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EXTREME SUPERSATURATION OF OXYGEN IN LOW TEMPERATURE EPITAXIAL SILICON AND SILICON-GERMANIUM ALLOYS

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Abstract

We report the low temperature growth (625 - 700 °C) of epitaxial silicon and silicon-germanium alloy films by vapor phase techniques with oxygen concentrations approximately 10^{20} cm^{-3}. These concentrations are well above the accepted solid solubility for oxygen in silicon. The films, however, have excellent structural and electrical properties with virtually no stacking faults or "haze". Infrared transmission analysis suggests the possible presence of OH, but the exact nature of the oxygen is not known.

Introduction

Generally, oxygen is a harmful contaminant in epitaxial films. The presence of oxygen precipitates may give rise to stacking faults in the epitaxial film and in extreme cases cause haze on the surface of the wafer. Here we report the low temperature growth of crystalline epitaxial films with oxygen concentrations reaching 10^{20} cm^{-3}.

Growth

The samples were grown by Limited Reaction Processing (LRP) [1], a combination of Chemical Vapor Deposition (CVD) and Rapid Thermal Processing (RTP). The reactor is a lamp heated system which utilizes no susceptor. Each sample is suspended on quartz pins in a quartz wall chamber above a bank of twelve tungsten halogen lamps. The radiation from the lamps heats the wafer directly while leaving the chamber walls cool. Another feature of the system is that has no load lock. During each loading process, the chamber must be vented to atmosphere. This is a possible source of contamination to the system.

The epitaxial films are grown at a pressure of 6 torr. Dichlorosilane and germane are used as the source gases and hydrogen is used as the carrier gas. Before growth, each

sample undergoes a high temperature clean (1200 °C). The clean is done in a hydrogen atmosphere and removes impurities form the wafer surface. The growth process begins with the growth of a silicon buffer layer (1000 °C), followed by a temperature drop to 700 °C for growth of silicon epitaxial layers or to 625 °C for growth of $Si_{1-x}Ge_x$ epitaxial layers. Typical sample structures are shown in Figure 1.

The epitaxial films grown at low temperature have excellent structural characteristics. They are all single crystals and exhibit no observable haze on the surface of the wafer in either the visible or ultra-violet regions. In plan view TEM, we notice misfit dislocations in some $Si_{1-x}Ge_x$ strained layer samples, but stacking faults are seldom observed. Stacking faults are virtually absent from our silicon samples as well.

Characterization

In order to characterize our system, we performed Secondary Ion Mass Spectrometry (SIMS), calibrated against implant standards, on our epitaxial samples. In Figure 2, it can be seen that the oxygen concentration in the silicon (grown at 700 °C) is nearly 5×10^{20} cm^{-3}. This is an extreme case, and it is more typical to see oxygen concentrations of 1×10^{20} cm^{-3} in these silicon films. The interface between the high temperature buffer and the low temperature epitaxial layers is clearly defined by the oxygen profile. The buffer layer has an oxygen concentration less than 10^{17} cm^{-3} while the layer grown at 700 °C has an oxygen concentration of approximately 5×10^{20} cm^{-3} throughout the film. This is two orders of magnitude above the accepted peak solid solubility of oxygen in silicon of 2×10^{18} cm^{-3}.

We have also performed SIMS on a Heterojunction Bipolar Transistor (HBT) structure (shown in Figure 1B). The silicon-germanium layer defines the narrow bandgap base region. The alloy base is sandwiched between two silicon layers which were grown at 850 °C and serve as the transistor's collector and emitter. As seen in Figure 3, an oxygen concentration of approximately 10^{20} cm^{-3} is found in the alloy layer grown at 625 °C. Since this is found in the base of the HBT, one might expect the electrical characteristics of the device to be degraded. As we will see in the next section, the electrical properties of the device are not adversely affected.

The source of oxygen is thought to be water vapor or oxygen that adsorbs on the walls of the sample chamber during the loading process. Careful loading procedures can reduce the oxygen levels somewhat, but they generally remain well above 2×10^{18} cm^{-3}. To establish the form taken by the oxygen, Fourier Transform Infrared Spectroscopy (FTIR) was performed at room temperature (Figure 4). Notice the large peak centered at

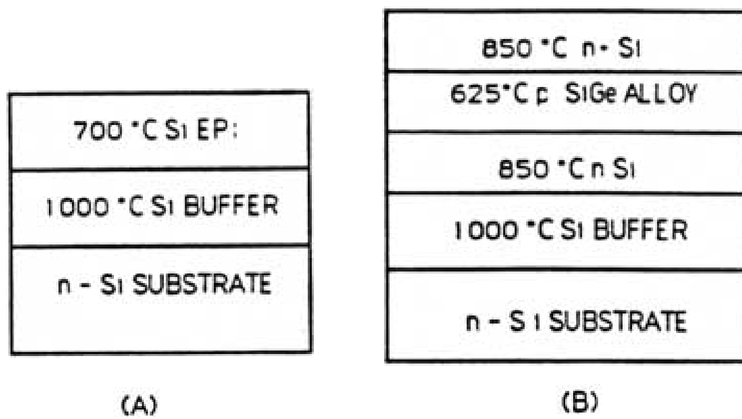

Figure 1: Typical Structures. A) Silicon epitaxial growth at the temperature of 700 °C. B) Silicon-germanium epitaxial growth at 625 °C for a Heterojunction Bipolar Transistor (HBT).

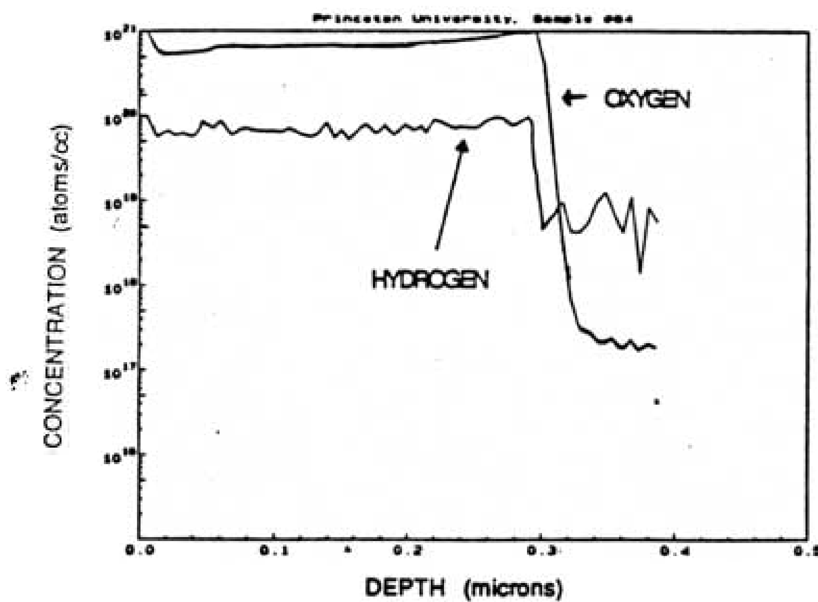

Figure 2: SIMS Profile. The top layer is 3000 Å of silicon grown at 700 °C with an oxygen concentration of approximately 5 x 10^{20} cm^{-3}. The 1000 °C buffer has an oxygen concentration less than 10^{17} cm^{-3}.

approximately 1000 cm^{-1} with a Full Width at Half Maximum (FWHM) of 100 cm^{-1}. This FWHM is much larger than the accepted FWHM (~32 cm^{-1}) for interstitial oxygen and is removed from the interstitial peak location (1107 cm^{-1}) [2] by more than 100 wavenumbers. Furthermore, the interstitial peak should be easily resolved on this scale yet there is no hint of this peak. The peak at 1000 cm^{-1} is also not characteristic of the formation of precipitates since precipitates are typically associated with a peak which is displaced toward an energy higher than that of the 1107 cm^{-1} peak [3].

The peak at 3400 cm^{-1} suggests the possible presence of an OH molecule. The OH bond has been studied extensively in fused silica and the O-H vibrational mode at 3690 wavenumbers is well documented. The fact that we see a peak at 3400 wavenumbers may be attributed to the difference between the two host materials. Stolen and Walrafen reported a Si-(OH) vibrational made at 970 cm^{-1} [4] (in a Raman spectrum) when studying wet optical fibers.The peak at 970 was noticed in fibers containing large amounts of OH as determined by the presence of the 3690 cm^{-1} peak. They also calculated a vibrational mode for this bond at 988 cm^{-1} using a modified model of an anchored SiO_4 tetrahedron. This theoretical oscillation corresponds well to their observed peak. We also performed a Raman analysis of our silicon layer and noticed a small peak at 970 cm^{-1}. However, we attribute this peak to a second order Raman mode for a Si-Si bond.

A second SIMS profile on the silicon layer (seen as Figure 2) confirms the presence of hydrogen. The hydrogen profile follows that of the oxygen (5×10^{20} cm^{-3}) but at a concentration of 7×10^{19} cm^{-3}. With these concentrations, one cannot account for every oxygen atom as an OH molecule since there is less than one hydrogen atom for each oxygen atom. However, the presence of hydrogen may explain the 1000 cm^{-1} peak in the FTIR. The shift of the peak toward a lower energy can be due to the effect of the hydrogen weakening the strength of the Si-O bond.

Electrical Properties

As Seen in Figure 3, the oxygen concentration reaches 10^{20} cm^{-3} in the base of the HBT structure. We have fabricated transistors in films with oxygen concentration of apprximately 10^{19} cm^{-3} and obtained gains on the order of twenty even with the base dopings two orders of magnitude above the emitter dopings (10^{19} cm^{-3} vs. 10^{17} cm^{-3}, respectively). A Gummel plot (log of the collector and base currents vs. base emitter voltage) in our previous work [5] shows the ideal collector current (60 mV/dec) in the transistor and a base current with an ideality factor of 1.3. King et al., at Stanford University, have fabricated HBT's with gains near 400 which exhibit ideal collector and

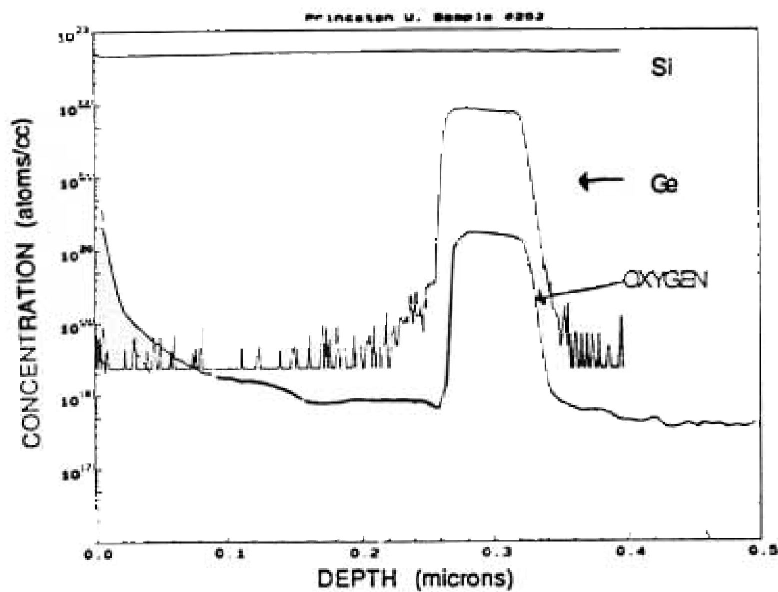

Figure 3: SIMS Profile. SIMS profile for a typical Heterojunction Bipolar Transistor structure. The base is defined by the $Si_{.80}Ge_{.20}$ layer.

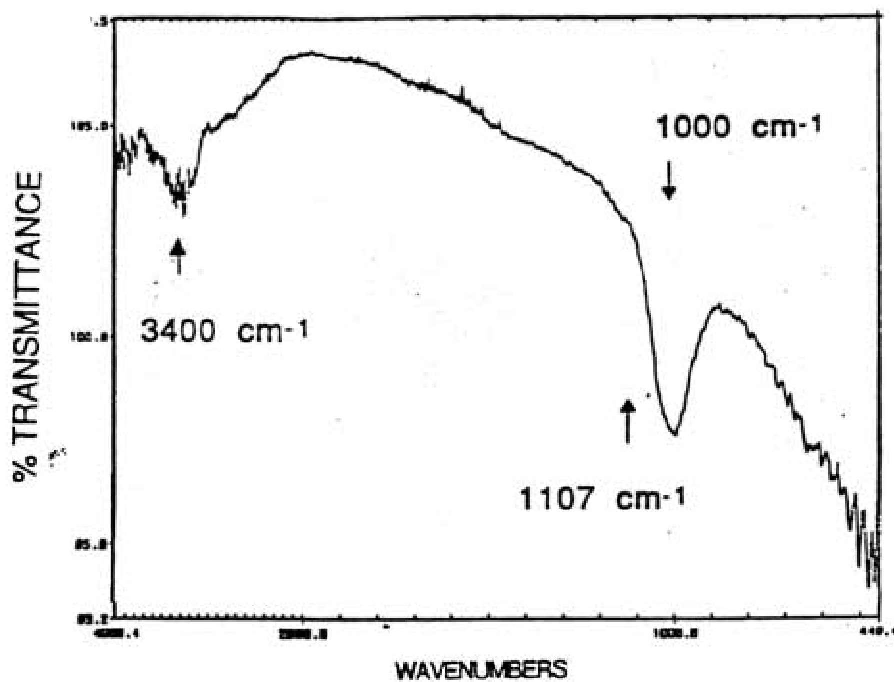

Figure 4: FTIR. Transmission spectrum for a typical silicon epitaxial layer grown at 700 °C. This sample was referenced to its substrate.

base currents [6]. The base regions of their transistors also contain large amounts of oxygen. Even though the oxygen concentration is large in the base region, it does not seem to degrade device performance.

Conclusion

We have grown epitaxial silicon and silicon-germanium layers with oxygen concentrations of approximately 10^{20} cm^{-3}. Even though there is a large amount of oxygen in the epitaxial films grown at low temperatures (625 - 700 °C), the films are still single crystals virtually free of stacking faults. There are also large amounts of hydrogen in these films and there is evidence that some of it exists as OH. However, the exact form of most of the oxygen is not known. The transistors fabricated in these films also exhibit excellent electrical characteristics showing that the oxygen does not seem to adversely effect device performance.

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References

1. J.F. Gibbons, C.M. Gronet and K.E. Williams, Appl. Phys. Lett. 47, 721-723 (1985)
2. W. Kaiser and P.H. Keck, J. Appl. Phys. 28, 882 (1957)
3. S.M. Hu, J.Appl. Phys. 51 (11), 5945-5948 (1980)
4. R.H. Stolen and G.E. Walrafen, J. Chem. Phys. 64, (6) 2623-2631 (1976)
5. J.C. Sturm, E.J. Prinz, P.M. Garone, P.V. Schwartz, Appl. Phys. Lett. 54 (26), 2702-2709 (1989)
6. C.A. King, J.L. Hoyt, C.M. Gronet, J.F. Gibbons, M.P. Scott, and J. Turner, Elect. Dev. Lett. 10 (2), 52-54 (1989)