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$Si_{0.85}Ge_{0.15}$ oxynitridation in wet-nitric oxide ambient

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Abstract

Nitric oxide (NO) aided $Si_{0.85}Ge_{0.15}$ wet-oxynitridation has been performed at 400–700 °C, while the wet-NO feed gas was preheated to higher temperatures before entering the reaction zone. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy data suggests that both nitrogen and oxygen incorporation increases within the dielectric bulk with increasing wet-oxynitridation temperature, while there is no apparent germanium segregation towards the dielectric/substrate interface at all temperatures studied. Moreover, angle-resolved XPS analysis suggests that wet-oxynitridation at temperatures higher than 600 °C volatilizes some germanium oxide from the surface region, while silicon monoxide is outgassed from the dielectric bulk and accumulates near the surface. Nitrogen incorporation is found to hinder germanium segregation. Z-contrast imaging with scanning transmission electron microscopy shows that oxynitrides grown in wet-NO have sharp interfaces with bulk $Si_{0.85}Ge_{0.15}$, while the roughness of the dielectric/$Si_{0.85}Ge_{0.15}$ substrate interface is less than 2 Å. These results are discussed in the context of an overall mechanism of SiGe wet-oxynitridation.

Keywords: Oxynitridation; Silicon germanium; X-ray photoelectron spectroscopy; Z-contrast imaging

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1. Introduction

Recently, SiGe alloys have received considerable attention due to their tunable band gap, enhanced hole mobility, improved high frequency behavior, and ease of integration with existing silicon technology. However, producing a high quality layer for insulating field effect devices has

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proved troublesome. At conventional high temperature (>400 °C) thermal oxidation of SiGe alloys in dry and wet O_2 or O_3 results in undesirable relaxation of strained layers [1,2] and formation of a Ge-rich layer below the oxide [1,3,4]. The Ge rich layer causes high interface trap density, high fixed charge, and poor breakdown characteristics [1,3,4]. Also, the scaling of oxide for use in sub-0.1 μm technologies raises fundamental problems (particularly, gate-to-substrate tunneling and dopant diffusion during a high temperature processing step). Thus, it is imperative to study new materials for use as future dielectrics on SiGe.

Since oxynitrides are among the leading contenders to replace oxides in future logic and memory applications, this work is intended to study the growth of hyper-thin oxynitride films on SiGe substrates. It aims at understanding the effect of temperature on wet NO-assisted oxynitridation of SiGe alloys, especially in ultrathin (i.e., <40 Å) dielectrics. Part of the rationale for wet oxynitridation is that the rate of oxidation of SiGe alloys has been observed to be significantly higher than that of pure Si during wet oxidation [5–12], whereas the oxidation rates of SiGe is the same as that of bulk Si in dry oxygen [5,13,14]. It has been demonstrated that Ge acts as a catalyst during the wet oxidation of SiGe [10,11]. Holland et al. [7] have suggested that the enhancement of the wet oxidation rate is the result of weak Si–Ge binding energy. In this work, the wet oxynitridation process is studied at 400–700 °C. X-ray photoelectron spectroscopy (XPS) is used to determine the extent and nature of bonding states of N, Si and Ge, while secondary ion mass spectroscopy (SIMS) is used to obtain the elemental concentration profiles at all conditions investigated, and Z-contrast imaging with scanning transmission electron microscopy to probe interfaces and complement the understanding of process–structure relationships.

2. Experiment

A resistively heated horizontal furnace (Lindberg/Blue, STF 55346C) is used for all processes. It consists of a quartz tube 3″ in diameter and 39″ in length. A removable cap at the inlet of the furnace allows a wafer boat to be pushed in and pulled out from the furnace. Three equally long heating zones occupy 24″ in the middle of the furnace. Here, 'zone I' is referred to the first zone encountered by the feed gases after entering the furnace, while 'zone II' and 'zone III' are the subsequent ones. When zone I is heated to 700 °C, while zones II and III are set to room temperature and 400 °C, respectively, the resulting temperature profile is 700/580/400 °C in zones I/II/III. Increasing the temperature of zone I to 800 °C, while zones II and III are set to room temperature and 500 °C, respectively, yields the temperature profile 800/670/500 °C in zones I/II/III. In the same manner, zone I/zone III were set 900/600 °C and 1000/700 °C. The sample wafers are always positioned in zone III, while the precursor gases are heated to the higher temperatures indicated upstream the sample.

The samples used in this study were 1500 Å thick epitaxial $Si_{0.85}Ge_{0.15}$ films deposited on p-type (1 0 0) Si wafers with resistivity 3–6 Ω cm. Before oxynitridation, the samples were cleaned with 2:1 H_2SO_4:H_2O_2 to remove organic contaminants. This was followed by a DI water rinse and a dip in buffered HF (NH_4F:49% HF, 10:1) to remove any native oxide. After etching, the samples were dipped in DI water for 30 s, blown dry in N_2, and immediately loaded into the reactor for processing. During this loading and unloading steps, the furnace was maintained in Ar ambient. The gases used were NO (AGA, 99.5% pure), Ar (AGA 99.996% pure) and liquid N_2. The reactor pressure was maintained at ~1 atm. and the NO gas flow rate at 0.5 l/min through a water bubbler kept at 95 °C.

A Cameca IMS 5f SIM Spectrometer was used for the depth profiles of Si, Ge, O and N in the oxynitride layer. To achieve slow sputtering rates, the Cs^+ primary beam was maintained at impact energy of 5.5 keV with a beam current of ~4 nA. The beam was rastered over an area of 350 × 350 μm^2 with data collected from a central circle 60 μm in diameter. The film thickness was measured with a M-44 Spectroscopic Ellipsometer (J.A. Woollam Co., Inc.) with an apriori-generated model that consisted of three layers: a variable