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(54) Title: SELF CLEANING SOLUTIONS FOR CARBON IMPLANTATION

(57) Abstract: Compounds and methods for use as source materials for pre-amorphization implantation in the formation of ultra-shallow junctions. Some compounds exhibit self-cleaning Cn (n= 5 - 30) ion source properties wherein each molecule of the compound includes a Cn (n= 5 - 30) ion source portion and a cleaning agent portion. Other compounds comprise binary solutions that exhibit self-cleaning Cn (n= 5 - 30) source properties wherein the solution contains a Cn (n= 5 - 30) ion source component and a cleaning agent component.



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SELF CLEANING SOLUTIONS FOR CARBON IMPLANTATION

FIELD OF THE INVENTION

(001) The present invention relates to self cleaning compounds for use as carbon implantation sources.

BACKGROUND OF THE INVENTION

(002) The use of semiconductors in our society is becoming more ubiquitous. For example, semiconductors are used in everyday items ranging from programmable coffee makers, to telecommunication devices to faster computers. The ability to scale down device structures, especially in trying to reach the <32 nm device technology, remains a goal. However, the requirements to achieve smaller and smaller sizes become more and more difficult to meet.

(003) One component of achieving smaller device sizes in the production of reduced junction depth, known as ultra-shallow junctions (USJ). However, forming USJ features present many challenges. In particular, dopants channeling penetration, transient enhanced diffusion, and clustering via interstitial sites or vacancies all present potential problems. These tendencies are recognized as causing an increase in the final junction depth and in sheet resistance. The basic challenge of forming high dopant activation and high junction steepness with a shallow penetration dopant profile remains. In addition, the elimination of residual effects, strong control of lateral diffusion, junction stability after post annealing and junction formation in new source and drain materials, such as SiGe/SiGeC/SiC/SiSn/GeSn, presents further challenges.

(004) To meet these challenges, there are several proposed processes and techniques. One of these is the pre-amorphization implant (PAI) of heavy ions, such as Ge and Xe ions or heavy C, F or N containing molecular ions, followed by dopant ions, e.g. B^+ , BF_2^+ , implantation. The PAI process helps to overcome the problems associated with channeling of the dopant ion as well as the limitation of solid solubility of the dopant ion. Cluster Carbon implant materials are available, such as from SemEquip, Inc. that can be used for PAI processes. Aromatic Carbon implant technology is also available from Axcelis Technologies. Those heavy carbon-based PAI methods have displayed advantages in performance and cost. They are also useful in making source and drain stressor materials. However, formation of hydrocarbon film residue in ion source chambers is a critical issue in this technology.

(005) There remains a need in the art for improvements related to PAI for use in the formation of ultra-shallow junctions.

SUMMARY OF THE PRESENT INVENTION

(006) The present invention provides improved methods and formulas for use in the PAI of substrates used in semiconductor manufacturing.

DETAILED DESCRIPTION OF THE INVENTION

(007) The present invention relates to methods and formulas for providing implantation ions to accomplish PAI of substrates, particularly for the formation of ultra-shallow junctions.

(008) In accordance with the present invention, the source ions are preferably carbon atoms, supplied from a C_n ($n=5-30$) molecular source. This source may

be provided in a liquid sub-atmospheric pressure package, such as the Genii technology available from the Linde Group. A preferred C_n (n=5 – 30) source is toluene which has shown promising results in both beam current and wafer characteristics. However, use of this C_n (n=5 – 30) source also resulted in the production of a large amount of hydrocarbon film residue inside the ionization chamber. This residue must be cleaned periodically from the chamber, requiring tool downtime with a resultant increase in semiconductor manufacturing time and cost.

(009) The present invention relates to compounds that exhibit self-cleaning C_n (n=5 – 30) ion source properties. According to one embodiment of the present invention, the compounds are single molecule liquid compound that exhibit self-cleaning C_n (n=5 – 30) ion source properties. Each molecule of the compounds of the present invention has a C_n (n=5 – 30) ion source portion and at least one cleaning agent portion, e.g. the portion containing reactive oxygen, chlorine, nitrogen, sulfur, fluorine, or the like species. The C_n (n=5 – 30) ion portion of the compound is preferable a toluene ion (C₇H₇⁺), when n=7. The compound liquid vapor pressure should be greater than 1 Torr at temperatures below 100°C, and the preferable vapor pressure is greater than 5 Torr and less than 100Torr at temperatures between 10°C and 100°C. In case of C₇ compound, upon ionization, the C₇ ions are highly concentrated in mass spectra with the C₇ ion (with a mass about 91 amu, C₇H₇⁺) being the most abundant ion peak in the mass spectra. The cleaning agent(s) dissociates from the parent molecule upon ionization and produces highly concentrated and reactive neutral or charged radicals. These radicals then react with hydrocarbon residue to form volatile gas produces, such as, CO₂, CO, H₂O, H₂S, CH₄, NH₃, CCl₄, or the like.

(010) In accordance with a second embodiment of the present invention, a binary liquid mixture may be used, the binary liquid mixture comprising a C_n (n=5 – 30)

source, e.g. toluene, mixed with a different cleaning agent compound, if C7 ion is required. For example, the cleaning agent compound could contain reactive oxygen function groups but it is not a source for C7 ion. In operation, the cleaning agent produces volatile products that help to avoid the formation of hydrocarbon film residue inside of the chamber. The cleaning agent may also produce oxygen, chlorine, nitrogen, or fluorine radicals to remove the hydrocarbon residue.

(011) For the binary liquid system to be viable, the vapor pressures of the C_n (n=5 – 30) source compound and the cleaning agent compound must be a good match to prevent concentration changes in the gas phase. Without the proper balance, results are compromised. For example, if cleaning agent concentration is increased, the chamber will remain clean, but the C_n (n=5 – 30) ion beam intensity is reduced, causing problems with the effectiveness of the PAI procedure. Alternatively, if the C_n (n=5 – 30) source concentration is raised higher than necessary for the beam intensity to be sufficient, then the cleaning capacity of the cleaning agent may be reduced, leading to the need for downtime cleaning of the chamber.

(012) For a binary liquid system using toluene as the C7 source, a number of cleaning agents having comparable vapor pressures may be used in the present invention. In particular, the vapor pressures of 1-chloropentane, cyclopentylamine, isopropyl butyl ether, ethyl isobutyrate, peracetic acid, 3-methyl-2-butanol and 2-methyl-1-propanol have vapor pressures near enough to that of toluene to be useful according to the present invention. These solutions provide results better than the use of toluene alone.

(013) Examples of single self-cleaning compounds useful as PAI sources according to the present invention include compounds having a C7 ion source portion with a composition of C7 or C7H_x, selected from benzyl chloride

($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$), benzyl acetate ($\text{C}_9\text{H}_{10}\text{O}_2$), benzyl ethyl ether ($\text{C}_9\text{H}_{12}\text{O}$), benzyl formate ($\text{C}_6\text{H}_5\text{CH}_2\text{OOCH}$), or benzyl mercaptan ($\text{C}_6\text{H}_5\text{CH}_2\text{SH}$). These compounds may also be useful as carbon sources for other carbon implantation purposes.

(014) The compounds according to the present invention may be packaged for use in several different ways. For example, the Genii technology from the Linde Group provides the compounds as standard sub-atmospheric pressure ion implantation sources in a cylinder with a membrane separator and with temperature control on the cylinder wall and delivery line up to 100°C . Alternatively, an inert carrier gas may be used, wherein the inert gas flows through the source liquid in a bubbler configuration at room temperature. In addition, the source compound may be delivered by direct liquid injection with a bubbler and liquid mass flow controller at room temperature. In general the compounds of the present invention will require heating between 50°C and 100°C if the pure vapor phase of liquid is delivered.

(015) The present invention provides many advantages. The compounds of the present invention are self-cleaning C_7 implantation sources that provide high C_7H_7 ion beam intensity as well as self-cleaning radicals with high concentration. For the single molecule liquid compound embodiment of the present invention, component separation is not necessary making processing simpler and less expensive. In addition, the single molecule liquid compounds of the present invention exhibit a single vapor pressure curve, reducing operation parameters and simplifying processing. The compounds of the present invention provide self-cleaning properties and therefore, longer ion chamber life can be achieved and the need for shutdown for cleaning can be reduced or eliminated. Consequently, manufacturing and operation costs are reduced.

(016) It is anticipated that other embodiments and variations of the present invention will become readily apparent to the skilled artisan in the light of the foregoing description, and it is intended that such embodiments and variations likewise be included within the scope of the invention as set out in the appended claims. For example, the compounds of the present invention may be useful for implantation of semiconductor devices, for implantation of structural engineered materials, or for implantation of photovoltaic materials. The variations of the present invention also include other carbon-based molecules other than C7.

CLAIMS

What is claimed:

1. A self cleaning solution for carbon implantation comprising a single molecule compound having a C_n ($n=5-30$) ion source portion and a cleaning agent portion.
2. The solution of claim 1, wherein the C_n ($n=5-30$) ion source portion is a C_7 ion source having a composition of C_7 or C_7H_x selected from benzyl chloride ($C_6H_5CH_2Cl$), benzyl acetate ($C_9H_{10}O_2$), benzyl ethyl ether ($C_9H_{12}O$), benzyl formate ($C_6H_5CH_2OOCH$), or benzyl mercaptan ($C_6H_5CH_2SH$).
3. The solution of claim 1, wherein the cleaning agent portion contains oxygen, chlorine, nitrogen, sulfur or fluorine.
4. The solution of claim 1, wherein the compound has a liquid vapor pressure greater than 1 Torr at temperatures below $100^\circ C$.
5. The solution of claim 4, wherein the liquid vapor pressure is greater than 5 Torr and less than 100 Torr at temperatures between $10^\circ C$ and $100^\circ C$.
6. A method of carbon implantation comprising:
delivering a self cleaning solution of a single molecule compound having a C_n ($n=5-30$) ion source portion and a cleaning agent portion to an ionization chamber;
dissociating the solution to produce a C_n ($n=5-30$) source ion and highly concentrated cleaning agent radicals;
implanting the C_n ($n=5-30$) source ions; and
reacting the cleaning agent radicals with hydrocarbon residue within the ionization chamber.

7. The method of claim 6, wherein the C_n ($n=5-30$) ion source portion is a C_7 ion source having a composition of C_7 or C_7H_x selected from benzyl chloride ($C_6H_5CH_2Cl$), benzyl acetate ($C_9H_{10}O_2$), benzyl ethyl ether ($C_9H_{12}O$), benzyl formate ($C_6H_5CH_2OOCH$), or benzyl mercaptan ($C_6H_5CH_2SH$).
8. The method of claim 7, wherein the C_7 ion source selected is the source having the highest ion intensity in mass spectra produced in the ionization chamber.
9. The method of claim 6, wherein the cleaning agent portion contains oxygen, chlorine, nitrogen, sulfur or fluorine.
10. The method of claim 6, wherein the compound has a liquid vapor pressure greater than 1 Torr at temperatures below $100^\circ C$.
11. The method of claim 10, wherein the liquid vapor pressure is greater than 5 Torr and less than 100 Torr at temperatures between $10^\circ C$ and $100^\circ C$.
12. The method of claim 6 wherein delivering comprises delivering the compound from a cylinder with a membrane separator having temperature control on the cylinder wall and the delivery line.
13. The method of claim 6 wherein delivering comprises flowing an inert carrier gas through the solution in a bubbler configuration at room temperature.
14. The method of claim 6 wherein delivering comprises direct liquid injection of the solution with a bubbler and liquid mass flow controller at room temperature.

15. The method of claim 6 wherein dissociating comprises heating the ionization chamber to a temperature between 50°C and 100°C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2012/030228

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 21/265 (2012.01)

USPC - 257/523

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(8) - H01L 21/00, 02, 20, 78, 265, 336 (2012.01)

USPC - 257/E21.334, E21.335, E29.166, E29.255, E29.257; 427/457, 523

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)

Patbase, Orbit.com, Proquest

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2009/0081874 A1 (COOK et al) 26 March 2009 (26.03.2009) entire document	1, 3, 6, 9 ----- 4, 5, 10-15
Y	US 2002/0070672 A1 (HORSKY) 13 June 2002 (13.06.2002) entire document	4, 5, 10, 11, 15
Y	US 2009/0252887 A1 (BARKER et al) 08 October 2009 (08.10.2009) entire document	12
Y	US 2005/0233529 A1 (POMAREDE et al) 20 October 2005 (20.10.2005) entire document	13, 14
A	US 2009/0206281 A1 (OVED et al) 20 August 2009 (20.08.2009) entire document	1-15

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

"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

"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

"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

"&" document member of the same patent family

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