Electrical Characterization of Photo-Oxidized $Si_{1-x-y}Ge_xC_y$ Films

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Abstract

Strained Silicon Germanium Carbon ($Si_{1-x-y}Ge_xC_y$ or SiGeC) on silicon was oxidized using a novel Photo-Oxidation process. The growth rate of the oxide was investigated and found to depend heavily on the germanium and carbon concentrations. MOS capacitors were fabricated with the resulting oxide and electrical characterization was done. The SiGeC MOS capacitors proved to have high leakage current through the gate oxide. The leakage current was found to be highly dependent on carbon concentration, and to a lesser degree, on germanium concentration, as well. Fixed oxide charge and interface state density were found to increase by a factor of ten over photo-oxidized silicon.

Keywords: Silicon Germanium Carbon (SiGeC), Silicon Germanium (SiGe), β-SiC formation, Ge Segregation, Photo-Oxidation, Oxidation Kinetics, MOS Capacitors, Leakage Current, Interface State Density.

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1. Introduction

Silicon Germanium Carbon ($Si_{1-x-y}Ge_xC_y$ or SiGeC) has demonstrated much potential for use in column IV Heterojunction Bipolar Transistors (HBT's) [1,2] and high hole mobility MOSFETs [3,4]. Like its more common counterpart, silicon germanium (SiGe), SiGeC is a narrow bandgap semiconductor that is compatible with most silicon-based processing. Its bandgap is adjustable, approximately according to Vegard's law and depending mainly on germanium content [5]. What distinguishes SiGeC from SiGe is the potential strain compensating effect of substitutional carbon.

As SiGe is epitaxially grown on silicon, lattice parameter mismatch between silicon and germanium introduces strain into the crystal. When the grown film reaches critical thickness, the built-up strain can no longer be accommodated by the crystal and misfit dislocations are introduced [6]. These dislocations are detrimental to active devices; therefore, SiGe epitaxial layers must be kept thinner than the critical thickness. This constraint can limit SiGe potential uses.

SiGeC overcomes this limitation by including small amounts of substitutional carbon. The small lattice parameter of carbon (3.5670 Å) alleviates the strain produced by the large germanium atom (lattice parameter of 5.6576 Å) in a silicon matrix (lattice parameter of 5.4305 Å) [7]. According to Vegard's Law, when carbon is incorporated substitutionally, with one carbon atom for every 8.2 germanium atoms, the strain is completely compensated [5]. With this strain compensation, epitaxial SiGeC is not limited by a critical thickness.

1.1 SiGeC - Metastability and β-SiC:

Unfortunately, because of carbon's extremely small solubility in silicon (0.0007% at silicon's melting point) and insolubility in germanium, extremely non-equilibrium growth methods are required [8-12]. One such method, Chemical Vapor Deposition (CVD), uses low temperature (<650^{o}C) and surface treatments to trap carbon on substitutional sites during film growth, creating a supersaturated solid solution. Enhancements in substitutional carbon solubility have been reported as high as 10^4 times the equilibrium value [8,10,14,15].

Because carbon is so far above its equilibrium solid solubility concentration, at higher temperatures (above 850^{o}C) it reverts to its equilibrium phase, and precipitates cubic silicon carbide (β-SiC), negatively affecting device performance [10,12,13,16]. This greatly limits SiGeC for MOS applications where high-temperature thermal oxidation is typically required for a high quality gate oxide.

1.2 SiGeC – Ge Segregation:

Even if β-SiC precipitation is avoided, another phenomenon exists which jeopardizes device performance, germanium segregation. During thermal oxidation of SiGeC, silicon and carbon react with oxygen to from SiO_2 (oxide) and CO (which diffuses away as a by-product). The germanium, however, is rejected by the growing oxide and "piles –

up” at the SiGeC surface. Surface germanium has been shown to increase interface traps and charging, degrading MOSFET performance. Germanium pile up amplifies this effect [16,18-20].

As germanium pile up was found to cease below 500^{o}C, alternatives to thermal oxidation have been explored to avoid high temperature processing. Deposited oxides, anodic oxides, plasma oxides, and wet oxides at low temperature have all been used on SiGeC (or SiGe) with limited success, though poor interface and oxide quality always resulted [20-23].

1.3 Photo-Oxidation:

Recently, a new technique to enhance low temperature oxidation has been developed that produces a high-quality oxide. This method, called “photo-oxidation,” uses vacuum ultraviolet light (VUV) to generate large amounts of atomic oxygen and ozone. These radicals, O and O_3, greatly enhance the oxidation rate in the linear region (initial stages of oxidation when oxide is very thin, <200 Å) of oxide growth. This allows for significant oxidation where molecular oxygen would grow almost none. Oxides with thickness greater than 100 Å have been grown at 250^{o}C with fairly good quality (fixed oxide charge concentration ~4×10^{10} cm^{-2}). This rate is 90 times the thermal oxidation rate at 612^{o}C [24-28].

Though photo-oxidation has been reported in the literature on SiGe, to the authors’ knowledge, this is the first investigation into the photo-oxidation of SiGeC. It is expected that photo-oxidation will not result in β-SiC formation, nor will it cause germanium segregation, due to the low processing temperatures. The un-oxidized SiGeC layer should remain of high quality and free of the mentioned phenomena.

As the germanium and carbon are not consumed during photo-oxidation, it remains to be seen what effect these elements will have on the oxide. Electrical testing of the resulting oxide is crucial to determine the usefulness of photo-oxidation in SiGeC MOS processing.

2. Experimental

Strained $Si_{1-x-y}Ge_xC_y$ (SiGeC) layers, heteroepitaxially grown on silicon substrates using Rapid Thermal Chemical Vapor Deposition (RTCVD) at 650^{o}C. Several compositions of SiGeC, in the range x=0 to 0.30 and y=0 to 0.02 were used in this experiment. The samples were cleaned and then oxidized using a novel photo-enhanced oxidation procedure. Photo-enhanced oxidation was achieved with a 172 nm excimer, Vacuum Ultraviolet (VUV), source used at 400^{o}C for 2 hours. All samples received identical processing, so the oxidation kinetics could be studied.

MOS capacitors were fabricated using lift-off photolithography with a titanium-tungsten and aluminum gate metal. Backside contacts were fabricated from aluminum. The capacitors were annealed in a forming gas (4% Hydrogen in Argon) at 425^{o}C for 30 minutes.

Current-Voltage (I-V) measurements were made with an HP4145B Semiconductor Parameter Analyzer and Capacitance-Voltage (C-V) measurements were made with an HP4284A Precision LCR meter. A 200-micron circular capacitor was used for each measurement.

3. Results and Discussion

The oxides resulting from the photo-oxidation treatment were measured via ellipsometry and were determined to be 70-130 Å thick. The compositional dependence of the thickness is depicted in Figure 1. The presence of germanium and carbon enhance the oxidation kinetics. Additionally, the two elements appear to interact with one another, creating a peak oxidation rate at certain ratios.

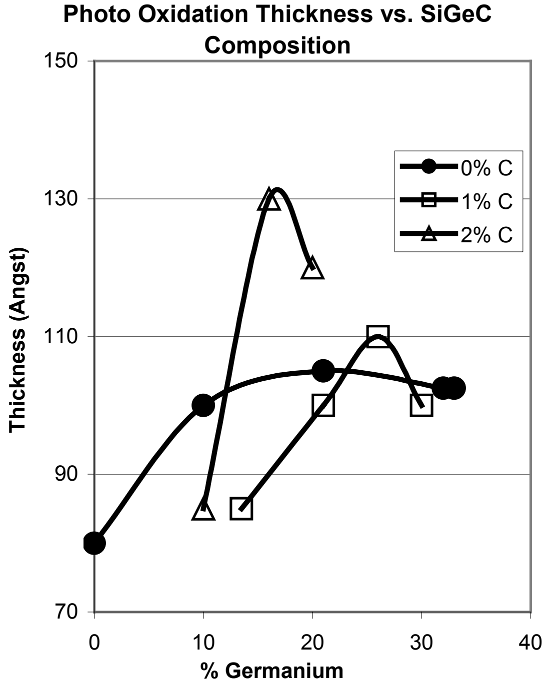

Figure 1: SiGeC Photo-Oxidation Kinetics

The results of the I-V measurements indicate that presence of either germanium or carbon in the oxide film decreased the hard breakdown voltage of the MOS Capacitor. Figures 2 and 3 demonstrate the effect of carbon on MOS capacitor leakage current for 10% and 30% germanium, respectively. Clearly, increased carbon increases leakage current in all cases.

Germanium has a less dramatic effect on the leakage current and does not exhibit a clear dependence like carbon.

All-silicon control samples, photo-oxidized and processed in an identical manner, were also measured and are included in each figure for comparison. These control samples demonstrated significantly lower leakage currents than either their SiGe or SiGeC counterparts.

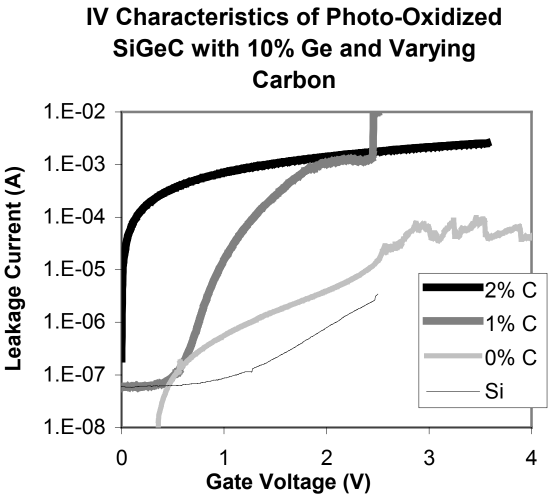

Figure 2: Leakage Current through Photo-Oxidized SiGeC MOS Capacitors with 10% Germanium Content.

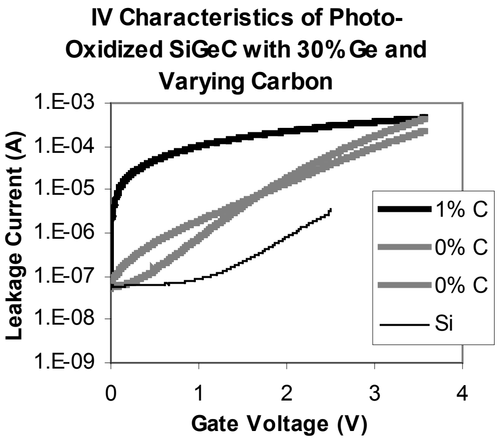

Figure 3: Leakage Current through Photo-Oxidized SiGeC MOS Capacitors with 30% Germanium Content.

The C-V curves could not be obtained in most cases, as high leakage currents obscured the results. Some samples, however, had low enough leakage to be able to take high frequency (1 MHz) capacitance measurements. Analysis of this data indicated that the fixed oxide charge concentration (N_{SS}) increased with both carbon and germanium. The silicon samples had $N_{SS} = 5.4 \times 10^{11}$ cm^{-3}, while samples with 10% Ge and 1% C had $N_{SS} = 1.9 \times 10^{12}$ to 1.1×10^{13} cm^{-3}. Higher concentrations could not be accurately evaluated due to excessive leakage current.

Density of interface states (D_{it}) measurements were also extracted for the few samples with low enough leakage. Using the Terman Method and the high frequency CV curve, D_{it} for the 10% Ge and 1% C is shown in Figure 4 [29]. An all-silicon sample is also shown for comparison. D_{it} is increased by a factor of ten, even for small amounts of germanium and carbon.

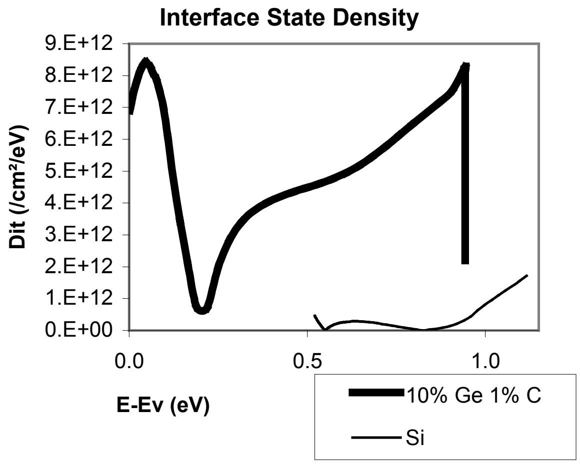

Figure 4: Interface State Density comparison of Photo-Oxidized MOS Capacitors fabricated from SiGeC and Si.

4. Conclusion

The kinetic study indicates that carbon and germanium increase the oxidation rate during photo-oxidation. The peak in the oxidation occurs at differing ratios of Ge:C. This suggests a possible strain dependence to photo-oxidation, as the Ge:C ratio heavily influences strain.

From the electrical data collected, it is apparent that carbon and germanium negatively affect the electrical quality of photo-oxidized SiGeC. High leakage currents through the oxide suggest that some conduction path exists; this conduction path demonstrates a large dependence on carbon concentration. Fixed oxide charge and interface state density are also increased by carbon/germanium.

Likely, the carbon trapped in the growing oxide is the primary source of the detrimental effects, since carbon had the greatest effect. Germanium in the oxide also influenced the oxide quality, but to a lesser degree.

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