Photonic Effects during Low-Temperature Ultraviolet-Assisted Oxidation of SiGe

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The behavior of Ge atoms during dry oxidation of $Si_{0.8}Ge_{0.2}$ films at 300°C under 10 mbar of oxygen induced by vacuum-ultraviolet (VUV) illumination from an array of Xe_2* excimer lamps (λ = 172 nm) has been studied. During VUV oxidation, samples are exposed to both a high concentration of ozone and atomic oxygen and a large flux of energetic photons. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy investigations showed that the layers grown for shorter periods of time contain mostly SiO_2 with a few percent GeO_2. Most of the Ge atoms, initially present uniformly within the SiGe layer, were segregated and accumulated at the interface between the grown oxide and remaining SiGe. Angle-resolved XPS showed that the amount of GeO_2 within the grown oxide layer decreased for longer irradiation times and was located adjacent to the SiGe layer. When the grown SiO_2 layer reached a thickness around ~70 Å and the amount of Ge that had accumulated in the segregated layer more than doubled, a sharp increase in the Ge oxidation rate was observed. Continuing the oxidation for longer irradiation times resulted in the formation of a mixed oxide layer. The Ge segregation was not previously observed during other low-temperature oxidation treatments, including ozone-assisted oxidation, which provides the same oxidation species as VUV-assisted oxidation and similar growth rates. It is, therefore, concluded that a VUV photon-irradiation enhancement effect on Si and Ge interdiffusion has been introduced, possibly involving either Si-Si or Si-Ge bond softening or even breaking.

Key words: VUV-assisted oxidation, SiGe, photon effects

INTRODUCTION

The SiGe alloys have been successfully employed for the production of bandgap engineered structures, such as heterojunction bipolar transistors, superlattices, and quantum wells.[1,2] To extend their use to high-performance metal-oxide semiconductor field-effect transistors either as a high p-type mobility channel or as a polycrystalline gate,[3,4] a process capable of growing high-quality oxide layers on SiGe needs to be devised. There is also a fundamental interest in understanding the physics of SiGe oxidation especially for thin oxide layers. Thermal oxidation usually produces Ge segregation at the interface between the grown oxide and the remaining SiGe layer, which degrades the electrical properties of the structure.[5–7] Several low-temperature oxidation techniques, such as plasma, electron-cyclotron resonance plasma, and atomic oxygen,[4,6–13] have been investigated to prevent Ge segregation, thermal relaxation of SiGe-strained layers, or unwanted-dopant redistribution.

We have previously investigated ultraviolet (UV) and vacuum-ultraviolet (VUV) assisted dry oxidation of SiGe layers at 450–550°C.[14–17] These studies showed that there are two major differences between UV-assisted and conventional thermal oxidation. First, there is an enhancement of the SiGe dry-oxidation rate over that of pure Si, which was previously observed only for thermal-wet oxidation. Recently, fluorine-assisted dry oxidation[6] and atomic-oxygen oxidation[12] studies reported a similar enhancement. It has been suggested[9] that because

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fluorine oxidation induces a high concentration of point defects (vacancies), perhaps the UV-assisted oxidation data[14–17] can be explained by a similar argument.

Second, Ge segregation to the boundary of the grown oxide has always been observed during the UV-oxidation process. This occurred even at 450°C for VUV-assisted oxidation.[17] Apart from one report using atomic-oxygen oxidation at 500°C where only partial Ge segregation was observed,[12] no other technique showed a similar trend. It has been further suggested that there could be a surface-reaction rate, limited-growth mechanism that leads to Ge segregation.[9] To clarify the Ge-segregation issue, we have investigated VUV-assisted oxidation of $Si_{0.8}Ge_{0.2}$ at 300°C, a temperature for which all other studies performed so far using various low-temperature oxidation techniques reported Ge incorporation into the grown oxide.[4,6–13]

EXPERIMENT

The $Si_{0.8}Ge_{0.2}$ layers, around 200-Å thick, grown by molecular-beam epitaxy (MBE) on (100) Si samples, cleaved from a 4-in. wafer, were cleaned in acetone, sonicated in methanol, dipped in 1% HF, blown dry with high-purity N_2, and then immediately loaded into a stainless-steel chamber containing an array of three Xe_2* excimer VUV lamps. The peak emission of the lamp system was at 172 nm, and the power-density incident onto the sample surface was around 25 mW/cm^2. More details of this VUV source can be found elsewhere.[18] The samples were mounted onto a heater stage whose nominal temperature, measured with an attached thermocouple, was set at 300°C. Prior to VUV irradiation for different exposure times, the chamber was evacuated, purged with electronic-grade (99.999%) N_2, and then with electronic-grade (99.999%) O_2, and finally backfilled with O_2 to the working pressure of 10 mbar. The low O_2 pressure employed in our study allows a significant fraction of the photons emitted by the lamps to reach the surface of the samples.

The chemical composition and atomic bonding were investigated by x-ray photoelectron spectroscopy (XPS, Perkin Elmer 5100, Al K_α radiation). Because we noticed that 4-keV Ar ion sputtering induced significant chemical changes in GeO_x, depth-profiling information was obtained from comparisons of the intensity of the XPS peaks acquired at 90° and 45° take-off angles. Fourier transform infrared (FTIR) (Perkin Elmer Paragon 100) spectroscopy was also used to analyze the chemical bonding of the grown layers. The optical properties and film thickness were measured by variable-angle spectroscopic ellipsometry (VASE) using a Woollam Company instrument.

RESULTS AND DISCUSSION

The XPS analysis of a sample, which after the cleaning procedure was exposed to the ambient atmosphere for a long period of time, revealed the presence of a thin mixed-native oxide $(Si,Ge)O_x$ ($x < 2$) layer on the surface, as shown in Fig. 1, where high-resolution scans of the Si 2p and Ge 3d regions are displayed. The thickness of this layer was estimated by VASE to be ~44 Å, much thicker than the usual ~25 Å-thick native oxide found on Si. For comparison, also shown in Fig. 1 are XPS spectra acquired from VUV-oxidized samples. One can immediately note that their chemical bonding is different. While the native oxide consists of a mixture of suboxides, the VUV grown layers contain a more fully oxidized type of Si and Ge. The binding-energy difference between Si^{x+} and Si^0 peaks of the VUV-oxidized samples increases for longer irradiation times, from 4.2 eV to 4.6 eV. It is also worth noting that the binding-energy difference between oxidized and unoxidized Ge peaks is almost constant and equal to 4.6 eV; the value corresponding to fully oxidized Ge.[19,20] For irradiation times longer than 90 min, there is a sudden increase in the size of the oxidized Ge peak simultaneous with a corresponding decrease of the unoxidized Ge peak. The sample oxi-

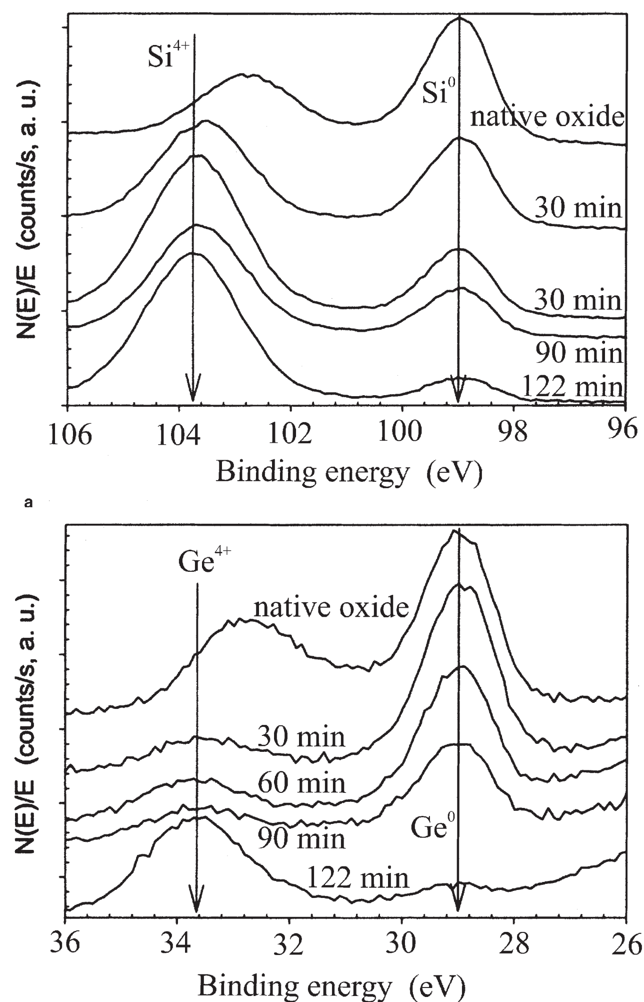


Fig. 1. The XPS high-resolution spectra (take-off angle was 45°) of the native oxide formed after cleaning and of the VUV oxidized-SiGe samples at 300°C for different times: (a) Si 2p and (b) Ge 3d regions.

dized for 122 min exhibits surface Si and Ge oxidized peaks located at 103.5 eV and 33.6 eV, which is very similar to those recorded for thick stoichiometric oxides,[3,8,10,15–17] i.e., Si^{4+} and Ge^{4+}. The amount of Si and Ge atoms bound in suboxides was estimated to be ~5% and ~20% after 30-min oxidation and decreased for longer oxidation times. It is also evident that the area of Ge^{x+} corresponding to Ge oxide is much smaller in the VUV-oxidized sample than in the native oxide and that it changes very little up to an irradiation time of 90 min. In addition, the Ge^0 peak attenuation for increased oxidation times is smaller than that of the Si^0 peak for these VUV-oxidized samples. This is evidence that there is a segregation process for unoxidized Ge atoms that are rejected from the growing oxide layer and accumulated at the interface.

In Fig. 2, scans of the Ge 2p and Ge 3d regions acquired at a 45° take-off angle from a sample oxidized for 90 min are displayed. While both the oxidized and unoxidized Ge 3d peaks, Ge^{4+} and Ge^0, respectively, are clearly visible in Fig. 2b, only the oxidized Ge 2p peak appears in Fig. 2a. Taking into account the inelastic mean-free paths of the Ge 3d and Ge 2p photoelectrons, which were estimated[9] to be 50 Å and 7 Å, respectively, the Ge 2p photoelectrons, contributing to the spectrum shown in Fig. 2a, originated from a region up to a depth of ~20 Å (three times the inelastic mean-free path). Therefore, all the unoxidized Ge atoms are completely rejected from the surface region during initial stages

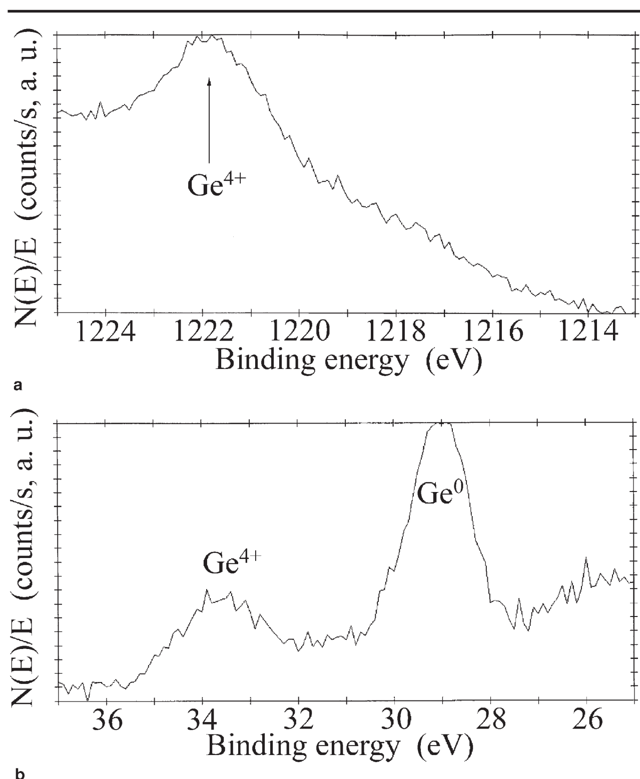


Fig. 2. The XPS high-resolution spectra of the (a) Ge 3d and (b) Ge 2p regions acquired from a SiGe sample oxidized for 90 min; take-off angle was 45°.

of the VUV-assisted oxidation at 300°C and accumulate in a buried SiGe layer. The evolution of the Ge concentration within the segregated SiGe layer with oxidation time, estimated from the areas of the Si 2p and Ge 3d peaks, is shown in Fig. 3. One can see that from an initial value of around 15–16%, it increases to almost 36% after 90-min oxidation time. Because of the limited depth resolution of the XPS technique, it is expected that the actual Ge concentration within this layer to be much higher.[12]

The evolution of the ratio between oxidized and unoxidized Si 2p and Ge 3d peak areas (Si^{4+}/Si^0 and Ge^{4+}/Ge^0), calculated after a Shirley-type background subtraction is plotted in Fig. 4. The data for zero oxidation time corresponds to the native oxide. The thickness of the oxide layers estimated by VASE is also indicated on the graph. From the data presented in this graph, one can clearly see that Si oxidation is a continuous process. There is an initial fast oxidation rate of around ~1.6 Å/min for the first 30 min, followed by a gradual transition to a slower oxidation rate, which becomes ~0.7 Å/min at 122 min. A similar trend, initial rapid linear growth followed by a transition toward a parabolic type of growth, was noticed for VUV-assisted oxidation of pure Si[21] and pure Ge.[20]

The behavior of Ge atoms during VUV-assisted oxidation was different from that of the Si atoms. The Ge peaks ratio, for both take-off angles, was smaller after 60-min and 90-min oxidation time than that measured after 30 min. The XPS analysis of the intensity and position of the Ge 2p peaks showed that there were no unoxidized Ge atoms left in the surface region. All unoxidized Ge atoms were buried under a SiO_2 layer, which becomes thicker with increasing irradiation time. Therefore, there is a decrease in Ge^0 peak intensity for longer irradiation times, as clearly shown in Fig. 1. The fact that the Ge^{4+}/Ge^0 ratio also decreases for longer oxidation times, as shown in Fig. 4, for both take-off angles suggests that the oxidized Ge atoms should also be buried at or very near the interface, and their quan-

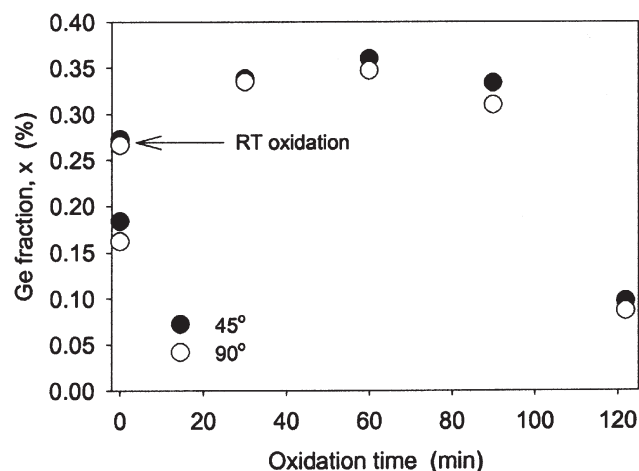


Fig. 3. The evolution of Ge fraction, x, within the segregated $Si_{1-x}Ge_x$ layer versus oxidation time.

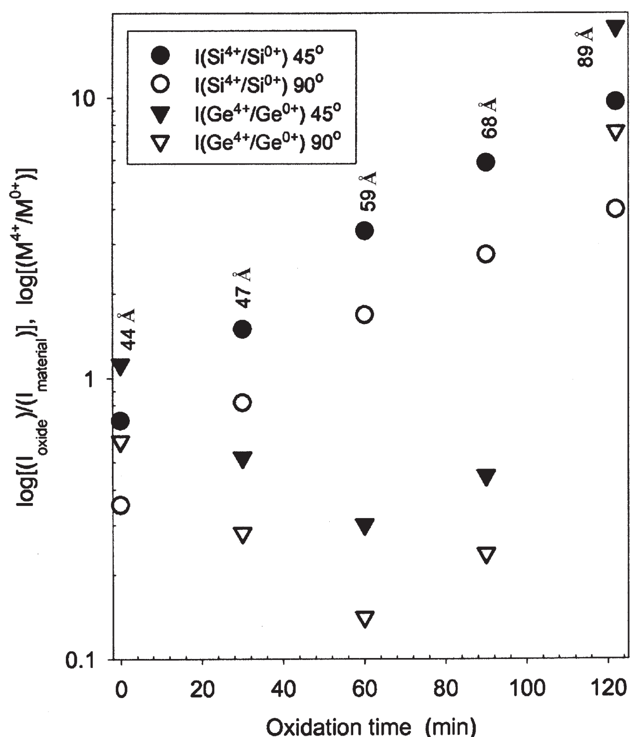
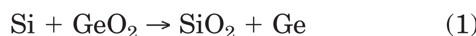


Fig. 4. The logarithm of the ratio of Si 2p and Ge 3d peak areas for oxide and elemental states acquired at 45° and 90° take-off angles versus oxidation time; the value for the native oxide is shown for zero time. The thickness of the oxide layer (in Å) is also indicated.

tity is lower after 60-min or 90-min oxidation time than that found after 30-min oxidation time or within the native oxide. This is evident from data shown in Fig. 5, where the fraction of oxidized Ge atoms within the grown oxide layer is plotted versus irradiation time. This is quite an unexpected result and can be understood as follows. There is always some Ge oxidation occurring at the interface at this low temperature but once formed most of the GeO_2 is immediately reduced by Si according to the following reaction:[6]



$$Si + GeO_2 \rightarrow SiO_2 + Ge \quad (1)$$

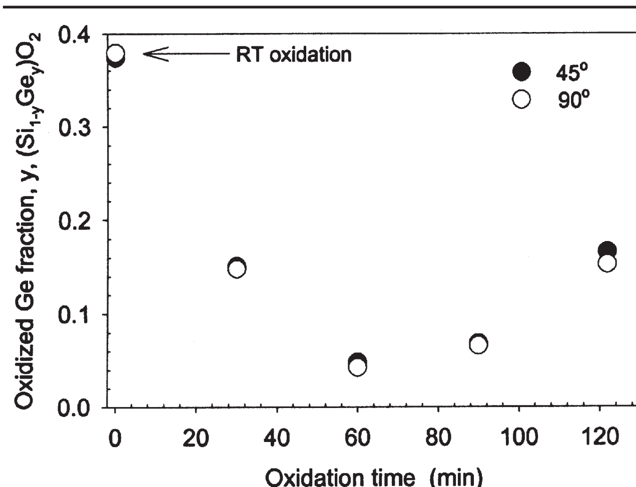


Fig. 5. The evolution of oxidized Ge fraction within the grown oxide layer versus VUV-irradiation time.

The free-energy change associated with this reaction is rather large; a value of $\Delta G_1 = -356$ kJ/mol O_2 was measured at 727°C.[22] The resulting Ge atoms should be completely segregated during the initial stages of VUV-assisted oxidation at the interface and then accumulated into the buried SiGe layer bcause their presence was not detected in the Ge 2p region of the XPS spectrum.

After 90-min oxidation time, when a ~70 Å-thick layer of almost pure SiO_2 was formed and the Ge concentration in the segregated layer more than doubled, there was a sudden increase in the Ge-oxidation rate. This resulted in a marked decrease of Ge concentration in the remaining SiGe layer, which reached 10% after 122-min oxidation. However, it is worth noting that, during VUV-assisted oxidation of SiGe at 300°C, Ge incorporation into the grown oxide layer does not begin during the initial fast-oxidation regime, as reported for atomic-oxygen oxidation[12] or plasma-assisted oxidation.[9]

The FTIR spectra acquired from samples oxidized for various times are shown in Fig. 6. The presence of Si-O-Si stretching and bending absorption bands located at approximately 1,080 cm^{-1} and 810 cm^{-1} is clearly visible. The areas of these absorption bands increase for longer irradiation times. One can also note that only the spectrum acquired from the sample oxidized for 122 min showed the presence of a new absorption band located at ~930 cm^{-1}, which confirms[19] the presence of a significant amount of GeO_2 also observed in the XPS spectra.

When comparing our data to those obtained using other low-temperature oxidation techniques, it is evident that only VUV-assisted oxidation resulted in almost complete Ge segregation for a significant oxidation time. It is especially instructive to compare these data with those obtained using ozone-assisted oxidation[11] because both techniques use the same oxidant species. The comparison is even more meaningful because similar initial growth rates (1.6

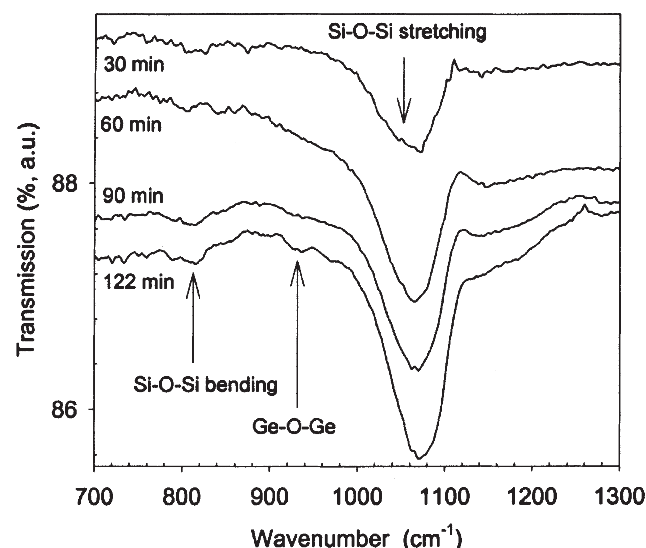


Fig. 6. The FTIR transmission spectra of oxidized SiGe samples.

Å/min and 2 Å/min) were measured in both experiments, indicating similar concentrations of the oxidizing species. For ozone-oxidation experiments, there was no measurable Ge segregation up to a temperature of 400°C. The main difference between these two techniques as well as other low-temperature techniques is the presence of highly energetic photons during VUV-assisted oxidation. It is well known that absorption of high-energy photons creates highly energetic electrons in the conduction band of the semiconductor, which can tunnel through the thin oxide layer and reach the surface, where they are captured by atomic oxygen.[23,24] However, this effect can only explain the enhancement of the semiconductor-oxidation rate. The trapping of Ge during SiGe-oxidation experiments has been explained by a competition between the oxidant flux from the surface and the Si atoms flux from the substrate:[5,6,9–12] as long as the flux of Si atoms is equal or greater than the oxidant flux, the grown oxide layer will contain only SiO_2, while all Ge atoms will be segregated from this newly formed oxide layer. Because the growth rates in our VUV-assisted oxidation experiment and ozone-assisted oxidation are very similar one can infer that the oxidant fluxes should also be very similar. The fact that Ge segregation was clearly observed only during VUV-assisted oxidation strongly suggests that the Si and Ge atoms interdiffusion was significantly enhanced. It has been recently shown that VUV photons can create point defects during Si oxidation.[25] There has been a suggestion that they can also soften or even break Si-Si bonds.[26] Both effects can significantly enhance Si and Ge interdiffusion and account for the observed Ge segregation during low-temperature VUV-assisted SiGe oxidation. Whatever effect is more important cannot be determined from the present data, we can only state that there should be a photonic effect to account for this singular Ge behavior, which is different from that observed during other low-temperature oxidation techniques. Further experiments at lower temperatures and different VUV wavelengths are in progress.

CONCLUSIONS

The VUV-assisted oxidation at 300°C of $Si_{0.8}Ge_{0.2}$ layers grown by MBE on (100) Si samples has been studied. The XPS results showed that for short oxidation times only a small fraction of the Ge atoms were oxidized, but afterward, they were almost completely reduced by Si atoms. All unoxidized Ge atoms were initially segregated from the grown oxide and accumulated at the interface within the remaining SiGe layer. When the thickness of the grown oxide layer reached ~70 Å and the Ge concentration within the remaining SiGe layer more than doubled with respect to the initial value, the Ge-oxidation rate suddenly increased. Further oxidation resulted in the formation of a mixed oxide layer. These results are very different from those observed when using any other low-temperature oxidation techniques. The fact that the Ge behavior is different even from that observed during ozone-assisted oxidation, a technique that uses similar oxidant species and resulted in similar growth rates, suggests that a photon-enhancement effect of Si and Ge interdiffusion is a very likely explanation. A high flux of energetic photons creates a high concentration of defects in the oxidized semiconductor and high-energy electrons that can account for enhanced-oxidation rates and diffusion of the atomic species.

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