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Bonding partner change reaction in oxidation of Ge on Si(001): Observation of two step formation of SiO₂

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Oxidation of 5 Å Ge deposited at room temperature on Si(001) and the dependence of temperature on the oxidation behavior are investigated by employing synchrotron radiation photoelectron spectroscopy. The sample on exposure to air forms a mixture of Ge oxides and a small amount of Si oxides. Upon annealing, oxygen changes its bonding partner from Ge to Si forming SiO₂ as the predominant final product. Two distinct steps have been observed in such a reaction. First step is the cleavage of all the Ge—O bonds and formation of Si—O bonds to form mainly Si suboxide. The second step is the rearrangement of Si—O bonds to form SiO₂. The former one takes place in the temperature range 200–300 °C whereas the latter one in the range 300–600 °C.

Considering the importance of SiGe material in high speed devices¹ we have been carrying out investigation of oxidation of ultrathin layers of Ge deposited on Si(001) to understand the early stages of the oxidation process. To address this problem, the authors have employed a combination of techniques such as photoelectron spectroscopies, medium energy ion scattering (MEIS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Recently we reported the occurrence of an annealing induced bonding partner change reaction of oxygen from Ge to Si^{2,3} in the case of a 5 Å Ge deposited on Si(001). The final result of this reaction is the formation of SiO₂. However, in this study, using conventional XPS, the early stages of formation of SiO₂ could not be revealed due to the comparatively low surface sensitivity of the technique. Therefore, we decided to investigate this reaction by employing highly surface sensitive synchrotron radiation photoelectron spectroscopy (SRPES). In this letter, we describe the results of such a study carried out on an air oxidized sample prepared by depositing 5 Å Ge on the Si(001) surface at room temperature [hereafter called 5 Å Ge/Si(001)RT].

The Si(001) wafers used are *n*-type with conductivity, ~5 Ω cm. After standard wafer cleaning, a thin layer of oxide was prepared by dipping the wafer in HNO₃ at room temperature. This oxide layer was removed in UHV by annealing to 900 °C and on this sample, a buffer layer of Si(200 Å) was deposited at 550 °C followed by an anneal at 900 °C. An ultrathin layer (5 Å, as monitored by the crystal thickness monitor) of Ge was deposited on this sample at room temperature. Depositions are carried out in a MBE chamber equipped with RHEED. The sample was oxidized in air for 10 h and was subsequently loaded into the ultrahigh vacuum chamber and annealed to various temperatures. After each annealing, the sample was cooled to room temperature and synchrotron radiation photoelectron spectra are measured. The measurements were carried out in a combined surface analysis system using a VG CLAM100 analyzer, at

the Photon Factory on NTT beam line BL-1A⁴ located in Tsukuba.

In Figs. 1 and 2 we plot the spectra in Si 2*p* and Ge 3*d* regions of oxidized 5 Å Ge/Si(001)RT and the spectra corresponding to anneal at various temperatures. The Si 2*p* spectra are background subtracted and corrected for band bending effects. The RT spectrum corresponds to the 5 Å Ge/Si(001)RT exposed to air for 10 h. As seen in the spectra, sample exposure to air partially oxidizes the Si atoms present underneath the Ge layer. The Si 2*p* due to elemental Si exhibits a peak at a binding energy of 99.3 eV and the oxide peak at around 102.2 eV. This binding energy separation of 2.9 eV is quite characteristic of a suboxide, comprising Si atoms with threefold oxygen coordination. The concentration of 3 coordinated Si atoms is little higher than that reported by Hollinger and Himpsel for an oxide layer of similar

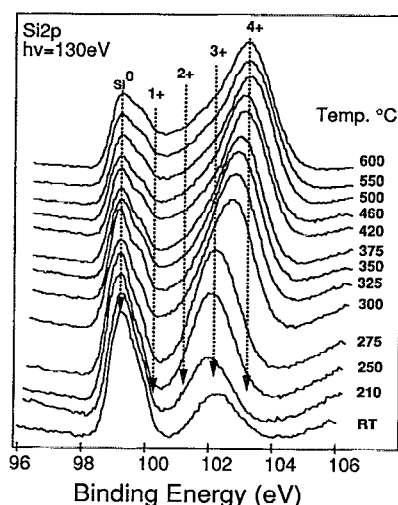


FIG. 1. The Si 2*p* spectra of 5 Å Ge/Si(001)RT exposed to air for 10 h and annealed to various temperatures. The spectra are background subtracted and corrected for band bending effects. The vertical lines show the peak positions of the components.

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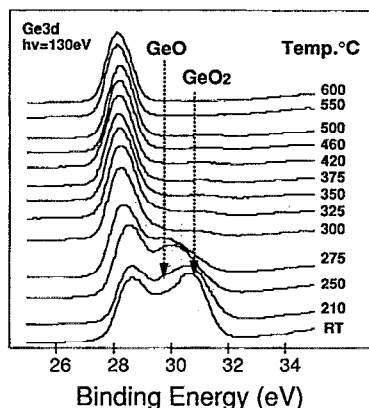


FIG. 2. Ge 3d raw spectra of 5 Å Ge/Si(001)RT exposed to air for 10 h and annealed to various temperatures. The spectra are not corrected for band bending effects.

thickness.⁵ The peak due to elemental Si is broad due to two factors. First, it is due to the mixed contribution to the signal by bulk and surface Si atoms. Second, the spin orbit splitting could not be resolved clearly due to the instrumental limitations. The contribution by bulk Si atoms to the signal was clearly demonstrated by Himpsel *et al.*⁶ in a geometry dependent surface core level excitations study. The Ge 3d spectrum of the air oxidized sample shows the presence of a mixture of oxides namely GeO and GeO₂. Ge 3d due to elemental Ge is observed at 28.55 eV and the components due to GeO and GeO₂ are observed, respectively, at 29.55 and 30.7 eV.

The spectra recorded after annealing the sample to around 210 °C shows noticeable changes. The Ge 3d signal due to oxide shows depletion in intensity and the signal due to oxide in Si 2p gains in intensity. This continues until around 300 °C when the oxide signal in Ge 3d completely disappears. This is accompanied by an increase in intensity of the oxide signal in Si 2p spectra. The total concentration of oxygen present on the surface remains the same as that before the anneal as noted by the intensity of the O 2p and O 2s signals in a wide scan. This means that all the Ge—O bonds are broken and oxygen atoms thus generated bond with Si atoms. Figure 3 describes the variation in the intensity ratio of Si 2p due to element and oxides as a function of temperature. In deducing the intensity of the peak due to oxide, the integrated area under the peak encompassing all the peaks due to suboxides and SiO₂ was measured from the background subtracted spectra. In Fig. 3 we have also plotted the energy separation between the Si 2p element and that due to the oxide. The peak position is noted from the background subtracted spectra and is the peak position of the combined peak due to suboxides and SiO₂. Although this procedure is not entirely accurate, the values thus obtained describe the general growth pattern of the oxide layer as demonstrated by Grunthaner *et al.*⁷ As shown, the intensity ratio of Si to Si oxides decreases in the temperature range 25–300 °C and then remains nearly constant at higher temperatures. At the same time the separation between the Si 2p element and the oxide remains the same as that correspond-

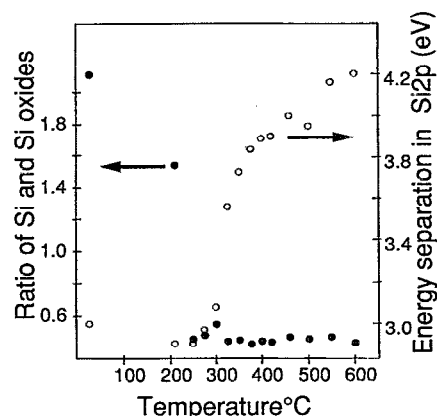


FIG. 3. The ratio in intensity of Si 2p due to element and that due to the oxides as a function of temperature. The right axis is a measure of the separation between the peak positions due to elemental Si and that due to the combined oxides.

ing to the room-temperature spectrum, i.e., ~3 eV. This means that all the oxygen atoms formed by the breakage of Ge—O bonds form bonds with Si atoms. At this stage those Si atoms are in a 3⁺ state which means 3 oxygen atoms attached to a single Si atom. This process continues until all the Ge—O bonds are broken. On annealing at higher temperatures, the Si to oxygen coordination number changes and forms SiO₂ as seen by the increased energy separation between elemental and oxide peaks in Si 2p spectra. This finding shows that the energetics of the formation of Si—O bonds to form SiO₂ is different from that of the formation of Si suboxides. This rearrangement of oxygen atoms around Si also consists of breakage of some of the Si—O bonds to form the 4 coordinated SiO₂. This is because of the limited amount of oxygen atoms available. During this process some lower coordinated Si atoms are also generated.

In Fig. 4 we plot the approximate individual intensities due to differently coordinated Si atoms. The spectrum of the air oxidized sample contains almost same amount of 1⁺, 2⁺, and 4⁺ Si and a slightly higher concentration of 3⁺ Si. These

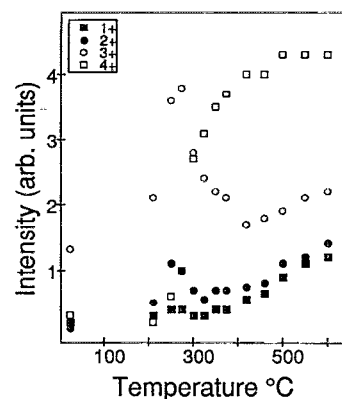


FIG. 4. The variation in individual intensity of various species of Si as a function of temperature. The intensity data are derived from the Si 2p spectra.

formal valences mean that each Si atom is coordinated with the corresponding number of oxygen atoms.⁷ The intensity due to 3 coordinated Si increases up to 275 °C and then decreases at higher temperatures. At the same time, the intensity due to the 4 coordinated Si remains nearly the same up to 275 °C and then increases on annealing the sample. This variation explains the two step formation of SiO₂ as a result of the bonding partner change reaction between Ge and Si atoms. Interestingly, in the temperature range, 450–600 °C, the transformation of 3 coordinated Si to generate 4 coordinated Si produces some 1 and 2 coordinated Si atoms. This is seen by the increase in the intensity due to 1 and 2 coordinated Si on annealing to higher temperatures. This can be understood more clearly on comparison with a study on oxidation of clean Si surfaces^{8,9} where the concentration of 1, 2, and 3 coordinated Si atoms decrease and that of 4 coordinated Si continue to increase. In this case, since there is a continuous supply of oxygen atoms, 1⁺ and 2⁺ Si species continue to get transformed to Si 4⁺. However, in the present experiment, the available amount of oxygen is limited and hence transformation of 3 coordinated Si to 4 coordination is followed by formation of a small amount of 1 and 2 coordinated Si atoms. The distribution of intermediary states indicate during the formation of SiO₂, the interface is not completely abrupt and the suboxide layer has a finite thickness as concluded by Hollinger and Himpsel.⁵ Some time ago there were reports that Ge catalyzes the oxidation of Si when the oxidation is carried out on SiGe layers.¹⁰ However in this study the presence of Ge—O bonds were not detected. We believe this catalytic action is due to the bonding of oxygen to the Ge sites which are available on the surface initially and its subsequent cleavage forming Si—O bonds. The first phase results in trapping the oxygen atoms which helps to make it available for bonding with Si. This process is accompanied by movement of Ge atoms leading to its pile up at the SiGe/Si interface. We have observed this in the case of ultrathin SiGe layer on Si(001) through medium energy ion scattering (MEIS).¹¹

As the oxidation of Si as a result of this bonding partner change reaction proceeds a shift of elemental Si 2*p* to lower binding energies by 0.5 eV is observed. This is as a result of increase in band bending. Similarly, Ge 3*d* shifts to lower binding energies by 0.5 eV, as the reduction reaction proceeds. Ge 3*d* due to elemental Ge is observed at a binding energy of 28.15 eV upon reduction. This is also due to the increase in band bending. As the oxidation of Si occurs on annealing, the components due to spin orbit splitting begin to resolve. This is attributed to the disappearance of the surface Si contribution from the RT spectrum, as they are preferentially oxidized in the initial stages. The O 2*p* and O 2*s* peaks shift to higher binding energies by ~1.9 eV upon completion of the bonding partner change reaction from Ge to Si form-

ing SiO₂. This difference is due to the difference in ionicity of Ge—O and Si—O bonds. Similar shifts were observed in the O 1*s* levels as well.² The O 1*s* corresponding to GeO is observed at 531.3 eV and that due to SiO₂ is observed at 532.5 eV. A study on oxidation of Ge and Si surfaces based on work function measurements show that the elementary dipole moments are 0.31 and 0.04*e*, respectively, for Si—O and Ge—O bonds.¹² Thus the Si—O bond is more ionic than the Ge—O bond suggesting a higher covalency in the Ge—O bond.

We had reported earlier on the surface morphology of these samples at various stages of the bonding partner change reaction. It was observed that the formation of SiO₂ leads to the formation of voids on the surface. We believe, that significant atomic movements take place causing the ejection of Si atoms from the substrate due to the exothermic nature of the reaction. This may also cause local heating thus forming hot Si atoms. The hot nature of the Si atoms make their movements more facile. This process forms nanometer sized voids on the surface.

To conclude, the early stages of the bonding partner change reaction of oxygen from Ge to Si sites occurring on an oxidized sample of 5 Å Ge deposited on Si(001) upon annealing is investigated by SRPES. The formation of SiO₂ as a result of this reaction takes place in two distinct steps. The first step is the breakage of the Ge—O bonds and making of Si—O bonds forming predominantly, suboxides of Si. This process continues until all the Ge—O bonds are broken. The second step is the rearrangement of oxygen atoms around Si forming the thermodynamically more stable 4 coordinated SiO₂.

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