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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

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 (HBTs) [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.

Since 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

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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]. Consequently, epitaxial SiGeC is not limited by a critical thickness.

1.1. SiGeC – metastability and β-SiC

Unfortunately, because of carbon's extremely limited solubility in silicon (0.0007% at silicon's melting point) and near insolubility in germanium, non-equilibrium growth methods are required [8–12]. One such method, chemical vapor deposition (CVD), uses low temperature (<650 °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].

At higher temperatures (above 850 °C), the excess carbon atoms revert to their equilibrium phase, and precipitate as cubic silicon carbide (β-SiC), thereby negatively affecting device performance [10,12,13,16]. Since high-temperature thermal oxidation is typically required for a high-quality gate oxide, utilizing SiGeC for MOS applications is severely limited.

1.2. SiGeC–Ge segregation

Even if β-SiC precipitation is avoided, another thermally enhanced phenomenon i.e., germanium segregation, also jeopardizes device performance. 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 [16–20].

Below 500 °C, germanium pile-up ceases. As a result, alternatives to thermal oxidation at high temperatures have been explored. Several, including deposited oxides, anodic oxides, plasma oxides, and wet oxides at low temperature have been used on SiGeC (or SiGe) but with limited success. In all instances, interface and oxide quality are inferior to high-temperature silicon oxidation [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 very active radicals, O and O_3, greatly enhance the oxidation rate in the initial linear growth region when the oxide is very thin, <200 Å. Oxides with a thickness greater than 100 Å have been grown in silicon at 250 °C with good quality (fixed oxide charge concentration $\sim 4 \times 10^{10}$ cm^{-2}). This rate is 90 times the thermal oxidation rate at 612 °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. Because of the low processing temperatures, it is expected that photo-oxidation will not promote β-SiC formation nor germanium segregation. Therefore, the un-oxidized SiGeC layer should remain of high quality and free of the afore mentioned phenomena.

Since the germanium and carbon atoms are not consumed during photo-oxidation, it remains to be seen what effect these elements will have on the oxide. Studies of various low temperature oxidation techniques on SiGe suggest that GeO_2 is trapped in the growing SiO_2 oxide [20,21]. Carbon's behavior has yet to be characterized, however it is postulated that CO, or some other carbonaceous gas, is formed and diffuses away. Electrical testing of the resulting oxide is crucial to determine the usefulness of photo-oxidation in SiGeC MOS processing.

2. Experimental

Strained $Si_{1-x-y}Ge_xC_y$ layers, have been heteroepitaxially grown on silicon substrates using rapid thermal chemical vapor deposition (RTCVD) at 650 °C. Several compositions of $Si_{1-x-y}Ge_xC_y$, in the range $x = 0$–0.30 and $y = 0$–0.02 were used in this experiment. The samples were first cleaned and then oxidized using a novel photo-enhanced oxidation procedure. Photo-enhanced oxidation was achieved with a 172 nm excimer, VUV, source used at 400 °C for 2 h. All samples received identical processing, to permit the study of their oxidation kinetics.

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 °C for 30 min.

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-μm 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. Most oxidation techniques used on SiGe and SiGeC are kinetically enhanced by the addition of carbon and germanium; photo-oxidation is no exception. The compositional dependence of the thickness is depicted in Fig. 1. The presence of germanium and carbon enhance the oxidation kinetics. Additionally, the two elements appear to interact, creating a peak oxidation rate at certain ratios.

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. Figs. 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.

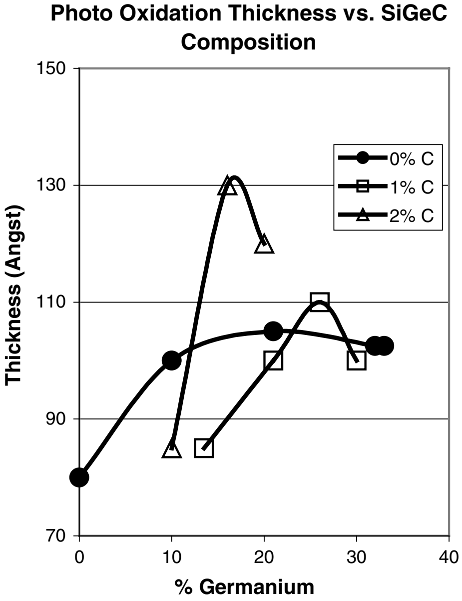

Fig. 1. SiGeC photo-oxidation kinetics.

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

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

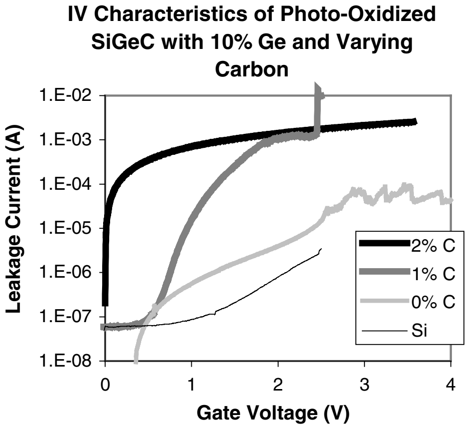

Fig. 2. Leakage current through photo-oxidized SiGeC MOS capacitors with 10% germanium content.

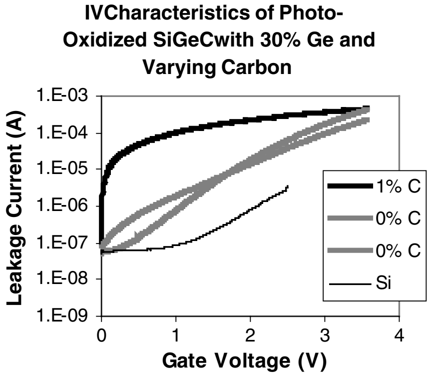

Fig. 3. Leakage current through photo-oxidized SiGeC MOS capacitors with 30% germanium content.

significantly lower leakage currents than either their SiGe or SiGeC counterparts.

The capacitance–voltage curves could not be obtained in most cases, as high leakage currents obscured the results. Some samples, however, had sufficiently low leakage to be able to make 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}. Samples with 10% Ge and 1% C had $N_{SS} = 1.9 \times 10^{12}$–$1.1 \times 10^{13}$ cm^{-3}, while samples with 21% Ge and 1% C had $N_{SS} = 1.2 \times 10^{13}$ cm^{-3}. Although more concentrations could not be accurately evaluated because of excessive leakage current, it is clear that the addition of Ge and C greatly increase the fixed oxide charge.

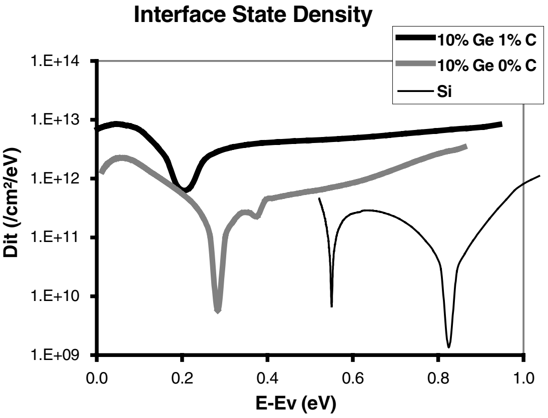

Fig. 4. Interface state density comparison of photo-oxidized MOS capacitors fabricated from SiGe, SiGeC and Si.

Density of interface states (D_{it}) measurements were also extracted for the few samples with acceptably low leakage. Employing the Terman method and the high frequency C–V curve, D_{it} behavior for the measurable cases is presented in Fig. 4 [29]. For comparative purposes the D_{it} behavior of a photo-oxidized all-silicon sample is also depicted. Evaluation of a 21% Ge and 1% C sample, not shown in the figure, yielded a maximum D_{it} of 1.5×10^{13} cm^{-2} eV^{-1}. D_{it} is increased somewhat by the incorporation of germanium, but carbon increases D_{it} by a factor of 10, even for small percentages.

4. Conclusion

Concordant with most SiGe(C) oxidation studies, the present kinetic study indicates that carbon and germanium atoms increase the rate of oxide formation during photo-oxidation. However, the peak in oxide layer thickness occurs at differing ratios of Ge:C, with the inclusion of the smaller carbon atoms being the more influential. Since strain is strongly affected by the incorporation of both Ge and C atoms, these findings solidly imply a strain dependence in the oxidation rate.

From the electrical data collected, it is apparent that carbon and germanium negatively affect the electrical quality of photo-oxidized SiGeC. High leakage currents are indicative of conduction paths through the oxide layer, consequently, the current I–V findings demonstrate that these conduction paths are strongly affected by the carbon concentration. Fixed oxide charge and interface state density are also increased by carbon, and to a lesser extent, by germanium.

Some of the electrical degradation of the oxide can be attributed to GeO_2 trapped in the growing SiO_2, but the collected data clearly show that germanium's effect on the electrical properties of the oxide is less significant than carbon's.

Carbon is the primary source of the detrimental effects observed. Most likely, its atoms are also trapped in the growing oxide, probably as a compound that does not diffuse away, as has been postulated.

Further study is needed to more fully explore the mechanisms of electrical degradation of SiO_2 due to carbon and germanium in photo-oxidation. It is clear, however, that direct oxidation of SiGeC layers by photo-oxidation for MOS applications offers little promise unless the noted deficiencies can be overcome.

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