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Study of Ge bonding and distribution in plasma oxides of $Si_{1-x}Ge_x$ alloys

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Secondary ion mass spectroscopy (SIMS) and Fourier transform infrared (FTIR) absorption have been studied in thin oxides of $Si_{1-x}Ge_x$ grown by plasma oxidation. SIMS analysis reveals that Ge can migrate to the oxide film surface leaving the oxide in the SiGe interface region Ge-depleted. This is in contrast to thermally grown oxides. Water selectively attacks the Ge-rich part of the oxide. In the FTIR spectra of the SiGe oxides, specific peaks identified with the vibration of O in Si–O–Ge and Ge–O–Ge bonds have been observed for the first time. These latter observations confirm that for the plasma oxidized films, the Ge is chemically bonded in the oxide network. © 1998 American Institute of Physics. [S0003-6951(98)03320-8]

The integration of binary, semiconductor alloys such as SiGe in present day Si based microelectronics opens the way to concepts such as band-gap engineering¹ and improved carrier mobility in metal–oxide–semiconductor field effect transistors (MOSFETs).^{2,3} However, the introduction of binary compounds may result in restrictions on the thermal budgets used in processing because of phenomena such as precipitation and segregation. Ge precipitation at the oxide–SiGe interface during thermal oxidation is an excellent example of this.^{4–6}

Plasma assisted oxidation is a potentially promising technique for the fabrication of homogeneous oxides of binary semiconductor compounds because it can be performed at low temperatures (as low as room for SiGe) where thermally induced diffusion of species is limited. For the case of SiGe, various authors have reported successful plasma assisted oxidation for temperatures in the range 15–500 °C.^{7–12} Secondary ion mass spectroscopy (SIMS) studies, however, indicate that Ge migration to the oxide–semiconductor interface still occurs at 500 °C¹² (to our knowledge, SIMS studies of oxides grown below 500 °C have not been reported).

In this letter we report a study of SiGe oxides grown anodically in a microwave excited plasma at temperatures around 100 °C. The oxide growth was monitored *in situ* using spectroscopic ellipsometry and the network bonding in the films was characterized *ex situ* using SIMS and Fourier transform infrared (FTIR) spectroscopy. Si_{1-x}Ge_x layers (x= 0.08, 0.2, 0.35 and 1) were grown heteroepitaxially on *p*-type (100) Si using an industrial 200 mm diameter wafer chemical vapor deposition (CVD) module (ASM Paragon) operating at either atmospheric or reduced pressure. Prior to epitaxial growth, the wafers were wet cleaned in dilute hydrofluoric acid followed by rinsing in isopropanol, then dried. Gaseous precursors for the CVD were SiH₄ and GeH₄ (diluted to 10% in H_2). The growth temperature was 650 °C. The thickness of the grown SiGe layers was 500 nm for x=0.08, 0.2 and 1 and 3 μ m for x=0.35, where the films were fully relaxed. Following removal of any native oxide in hydrofluoric acid, a 250 nm thick Al film was deposited on the back face of the wafers to ensure electrical contact during the anodization process in the oxygen plasma reactor. An O_2 pressure of 1 mTorr and a microwave (2.45 GHz) power of 500 W was used in the reactor during oxidation. Details of the reactor can be found elsewhere.¹³ The anodic oxidation was carried out in the so-called constant current mode with total currents in the range 1.1-1.3 A for sample areas on the order of 16 cm². Such current densities have been found previously¹⁴ to result in maximum temperature rises of about 100 °C. The SIMS profiles were measured using a CAMECA IMS 3F/4F machine. Although it is straightforward to measure the concentration of the $Si_{1-x}Ge_x$ film using this method,¹⁵ quantitative analysis of the mixed oxide film is more difficult. In order to minimize error, various modes of operation were used to obtain the concentration profiles, they include: (a) sputtering with O_2^+ ions at 4.5 keV, (b) the same as (a) but including flooding with O_2 , and (c) sputtering with Cs⁺ primary ions with an energy of 5.5 keV. FTIR absorption spectroscopy was carried out in a reflection configuration (due to the Al layer on the backface of the sample) using a Bruker IFS 66 spectrometer. The angle of incidence of the infrared (IR) beam was about 45°. Reference samples for the FTIR studies were obtained by taking part of the oxidized sample and removing the oxide via an HF acid dip.

In Fig. 1 we show a typical anodic oxide growth curve for a $Si_{0.8}Ge_{0.2}$ sample. The potential applied between the SiGe substrate and the body of the reactor (V_S), which is varied during growth to maintain a constant total direct current through the growing oxide, is found experimentally to vary linearly with oxide thickness (inset of Fig. 1). The slope of the curve yields the electric field applied across the oxide

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FIG. 1. Growth curve of the oxide and evolution of the sample potential for anodization of $Si_{0.8}Ge_{0.2}$ at 1.2 A. The slope of the curve in the inset corresponds to the electric field across the growing oxide.

which is of the order of 9.1 MV/cm for the example shown. A linear relation has been found previously in studies on the anodic oxidation of Si.¹⁶ In Table I we summarize the initial oxide growth rates and electric fields for three $Si_{1-x}Ge_x$ samples and for pure Si subjected to the same constant current growth conditions (1.2 A). Despite our efforts we were unable to grow oxide thicker than 5 nm on the pure Ge sample. We observe that $Si_{1-x}Ge_x$ alloys oxidize significantly faster that pure Si for the same total current (O⁻ plus electrons) consistent with thermally induced oxidation. However, the electric field necessary to maintain this level of current is much larger.

The SIMS analysis reveals that the anodic grown oxide, although grown at low temperature, is not perfectly homogeneous. Figure 2(a) shows a typical depth profile for an oxide film on Si_{0.8}Ge_{0.2}. There is clear evidence of the accumulation of Ge at the oxide surface and Ge depletion near the oxide-semiconductor interface. The former effect was observed by Hall et al.⁷ but not the latter. The data shown in Fig. 2(a) were obtained using O_2^+ primary ions together with O_2 flooding. Similar behavior was detected when using Cs^+ primary ions. The intensity ratio, Ge⁺/Si⁺, in the substrate (unoxidized part) corresponds to a Ge concentration of 20% as expected.¹⁵ The Ge/Si atomic ratio in the center of the oxide is close to that in the substrate, suggesting that in this region the oxide is stoichiometric $Si_{0.8}Ge_{0.2}O_2$ [see Fig. 2(b)]. Furthermore, by integrating the different concentrations over the whole oxide volume the same average concentration is again recovered. The Ge missing in the region of the oxide-semiconductor interface is then located at the ox-

TABLE I. Measured growth parameters for plasma oxidation of SiGe at 1.2 A.

Ge content (%)	Initial growth rate (nm/min)	Electric field (MV/cm)
0	2.0	2.5
8	3.7	9.0
20	6.4	9.1
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FIG. 2. SIMS profile of a plasma oxide of $Si_{0.8}Ge_{0.2}$, using O_2^+ primary ions with additional oxygen flooding. (a) raw data, (b) Ge/Si ratio, normalized to 0.2/0.8=0.25 in the unoxidized SiGe layer. The oxide thickness is 22 nm.

ide surface. Migration of the Ge atoms to the oxide surface is the opposite of what is observed during thermal oxidation of SiGe (Ref. 4) and may be related to the presence of the electric field during anodic oxidation inducing field assisted drift.

Water attacks the oxidized $Si_{1-x}Ge_x$ films. We have measured this effect by immersing samples at room temperature and measuring the film thickness by ellipsometry. For a nominally 30 nm thick oxide, the maximum thicknesses ~7 and 2 nm were removed for samples with x=0.35 and 0.2, respectively, and this was within a few tens of seconds. The $Si_{0.92}Ge_{0.08}O_2$ oxide was water resistant and the thickness of the oxide did not change. We conclude from these measurements that water attacks Ge-rich oxide when the Ge concentration exceeds some threshold level. This observation is consistent with data on thermally grown oxides.¹⁷

The forementioned water solubility of Ge-rich oxide provides a useful means of interpretation of the FTIR absorption data. Figure 3(a) shows the spectra observed in $Si_{1-x}Ge_x$ oxides for x = 0.35, 0.2 and 0 in the wave number range 750-1400 cm⁻¹, because of the oblique incidence of the beam, both transverse optic (TO) and longitudinal optic (LO) vibrational modes of the bridging oxygen asymmetric stretch mode are excited.¹⁸ In the "pure" GeO₂ sample case (where we obtained a maximum thickness of 5 nm of oxide) a single peak (TO) is observed centered on 850 cm^{-1} with a full width at half peak height on the order of 80 cm^{-1} . This half width is substantially smaller than the value¹⁹ for bulk GeO_2 (~200 cm⁻¹) and shifted to lower wave numbers from the bulk value ($\sim 885 \text{ cm}^{-1}$). This behavior is similar to that observed¹³ in thin film and bulk SiO₂. Concentrating on the TO peak in the $Si_{1-x}Ge_xO_2$ samples, we see that as x increases, the mode centered at $\sim 1050 \text{ cm}^{-1}$ in the SiO₂ sample broadens and shifts to lower wave numbers. Such



FIG. 3. (a) FTIR absorption spectra of plasma oxidized $Si_{1-x}Ge_x$ with different Ge content *x*. The thickness of the oxides is close to 30 nm. (b) Spectrum of the oxide of $Si_{0.65}Ge_{0.35}$ before and after immersion in water. The oxide thickness is reduced from 28 to 21 nm. (c) Spectrum of the Ge-rich part of the oxide, obtained by subtracting the spectrum of either (solid line) the water rinsed oxide or (dotted line) pure SiO₂ from the spectrum of the oxide of $Si_{0.65}Ge_{0.35}$.

behavior would be consistent with the appearance of vibrational modes associated with bridging oxygens in Si–O–Ge and Ge–O–Ge structures. In Fig. 3(b) we compare the spectra of an oxide on Si_{0.65}Ge_{0.35} before and after immersion in de-ionized water for 15 mins. The solid line in Fig. 3(c) shows the absorption spectra obtained if one subtracts the "water rinsed" spectrum from the "as-made" spectrum of Fig. 3(b). One observes that the water etch has removed two clear peaks at 850 and 1000 cm⁻¹. From our measurements on plasma oxidized "pure" Ge films we identify the former peak with asymmetric O vibrations in Ge–O–Ge bonds. The latter peak at 1000 cm⁻¹ can then be associated with vibrations of the O in Si–O–Ge bonds. The dotted line in Fig. 3(c) corresponds to the the difference spectrum obtained by subtracting a weighted spectrum for plasma oxidized Si ("pure" SiO₂) from the unetched spectrum of Si_{0.65}Ge_{0.35}O₂ [solid line in Fig. 3(b)]. We observe, again, evidence for the presence of two peaks at 1000 and 850 cm⁻¹ in the Ge containing sample. The weighting factor used was 0.43 which corresponds to the statistical number of Si–O–Si bonds in Si_{0.65}Ge_{0.35}O₂.

We have successfully oxidized $Si_{1-x}Ge_x$ thin films using plasma assisted oxidation at temperatures <100 °C and characterized these films using SIMS and FTIR. The high Ge concentration films show evidence for separated regions of Ge-rich oxide and Si-rich oxide, the former being close to the oxide surface, in contrast to thermally oxidized films where Ge excess and/or precipitation near the oxide– semiconductor interface is observed. This effect has been confirmed both by SIMS analysis and FTIR combined with water etching. Our FTIR data enable us, for the first time, to identify clearly vibrational modes associated with O in Si– O–Si, Si–O–Ge and Ge–O–Ge structures in the thin films, confirming that the plasma oxides of SiGe are mixed on an atomic scale.

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