Oxidation of Si surfaces is one of the most widely investigated systems in the field of surface science, dating back a couple of decades, and it has been reviewed as well by several groups.1–3 However, some of the basic issues regarding the early stages of oxide growth as well as its thermal decomposition behavior are still being debated. There are many papers that address understanding of the nature of the adsorbed species as well as the desorbing species. In the latter case, the transformation of the adsorbed species to the desorbing species is important in understanding the surface and interface properties. In the industrial microelectronics fabrication process, the wafers go through several wet chemical treatments and it is therefore important to understand the surface chemistry4 at each stage. Studies on Ge surfaces are also especially important due to the growing interest in SiGe as a promising candidate for the fabrication of high performance devices.5 In this letter, we describe the effect of annealing on a chemically prepared ultrathin oxide layer on Ge(100) and Si(100) surfaces. The advantage of using synchrotron radiation for studying this system is its unique surface sensitivity which enables one to probe the topmost layer in the solid. In conventional x-ray photoelectron spectroscopy the signals are dominated by contributions from the deeper layers and the features due to the surface appear very weak, as demonstrated in our own earlier work.6,7

The synchrotron radiation photoelectron spectroscopy (SRPES) measurements were performed at the NTT SR source located in Atsugi on beam line ABL-3B. The front end of the beam line consists of a “grasshopper” monochromator and provides sufficient photon flux for measuring Ge3d and Si2p core levels (hv = 90 and 130 eV, respectively).8 Ge and Si wafers (n type, 5–10 Ω cm) were cleaned by standard methods. The oxide on the Ge surface was prepared by reacting the wafer with concentrated H2O2, described in detail elsewhere,9 and silicon oxide was prepared by treatment with concentrated HNO3 after proper chemical cleaning (~1 nm thick). The samples were brought to the ultrahigh vacuum chamber through a load-lock chamber in 5–10 min. In order to monitor the annealing effect, the samples were brought to a particular temperature and kept for 15–20 min and the measurements were carried out at room temperature (RT).

In Figs. 1 and 2, we display the raw Ge3d and Si2p spectra from the respective oxides as a function of temperature. The spectra at RT from the as-prepared oxide samples indicate the presence of elemental Ge and a mixture of oxides, which are marked GeO and GeO2 (elemental Si, SiOx and SiO2, in the case of the Si oxide surface). The GeOx and SiO2 species (where x<2) are actually a mixture of oxides called the suboxides and consist of a structure with less than four oxygen atoms attached to one Ge or one Si atom. Since...
the predominant signal in the suboxide is due to the monoxide, we refer to only the monoxide species in further discussions in this letter. The assignments are based on the work of several groups as well as on our own in situ oxidation experiments carried out independently on clean Ge and Si substrates.\textsuperscript{10–12} The spin-orbit split components in Ge\textsuperscript{3d} (3d\textsubscript{5/2} and 3d\textsubscript{3/2}) and Si\textsuperscript{2p} (2p\textsubscript{3/2} and 2p\textsubscript{1/2}) are observed. Upon annealing the Ge oxides, (see Fig. 1), the intensity of the spectral component due to the dioxide species decreases with a concomitant increase in intensity of the peak due to the monoxide species (marked GeO\textsubscript{x} in Fig. 1). This intensity variation results in a shift of the overall peak due to oxide towards lower binding energy. The chemical shift of the peak due to the combined oxides is plotted as a function of temperature in Fig. 3 for both Ge oxides and Si oxides. GeO is known to exhibit a signal at binding energies lower than that of GeO\textsubscript{2}.\textsuperscript{10} The insets in Figs. 1 and 2 show a comparison of the spectrum from the as-mounted sample and that after annealing to the highest temperature (prior to desorption). These results suggest the occurrence of the surface transformation reaction,

\[ \text{GeO}_x + \text{Ge} \rightarrow 2\text{GeO}_2. \]

As the temperature is raised further, the amount of monoxide species on the surface increases. In order to clearly show this transformation, we plotted the intensity ratio, GeO/GeO\textsubscript{2}, (obtained from the area of the component peaks, after de-\textsuperscript{composition of Ge\textsuperscript{3d} spectra}) as a function of temperature in Fig. 4. Inset shows a typical fit with six components due to three species, Ge, GeO and GeO\textsubscript{2}. It is to be noted that during this temperature induced surface transformation, the amount of surface oxygen remains the same, as shown by the inset in Fig. 4. At \( \sim 420^\circ \text{C} \), the signal due to the monoxide species is more than that of GeO\textsubscript{2} and this stage is a precursor to the desorption. At \( \sim 430^\circ \text{C} \) complete desorption takes place, leading to the formation of a clean surface. The desorption product is known well to be the monoxide GeO.\textsuperscript{13}

The results of similar experiments performed on Si surfaces are given in Fig. 2. As can be seen, upon annealing, the peak due to the oxide moves towards higher binding energy, due to the depletion of the monoxide signal. The chemical shift corresponding to the spectrum recorded after annealing at high temperature (\( \sim 745^\circ \text{C} \)) is 4.2 eV (shown in Fig. 3), which is similar to that of SiO\textsubscript{2}. At this temperature, the full width at half maximum of the peak due to the oxide is reduced to about 0.88 eV, indicating the existence of nearly a single type of species. This shows that the following transformation reaction takes place on the surface during the early stages of the annealing process (see the inset in Fig. 2 also):

\[ 2\text{SiO} \rightarrow \text{SiO}_2 + \text{Si}. \]

This behavior is exactly opposite to that of Ge oxides, as described earlier. The total amount of oxygen remains unchanged throughout the transformation process, as confirmed by the constant intensity of the O\textsubscript{2s} signal. Upon annealing the sample at higher temperatures (>780 °C), the oxide decomposes and desorbs as SiO\textsubscript{3}.

Independently measured spectral changes of the valence band, upon annealing (Fig. 5), are in agreement with this interpretation. In the inset, an overlay of the RT spectrum and that recorded after annealing close to the desorption temperature (\( \sim 400^\circ \text{C} \) for the Ge oxide and around 780 °C for the Si oxide) are plotted. Both the oxides exhibit two peaks.
respectively. The peak energies, separation between the high binding energy peak increases and this can be taken with a solid line in the insets. However, the intensity of these experiments were performed independently, in a separate chamber.

(7.3 and 11.3 eV from the Si oxide and 5.8 and 8.7 eV from the Ge oxide). They are assigned as originating from non-bonding or $\pi$ bonding O2$p$ orbitals and from the intermediate state between nonbonding and $\sigma$ bonding O2$p$ orbitals, respectively. The peak energies, separation between the two peaks, and their intensity ratio are known to show changes when the surface species undergo transformation. In the case of Si oxide, the peak positions (7.3 and 11.3 eV) are very similar to those from a predominantly SiO2 like oxide, and do not shift significantly even when the sample is annealed close to the desorption temperature (solid line, ~400 and ~780 °C, respectively, for Ge and Si). These experiments do not cause major shifts in the corelevels. Therefore, the large core level shifts in the present experiments are indeed due to the transformation of the surface chemical entities. In order to give a proper explanation for these transformation reactions, one has to take into consideration a variety of factors, such as thermodynamic and structural parameters of the individual species. For example, the heat of formation (~910 kJ/mol) of SiO2 seems to suggest a higher stability over other oxides. Similar data for crystalline SiO are not available in data books. However, the transformation of GeO2 to GeO cannot be explained this way. Therefore, we believe that the surface and interface properties play crucial roles in influencing the surface transformation and thermal decomposition pathway.

To conclude, we report that the thermal decomposition pathways of ultrathin oxide layers formed on germanium and silicon surfaces are different, even though the desorbing species are the respective monoxides in both the cases. Annealing Ge oxides results in the transformation of GeO2 to GeO on the surface (up to ~420 °C), and desorbs as GeO at higher temperatures. In contrast, during the initial stages of the annealing of Si oxides (up to ~780 °C), SiO gets transformed into SiO2. At higher temperatures, SiO2 decomposes, implying a reverse transformation to volatile SiO.

The authors thank Dr. D. Bottomley for fruitful discussions.

The early stages of the thermal decomposition of ultrathin Si oxides was examined in detail by various groups. The consensus is that, on raising the surface temperature, the oxide layer undergoes clustering (partly to reduce the strain in the oxide layer), which is followed by void formation, facilitating the desorption of SiO molecules. This is accompanied by structural changes, such as changes in Si–O–Si bond angles, Si–O bond lengths and so on. However, these do not cause major shifts in the corelevels.

FIG. 5. He I ultraviolet photoelectron spectroscopy of the Ge oxides/Ge(100) and Si oxides/Si(100) after annealing to various temperatures. The inset shows a comparison of the spectrum from the as-mounted sample (broken line) and after annealing to a temperature prior to the desorption (solid line, ~400 and ~780 °C, respectively, for Ge and Si). These experiments do not cause major shifts in the corelevels. Therefore, the large core level shifts in the present experiments are indeed due to the transformation of the surface chemical entities. In order to give a proper explanation for these transformation reactions, one has to take into consideration a variety of factors, such as thermodynamic and structural parameters of the individual species. For example, the heat of formation (~910 kJ/mol) of SiO2 seems to suggest a higher stability over other oxides. Similar data for crystalline SiO are not available in data books. However, the transformation of GeO2 to GeO cannot be explained this way. Therefore, we believe that the surface and interface properties play crucial roles in influencing the surface transformation and thermal decomposition pathway.

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