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GASEOUS NONPREFERENTIAL ETCHING OF SILICON

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ABSTRACT OF THE DISCLOSURE

A silicon surface is etched or polished with a gaseous mixture comprising sulfur hexafluoride, SF_6, of high purity and a carrier gas such as hydrogen at temperatures between 950° C. and 1250° C. The sulfur hexafluoride should have a low nitrogen concentration with a preferred nitrogen concentration being less than 200 parts per million by weight.

BACKGROUND OF THE INVENTION

This invention relates to the vapor phase etching of silicon and more particularly to the etching of silicon with a gaseous mixture containing high purity sulfur hexafluoride.

In the processing of semiconductor materials such as silicon, the need for extremely smooth, flat, and clean surfaces has been well established. Such surfaces were once prepared by a sequence of steps involving lapping and mechanical polishing of a surface, followed by liquid phase chemical etching. Although improved chemical etching and polishing techniques are now available, with the advent of vapor phase etching as described in U.S. Pat. 3,243,-323 to Wilfred J. Corrigan et al., the liquid phase chemical etching has been replaced to a substantial extent by the vapor phase etching technique. As explained in the Corrigan et al. patent, gas phase etching is carried out by mounting the semiconductor material in a suitable high temperature reaction chamber and passing a gaseous mixture comprising hydrogen and hydrogen chloride in contact with the heated semiconductor material. While the gas phase etching process involving mixtures of hydrogen and hydrogen chloride has been widely accepted by the semiconductor industry as the predominant etching process, extreme care must be utilized with this corrosive gaseous mixture to avoid corrosion problems.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved vapor etching method for silicon. It is another object of this invention to provide an etchant which will not corroide process equipment at room temperature. It is yet another object of this invention to provide an etchant and an etching method for temperatures in the range of 950 to 1250° C. that will etch at a fast rate. It is still another object of this invention to provide an etching method which uses a non-toxic etchant.

These and other objects of this invention are accomplished by a method which comprises passing a gaseous mixture containing sulfur hexafluoride having a low nitrogen concentration and preferably below 200 parts per million by weight of nitrogen and a carrier gas such as hydrogen. The temperature of the silicon is between 950° C. and 1250° C. as this gaseous mixture is passed thereover.

DETAILED DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

In accordance with this invention, it has been determined that sulfur hexafluoride having a relatively high purity may be used as an effective etchant for silicon. Sulfur hexafluoride containing 0 to about 1300 parts per million by weight of nitrogen is diluted with a carrier

gas such as hydrogen, argon, or helium to provide an etching mixture which when passed over silicon at a temperature between 950° C. and 1250° C. readily etches the silicon.

The purity of the sulfur hexafluoride is critical in the practice of the method of this invention. Commercially available sulfur hexafluoride containing 98.5 percent SF_6 contains, according to the specification sheets, a maximum of about 3000 to 5000 parts per million of nitrogen by weight. Sulfur hexafluoride of this purity (a maximum of 3000 to 5000 parts per million by weight of nitrogen) has been found to be unsuitable as an etchant for silicon except at low etch rate at 1150° C. or higher. Sulfur hexafluoride of 99 percent purity containing a maximum of about 1300 parts per million of nitrogen by weight has been found to be a marginal material to use as an etchant on silicon at temperatures between 950 and 1050° C. Sulfur hexafluoride of this purity does, however, yield good results as an etchant in the temperature range of 1050 to 1250° C.

Sulfur hexafluoride of 99.98 percent purity containing less than 200 parts per million of nitrogen by weight (the minimum detectable nitrogen quanty in SF_6) is a very effective etchant on silicon over the entire temperature range of 950 to 1250° C. It is quite clear that the efficiency and/or effectiveness of the sulfur hexafluoride as a silicon etchant is directly dependent upon the concentration of the nitrogen in the SF_6. Nitrogen concentrations above 1300 p.p.m. tend to render the sulfur hexafluoride ineffective, whereas substantially nitrogen free sulfur hexafluoride provides excellent etching results.

In accordance with this invention, the SF_6 etchant is used in the etching method described below.

Silicon wafers are placed on a slab of quartz which serves as a planar support resting on a susceptor of graphite. The susceptor is heated by any suitable means, for example, by radio frequency energy from induction coils about the reaction chamber. The silicon is heated primarily by conduction from the susceptor although substantial direct heating of the semiconductor by induction does occur in the event substantially elevated temperatures are employed.

The silicon wafer is then heated to a temperature between 950 and 1250° C.

Sulfur hexafluoride of high purity containing less than about 1300 parts per million by weight of the nitrogen and preferably below 200 parts by weight nitrogen, is mixed with a carrier gas such as hydrogen, argon, or helium, with hydrogen being the preferred gas. The sulfur hexafluoride gas mixture is passed over the heated silicon for a given period of time to etch the silicon surface. When the desired amount of silicon has been etched away, the flow of sulfur hexafluoride is stopped, while the flow of the diluent gas is continued.

The mole ratio of the sulfur hexafluoride in hydrogen is about 1×10^{-3} percent to 1 percent. The mole ratio is determined at a given temperature experimentally to obtain the optimum processing conditions, that is, a convenient rate and an adequate surface quality. This will be apparent from the following examples.

Example 1

A series of silicon wafers were placed on a slab of quartz on a graphite susceptor. The susceptor was heated by induction coils surrounding the reaction chamber. The susceptor in turn provided sufficient heat to heat the silicon wafers to a temperature of 1000° C. Sulfur hexafluoride containing a maximum of 200 parts per million by weight nitrogen was mixed with hydrogen to form a gaseous mixture containing 21×10^{-3} mole percent SF_6. The sulfur hexafluoride-hydrogen mixture was passed over the heated silicon for about 7 minutes to etch the silicon surface to a depth of four microns. The flow of sulfur hexafluoride was stopped while the flow of the hydrogen was continued.

The resultant silicon wafer had a good surface and had been etched at a rate of 0.59 micron per minute. The definition of a good surface was a surface in which oblique light from a microscope lamp did not show any haze.

Other examples of sulfur hexafluoride used as an etchant with hydrogen as a carrier gas are given in the tables below.

TABLE 1

SF_6 (containing less than 200 p.p.m. N_2)

	Good surface		Borderline surface		Bad surface	
Temp., ° C.	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2
800						
900					0.024	5.2×10^{-3}
950	0.136	5.2×10^{-3}			0.23	10.5×10^{-3}
1,000	0.59	21×10^{-3}	0.83	30×10^{-3}	1.1	41×10^{-3}
1,050	1.35	41×10^{-3}	2.80	100×10^{-3}		
1,100	2.36	73×10^{-3}	3.80	100×10^{-3}		
1,150	3.89	100×10^{-3}				

Table 1 lists results obtained when using sulfur hexafluoride having a purity in which the nitrogen content was less than 200 parts per million by weight. Good surfaces were obtained at temperatures between 950° C. and 1150° C. with an etchant rate going from 0.136 up to 3.89 microns per minute, respectively. At 900° C., the surface was unsatisfactory, unsatisfactory meaning that the surface of the wafer was hazy when observed under room light. A borderline surface is a surface which looks good under room light but which looks hazy when observed under oblique light from a microscope lamp. Table 1 indicates the preferred etching rates at a given temperature. For example, the etching rate at 1000° C. which is preferred is .59 micron per minute or less since .83 micron per minute gave borderline surfaces and an etching rate of 1.1 microns per minute gave a bad surface.

TABLE 2

SF_6 (containing less than 1,300 p.p.m. N_2)

	Good surface		Borderline surface		Bad surface	
Temp., ° C.	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2
900					0.023	5.2×10^{-3}
950					0.11	5.2×10^{-3}
1,000					0.14	5.2×10^{-3}
1,050	0.32	10.5×10^{-3}	0.42	12.5×10^{-3}	0.74	20.8×10^{-3}
1,100	0.92	20.8×10^{-3}	1.95	41.8×10^{-3}	3.0	71.8×10^{-3}
1,150	1.62	30×10^{-3}	2.25	41.8×10^{-3}	3.5	71.8×10^{-3}

Table 2 lists results obtained with sulfur hexafluoride containing less than 1300 parts per million by weight nitrogen. Good surfaces were obtained at temperatures of 1050 through 1150° C. with etching rates of from 0.32 micron per minute to 1.62 microns per minute, respectively. Bad surfaces were obtained at temperatures below 1000° C.

TABLE 3

SF_6 (containing less than 3,000–5,000 p.p.m. N_2)

	Good surface		Borderline surface		Bad surface	
Temp., ° C.	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2	Etching rate, μ/min.	Mole percent SF_6 in H_2
950					0.23	5.2×10^{-3}
1,000					0.23	5.2×10^{-3}
1,100			0.16	5.2×10^{-3}		
1,150	0.17	5.2×10^{-3}	0.40	10.5×10^{-3}	0.57	12.5×10^{-1}
1,200	0.44	10.5×10^{-3}			1.35	20.8×10^{-3}

Table 3 lists results obtained using sulfur hexafluoride containing less than 3000 to 5000 p.p.m. nitrogen. Unsatisfactory results were obtained at temperatures below 1000° C. A good surface was obtained at a temperature of 1200° C., however, the etching rate was only 0.4 micron per minute. This etching rate is considered too slow in most cases at this temperature.

The advantage of etching with sulfur hexafluoride is that the etching reaction $Si+SF_6+H_2\rightarrow H_3SiF+SiS$ is substantially irreversible in the temperature range of from 950 to 1250° C. As a result, this method does not have any redeposition of volatile impurities occurring.

The examples have shown sulfur hexafluoride mixtures with hydrogen as the carrier gas. Sulfur hexafluoride may be mixed with other etchants such as ClF_3, HCl, HF, H_2S, or combinations thereof, to provide an alternate etchant gaseous mixture in accordance with this invention.

I claim:

1. The method for the nonpreferential vapor phase etching of a mirror-like silicon surface while maintaining the mirror-like quality of the silicon surface for assuring a suitable silicon surface for semiconductor processing, comprising the steps of:

providing a silicon wafer having a mirror-like surface to be etched;

heating said wafer to a temperature lying within the range between 950° C. to 1200° C.;

passing a gaseous mixture of hydrogen and sulfur hexafluoride over said heated silicon surface for obtaining an oxidizing reaction between said mixture and said silicon surface through the reaction

$$Si+SF_6+H_2\rightarrow H_3SiF+SiS$$

and etchably removing portions of said silicon while maintaining the mirror-like quality of said silicon surface; and

said gaseous mixture having a nitrogen content less than 5000 parts per million by weight, and containing a percentage of sulfur hexafluoride lying within the range between 0.001 and 0.1 mole percent.

2. The method for the nonpreferential vapor phase etching of a mirror-like silicon surface while maintaining the mirror-like quality of the surface for assuring a suit-

able silicon surface for semiconductor processing, comprising the steps of:

providing a silicon wafer having a mirror-like surface to be etched;

heating said wafer to a temperature lying within the range between 950° C. to 1200° C.;

passing a gaseous mixture of an inert carrier gas and sulfur hexafluoride over said heated silicon surface for etchably removing portions of said silicon while maintaining the mirror-like quality of said silicon surface;

said carrier gas being selected from the group consisting of hydrogen, argon and helium; and

said gaseous mixture containing a nitrogen content less than 5000 parts per million by weight, and containing a percentage of sulfur hexafluoride laying within the range between 0.001 and 0.1 mole percent.

3. The method for the monopreferential vapor phase etching of a mirror-like silicon surface while maintaining the mirror-like quality of the surface for assuring a suitable silicon surface for semiconductor processing, comprising the steps of:

providing a silicon wafer having a mirror-like surface to be etched;

heating said wafer to a temperature lying within the range between 1050° C. to 1150° C.;

passing a gaseous mixture of a carrier gas and sulfur hexafluoride over said heated silicon surface for etchably removing portions of said silicon while maintaining the mirror-like quality of said silicon surface;

said inert carrier gas being selected from the group consisting of hydrogen, argon and helium; and

said gaseous mixture containing a nitrogen content less than 1310 parts per million by weight, and containing a percentage of sulfur hexafluoride lying within the range between 0.0105 and 0.0418 mole percent.

4. The method for the nonpreferential vapor phase etching of a mirror-like silicon surface while maintaining the mirror-like quality of the surface for assuring a suitable silicon surface for semiconductor processing, comprising the steps of:

providing a silicon wafer having a mirror-like surface to be etched;

heating said wafer to a temperature lying within the range between 950° C. to 1250° C.;

passing a gaseous mixture of hydrogen and sulfur hexafluoride over said heated silicon surface for obtaining an oxidizing reaction between said mixtures and said silicon surface through the reaction

$$Si+SF_6+H_2 \rightarrow H_3SiF+SiS$$

and etchably removing portions of said silicon while maintaining the mirror-like quality of said silicon surface; and

said gaseous mixture having a nitrogen content less than 200 parts per million by weight, and containing a percentage of sulfur hexafluoride lying within the range between 0.005 and 0.1 mole percent.

5. The method for the nonpreferential vapor phase etching of a mirror-like silicon surface while maintaining the mirror-like quality of the surface for assuring a suitable silicon surface for semiconductor processing, comprising the steps of:

providing a silicon wafer having a mirror-like surface to be etched;

heating said wafer to a temperature lying within the range between 1050° C. to 1150° C.;

passing a gaseous mixture of hydrogen and sulfur hexafluoride over said heated silicon surface for obtaining an oxidizing reaction between said mixture and said silicon surface through the reaction

$$Si+SF_6+H_2 \rightarrow H_3SiF+SiS$$

and etchably removing portions of said silicon while maintaining the mirror-like quality of said silicon surface; and

said gaseous mixture having a nitrogen content less than 1300 parts per million by weight, and containing a percentage of sulfur hexaflouride lying within the range between 0.0105 and 0.0418 mole percent.

References Cited

UNITED STATES PATENTS

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