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(54) **Title:** SAWING WIRE WITH BARE STEEL SURFACE AND METHOD TO MAKE THE SAME

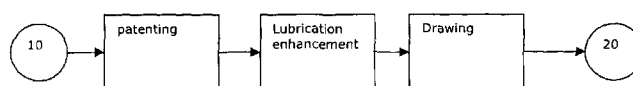


Figure 1

(57) **Abstract:** A sawing wire (20) has a bare steel surface wherein lubricant is present on the surface. And a method to manufacture said sawing wire (20) comprises the steps of, patenting a starting steel wire (10), applying lubrication enhancement substances on the surface of the starting steel wire (10), and drawing the starting steel wire (10) through a plurality of drawing dies to a finish diameter. The bare steel surface of the sawing wire does not have copper or copper alloy coatings to contaminate the wafers, and scratches on the surface of the sawing wire can pick more slurry to improve the cutting process.



Sawing wire with bare steel surface and method to make the same

Technical Field

[0001] This invention relates to a steel wire for use in a wire saw to cut semiconductor ingots into wafers, and in particular to a sawing wire with bare steel surface. This invention also provides the method to manufacture a sawing wire with bare steel surface.

Background Art

[0002] Semiconductor wafers are generally prepared from a single crystal ingot, such as a silicon ingot, that is cylindrical in shape. The ingot is sliced in a direction normal to its longitudinal axis to produce as many as several hundred thin, disk-shaped wafers. The slicing operation may be accomplished by means of a wire saw, wherein the ingot is contacted with a reciprocating wire while liquid slurry containing abrasive grains is supplied to a contact area between the ingot and the wire. As the abrasive particles in the slurry are rubbed by the wire against the ingot, silicon crystal is removed and the ingot is gradually sliced. The wire saw provides a gentle mechanical method for slicing which makes it ideal for cutting silicon crystal, which is brittle and could be damaged by other types of saws.

[0003] Conventionally, the sawing wire is generally plated with copper or copper alloy. The reason for plating a sawing wire with copper or copper alloy is to impart a corrosion preventive effect and to impart a lubricating effect during a drawing process in which a starting wire passes through several dies having different sizes of holes so as to be drawn in several steps. When a starting wire without copper or copper alloy plating is drawn, not only does the drawing speed significantly decrease due to poor lubrication between the wire and the die, but also there are formed many scratches on the wire surface,

which impair quality characteristics that a sawing wire is required to have, for example tensile strength. Thus, this lubricating effect is particularly important.

[0004] However, when a sawing wire with copper or copper alloy plating is used to slice a semiconductor ingot, not only does the copper or copper alloy plating exfoliate from the wire surface during slicing and accumulates in the collected abrasive slurry, but also copper or other metallic impurities contained in copper or copper alloy plating directly contact the sliced surface of the semiconductor ingot, resulting in contaminated product wafers. Copper has a greater coefficient of diffusion within silicon than does iron, which is the material used for the sawing wire. Therefore, when semiconductor silicon is contaminated with copper, copper is highly likely to diffuse from the sliced surface into the bulk of a silicon wafer due to the heat generated by slicing friction between a sawing wire and a silicon ingot. Thus, product wafers are difficult to be decontaminated by merely cleaning the surface thereof.

[0005] Prior art US5927131 provides a sawing wire without copper or copper alloy plating, wherein the copper or copper alloy plating is removed by physical polishing and/or chemical polishing after the finish drawing stage. Prior art KR20010002690A provides a sawing wire without copper or copper plating, wherein the copper or copper alloy plating is dissolved into a chemical solution. Both prior art documents have the drawback that copper or copper alloy is firstly plated on the starting wire as a lubricant for followed wire drawing process, and secondly removed either physically or chemically from the surface of the sawing wire.

Disclosure of Invention

[0006] It is the objective of present invention to provide a sawing wire with bare steel surface. It is also the objective of present invention to provide the method to manufacture a sawing wire with bare steel surface.

[0007] According to present invention, a sawing wire with bare steel

surface wherein lubricant is present on the surface in an amount corresponding to between 5 to 50 mg/m² of carbon, and preferably between 15 and 50 mg/m² of carbon.

[0008]According to present invention, a sawing wire with bare steel surface wherein phosphorus is present on the surface in an amount corresponding to between 2 to 30 mg/m², and preferably between 5 to 15 mg/m².

[0009]According to present invention, a sawing wire with bare steel surface wherein boron is present on the surface in an amount corresponding to between 2 to 30 mg/m², and preferably between 5 to 15 mg/m².

[0010]As phosphorous and boron are the elements that are used to make the silicon n-type (phosphorus) or p-type (boron), it is important to the invention that their remnants on the wire are controlled as this could lead to contamination of the wafers.

[0011]According to present invention, a sawing wire with bare steel surface wherein grooves are present on the surface with depth between 0.5μm to 10μm on the cross-sectional view, and preferably between 1μm and 5μm.

[0012]According to the present invention, a method of manufacturing a sawing wire with bare steel surface, comprises the steps of:

- a. patenting the starting steel wire;
- b. applying a lubrication enhancing substance on the surface of the starting steel wire; and
- c. drawing the starting steel wire through a plurality of drawing dies to a final diameter.

Preferably the lubrication enhancing substance is Phosphate, or Borax or Borax and Phosphate salt.

Brief Description of Figures in the Drawings

[0013]Figure 1 is a process diagram showing a method of manufacturing

a sawing wire with bare steel surface according to present invention.

[0014]Figure 2 is a schematic illustration showing a magnified cross-sectional view of a sawing wire with bare steel surface according to present invention.

Mode(s) for Carrying Out the Invention

[0015]Preferred embodiments of the present invention will be described herein below with reference to the accompanying drawings.

[0016]Figure 1 is a process diagram showing a method of manufacturing a sawing wire with bare steel surface according to present invention. The starting wire 10 goes through steps, patenting, lubrication enhancement, and drawing, to a final sawing wire 20.

[0017]Patenting is a thermal treatment applied to rods and wires. The object of patenting is to obtain a structure which combines high tensile strength with high ductility so that the wire is able to withstand heavy drafting, i.e. reduction in diameter by drawing, to produce the desired finished sizes with a combination of high tensile strength and good toughness. Conventionally patenting treatment comprises heating the starting wire until above the austenitizing temperature and followed by cooling the starting wire down to between 500C and 680C thereby allowing transformation from austenite to pearlite. US3458365 provides a patenting treatment for rods and wire, while UK1011972 provides another patenting treatment.

[0018]Lubrication enhancement is a surface treatment on the starting wire 10 to provide the wire with a coating which can enhance the lubrication on the starting wire 10 to go through the drawing thereafter. Phosphate coating is a good lubrication enhancement, in which phosphate coating binds a subsequently applied lubricant so firmly that it virtually will not be removed by the next drawing operation, because the combination of the phosphate coating and the lubricant permits a repeated strong cold working, without a

new intermediate treatment with lubricant. EP403241A and EP414301A provide solutions and process to form phosphate coating. Borax is another lubrication enhancement. GB9788124A and US5614261A provide method to apply Borax on the steel wire as lubrication enhancement before drawing. Besides, Borax can be applied after the phosphate coating to neutralize the phosphate coating because the borax solution is alkaline and the solution for phosphate coating is acidic.

[0019]Drawing is a mechanical deformation in that a starting wire 10 passes through a series of dies having decreasing size of holes so as to be drawn in several steps. There are types of drawing processes, dry drawing and wet drawing, depending on whether the drawing process is conducted in a coolant (wet drawing) or not (dry drawing). US3961511A discloses a dry drawing process wherein a lubricating or drawing mixture made up of three essential ingredients, namely soap powder, powdered fire clay, and powdered graphite, is used. US5189897A discloses a wet wire drawing process and apparatus to produce high tensile strength steel wire.

[0020]Going through the above manufacturing step, the finished sawing wire with bare steel surface has residual of lubricant, phosphorus, and boron on the surface.

[0021]The residual of lubricant can be tested on a surface carbon analyser STROHLEIN C-MAT 5500 machine. The sample of sawing wire is weighed in tarred sample boat. The sample boat is heated in a quartz combustion tube, under an O₂ purge. Organic material on the sample surface is vaporized or decomposed into CO or CO₂. The evolved gas is lead through a catalyst where a full conversion of organics and CO into CO₂ takes place. After being lead through a moisture trap, the gas flows through a selective infra-red detector and the amount of CO₂ is quantified. By means of an experimentally determined calibration factor, the amount of carbon in the gas flow and thus on the samples surface is calculated.

[0022]The residual of phosphate and boron can be tested by means of an Inductively Coupled Plasma spectrophotometer. The test method comprises: cut a sample of G gram of a finished sawing wire and merge the sample into M ml of 0.01 mol/L HCl for 15 seconds with shake, transfer the solution into a test tube and mount the tube on ICP test machine, set the detection wavelength of phosphate at 214.914nm and set the detection wavelength of boron at 249.772nm, read P the concentration of phosphate in the solution in mg/l and B the concentration of boron in the solution in mg/l. The amount of residual phosphate on the surface in mg/m^2 can be calculated according to following formula, $P \times M \times (D \times 1.963) / (G \times 3.0645)$, in which P is the concentration of phosphate test on ICP in mg/l, M the volume of 0.01mol/L HCl used in ml, D the diameter of the sawing wire in mm and G the amount of sample in gram. The amount of residual boron on the surface in mg/m^2 can be calculated according to following formula, $B \times M \times (D \times 1.963) / (G \times 3.0645)$, in which B is the concentration of boron test on ICP in mg/l, M the volume of 0.01mol/L HCl used in ml, D the diameter of the sawing wire in mm and G the amount of sample in gram.

[0023]In a first embodiment of present invention, a starting wire 10 with 1.05 mm diameter firstly goes through the patenting process, secondly the lubrication enhancement with borax, and finally the dry drawing process to a final sawing wire 20 with 0.175 mm diameter. In a second embodiment, a starting wire 10 with 1.05 mm diameter firstly goes through the patent process, secondly the lubrication enhancement with phosphate coating and borax, and finally the wet drawing process in oil, to a final sawing wire 20 with 0.12 mm diameter. Comparatively the second embodiment is better than the first one, on the productivity (high drawing speed), draw-ability (small diameter with less fracture), and durability (little wear on drawing dies and long life), because of the improved lubrication and cooling of the drawing of process.

[0024]Even when the wire goes through the enhanced lubrication

process, there are scratches on the surface of the sawing wire because of the attrition between the wire and the drawing dies. Figure 2 schematically illustrates a magnified cross-sectional view of a sawing wire with bare steel surface according to present invention, wherein the depth of the scratch is defined as the radial distance from the lowest point of the scratch to the smallest imaginary circle covering the cross-sectional view of the wire. The scratches on the surface, on one hand may decrease the sawing wire tensile strength as a surface defect, on the other hand can pick more slurry to improve the cutting process.

Claims

1. A sawing wire having a bare steel surface wherein lubricant is present on the surface in an amount corresponding to between 5 to 50 mg/m² of carbon.

2. A sawing wire having a bare steel surface as claimed in claim 1, wherein lubricant is present on the surface in an amount corresponding to between 15 to 50 mg/m² of carbon.

3. A sawing wire having a bare steel surface as claimed in claim 1, wherein phosphorus is present on the surface in an amount corresponding to between 2 and 30 mg/m².

4. A sawing wire having a bare steel surface as claimed in claim 3, wherein phosphorus is present on the surface in an amount corresponding to between 5 and 15 mg/m².

5. A sawing wire having a bare steel surface as claimed in claim 1, wherein boron is present on the surface in an amount corresponding to between 2 to 30 mg/m².

6. A sawing wire having a bare steel surface as claimed in claim 5, wherein boron is present on the surface in an amount corresponding to between 5 to 15 mg/m².

7. A sawing wire having a bare steel surface as claimed in claim 1, wherein scratches are present on the surface with depth between 0.5 μm to 10μm on the cross-sectional view.

8. A sawing wire having a bare steel surface as claimed in claim 7, wherein scratches are present on the surface with depth between 1μm to 5μm on the cross-sectional view.

9. A method of manufacturing a sawing wire having a bare steel surface, comprising the steps of
patenting the starting steel wire;

applying a lubrication enhancement substance on the surface of the starting steel wire;

drawing the starting steel wire through a plurality of drawing dies to a finish final diameter;

10. A method of manufacturing a steel wire having a bare steel surface according to claim 9, wherein said lubrication enhancement substance is Borax.

11. A method of manufacturing a steel wire having a bare steel surface according to claim 9, wherein lubrication enhancement substance is Borax and Phosphate salt.

12. A method of manufacturing a steel wire having a bare steel surface according to claim 9, wherein lubrication enhancement substance is phosphate.

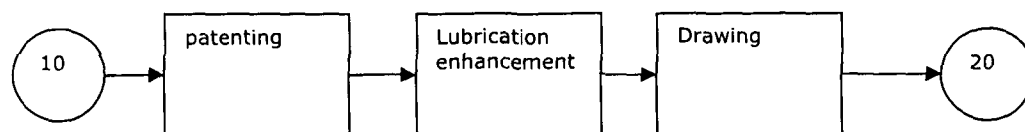


Figure 1

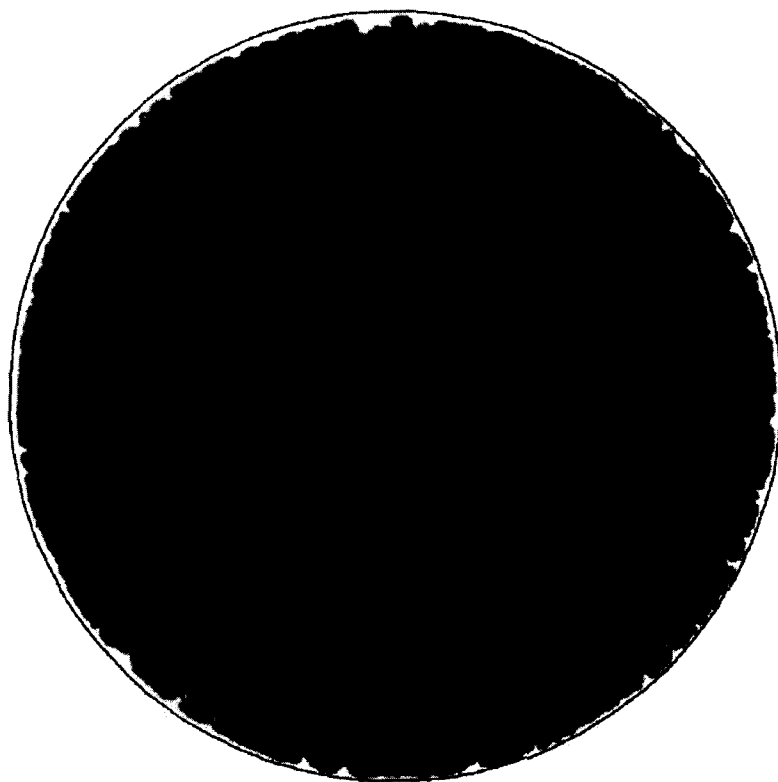


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/077385

A. CLASSIFICATION OF SUBJECT MATTER

B23D61/18 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC:B23D61/18, B21C1/+

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI,EPODOC,CNPAT,CNKI: sawing, wire, rope, cable, fibre, fiber, thread, phosphorus, boron, lubricat+, draw+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1143903C(KOBE STEEL LTD) 31 Mar.2004(31.03.2004) see description page 3, line 5 to page 10, line 1, figure 1	1,2,7,8,9
Y		3-6,10-12
Y	CN101875059A(SHANGHAI NO 2 STEEL CO LTD BAOSTEEL GROUP) 03 Nov.2010 (03.11.2010) see description paragraph [0007]	3-6,10-12
A	CN102421538A(BEKAERT SA NV)18 Apr.2012(18.04.2012) see the whole document	1-12
A	CN101965413A(BEKAERT SA NV)02 Feb.2011(02.02.2011) see the whole document	1-12
A	CN102413983A(BEKAERT SA NV)11 Apr.2012(11.04.2012) see the whole document	1-12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 21 Feb.2013(21.02.2013)	Date of mailing of the international search report 28 Mar. 2013 (28.03.2013)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer LI Xiaoli Telephone No. (86-10)62085373

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/077385

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US5927131A(SHINETSU HANDOTAI KK)27 Jul.1999(27.07.1999) see the whole document	1-12
A	US5614261A(WIRELUBE RES CO)25 Mar.1997(25.03.1997) see the whole document	1-12

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/077385

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN1143903C	31.03.2004	KR20030022715A	17.03.2003
		EP1293582A	19.03.2003
		JP2003082437A	19.03.2003
		US2003066575A	10.04.2003
CN101875059A	03.11.2010	None	
CN102421538A	18.04.2012	WO2010130533A	18.11.2010
		US2012060980A	15.03.2012
		EP2429722A	21.03.2012
		JP2012527065A	01.11.2012
CN101965413A	02.02.2011	WO2009109495A	11.09.2009
		EP2268839A	05.01.2011
		US2011000593A	06.01.2011
		EA201001411A	28.02.2011
		JP2011517330A	02.06.2011
CN102413983A	11.04.2012	WO2010125085A	04.11.2010
		TW201119772A	16.06.2011
		SG175811A	29.12.2011
		US2012017741A	26.01.2012
		EP2424703A	07.03.2012
		JP2012525264A	22.10.2012
US5927131A	27.07.1999	JP9254145A	30.09.1997
		EP0799655A	08.10.1997
		TW393387B	11.06.2000
US5614261A	25.03.1997	None	