at room temperature for five minutes or more. Next, the plate is swabbed with cotton to remove particulate matter, and thereafter subjected successively to three separate one minute rinses in distilled deionized water to eliminate water spot formations and liquidous surface acidity. The plate is then subjected to ultrasonic agitation in a distilled deionized water bath for about five minutes, or more. Thereafter, the plate is again rinsed in distilled deionized water to remove any surface matter which may have been collected on the plate during the foregoing ultrasonic agitation step.

The plate is blown dry with filtered clean dry air to remove water droplets and spots. A conventional vapor degreaser is thereafter used to rinse away any remaining water from the plate with isopropyl alcohol vapor. Finally, the plate is baked in clean filtered dry air for about thirty minutes or more in a temperature range between about 180° C. and 200° C. In the foregoing manner, surface contamination of the plate is substantially reduced thereby eliminating a possible source of film defect formation.

The cleaned substrate is disposed in a conventional vacuum evaporation chamber, and a film is formed by electron beam evaporation of a pellet of 50% Fe₂O₃ powders and 50% Fe₃O₄ powders at a pressure of 10⁻⁵ torr. This mixture of iron oxide powders is preferred to the use of Fe₂O₃ powder alone or Fe₃O₄ powder alone since it reduces the violence of the reactions occurring during melting in the evaporation boat which can result in the emission of large particles of powder from the source material. The mixture of Fe₂O₃ powders and Fe₃O₄ powders provided a much smoother evaporation process.

The resultant film is a black, highly permeable non-crystalline form of iron oxide physically similar to FeO. This film is then subjected to heat treatment in air at a temperature of 550° C. for five minutes. The result is a highly crystalline film of hematite, alpha Fe₂O₃. While being oxidized to Fe₂O₃, the film may grow by a factor of about 40% in thickness, becoming definitely crystalline hematite.

The optical characteristics of the resultant film of alpha Fe₂O₃ are particularly suitable for microcircuit mask applications when film thickness is between 1000 Å. and 3600 Å. The graph shown in FIG. 1 illustrates the optical density per 1000 Å. vs. wavelength for iron oxide films formed by various processes. Curve 12 relates to a film which is formed in accordance with the above-described process. Curve 14 relates to a film formed by the fuming process whereby chemical vapors from such source materials as iron carbonyl or ferrocene are carried by an inlet gas to a hot substrate where the vapors decompose and form an iron oxide film. Curve 16 relates to a film produced by the RF sputtering technique disclosed in my co-pending U.S. patent application Ser. No. 50,670 entitled "Microcircuit Mask and Method" filed on even date herewith.

Box 18 illustrates the band of light to which common photosensitive resists are sensitive. This graph indicates that the RF sputtered films are more opaque to ultraviolet light than films deposited by other methods, but films produced by the method of this invention have a much lower optical density in the visible portion of the spectrum. Moreover, a comparison of iron oxide films formed by each of these three methods reveals that films formed in accordance with the method of this invention are more transparent in the visible portion of the spectrum provided that film thicknesses are such that all films provide similar opacity to ultraviolet light. This fact is clearly evident from the graph in FIG. 2 wherein transmission is plotted as a function of wavelength for iron oxide films deposited by different methods. Curve 22 relates to a film deposited

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in accordance with the method of this invention, curve 24 relates to an RF sputtered film and curve 26 relates to a chemically fumed film. The thicknesses of the films is such that all films have about 0.032% transmission, or an optical density of about 3.5, at 4000 Å., which is in the middle of the photoresist exposure range of interest. At wavelengths greater than about 5750 Å. the mask produced in accordance with this invention provides significantly more transmission than the other masks. The RF sputtered mask provides slightly more transmission at wavelengths between about 4500 Å. and 5750 Å.; however, this effect is diminished by two factors. First, the incandescent light source utilized in the process of aligning microcircuit masks provides a much greater light output at wavelengths above 5750 Å. than it does below this wavelength. Also, a filter is used in conjunction with the incandescent alignment light to absorb resist exposing wavelengths below 5000 Å. Thus, for films which provide similar opacity to ultraviolet light, the evaporated film of this invention transmits substantially more visible light which can be used for alignment purposes.

After the film of alpha iron oxide is deposited on the glass substrate, the film can be patterned in accordance with well known techniques, one of which is disclosed in U.S. Patent application Ser. No. 50,668 entitled "Transparent Iron Oxide Microcircuit Mask" filed on even date herewith in the name of Edward M. Griest. Briefly, in accordance with this method, a layer of a photosensitive resist is applied to the surface of the iron oxide film and is baked to improve its adherence and quality. Thereafter, the layer of photoresist is suitably masked to avoid exposure of selected portions thereof to ultraviolet light. A mercury vapor lamp of the type conventionally used in photoresist exposure work is employed to expose selected portions of the photoresist layer through the mask. Thereafter the mask is removed and the soluble portions of the photoresist layer are removed in a conventional developer solution such as trichloroethylene, or the like. The remaining insoluble portions of the photoresist layer, being unaffected by the developer solution, remain adhered to the plate to protect selected portions of the iron oxide film during a following acid etching step.

The iron oxide microcircuit mask pattern is formed by immersing the unit so formed in any suitable iron oxide etchant such as hydriodic acid to remove exposed portions of the iron oxide film. After the etching action is completed, the protecting mask of photoresist is removed, leaving a transparent microcircuit mask.

In accordance with conventional practice, transparent microcircuit masks are aligned face down with a pattern or other idicia carried by a semiconductor body under visible light passing through the pattern carried by the transparent mask. Coarse alignment of the mask with the semiconductor body may be obtained by providing guides or alignment surfaces which contact both the semiconductor body and the mask. After the mask has been aligned with the semiconductor body, the photoresist carried by the semiconductor body is exposed to ultraviolet light which passes from a suitable source through the mask. After the photoresist carried by the semiconductor body has been exposed in accordance with the pattern carried by the mask, the semiconductor body can be processed in the conventional manner to provide a plurality of chips or dies, each of which carries an integrated circuit of other semiconductor device. Since a mask made from a blank resulting from the previously described method passes a greater amount of visible light than masks made from iron oxide films produced by other methods, this mask can be more easily and quickly aligned.

I claim:

1. A method of forming a thin film of iron oxide, alpha Fe_2O_3 , comprising the following steps:

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providing a substantially alkali-free glass substrate, cleaning the surface of said substrate to substantially remove foreign contaminants, disposing said substrate in a vacuum chamber in an unheated condition,

disposing in said vacuum chamber a source of iron oxide selected from the group consisting of Fe_2O_3 powder, Fe_3O_4 powder and mixtures thereof, applying to the surface of said substrate a film of a black, highly permeable non-crystalline form of iron oxide by subjecting said substrate to vapor produced by evaporating said source of iron oxide at a pressure less than 10^{-4} torr, and

heating the film so formed in an oxidizing atmosphere at a temperature between 425°C . and 550°C . for a period of time between one hour and five minutes which is sufficient to convert the initially deposited film to a stable, crystalline film of hematite, alpha Fe_2O_3 .

2. A method in accordance with claim 1 wherein said source of iron oxide comprises a mixture of Fe_2O_3 powder and Fe_3O_4 powder.

3. A method in accordance with claim 1 wherein said source of iron oxide comprises substantially equal amounts of Fe_2O_3 powder and Fe_3O_4 powder.

4. A method in accordance with claim 1 wherein said oxidizing atmosphere is air.

5. A method of making a transparent microcircuit mask comprising the step of:

providing an unheated, substantially alkali-free glass substrate that is substantially transparent to visible and ultraviolet light,

cleaning the surface of said substrate to substantially remove foreign contaminants,

applying to the surface of said substrate a film of a black, highly permeable, non-crystalline form of iron oxide by subjecting said substrate to a vapor produced by evaporating a source of iron oxide selected from the group consisting of Fe_2O_3 powder, Fe_3O_4 powder and mixtures thereof at a pressure less than 10^{-4} torr,

heating the film so formed in an oxidizing atmosphere at a temperature between 425°C . and 550°C . for a period of time between one hour and five minutes which is sufficient to convert the initially deposited film to a stable, crystalline form of hematite, alpha Fe_2O_3 , the thickness of said film of alpha Fe_2O_3 being between 1000 Å. and 3600 Å., and

forming a pattern in said film of alpha Fe_2O_3 by removing selected portions thereof.

6. A method in accordance with claim 5 wherein said source of iron oxide comprises a mixture of Fe_2O_3 powder and Fe_3O_4 powder.

7. A method in accordance with claim 6 wherein said oxidizing atmosphere is air.

8. The article produced by the method of claim 5.

9. A method in accordance with claim 7 wherein said source of iron oxide comprises substantially equal amounts of Fe_2O_3 powder and Fe_3O_4 powder.

10. In a transparent mask for use in the photographic exposure of a photosensitive resist carried by a body, said mask being of the type comprising a glass substrate having at least one smooth surface, said substrate being substantially transparent to visible and ultraviolet light, and a patterned film of masking material disposed on said planar surface, said masking material being characterized in that it comprises a film of iron oxide, alpha Fe_2O_3 , formed by the method comprising the following steps

disposing said substrate in a vacuum chamber,

disposing in said vacuum chamber a source of iron oxide selected from the group consisting of Fe_2O_3 powder, Fe_3O_4 powder and mixtures thereof,

applying to said substrate a film of a black, highly

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permeably non-crystalline form of iron oxide by subjecting said substrate to a vapor produced by evaporating said source of iron oxide at a pressure less than 10^{-4} torr,

heating the film so formed in an oxidizing atmosphere 5
at a temperature of at least 425° C. for a period of time up to one hour which is sufficient to convert the initially deposited film to a stable, crystalline form of hematite, α Fe_2O_3 , the thickness of said film of α Fe_2O_3 being between 1000 A. and 10
3600 A., and

forming a pattern in said film of α Fe_2O_3 by removing selected portions thereof,

said film of α Fe_2O_3 providing increased transmission 15
in the visible portion of the spectrum at wavelengths greater than about 5750 A. for a given optical density in the ultraviolet portion of the spectrum so that said resist-coated body can be relatively easily viewed through said iron oxide film and so that said photosensitive resist

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can be exposed to ultraviolet light in accordance with the pattern of said iron oxide film.

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117—33.3, 54, 106 R, 124 A