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MANUFACTURING IN-PROCESS CONTROL AND MEASURING TECHNIQUES
FOR SEMICONDUCTORS SURFACE ETCHING
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FIG. 2

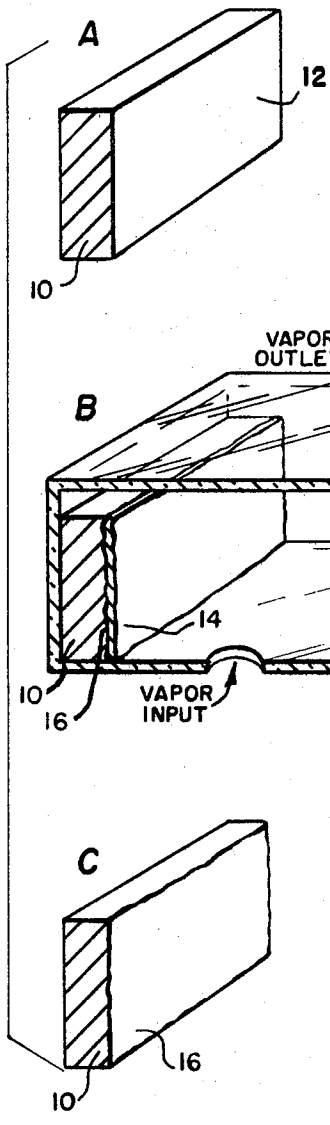


FIG. 1

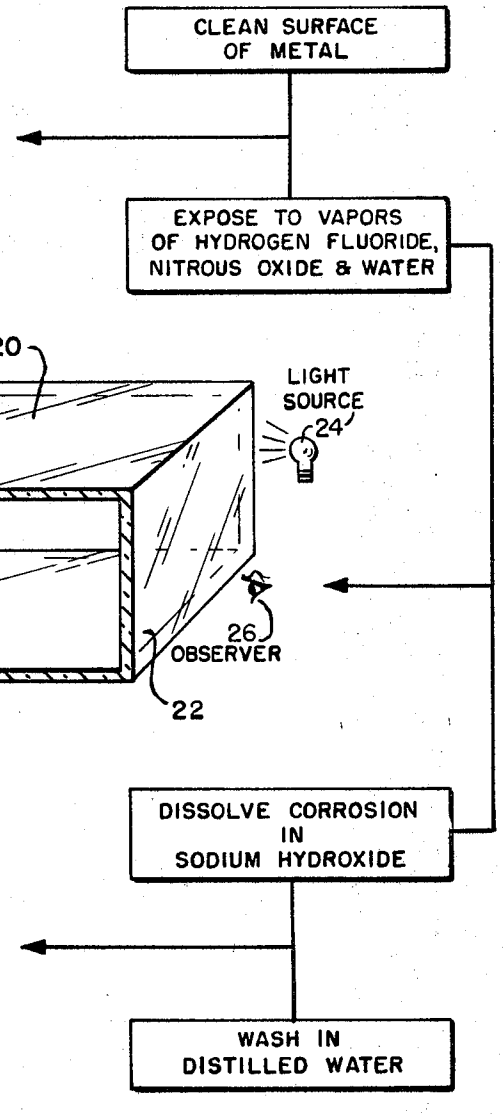
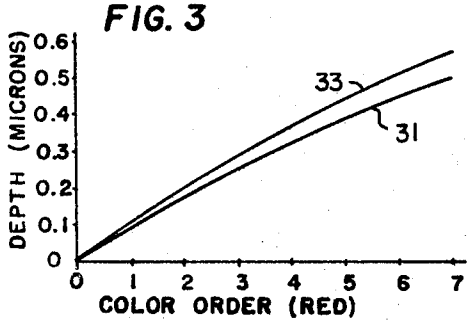


FIG. 3



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MANUFACTURING IN-PROCESS CONTROL AND MEASURING TECHNIQUES FOR SEMICONDUCTORS SURFACE ETCHING

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U.S. Cl. 156—17 7 Claims

ABSTRACT OF THE DISCLOSURE

This is a method for controlling the depth of an etch in a metallic surface such as that of a semiconductor. The etch is produced by corroding the surface of the semiconductor with an atmosphere of hydrogen fluoride, nitrous oxide and water vapors, and removing the corrosion layer. The depth of the etch is proportional to the thickness of the corrosion layer. The actual, in-process control of the ultimate depth of the etch is achieved by observing the interference-pattern colors reflected, by the corroded surface layer, from a source of incident, white light. The interference-pattern colors change as the corrosion layer on the surface increases and the process is terminated when a given color—or number of cycles of color—indicate the correct thickness. The corrosion layer is removed from the metal by a wash of dilute alkaline solution such as sodium hydroxide, leaving the surface etched to the correct depth.

This invention relates to etching processes and particularly to low-temperature, corrosive, vapor processes for producing an etch in semiconductor materials. More particularly this invention relates to an in-process method for controlling the depth of the etch produced by a low temperature, corrosive vapor.

A typical, low-temperature, vapor etching process of the ytpe that would be applicable here is taught in my copending application, Ser. No. 564,705 for a "Corrosive Vapor Etching Process" filed July 12, 1966. This process includes the steps of cleaning the surface of a metallic sample; exposing the surface of the metallic sample to vapors of hydrogen fluoride and nitrous oxide for a given time at room temperature to corrode the surface; dissolving the layer of corrosion from the surface of the metallic sample in a wash of dilute alkaline solution, such as sodium hydroxide, for a given time at room temperature; and washing and drying the resultant, etched surface.

This is a very simple and effective method of producing an etch but, as in all etching processes, there is the problem of how to obtain the precise depth of etch required for any given purpose. The problem exists because there are several variables in any etch process and, in this particular vapor etching process, the temperature, the pressure, the concentration of the various vapors, and the circulation of vapors past the surface—as well as the time of exposure—all influence the final depth of the etch. Even when all these factors are being controlled, there is, at present, no device available for indicating, or no method available for determining, the actual depth of the etch until the sample has been removed from the vapors and cleaned. If the etch is not deep enough, the sample has to be put back into the vapor chamber for another interval of time. If the etch is too deep the sample may have to be discarded.

It is therefore an object of this invention to provide

an improved method for etching the surface of a metal to a given depth.

It is a further object of this invention to provide an improved method for controlling the depth of the etch produced by a corrosive vapor etching process.

It is a further object of this invention to provide an improved, simple, and effective method for controlling the thickness of the corrosion layer that determines the depth of the etch in a corrosive vapor etching process.

These and other objects are accomplished by exposing the clean surface of the metallic sample to vapors of hydrogen fluoride, nitrous oxide, and water to initiate the growth of a corrosion layer on the metallic surface; observing the changing colors of the interference patterns resulting from white light incident on the growing corrosion layer; and terminating the exposure of the metallic surface to the vapors of hydrogen fluoride, nitrous oxide, and water at the time when the interference pattern shows the correct color, or has passed through the correct number of color cycles.

This invention will be better understood and further objects of this invention will become apparent from the following specification and the drawings of which:

FIG. 1 shows a series of blocks labeled to illustrate the sequence of steps of this process and

FIG. 2 shows a series of isometric views including cross-sections to illustrate the changes in the surface during the etching processes and

FIG. 3 is a graph illustrating the changes in the thickness of the corrosion layer and in the resultant depth of the final etch with respect to sequential orders of color.

Referring now particularly to the steps listed in FIG. 1, the surface of the metallic sample to be etched is first cleaned in a well-known manner and then the sample is placed in a container of inert material, such as Teflon or polyethylene, with suitable input and outlet facilities to introduce into and to exhaust the vaporous reagent from the container. When the surface of the sample is exposed to the corrosive vapors of hydrogen fluoride, nitrous oxide, and water to produce a corrosion layer of the desired thickness on the surface of the metallic sample, as detailed by this method, the sample is removed from the container, the corrosion layer is dissolved in a bath of sodium hydroxide, and the surface is washed in distilled water in a well-known manner.

FIG. 2A shows an isometric view of a typical sample **10** of a metallic material with a mechanically smooth surface **12** that has been cleaned in preparation for etching in accordance with the first step of this process.

FIG. 2B shows another isometric view of the sample **10** positioned in a container **20** of an inert material. This container has suitable vapor input openings and vapor outlet openings which are so labeled. The container may be transparent along an area **22** opposite to the position of the sample. If the material of the container is not transparent enough for observation of the sample from outside of the container, provision may be made for a window of transparent material in the side of the container opposite to the position of the surface of the sample. This window must also be inert to the reagents used in this process. The transparent portion **22** of the container is also used to transmit light from the light source **24** to the corrosion layer **14** during its growth on the surface of the sample **10**. The transparent portion also serves for an observer **26** to see the changing color of the interference pattern produced by the light incident on the growing corrosion layer on the surface of the sample to know at what time corrosion process is to be stopped. At this time the sample **10** is removed from the inert container **20** so that the corrosion layer **14** can be

dissolved in a bath of sodium hydroxide to produce the etched surface **16**.

FIG. 2 shows another isometric view of the sample **10**. The corrosion layer has been removed, exposing the surface **16** which may then be washed, dried, and used.

FIG. 3 is a graph of a typical relationship between the thickness of the corrosion layer, the ultimate depth of etch, and the interference patern colors. In a typical corrosive growth the increasing thickness of the corrosion layer in microns with respect to the changing colors through several sequences of the color red would be approximately that shown by curve **31**. The corresponding depth in microns of the resulting etch after the corrosion layer is removed would be approximately that illustrated by curve **33**. It is obvious that the interference pattern will appear as successive colors of increasing wavelength as the thickness of the corrosion layer increases. Each repetition of the color red would be preceded by the usual sequence of visible colors of shorter wavelength.

It is seen from these curves that an etch of a given depth can be obtained by stopping the corrosion of the surface at a particular color or after a given number of cycles of color have occurred.

The actual, corrosive-growth etching process is described in detail in my above-mentioned, copending application which includes details of reagents, desirable concentrations, temperatures, approximate times, and some of the variations in the reagents that are acceptable to this process; as well as typical container dimensions and mechanical details. For this in-process method for controlling the depth of the final etch, the container itself may provide the transparent surface **22** of FIG. 2B, if the inert plastic material of the container is optically clear enough to permit adequate observation of the more significant of the interference-pattern color changes and if the surface **22** is suitable situated for observing the corrosive growth.

The main difference between this in-process method of etch control and that of the above-mentioned, copending application is in the timing of the action of the corrosive vapors corrosion of the surface. In practicing this in-process method, a source of light is positioned to shine on the corroding surface in such a manner that the interference-pattern colors produced by the surface are clearly visible. These colors will, of course, change as the corosion layer thickens and produces longer wavelength interference patterns. The corrosion is stopped when the correct color appears or when the interference patterns have passed through a given series of cycles of color. At this time, the incoming vapor can be cut off and the corrosive vapor driven away from the surface by other neutral gases, such as argon, to terminate the active corroding of the surface.

If the container material or surface at **22** are not optically suitable, a port or window may be cut in the container at **22** and replaced with an optically suitable window of a material, such as Celluloid, that is also inert to the vapor necessary for this process.

The samples in FIG. 2 are shown vertically and positioned in sequence to suggest the order of steps and to permit the most orderly, graphic illustration of the fundamental part of this method, which is seen in FIG. 2B. It is obvious that the sample could and probably would be placed flat in the container and that the light source and the observer could be located at any corresponding point, compatible for the transparent surface and the location of the sample, and that the vapor inputs and outlets could be situated in any other convenient parts of the container.

The light source **24** is intended to suggest a common, low-wattage light bulb that will produce a substantially white light of suitable strength for this purpose. It is obvious that any other source of white light can be used and that the wattage may be increased, or the light focused or directed in any of the ways well-known in the art, to provide adequate light for clearly distinguishable interference patterns.

The angle between the light source and the surface of the corrosive layer may be adjusted to produce the most clearly visible interference patterns. The position of the observer also may be varied to a distance and angle most suitable for observation or for giving the clearest indication of color. It has been found in practice that moving the sample with respect to the light and to the observer gives a trained observer a very quick and accurate indication of the existing interference-pattern color.

It should also be noted that color-sensitive indicators and controls are available, or can be provided within the state of the art, to establish, automatically, when a certain color is reached or when a certain series of color changes have been accomplished. These automatic indicators and controls can be combined with readily-available electromechanical valves and devices to cut off the input of the corrosive vapors and to move the sample on to the next step of this method when the color-sensitive optical devices indicate the correct condition.

In practice the colors are clearer during the first few orders because dispersion and other losses weaken the colors in the higher orders. However, the cycle of change is visible or recognizable to a trained eye considerably beyond the point where any specific wavelength of color is identifiable. In any case the percentage change in depth for a given color change is much less in the higher orders, so the degree of accuracy of this system is fairly constant.

In etching to depths that require corrosion layers of thickness that pass through many orders of interference-pattern colors the use of monochromatic light might be desirable to produce clear indication of increases of one wavelength rather than the vague sweep of weaker colors.

What is claimed is:

1. An etching process comprising the steps: cleaning a silicon surface to be etched; exposing said surface to be etched to a combination of hydrogen fluoride and oxilizing vapors to cause a growth of a corrosion layer on said surface; shining visible light on said corrosion layer; observing the changing colors of the interference patterns produced by said light on said growing corrosion layer; terminating said exposure of said surface to said combination of hydrogen fluoride and oxidizing vapors when said interference pattern has passed through a given color sequence that is indicative of a desired thickness of said corrosion layer; and dissolving said corrosion layer in a hydroxide bath to leave said surface etched to a given depth; and washing said etched surface.

2. An etching process as in claim **1** wherein said given color sequence includes more than one cycle of the spectrum of the wavelengths of visible light.

3. An etching process as in claim **1** including means sensitive to said given color sequence of said interference pattern and means responsive to said means sensitive to said given color sequence for automatically terminating said exposure of said surface to said combination of hydrogen fluoride and oxidizing vapors when said interference pattern passes through said given color sequence.

4. An etching process as in claim **1** wherein said oxidizing vapor is one of nitrous oxide.

5. An etching process as in claim **1** wherein said oxidizing vapor is one of nitric oxide.

6. An etching process as in claim **1** wherein said incident light is monochromatic.

7. A process for etching the surface of a silicon semiconductor comprising the steps; cleaning said surface of said semiconductor in a bath of organic solvent; oven drying said surface of said semiconductor; mounting said semiconductor in an inert container having an intake port, an exhaust port, and a transparent window, said surface of said sample being visible through said window; directing white light through said window to said surface of said semiconductor; applying a combination of 1% hydrogen fluoride vapor, 1% nitrous oxide vapor, and 1%

water vapor through said intake port into said container to initiate a corrosive growth on said surface of said semiconductor; observing the color of the interference patterns in said corrosive growth on said surface of said semiconductor; removing said combination of vapors from said container through said exhaust port to terminate said corrosive growth when said interference pattern in said corrosive growth produces a given color; removing said semiconductor from said container; dissolving said corrosive growth from said surface of said semiconductor in a 10% solution of sodium hydroxide for ½ minute; and washing the resultant, etched surface of said semiconductor in hot distilled water for at least five minutes.

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U.S. Cl. X.R.

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