

PATENT SPECIFICATION

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(54) PROCESS FOR CLEANING SILICON SEMICONDUCTOR MATERIALS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, 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:-

The invention relates to a process for removing metallic impurities from the surface of a silicon semiconductor material and the use of the process in the manufacture of silicon semiconductor devices.

The manufacture of semiconductor devices such as silicon integrated circuits and charge coupled devices requires that impurities be kept from residing on the surface of such devices. Impurities such as copper, iron and gold are especially troublesome since they form undesirable charge traps at the surface of the device, and can diffuse into the silicon bulk to form hot spots, or noise sources, which adversely affect the performance of the device.

In addition to impurities present in starting materials, impurities are necessarily added during processing. Therefore, in addition to ab initio attempts to minimize impurity contamination, present practice is to getter impurity atom at various stages of the manufacture of the device. Conventionally, devices may be formed from a silicon wafer which is photolithographically processed through successive steps, many of which involve

1. the thermal diffusion of dopants into the silicon, or

2. The thermal growth of an oxide over part of or the whole of the silicon. Before each thermal step (which takes place in a gaseous environment within a high-temperature oven), it is customary to clean the silicon wafer. Typically, this is done by immersing the wafer in a dilute solution of ammonium hydroxide and hydrogen peroxide for 20 minutes at 80°C; rinsing the wafer with distilled water; immersing the wafer in a solution of hydrogen peroxide and hydrochloric acid for 20 minutes at 80°C; and again rinsing the wafer with distilled water. Such a technique, while working to clean away trace amounts of impurities leaves something to be desired, primarily because it requires handling and processing by wet solutions; and because it takes a fair amount of time to do.

In accordance with the invention, there is provided a process for removing metallic impurities from the surface of a silicon semiconductor material which process comprises exposing the surface of the material to a cleaning gas comprising nitric oxide at a temperature sufficient to remove the impurities.

Although nitric oxide has been found to be alone effective to clean away metallic impurities from a silicon semiconductor material (e.g., 99.85% of copper was removed from a semiconductor wafer in ten minutes of exposure to nitric oxide at 1000°C), according to a preferred embodiment of the invention, the nitric oxide is combined with anhydrous hydrochloric acid. This anhydrous mixture of gases may efficiently clean even gold from the water, it being interesting to note that, in general, neither nitric oxide nor anhydrous hydrochloric acid are singularly effective for cleaning away gold.

The cleaning gas may further comprise a carrier gas.

Preferably, the cleaning step is performed at a temperature of from 850°C to 1100°C, with the best results being obtained from 900°C to 1000°C.

In another aspect, the invention provides a method for the manufacture of a silicon semiconductor device comprising at least one step in which the device is exposed to a high-temperature gaseous environment wherein, prior to said step, metallic impurities are

removed from the surface of the device by the process of the invention.

The device may be exposed to a high-temperature gaseous environment which causes the growth of an oxide on the surface of the device.

Gaseous cleaning may be performed at selected steps of wafer-processing. From the standpoint of how long it takes to effect good cleaning, gaseous cleaning according to the invention permits cleaning to be done generally in less than 10 minutes and normally in less than about five minutes. In a typical implementation of the invention, a mixture of nitric oxide, anhydrous hydrochloric acid, and a carrier gas of nitrogen, at 900°C, and respective flow rates of 112.5 cc/min, 135 cc/min, and 2250 cc/min, was for two minutes used effectively to clean a silicon wafer of impurities; and, with respect to gold, about 60% was removed.

An interesting feature of the invention is that, at moderate flow rates and lower temperatures, the tendency to form an undesirable nitride or oxynitride coating on silicon may be limited. For example, for a cleaning cycle preparatory to a thermal oxidation step, it would be desirable to avoid formation of a nitride/oxynitride film on the silicon because such a film has a tendency to inhibit formation of the desired oxide film. The above-noted typical implementation of the invention does not inhibit forming of the oxide film. Of course, in some instances there is little or no concern for nitride or oxynitride forming during cleaning. In such cases, the operating conditions may be chosen to optimize, say, gettering of gold: by doubling the flow rate of nitric oxide in the above-noted typical implementation, the gettering of gold increases to 70.5%, although the oxidation inhibition is increased.

The invention will be further described with reference to the Figure which shows schematically one implementation of the invention.

Referring to the Figure, a system for practicing the invention employs a source 10 of nitric oxide, a source 12 of anhydrous hydrochloric acid, and a source 14 of carrier gas such as nitrogen, or argon. Adjustable valves 16, 18 and 20, respectively, regulate the flow of nitric oxide, anhydrous hydrochloric acid and carrier gas into a mixing chamber 22 connected to a furnace tube 24 of a conventional type. Silicon wafers 26 are stacked in a boat 28 within the furnace, the mixed gases flowing into and out of furnace ports 30 and 32, respectively. The furnace temperature is regulatable by means of a temperature regulator 34. Gettering is a relatively complex phenomenon resulting from the interplay of many influences. Although some sets of parameters for the gettering operation work better than others, the chart below shows some parameters sets which are especially attractive, or representative. In the right-hand column of the chart, the percentage of gold removal is indicated, gold being so indicated because it is perhaps the most difficult of impurities to getter.

	Flow Rates (cc/min)		N ²	Temp. °C	Time (min)	% Gold Gettered	
	NO	HCl					
40	67.5	67.5	2250	900	2	57.5	40
	135	135	2250	900	5	67.4	
	225	67.5	2250	900	2	62.8	
45	225	135	2250	900	5	70.5	45
	225	270	2250	900	5	69.9	
	112.5	67.5	2250	1000	5	88.6	
	225	67.5	2250	1000	1	65.0	
50	135	135	2250	1000	1	62.9	50
	225	135	2250	1000	3	65.9	

The invention may be used as the sole process for cleaning a silicon semiconductor material or it may be used in addition to conventional processes.

For example, the invention may be used to complement, not replace, one or more wet cleaning steps used in the cleaning of a silicon wafer. That is, having conventionally cleaned a wafer, it may be subjected to nitric oxide and anhydrous hydrochloric acid as indicated in one of the examples depicted in the above chart.

WHAT WE CLAIM IS:-

1. A process for removing metallic impurities from the surface of a silicon semiconductor material which process comprises exposing the surface of the material to a cleaning gas comprising nitric oxide at a temperature sufficient to remove the impurities.

2. A process as claimed in Claim 1 wherein the cleaning gas further comprises anhydrous hydrochloric acid.

3. A process as claimed in Claim 1 or Claim 2 wherein the cleaning gas further



removed from the surface of the device by the process of the invention.

The device may be exposed to a high-temperature gaseous environment which causes the growth of an oxide on the surface of the device.

5 Gaseous cleaning may be performed at selected steps of wafer-processing. From the standpoint of how long it takes to effect good cleaning, gaseous cleaning according to the invention permits cleaning to be done generally in less than 10 minutes and normally in less than about five minutes. In a typical implementation of the invention, a mixture of nitric oxide, anhydrous hydrochloric acid, and a carrier gas of nitrogen, at 900°C, and respective flow rates of 112.5 cc/min, 135 cc/min, and 2250 cc/min, was for two minutes used effectively to clean a silicon wafer of impurities; and, with respect to gold, about 60% was removed. 10

An interesting feature of the invention is that, at moderate flow rates and lower temperatures, the tendency to form an undesirable nitride or oxynitride coating on silicon may be limited. For example, for a cleaning cycle preparatory to a thermal oxidation step, it would be desirable to avoid formation of a nitride/oxynitride film on the silicon because such a film has a tendency to inhibit formation of the desired oxide film. The above-noted typical implementation of the invention does not inhibit forming of the oxide film. Of course, in some instances there is little or no concern for nitride or oxynitride forming during cleaning. In such cases, the operating conditions may be chosen to optimize, say, 15 gettering of gold: by doubling the flow rate of nitric oxide in the above-noted typical implementation, the gettering of gold increases to 70.5%, although the oxidation inhibition is increased. 20

The invention will be further described with reference to the Figure which shows schematically one implementation of the invention.

25 Referring to the Figure, a system for practicing the invention employs a source 10 of nitric oxide, a source 12 of anhydrous hydrochloric acid, and a source 14 of carrier gas such as nitrogen, or argon. Adjustable valves 16, 18 and 20, respectively, regulate the flow of nitric oxide, anhydrous hydrochloric acid and carrier gas into a mixing chamber 22 connected to a furnace tube 24 of a conventional type. Silicon wafers 26 are stacked in a boat 28 within the furnace, the mixed gases flowing into and out of furnace ports 30 and 32, respectively. The furnace temperature is regulatable by means of a temperature regulator 34. Gettering is a relatively complex phenomenon resulting from the interplay of many influences. Although some sets of parameters for the gettering operation work better than others, the chart below shows some parameters sets which are especially attractive, or representative. In the right-hand column of the chart, the percentage of gold removal is indicated, gold being so indicated because it is perhaps the most difficult of impurities to 35 getter.

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	135	135	2250	900	5	67.4	
	225	67.5	2250	900	2	62.8	
45	225	135	2250	900	5	70.5	45
	225	270	2250	900	5	69.9	
	112.5	67.5	2250	1000	5	88.6	
	225	67.5	2250	1000	1	65.0	
	135	135	2250	1000	1	62.9	
50	225	135	2250	1000	3	65.9	50

The invention may be used as the sole process for cleaning a silicon semiconductor material or it may be used in addition to conventional processes.

55 For example, the invention may be used to complement, not replace, one or more wet cleaning steps used in the cleaning of a silicon wafer. That is, having conventionally cleaned a wafer, it may be subjected to nitric oxide and anhydrous hydrochloric acid as indicated in one of the examples depicted in the above chart.

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60 1. A process for removing metallic impurities from the surface of a silicon semiconductor material which process comprises exposing the surface of the material to a cleaning gas comprising nitric oxide at a temperature sufficient to remove the impurities.

2. A process as claimed in Claim 1 wherein the cleaning gas further comprises anhydrous hydrochloric acid.

65 3. A process as claimed in Claim 1 or Claim 2 wherein the cleaning gas further



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comprises a carrier gas.

4. A process as claimed in any one of the preceding Claims wherein the cleaning gas has a temperature of from 850° to 1100°C.

5 5. A process as claimed in any one of Claims 1 to 3 wherein the cleaning gas has a temperature of from 900° to 1000°C. 5

6. A process as claimed in Claim 1 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.

7. A semiconductor material when cleaned by a process as claimed in any one of the preceding Claims.

10 8. A method for the manufacture of a silicon semiconductor device comprising at least one step in which the device is exposed to a high-temperature gaseous environment wherein, prior to said step, metallic impurities are removed from the surface of the device by a process as claimed in any one of Claims 1 to 6. 10

15 9. A method as claimed in Claim 8 wherein the device is exposed to a high-temperature gaseous environment which causes the growth of an oxide on the surface of the device. 15

10. A semiconductor device when prepared in accordance with a method as claimed in Claim 8 or Claim 9.

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