Instability of a $Ge_xSi_{1-x}O_2$ film on a Ge_xSi_{1-x} layer

W. S. Liu, J. S. Chen, and M.-A. Nicolet
California Institute of Technology, Pasadena, California 91125

V. Arbet-Engels and K. L. Wang
University of California, Los Angeles, California 90024

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The stability of an amorphous $Ge_xSi_{1-x}O_2$ in contact with an epitaxial (100)Ge_xSi_{1-x} layer obtained by partially oxidizing an epitaxial Ge_xSi_{1-x} layer on a (100)Si substrate in a wet ambient at 700 °C is investigated for $x=0.28$ and 0.36 upon annealing in vacuum at 900 °C for 3 h, aging in air at room temperature for 5 months, and immersion in water. After annealing at 900 °C, the oxide remains amorphous and the amount of GeO_2 in the oxide stays constant, but some small crystalline precipitates with a lattice constant similar to that of the underlying GeSi layer emerge in the oxide very near the interface for both x. Similar precipitates are also observed after aging for both x. The appearance of these precipitates can be explained by the thermodynamic instability of $Ge_xSi_{1-x}O_2$ in contact with Ge_xSi_{1-x}. In water at RT, 90% of GeO_2 in the oxide is dissolved for $x=0.36$, while the oxide remains conserved for $x=0.28$.

The oxidation of Ge_xSi_{1-x} has become of interest recently,[1-12] due to the potential of GeSi devices and the importance of oxidation in device technology. It was initially reported that for GeSi samples of low Ge content ($x<0.2$) at high temperature ($T>800$ °C), a pure SiO_2 layer grows with Ge piling up behind it.[1-6] This resulting pileup of Ge greatly increases the interface trap density of the oxide[3] and thus should be avoided if the oxide is to be used in a device environment. At low temperatures ($T<700$ °C)[9-12] or for high Ge content,[7,8] the Si supply at the reaction interface is restricted, and Ge can also be oxidized, resulting in the formation of a GeSi oxide. The oxide that formed at low temperature in wet ambient shows a uniform composition with the same Ge/Si ratio as that of the virgin GeSi epilayer. No pileup of Ge is observed in that case and the oxidation rate is very large.[12] The consequent low thermal budget of this wet oxidation process of GeSi at low temperature is of practical interest.

It has been reported that GeO_2-SiO_2 glasses can, in the proper composition range, exhibit thermal coefficients of expansion that approximate that of the silicon (approximately 40×10^{-7}/°C between 25 and 700 °C).[13] The interfacial stress between these two materials, indeed, is less than 10^9 dyn/cm^2 (almost stress free) over a wide composition range of GeO_2.[14] The thermal coefficient of expansion of Ge is about 70×10^{-7}/°C in the same temperature range. The $Ge_xSi_{1-x}O_2/Ge_xSi_{1-x}$ system therefore exhibits much closer thermal coefficients of expansion between the protective insulating layer and the underlying GeSi film than the SiO_2/Ge_xSi_{1-x} system does. This fact is of interest especially for epitaxial GeSi films, whose metastability might be affected by this interfacial stress. However, the properties of the oxide, and especially its stability, need to be examined since the resulting interface between $GeSiO_2$ and GeSi is thermodynamically unstable and germanium oxide is also known to be unstable at high temperature or in moisture. We present here the results of experiments that investigate the stability of $Ge_xSi_{1-x}O_2$ on GeSi upon annealing, aging, and exposure to moisture.

The GeSi samples for this study were grown epitaxially onto a (100)Si substrate by molecular beam epitaxy without intentional doping. One sample is a layer of $Ge_{0.36}Si_{0.64}$ about 470 nm thick, the other a layer of $Ge_{0.28}Si_{0.72}$ about 550 nm thick. Both films are elastically relaxed as determined from x-ray double-crystal diffractometry. Samples from the wafers were oxidized in a tube furnace at 700 °C for 1 h in wet ambient obtained by bubbling nitrogen gas through 95 °C de-ionized water. For the annealing test, the oxidized samples were vacuum annealed at 900 °C for 3 h. Other oxidized samples were stored in air at room temperature for about 5 months. Additional oxidized samples were placed in de-ionized water at room temperature from several hours up to several days. The water sometimes was heated up to the boiling point to accelerate the test. The oxide film of all these samples was investigated by transmission electron microscopy and backscattering spectrometry before and after the tests.

The backscattering spectra for the oxide of $Ge_{0.36}Si_{0.64}$ before and after the vacuum annealing test are indistinguishable. The oxide thus remains uniform. No Ge is lost during annealing. Similar results are also found in the case of the oxide of $Ge_{0.28}Si_{0.72}$. This is noteworthy because germanium dioxide tends to volatize at elevated temperatures in the presence of pure germanium due to the following reaction: $GeO_2+Ge=2\,GeO_{(g)}$.[15] The conservation of Ge in the present case could be due to the absence of pure Ge or the action of the oxide as a protective cap.

Figure 1 shows cross-sectional transmission electron micrographs of the oxide of $Ge_{0.36}Si_{0.64}$ after 3 weeks and 5 months aging in air at room temperature and after the

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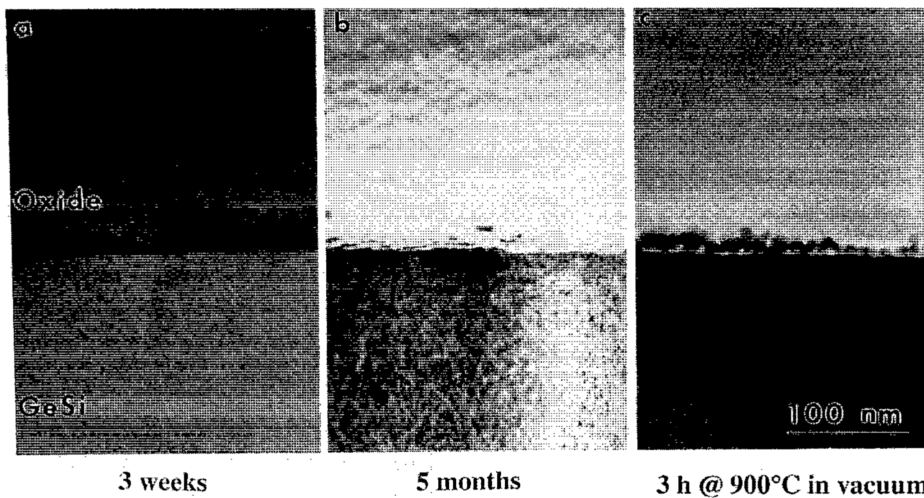

FIG. 1. Cross-sectional transmission electron micrographs of the GeSi oxide/GeSi layer interface for (a) 3 weeks aging in the air, (b) 5 months aging in the air, and (c) 900 °C annealing for 3 h after oxidation.

vacuum annealing test. Small precipitates emerge in the oxide near the interface and alter the initially sharp interface after 5 months aging and 900 °C annealing. In both cases, the precipitates are mostly located at about 10 nm from the interface. The size of the precipitate after 900 °C annealing is generally larger than that after 5 months aging at room temperature. The precipitates are crystalline with a lattice constant similar to that of the underlying GeSi layer, as shown in Fig. 2 which is a high-resolution micrograph of the oxide/GeSi region after 5 months aging. Similar features are also observed in the oxide of $Ge_{0.28}Si_{0.72}$ after the vacuum annealing and aging tests. By the lattice constants, these precipitates could be elemental Ge, elemental Si, GeSi solution, or even tetragonal GeO_2, which can grow epitaxially on the (110) plane of germanium.[16] Thermodynamic arguments given as follows predict that these precipitates should be Ge_xSi_{1-x} solid solution or in the limit, elemental Ge.

FIG. 2. High-resolution cross-sectional transmission electron micrograph of a $GeSiO_2$/GeSi interfacial region after aging for 5 months in air at room temperature. Crystalline precipitates with a lattice constant similar to that of the underlying GeSi layer are observed near the interface as the arrows indicate.

The Ge-Si-O ternary phase diagram calculated by Pain *et al.*[10] has tielines connecting SiO_2 with GeO_2 and Ge_xSi_{1-x} at 1000 K. The phase diagram is similar from room temperature to 900 °C according to our calculation similar to Pain *et al.* Any compound below the GeO_2-SiO_2 tieline, i.e., of composition $Ge_zSi_{1-z}O_{2-\delta}$ ($0 \leqslant z \leqslant 1$, $0 < \delta < 1$), will decompose into SiO_2 plus GeO_2 and Ge, or into SiO_2 and a Ge_ySi_{1-y} solution, depending on what the ratio of O/(Ge+Si) is. Cross-sectional transmission electron micrographs show that the interface between the GeSi layer and the Si substrate is still sharp after 900 °C annealing, indicating only insignificant interdiffusion between them. We can thus exclude the Si substrate from the system and only consider the equilibrium between the oxide and the remaining GeSi layer. Thermodynamically, the oxide then becomes unstable when it contacts GeSi, since the ratio of O/(Ge+Si) for this system is less than 2 and will locate this system below the GeO_2-SiO_2 tieline in the Ge-Si-O phase diagram. To explain the particular location of the precipitates seen in Fig. 1 requires a model of the kinetics involved with nucleation and growth. This instability also exists with pure Si and is unacceptable from a device point of view.

The backscattering spectra of the oxide before and after immersion in water at room temperature for one day are shown in Fig. 3. After this test, the oxide remains uniform but with a Ge content that decreases from $Ge_{0.36}Si_{0.64}O_2$ to about $Ge_{0.05}Si_{0.95}O_2$, or equivalently, a reduction from 2000 to 1400 f.u./cm^2. This result means that about 90% of the GeO_2 is lost in the water. To see if GeO_2 could be totally dissolved in the water, the sample of Fig. 3

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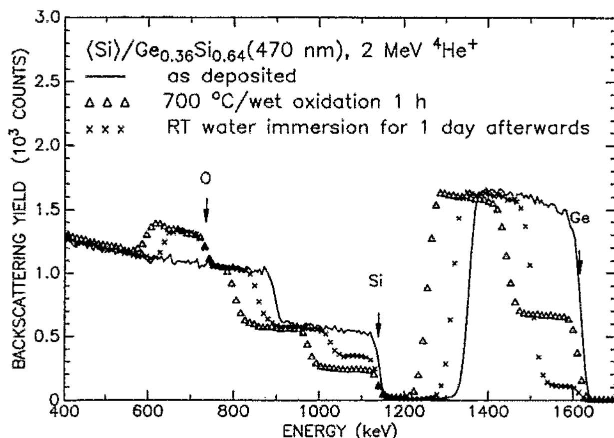

FIG. 3. 2 MeV $^4He^+$ backscattering spectra of a $Ge_{0.36}Si_{0.64}O_2$ layer before and after immersion in water at room temperature for 1 day (Near-normal radiation beam incidence; the scattering angle of detected particles: 170°).

was placed back in fresh de-ionized water for a week with water being replaced every day. No significant change was observed by backscattering spectrometry. The whole oxide including SiO_2 is totally lost after 16 h immersion in boiling water. For $Ge_{0.28}Si_{0.72}O_2$, the oxide is conserved after immersion in the water at room temperature for one day according to the backscattering spectrometry measurements, indicating the solubility of this oxide in the room temperature water is negligible. However, some amount of GeO_2 is lost after 16 h immersion in boiling water.

Hexagonal GeO_2 is known to be rapidly soluble in water; tetragonal GeO_2, on the other hand, is only very slightly soluble in the room-temperature water (<0.005 g/ℓ).[17] According to IR absorption spectrometry, the state of GeO_2 in the present $Ge_{0.36}Si_{0.64}O_2$ and $Ge_{0.28}Si_{0.72}O_2$ films is mostly in the from of tetrahedrally coordinated $[GeO_4]$ germanium (hexagonal form of GeO_2) with a little octahedrally coordinated $[GeO_6]$ germanium (tetragonal form of GeO_2).[12] By that observation, most of the GeO_2 should be water soluble in both cases. Most of the GeO_2 in $Ge_{0.36}Si_{0.64}O_2$ is in fact lost upon immersion in water at room temperature. $Ge_{0.28}Si_{0.72}O_2$, however, is completely water insoluble. Similar water tests have been performed on the GeO_2-SiO_2 glasses deposited on Si substrates by low pressure chemical vapor deposition.[14] They also found a limit (about 20% GeO_2) below which the glasses is water insoluble. To what extent the unequal solubility of $Ge_xSi_{1-x}O_2$ films can simply be explained by a tetragonal versus hexagonal coordination of Ge thus remains an open question.

Compositional and structural inhomogeneities can also affect the solubility. If enough SiO_2 surrounds GeO_2, it can be shielded from attack by water even though it may be tetrahedrally coordinated. The ratio of GeO_2/SiO_2 below which the oxide is completely room-temperature water insoluble is then decided by the detailed structure of the oxide, which could be affected by the ways the oxide is formed. The effect of hot water could be to accelerate the breakup of this shielding until the remaining oxide is so porous that even the SiO_2 is eroded away.

The interface between $Ge_xSi_{1-x}O_2$ films and Ge_xSi_{1-x} or Si is thermodynamically unstable. This instability leads to the formation of GeSi precipitates by a reduction of GeO_2 near the interface. The phenomenon is detectable a few months after the formation of the interface and storage at room temperature meaning that it is a major consideration in any proposed application of $Ge_xSi_{1-x}O_2$ in Ge_xSi_{1-x} devices. The mixed oxides are also sensitive to moisture, in ways not explained yet.

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