Epitaxial Ge Layers on Si via Ge$_x$Si$_{1-x}$O$_2$ Reduction: The Roles of the Hydrogen Partial Pressure and the Ge Content

W.S. LIU and M.-A. NICOLET
California Institute of Technology, Pasadena, CA 91125
T.K. CARNES and K.L. WANG
University of California, Los Angeles, CA 90024

The epitaxial growth of an epi-Ge layer via Ge$_x$Si$_{1-x}$O$_2$ reduction in hydrogen annealing is reported. Ge$_x$Si$_{1-x}$ alloys with $x = 0.52$ and $0.82$ were first grown epitaxially on Si substrates. They were then oxidized in a wet ambient and subsequently annealed in 5% or 100% H$_2$. The reduction of Ge from its oxide state is observed in both samples with both ambients. However, an epitaxial Ge growth is only observed in the sample with $x = 0.82$ after the 5% H$_2$ annealing. The other three cases result in the formation of polycrystalline Ge. The roles of the hydrogen partial pressure and the Ge content are discussed and conditions under which this novel mode of solid-phase epitaxy can occur are explained.

Key words: Epi-Ge, GeSiO$_2$ reduction, H$_2$ annealing, Si

INTRODUCTION

To grow device-grade GaAs epitaxially on a single crystalline Si substrate for integrated electronic and optical devices is of great technological interest. Because the lattice constant and thermal expansion coefficient of Ge are close to those of GaAs but those of Si are not, efforts to form an epitaxial interlayer of Ge on Si started early.\cite{1-5} The fact that device-quality heteroepitaxial GaAs has been grown on Ge substrates vindicates this concept.\cite{6}

We have demonstrated very recently a novel way to grow an epitaxial Ge film on a Si substrate via the reduction of Ge$_x$Si$_{1-x}$O$_2$.\cite{7} The process sequence involves the oxidation of an epitaxial GeSi film grown on a Si single crystalline substrate and a subsequent reduction of the GeO$_2$ of this oxide to elemental Ge in an ambient of forming gas (95% N$_2$ + 5% H$_2$). The reduction process is driven by the reaction:

$$\text{GeO}_2 \text{(in solution with SiO}_2\text{)} + 2\text{H}_2 \rightarrow \text{Ge + 2H}_2\text{O} \quad (1)$$

The Ge that precipitates out of the oxide grows epitaxially on the unoxidized part of GeSi (Fig. 1). The seed for this epitaxial growth is provided by a percolation layer that consists of a network of epitaxial Ge with islands of silicon oxide imbedded in it. Most underlying dislocation will terminate in that percolation layer, so that Ge that grows on it has a better crystalline quality than that of the underlying seeding GeSi layer.\cite{7}

In this paper, we investigate the effect of the hydrogen partial pressure on this epitaxy growth. It is shown that two quite different Ge structures can be obtained by changing the hydrogen partial pressure, which we depict schematically in Fig. 1. The role of the Ge content in the sample is also examined. Finally, conditions under which this epitaxy growth takes place are discussed.

EXPERIMENT

Elastically relaxed Ge$_x$Si$_{1-x}$ alloys with $x = 0.52$ and 0.82 were grown epitaxially on (100)Si substrates by molecular beam epitaxy. The thickness for $x = 0.52$ and $x = 0.82$ are 540 and 580 nm, respectively. Both samples are then oxidized in a tube furnace at 700°C in a wet ambient. In order to produce a similar oxide thickness, the sample with $x = 0.52$ was oxidized for
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Figure 2 shows the backscattering spectra of the oxidized samples $x = 0.82$ before and after the annealing in $5\% H_2$ at 700°C for 1 and 4 h. The sample annealed in pure hydrogen at 700°C for 1 h is also included for comparison. After the annealing in $5\% H_2$ for 1 h, a Ge peak emerges near 1.42 MeV. The thickness of the initially unoxidized GeSi layer of about 280 nm (corresponding to the Ge signal from 1.07 to 1.27 MeV, solid line) decreases to about 200 nm (Ge signal from 1.23 to 1.35 MeV, dash-dotted line). This remaining unoxidized GeSi layer maintains its original composition. A layer containing all three elements Ge, Si, and O (signals at 1.35, 0.95, and 0.55 MeV) is also observed between the emerging Ge layer and the underlying GeSi layer. The decrease of the Ge and oxygen signal areas shows that some Ge and oxygen escapes the sample from the surface. A SiO$_2$-rich layer is formed near the surface which, however, still contains a substantial amount of Ge. This layer of SiO$_2$ evidently acts as a cap for further loss of Ge because such a loss is not observed beyond the first hour of annealing. After 4 h of annealing, the signal of this Ge moves to the nearby Ge peak and a well-defined rectangular Ge signal is observed whose height and width indicate that a uniform, pure Ge layer has developed (Ge signal from 1.45 to 1.53 MeV, circle symbol). No such Ge peak is observed after annealing in pure $H_2$ for 1 h. Rather, Ge is uniformly distributed throughout the oxide. A SiO$_2$-rich layer is also observed near the surface. Excluding this surface oxide, the composition of the oxide that remains after 1 h in pure $H_2$ is calculated to be Ge$_{0.8}$Si$_{0.2}$O$_{0.4}$, which is equivalent to 0.8 Ge + 0.2 SiO$_2$ and strongly suggests that this oxide layer is a mixture of elemental Ge and silicon dioxide. This also indicates that almost all the Ge$_2$O$_3$ in the GeSi oxide is reduced to the elemental state after the pure hydrogen annealing. The area of the Ge signal is indeed observed to decrease only by 5% in that case.

To clarify their crystalline structure, we analyzed the samples by double crystal x-ray diffraction using the Fe K$_{\alpha1}$ line ($\lambda = 1.936\,\text{Å}$) and the (400) diffraction (Fig. 3). As we pointed out previously, the striking outcome of this annealing with forming gas is that the formed Ge layer is epitaxial and is of better quality than that of the underlying GeSi seeding layer. This is also evidenced by comparing the full-width at half-