

NOVEL METHODS FOR GAS PHASE SELECTIVE ETCHING OF SILICON-GERMANIUM LAYERS

Field of Invention

[0001] This invention relates to selective etching of silicon-germanium layers on a wafer in connection with semiconductor fabrication. More particularly, the invention pertains to novel methods for improving the selectivity ratio of silicon-germanium layer relative to silicon during semiconductor fabrication that is not possible with conventional etchant techniques.

Background of the Invention

[0002] Amorphous silicon (a-Si), polycrystalline silicon (poly-Si) and single crystal Si, in conjunction with silicon-germanium (“SiGe”) are widely used in the semiconductor industry for different applications. For sub-20 nm technology nodes and below, the integration of SiGe as a source-drain material has shown potential to improve electrical performance for transistors. Various transistors can be formed on a substrate.

[0003] In scaling beyond 5 nm technology nodes, the semiconductor device industry is moving away from FinFet transistor structures towards so-called gate all-around (GAA) device architectures. One fundamental requirement for GAA implementation is the formation of SiGe and Si nanowires (NW) and Si nanosheets (NS). Specifically, horizontally-stacked silicon nanowires (HNW), and horizontally stacked nanosheets (HNS) are being investigated. HNS has been identified as the next generation device structure at 3 nm node and sub-3nm nodes.

[0004] However, in order to successfully manufacture HNS structures, advanced methodologies are required to address the challenges and meet the demands for aggressive patterning that continue to reduce the size of the critical features. The ability to successfully integrate patterning schemes with highly selective etch processes is critical to reliable pattern transfer. Pattern transfer can be carried out as follows. After the circuit pattern is formed, a protective layer (e.g., photo-sensitive material patterned using optical lithography, a mechanically imprinted patterned layer or a direct self-assembled layer) is

used to mask certain regions of the semiconductor substrate, while other regions of the semiconductor substrate remain exposed. The remaining exposed regions allow the transfer of the circuit pattern onto an underlying layer of the substrate by utilizing a dry etching process. The ability to fabricate the HNS features requires high etch selectivity of SiGe to Si that is not currently available. The etch selectivity is defined as the ratio of etch rate for two different surfaces when exposed to an etchant process. For example, an etch selectivity of 100:1 for SiGe to Si under exposure to a certain etchant process means that the etch rate for SiGe surface is 100 times higher than a Si surface when using the etchant process.

[0005] Conventional etchant techniques such as direct plasma etch, plasma atomic layer etching (ALE), or ion milling are not capable of achieving the higher etch selectivity ratios of SiGe to Si required for creating HNS features. By way of example, for three stacked silicon NS's, there are four SiGe sacrificial layers. The removal of the SiGe sacrificial layers without Si NS damage is required and represents a critical process step in GAA HNS devices. The undercut or cavity SiGe etch requires high precision and high selectivity isotropic chemical etches not possible by conventional etch techniques.

[0006] Other traditional etchant methods involve oxidative wet etch methods that are commonly seen in selective etching of SiGe over Si in the micro-electromechanical systems (MEMS) industry and in early GAA HNS research. However, generally speaking, the semiconductor industry prefers not to utilize a wet-based etchant method. Instead, the industry desires a selective dry chemical etch for better Si HNS release quality and easier high-volume manufacturing processes.

[0007] Dry thermal etch processes are being created for the selective etching of SiGe over Si, SiO₃, SiC, and Si₃N₄. However, such dry thermal etchant processes remain deficient. Specifically, current methods, such as remote CF₄/O₂ based plasmas, are only capable of producing an etch selectivity of 50:1. In other words, the etch rate for SiGe surface is 50 times higher than a Si surface when using the CF₄/O₂ remote plasma process.

[0008] Currently, as other alternatives, thermal dry etching process using interhalogen species such as ClF₃, or different mixtures of F₂ and inert gases from early MEMS research activities has been investigated (U.S. Patent Publication No. 2020027741;

and Loubet et al., *A Novel Dry Selective Etch of SiGe for the Enablement of High Performance Logic Stacked Gate-All-Around NanoSheet Devices*, *IEDM*, pp. 1-4, 2019).

Etch selectivity of up to 150:1 for superlattice SiGe:Si layers have been reported when utilizing ClF_3 as an interhalogen etchant.

[0009] Despite current developmental activities, there remains a continued demand for higher etch selectivity to improve GAA nanostructure performance and increase manufacturing productivity. There is currently an unmet demand for etch selectivity of SiGe to Si, SiO_2 , Si_3N_4 and SiC that is greater than 150:1.

Summary of the Invention

[0010] In one aspect, a method of selectively dry etching a substrate, comprising the steps of: providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer; introducing a fluorine-containing interhalogen gas into the etch chamber; selectively etching a first portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a first portion of volatilized fluorides of silicon and germanium; ; converting the silicon layer into a non-volatized fluorinated silicon layer; withdrawing any residual amount of the fluorine-containing interhalogen gas from the etch chamber; introducing a passivating gas into the etch chamber selectively convert the non-volatized fluorinated silicon layer into a passivating silicon layer, whereby the passivating gas does not substantially react with the silicon-germanium alloy layer, wherein the passivating gas is introduced after introducing the fluorine-containing interhalogen gas; withdrawing any residual amount of the passivating gas from the etch chamber; re-introducing the fluorine-containing interhalogen gas into the etch chamber; and selectively etching a second portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a second portion of volatilized fluorides of silicon and germanium without substantial etching of the passivating silicon layer.

[0011] In a second aspect, a method of selectively dry etching a substrate, comprising the steps of: providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer; introducing a first etchant

gas into the etch chamber, wherein said first etchant gas comprises a fluorine-containing interhalogen gas; selectively etching a first portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a first portion of volatilized fluorides of silicon and germanium; converting the silicon layer into a non-volatilized fluorinated silicon layer; withdrawing any residual amount of the fluorine-containing interhalogen gas from the etch chamber; introducing a passivating gas into the etch chamber to selectively convert the non-volatilized fluorinated silicon layer into a passivating silicon layer, whereby the passivating gas does not substantially react with the silicon-germanium alloy layer, wherein the passivating gas is introduced after introducing the fluorine-containing interhalogen gas; withdrawing any residual amount of the passivating gas from the etch chamber; introducing a second etchant gas into the etch chamber; and selectively etching a second portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a second portion of volatilized fluorides of silicon and germanium without substantial etching of the passivating silicon layer.

[0012]

[0013] In a third aspect, a method of selectively dry etching a substrate, comprising the steps of: providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer; and selectively etching the silicon-germanium alloy layer with solely the use of an interhalogen fluorine-containing gas to form a fluoride terminated-layer on the silicon layer while creating and maintaining a passivating layer on the Si layer.

Brief Description of the Drawings

[0014] Fig. 1 illustrates a flow chart of an etchant process according to a first embodiment of the present invention;

[0015] Fig. 2 illustrates a representative resultant surface after etching a first portion of a SiGe alloy layer with a fluorine-containing interhalogen gas, and exposing the fluorine-containing interhalogen gas to a Si surface to form a fluorine terminated layer on

Claims

1. A method of selectively dry etching a substrate, comprising the steps of:
 - providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer;
 - introducing a fluorine-containing interhalogen gas into the etch chamber;
 - selectively etching a first portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a first portion of volatilized fluorides of silicon and germanium;
 - converting the silicon layer into a non-volatilized fluorinated silicon layer;
 - withdrawing any residual amount of the fluorine-containing interhalogen gas from the etch chamber;
 - introducing a passivating gas into the etch chamber to selectively convert the non-volatilized fluorinated silicon layer into a passivating silicon layer, whereby the passivating gas does not substantially react with the silicon-germanium alloy layer, wherein the passivating gas is introduced after introducing the fluorine-containing interhalogen gas;
 - withdrawing any residual amount of the passivating gas from the etch chamber;
 - re-introducing the fluorine-containing interhalogen gas into the etch chamber; and
 - selectively etching a second portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a second portion of volatilized fluorides of silicon and germanium without substantial etching of the passivating silicon layer.
2. The method of claim 1, further comprising repeating the step of re-introducing the fluorine-containing interhalogen gas into the etch chamber one or more times to further react with the silicon-germanium alloy layer until a predetermined amount of the silicon-germanium alloy layer is selectively etched and subsequently removed from the etch chamber without substantial etching of the passivating silicon layer.
3. The method of claim 2, further comprising the steps of:

removing the passivating silicon layer to expose the silicon layer when the predetermined amount of the silicon-germanium alloy layer has been selectively etched and subsequently removed from the etch chamber.

4. The method of claim 1, wherein the passivating gas is selected from the group consisting of NH_3 , H_2O , O_2 , compounds with an alcohol functional group, H_2S , H_2Se and any combination thereof.

5. The method of claim 1, wherein the passivating silicon layer is selected from the group consisting of silicon oxide, silicon sulfide, silicon nitride, silicon selenide and a fluorosilicate salt.

6. The method of claim 1, wherein the passivating silicon layer comprises incorporation of carbon or hydrogen as a self-assembled monomer or alkyl chain.

7. The method of claim 2, further comprising re-introducing the passivating gas into the etch chamber to re-establish the passivating silicon layer prior to the step of repeating the re-introducing of the fluorine-containing interhalogen gas into the etch chamber one or more times.

8. The method of claim 1, further comprising withdrawing the residual amount of the fluorine-containing interhalogen gas after converting the silicon layer into the non-volatized fluorinated silicon layer, and prior to introducing the passivating gas into the etch chamber.

9. The method of claim 1, wherein the step of withdrawing the residual amount of the passivating gas occurs after converting the non-volatized fluorinated silicon layer into the passivating silicon layer and prior to re-introducing the fluorine-containing interhalogen gas into the etch chamber.

10. A method of selectively dry etching a substrate, comprising the steps of:
providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer;
introducing a first etchant gas into the etch chamber, wherein said first etchant gas comprises a fluorine-containing interhalogen gas;
selectively etching a first portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a first portion of volatilized fluorides of silicon and germanium;
converting the silicon layer into a non-volatized fluorinated silicon layer;
withdrawing any residual amount of the fluorine-containing interhalogen gas from the etch chamber;
introducing a passivating gas into the etch chamber to selectively convert the non-volatized fluorinated silicon layer into a passivating silicon layer, whereby the passivating gas does not substantially react with the silicon-germanium alloy layer, wherein the passivating gas is introduced after introducing the fluorine-containing interhalogen gas;
withdrawing any residual amount of the passivating gas from the etch chamber;
introducing a second etchant gas into the etch chamber; and
selectively etching a second portion of the silicon-germanium alloy layer that is subsequently removed from the etch chamber as a second portion of volatilized fluorides of silicon and germanium without substantial etching of the passivating silicon layer.
11. The method of claim 10, wherein the second etchant gas is selected from the group consisting of CF₄, C₄F₈, C₄F₆, CH₃F, F₂, XeF₂, NF₃ and any combination thereof.
12. The method of claim 10, further comprising the step of re-introducing an additional amount of the second etchant gas into the etch chamber to further react with the silicon-germanium alloy layer until a predetermined amount of the silicon-germanium alloy layer is selectively etched without substantial etching of the passivating silicon layer.
13. The method of claim 12, further comprising the step of:

removing the passivating silicon layer when the predetermined amount of the silicon-germanium alloy layer is selectively etched and subsequently removed from the etch chamber.

14. The method of claim 12, further comprising re-introducing the passivating gas into the etch chamber to re-establish the passivating silicon layer prior to the step of re-introducing the additional amount of the second etchant gas into the etch chamber.

15. The method of claim 10, further comprising withdrawing the residual amount of the fluorine-containing interhalogen gas after converting the silicon layer into the non-volatized fluorinated silicon layer and prior to introducing the passivating gas into the etch chamber.

16. The method of claim 10, further comprising withdrawing the residual amount of the passivating gas after converting the non-volatized fluorinated silicon layer into the passivating silicon layer and prior to introducing the second etchant gas into the etch chamber.

17. A method of selectively dry etching a substrate, comprising the steps of:
providing a substrate in an etch chamber, said substrate comprising a silicon-germanium alloy layer and a silicon layer; and
selectively etching the silicon-germanium alloy layer with solely the use of an interhalogen fluorine-containing gas to form a fluoride terminated-layer on the silicon layer while creating and maintaining a passivating layer on the Si layer.

18. The method of claim 17, wherein the passivating layer is formed by flowing a passivating gas into the etch chamber towards an exposed surface of the silicon layer.

19. The method of claim 18, wherein the passivating gas is flowed into the etch chamber after etching a first portion of the silicon-germanium alloy layer with the

interhalogen fluorine-containing gas, thereby exposing at least a portion of the silicon layer.

20. The method of claim 17, further comprising introducing an additional gas species into the etch chamber, said additional gas species comprising a rate inhibitor species to reduce a rate of etching on the Si layer more than that of the silicon-germanium alloy layer.

21. The method of claim 17, further comprising introducing an additional gas species into the etch chamber, said additional gas species comprising a rate enhancer species to increase a rate of etching on the silicon-germanium alloy layer more than that of the Si layer.

22. The method of claim 17, further comprising introducing additional gas species into the etch chamber, said additional gas species comprising a rate inhibitor species and a rate enhancer species.