Low-temperature hetero-epitaxial growth of Ge on Si by high density plasma chemical vapor deposition

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ABSTRACT

Demand for integration of optoelectronic functionality (e.g., optical interconnects) with silicon complementary metal oxide semiconductor (CMOS) technology has for many years motivated the investigation of low temperature (~ 450ºC) germanium deposition processes that may be integrated in to the back-end CMOS process flow. A common challenge to improving the germanium quality is the thermal budget of the in-situ bake, which is used to reduce defect forming oxygen and carbon surface residues [1, 2]. Typical cleaning temperatures to remove significant concentrations of oxygen and carbon have been reported to be approximately 750ºC for thermal hydrogen bakes in standard chemical vapor deposition chambers [3]. Germanium device performance using lower peak in-situ cleans (i.e., ~450°C) has been hampered by additional crystal defectivity, although epitaxy is possible with out complete removal of oxygen and carbon at lower temperatures [4].

Plasma enhanced chemical vapor deposition (PECVD) is used to reduce the processing temperature. Hydrogen plasma assisted in-situ surface preparation of epitaxy has been shown to reduce both carbon and oxygen concentrations and enable epitaxial growth at temperatures as low as ~150°C [5, 6]. The hydrogen is believed to help produce volatile Si-O and H_2O species in the removal of oxygen, although typically this is not reported to occur rapidly enough to completely clear the surface of all oxygen until ~550ºC. In this paper, we describe the use of an in-situ argon/germane high density plasma to help initiate germanium epitaxy on silicon using a peak temperature of approximately 460ºC. Germanium is believed to readily break Si-O bonds to form more volatile Ge-O [7-9], therefore, argon/germane plasmas offer the potential to reduce the necessary in-situ clean temperature while obtaining similar results as hydrogen in-situ cleans. To the authors knowledge this report is also the first demonstration of germanium epitaxy on silicon using this commercially available high density plasma chamber configuration instead of, for example, remote or electron cyclotron resonance configurations.

INTRODUCTION

Germanium-silicon heterostructures are currently being considered for near infrared (NIR) optoelectronic (e.g., detectors [4], and modulators [10]) that are compatible with the complementary metal oxide semiconductor (CMOS) platform. A common challenge to advancing this technology is minimizing the defects that form in the germanium (Ge) due to the

lattice mismatch with the Si substrate. Recently Ge (p)/Si (n) diodes that include the interface in the junction were reported to produce detectors with potentially useful NIR performance despite the defective interface (e.g. J_d ~ 10 mA/cm^{-2}, and responsivity as high as 0.59 A/W, at 1550 nm) [11]. Most if not all reported low temperature (T < 450ºC) Ge detectors have used either e-beam evaporation (i.e., in some cases polycrystalline Ge, or molecular beam epitaxy (MBE)) [4, 12]. Improvement upon these results using a more commercially standard deposition technique while maintaining the low deposition temperature would be desirable.

In this paper, we describe the development of a high density plasma chemical vapor deposition (HDP-CVD) process that uses a low temperature (~460ºC) surface preparation step (i.e., in-situ argon/germane plasma) that assists in the initiation of germanium epitaxy. The use of this surface preparation step to initialize the germanium epitaxy demonstrates an alternative way to produce Ge epitaxy at temperatures very close to 450ºC for back-end CMOS compatible deposition. The use of germanium to assist in oxygen removal at lower temperatures is also discussed.

EXPERIMENT & DISCUSSION

Germanium was deposited on Si (100) p-type (2-10 Ω-cm) substrates using HDP-CVD. The HDP-CVD used in this work is a commercially available chamber typically used for high density plasma chemical vapor deposition of oxides [13] that was modified so that a germane/argon mixture (1% germane in argon) could be injected for SiGe deposition. Unless otherwise noted all wafers received a 1 minutes 100:1 DI:HF (DHF) dip to strip off the native oxide. Different in-situ cleans and deposition parameters were used to achieve either amorphous, poly-Ge or single crystal Ge epitaxy. For this work the deposition power, pressure, and germane partial pressure ranged from 1000-5000 W, 1-25 mtorr, and 10-85 µtorr, respectively. Deposition temperature at the center of the wafer depended directly on applied power to the argon/germane plasma and ranged from 250-550ºC. A transition from amorphous to poly-Ge deposition was observed with increasing power and temperature, Fig. 1. The solid-phase epitaxial recrystallization rates of amorphous germanium approach the deposition rate (~1-3 A/sec) at between 350 and 400ºC [14]. Thermally assisted motion of the atoms in the surface and near surface region may therefore be sufficient to explain the transition from amorphous to the crystalline phase of the growth at these increased powers.

To establish the crystallinity the films were measured initially with X-ray diffraction. Ellipsometry of the films was also used to rapidly evaluate films using the goodness of fit to either a hydrogenated amorphous germanium model or a single crystal germanium model. It was found that increasing coherency of the germanium single crystal with the substrate, estimated using the ratio of misaligned to <100> diffraction peak intensity to coherently aligned intensity, was found to correlate with increasingly close fits to the germanium single crystal model.

Representative samples were also examined using TEM to unambiguously determine the crystallinity and defect density (i.e., threading dislocation density) of the films.

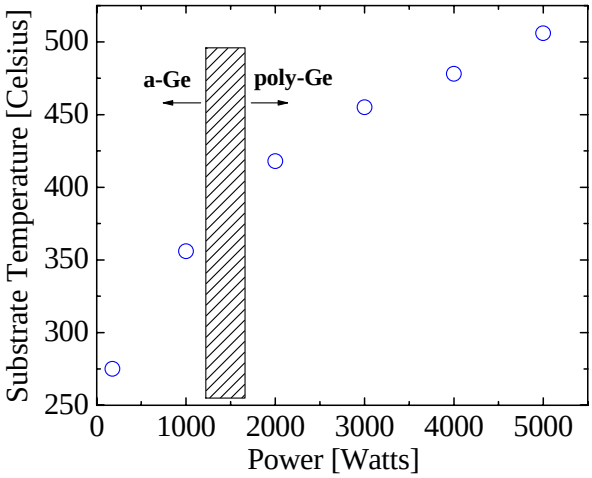
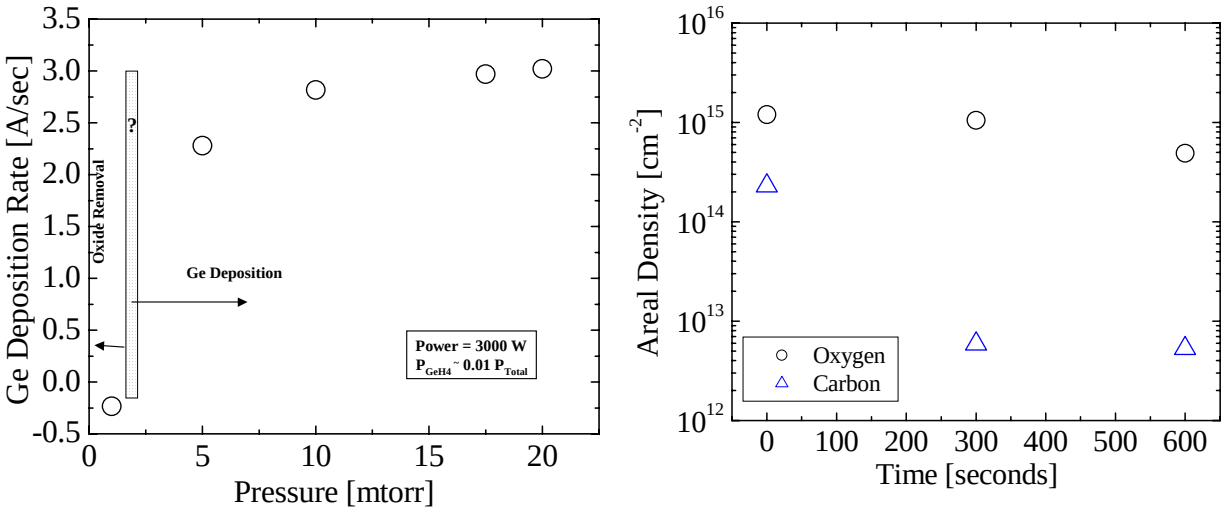


Figure 1. Substrate temperature dependence of HDP-CVD germanium films on applied power. A transition from amorphous to poly-Ge was observed at powers of 2000W and above. An additional low pressure in-situ surface preparation step was necessary to assist in the formation of single crystal epitaxy instead of poly-Ge.

Secondary ion mass spectrometry (SIMS) and Rutherford backscattering (RBS) measurements were also done on some samples to determine the chemical composition of the films as well as characterizing oxygen and carbon residue at the Ge/Si interfaces, Fig. 2. Amorphous films contained approximately 3% hydrogen, while crystalline films showed hydrogen contents well below the detection limits of RBS. Oxygen and carbon concentrations were found to be $\geq 10^{19}$ cm^{-3} and 10^{17} cm^{-3} within the films, respectively.

A necessary requirement to initiate germanium epitaxy is that the crystal template of the silicon surface have oxygen and carbon free areas at which the germanium atoms can coherently attach to the silicon atomic lattice sites. It is well known that silicon surfaces can be prepared with relatively low oxygen free hydrogen terminated surfaces through use of an ex-situ HF dips, which is sufficient for thermal CVD systems to grow relatively defect free epitaxy although oxygen and carbon are always found at the substrate growth interface using HF dips only. On the other hand, standard HF dips are not usually sufficiently stable to allow epitaxial growth in plasma systems despite the much lower peak temperatures [15]. All germanium deposited in this work was found to be polycrystalline when using HF dips followed by directly depositing germanium, which included an initial warm-up step of several minutes in the presence of a 3000W, 10 mtorr (or 1 mtorr) argon plasma followed by introducing 50 µtorr of germane to initiate the Ge deposition once the substrate reached it's steady-state temperature of 460°C. This is consistent with previous reports of plasma assisted epitaxial growth, which required an in-situ surface preparation step like a hydrogen plasma clean.



(a) **(b)**

Figure 2 (a) germanium deposition rate dependence on total pressure in plasma chamber (negative values represent the measured oxide removal rate); and (b) areal density of oxygen and carbon observed at the Ge/Si interface after different times of 1 mtorr, Ar/GeH_4 plasma surface preparation before Ge deposition.

Typical plasma cleans rely on hydrogen to assist the formation of volatile silicon oxide and steam from the surface [16].

$$SiO_2 + 2H \rightarrow SiO(g) + H_2O \qquad \text{eqn. 1}$$

However, hydrogen plasma cleans require substrate temperature of approximately 550°C or higher to completely remove the oxygen [6]. A reduction in in-situ clean temperature of approximately 100°C is desired to allow for deposition of germanium after all CMOS fabrication is completed (i.e., metal is deposited). Germanium oxide is known to be volatile at considerably lower temperatures than silicon oxide and is reported to readily break existing Si-O bonds [7-9]. The introduction of germane at low fluxes offers a potential way to reduce the temperature at which oxide may be removed from the silicon surface.

Deposition rate at a fixed power and substrate temperature was found to depend on plasma pressure. A transition from germanium deposition to oxide removal was subsequently observed when the argon/germane plasma pressure dropped to 1 mtorr, Fig 2. The dependence of deposition rate on pressure in the inductively coupled plasma is likely due to an increase in electron temperature, which results in both an increase in sheath potential and a sub-linear reduction in ion density. We speculate that a low energy sputtering component, due to the increased sheath potential, suppresses germanium deposition and ion assisted Ge and H bombardment of the Si surface leads to Si-O, Ge-O and H_xO desorption. The reduction in carbon in the presence of hydrogen ions is very rapid even at T ~ 350°C [3, 16].

The oxygen removing plasma condition at 1 mtorr was subsequently found to assist in initiating single crystal germanium epitaxy on silicon when the step was introduced directly before the deposition and after the plasma warm-up step. This is in contrast with the repeatable formation of poly-Ge when germane is removed from the 1 mtorr surface preparation step (i.e., a 1 mtorr argon plasma does not lead to the formation of Ge epitaxy), Fig 3. Ge films deposited using alternative in-situ surface preparation steps before the deposition, like exposing the surface to reactive NF_3 species from a remote plasma source, also resulted in poly-Ge films.

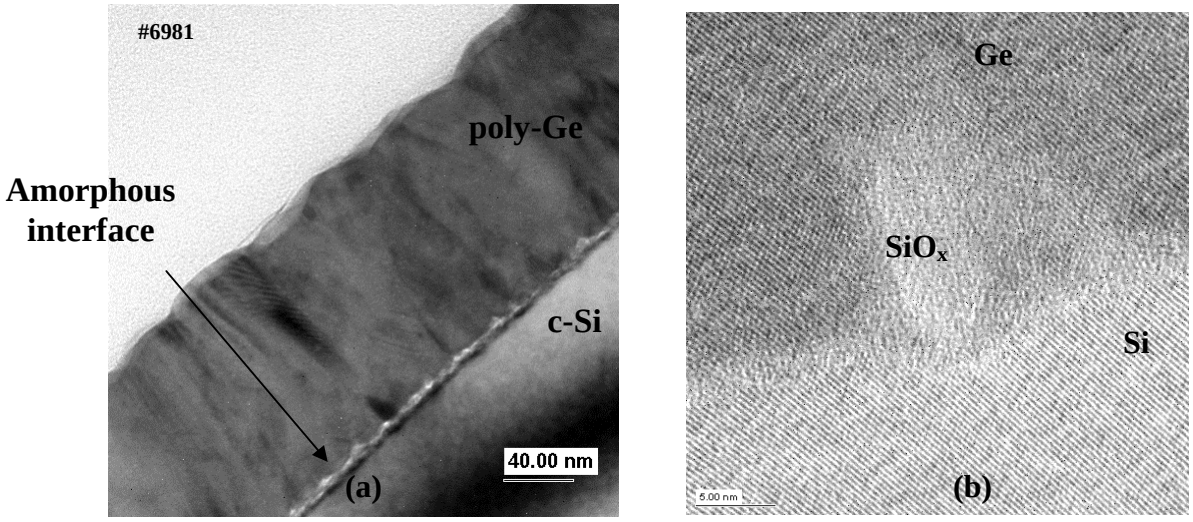


Figure 3 (a) TEM of Ge deposited on Si using a 1 mtorr argon plasma surface preparation step followed by the standard 10 mtorr Ge deposition step and (b) HRTEM of epitaxial germanium that results after germane is inserted into the 1 mtorr surface preparation step. Epitaxy grows through windows in amorphous regions at the Ge/Si interface.

A combination of XRD, ellipsometry and TEM confirm that the germanium crystal growth is coherent (i.e., <100> oriented) and epitaxial over the entire surface. TEM shows, furthermore, a large frequency of amorphous regions at the Ge/Si interface. High resolution TEM shows that the germanium crystal grows in between the amorphous regions and coalesces above the interface region as coherently aligned (100) crystal. A large concentration of oxygen is observed at the Ge/Si interface by SIMS, Fig. 3 (b), which suggests that the amorphous regions observed in TEM is residual oxide. Germanium epitaxy grown in nanowindows of the oxide has been reported before and when the size and spacing of the windows is tuned properly, this can also result in significantly reduced dislocation density [7, 17]. A large number of threading dislocations (~10^{10} cm^{-2}) is observed in this case, which is not atypical for germanium epitaxy on silicon when no special steps are taken (e.g., graded buffer layers or tuned nanowindow formation [17]).

Finally, the reduction of oxygen and carbon at 460°C is similar if not better than what has been reported for electron cyclotron resonance (ECR) hydrogen plasmas using similar total pressures, 1 mtorr, greater hydrogen partial pressures and temperatures constrained to below 550°C. Further investigation is proceeding to unambiguously clarify whether there is an enhanced removal of oxygen due to the presence of germanium or alternatively whether the oxygen and carbon reduction at the surface is only due to dissociated hydrogen from the germane molecules.

CONCLUSIONS

Low temperature (~460°C) germanium epitaxy was grown using a commercially available high density plasma chemical vapor deposition (HDP-CVD) chamber. To the authors knowledge this is the first report of Ge on Si epitaxy using this particular plasma chamber configuration. Furthermore, to assist in the growth of low temperature epitaxy we describe an alternative in-situ surface preparation step using a 1 mtorr, 3000W, 460°C argon/germane plasma that reduces oxygen and carbon concentration from the silicon surface and enables epitaxial growth. Introduction of germanium to form Ge-O volatile compounds to assist in reducing the temperature at which oxygen may be removed from the surface motivates this examination of germane/argon plasmas for in-situ cleaning.

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