crystallization temperature was reduced to as low as 350°C for 5 minutes. The crystallization behavior in this case was confirmed by x-ray diffraction and optical absorption results. In this case of selectively treating the surface and then annealed at 350°C for 5 minutes, crystallization occurred only in areas which were subjected to surface treatments. Hence, this process can be used to define a priori regions of amorphous silicon films that are to be crystallized and regions that are to remain amorphous. Electrical characterization in terms of conductivities and Schottky barrier device behavior is presented for these two distinct regions.


Low-temperature (<500°C) epitaxial growth of silicon will be required for future bipolar and CMOS devices to achieve ultra high-density and high-speed integrated circuits. Such epitaxial growth is contingent on damage-free substrate cleaning at low temperature. We report the first use of GeF$_4$-H$_2$ mixtures as etchant gas down to 350°C. Because no potential surface contaminant such as carbon is introduced, the use of GeF$_4$ will be of particular advantage in the preparation of surfaces for epitaxial growth of Si-Ge alloys for heterojunction bipolar transistors.

The thermodynamics of the Si-GeF$_4$ equilibrium favor etching: Si(s) + GeF$_4$(g) → SiF$_4$(g) + GeF$_2$(g) 

∆H$_{298}$ = -2.38 kJ, ∆S$_{298}$ = +26 kJ

Exponentially, we find that the etching rate achieved by simple exposure of Si to GeF$_4$ gas is high. Therefore, no plasma assistance is required to breakdown the GeF$_4$ molecule, so that damage by ion bombardment and radiation can be avoided.

At 350°C substrate temperature, the etch rate in 0.6 Torr of pure GeF$_4$ is 3 μm/min. Hydrogen dilution reduces the etch rate but eliminates the surface facetting observed by SEM for etching with pure GeF$_4$. We report our etching results over a range of substrate temperatures, gas pressures, and GeF$_4$/H$_2$ ratios.

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While it has long been known that oxygen surface contamination can give rise to defects in silicon epitaxial layers grown in the range of 1000-1200°C, the actual levels of oxygen incorporated in these layers is less than the solid solubility of ~2 x 10$^{17}$ cm$^{-3}$. In our work, we have investigated oxygen incorporation in epitaxial silicon and silicon-germanium films grown at low temperature (625-800°C). Depending upon growth temperatures and other conditions, oxygen concentrations as large as 1 x 10$^{18}$ cm$^{-3}$ (2 atomic percent) have been found in crystalline epitaxial films.

The layers were all grown in a single-wafer vapor-phase deposition system with quartz walls and exhausted by a mechanical pump. The wafer is radiantly heated without a susceptor by microprocessor-controlled lamps as in rapid thermal processing, and dichlorosilane and germane are used as the source gases in a hydrogen carrier at 6.0 torr. The wafers were loaded from one end of the tube with the system at atmosphere pressure. Substrate cleaning before growth was done at 1200°C in hydrogen, and the wafer was then cooled to 1000°C (in hydrogen) where a buffer layer was first grown before gradually dropping to the final growth temperature. Layers grown above 900°C consistently show low defect densities and good electrical properties.

Low temperature silicon epitaxial growth has been performed from 700 to 800°C. Oxygen levels have been measured by both calibrated SIMS and infrared absorption where appropriate. The primary source of oxygen in our system is water and/or oxygen absorbed on the walls of the system during sample loading. For example, by keeping the chamber walls warm and using a nitrogen shower during loading, silicon layers have been grown at 750°C with an oxygen concentration less than 2 x 10$^{15}$ cm$^{-3}$ (SIMS resolution limit). The growth rate was on the order of 10 nm/min, and p-n diodes fabricated in similar epitaxial layers had an excellent ideality factor in forward bias of 1.05 down to bias levels of 0.1V.

As an experiment, on the next run wafer loading was done with cold walls and without the nitrogen shower. Epitaxial silicon grown at 755°C on this wafer showed oxygen levels by SIMS of ~1 x 10$^{17}$ cm$^{-3}$. A more extreme case is demonstrated by a Si layer grown at 700°C with a cold-wall load, where SIMS measurements showed an enormous oxygen level of roughly 10$^{18}$ cm$^{-3}$. However, the sample showed excellent electron channeling patterns, demonstrating high crystalline quality, and no "haze" was visible in the sample. Infrared absorption measurements showed an anomalous peak at 1000 cm$^{-1}$, which is absent in SIMS. Assuming the absorption efficiency for interstitial oxygen, the area under the peak corresponds to an oxygen concentration on the order of that detected by SIMS. The peak does not match the known signals for either interstitial oxygen in silicon or for SiO$_2$, and we do not know the exact location or the form of the oxygen. TEM of this sample is in progress.

Silicon-germanium growth at 685°C was also investigated. Layers with on the order of 20% germanium typically show oxygen levels of roughly 10$^{18}$ cm$^{-3}$. Silicon layers grown on top of these in situ at 750°C (with similar growth rates) show negligible oxygen, suggesting that the growth temperature is more important than the growth rate in low-temperature oxygen incorporation. Similar levels of oxygen have been reported by another group in layers grown at 625°C which exhibit similar characteristics in transistor structures and have reported oxygen-induced growth defects such as stacking faults, etc.

In conclusion, oxygen levels several orders of magnitude in excess of solid solubility may be incorporated in low-temperature silicon and silicon-germanium epitaxial films grown by vapor-phase. However, it appears possible to incorporate these large amounts of oxygen without the traditional oxygen-related growth defects.

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4:50 PM, U10 Crystalline Defects in Low Temperature Epitaxial Silicon Growth by RPCVD: T. Hsu, L. Breux, B. Anthony, S. Banerjee and A. Tasch, Microelectronics Res. Ctr., The Univ. of Texas at Austin, Austin, TX 78712

A major thrust of research in silicon technology today is in low temperature processing which is required for future generation Ultra Large Scale Integration (ULSI). Also, novel Si-based devices, which require high-aberlity threshold drivers or heterostructures to achieve "energy band engineering," are critically dependent on the success of low temperature fabrication. Silicon homoeopitaxy at temperatures as low as 220°C has been demonstrated using Remote Plasma-enhanced Chemical Vapor Deposition (RPCVD). This paper discusses the characteristic of crystalline defects in low temperature (<300°C) epitaxial Si films grown by RPCVD. In RPCVD, unlike in conventional plasma-enhanced CVD, instead of directly exciting the reactant gas, a noble gas (Ar or He) excited by a rf coil is used to generate the metastable species and energetic electrons which then selectively excite the reactant gases which are introduced between the plasma column and the substrate. Since the reactant gases and the substrate are not immersed in the plasma, plasma-induced surface damage is minimized, and the morphology and crystalline quality of the deposited films is improved. The crystalline quality of the deposited films is strongly dependent on the substrate condition and growth conditions. The wafers discussed in this paper received an oxidation/annealing/oxide-stripping treatment by oxidizing at 950°C for ~220 minutes in dry oxygen atmosphere and annealing at 750°C for 15 hours in nitrogen to assure a smooth interface between Si and SiO$_2$, in accordance with the work of Hahn and Henzie. A combination of an ex-situ modified RCA clean and an in-situ remote plasma H$_2$ clean has been used to remove C and O. The in-situ H plasma cleaning process has been performed at 300°C at a chamber pressure of 44 mTorr, and plasma power of 10W for 30 minutes. The removal of C and O has been confirmed by in-situ Auger analysis, and supported by the observation (in-situ) of excellent KREED patterns. The films under investigation have all been deposited at 300°C and 450 mTorr with thicknesses between 250Å and 1000Å. For defect characterization, a modified Schimmel etch which has an etch rate of 1250Å/min on intrinsic Si, and a modified Yang etch have been used to delineate the defects such as dislocations and stacking faults in the epitaxial films. Nomarski optical