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Reactive ion etching of SiGe alloys using HBr

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We have studied reactive ion etching of $\text{Si}_{1-x}\text{Ge}_x$ alloys with $x \leq 0.15$ and Ge in HBr plasmas. The etch rate of SiGe increases monotonically with the Ge content of the alloy and for a $\text{Si}_{85}\text{Ge}_{15}$ alloy was $\approx 50\%$ greater than for Si. Etch profiles are identical to those formed in single-crystal Si. X-ray photoelectron spectroscopy studies shown that the surface of the etched SiGe alloys are depleted in Ge and consist of about one monolayer of brominated Si over the alloy.

Reactive ion etching of SiGe alloys is desirable for pattern transfer in the fabrication of heterojunction bipolar transistors using a SiGe base region. Such devices are of rapidly increasing technological importance, as it has been demonstrated that they may be used at speeds previously unattainable by Si-based devices.¹ Of particular technological importance are strained epitaxial SiGe alloys with a proportion of Ge of 20% or less.² Here, the reactive ion etching of SiGe, Si, and Ge in HBr plasmas has been studied. HBr etching plasmas have previously been examined for Si etching,³⁻⁵ and offer anisotropic etching which may be very selective with respect to an oxide mask. Another attractive feature of HBr etching processes on Si is the very thin reaction layer which is formed—about one monolayer thick.^{5,6}

Strained, epitaxial SiGe-alloy films with a Ge content of up to $\approx 15\%$ and a film thickness of up to 800 nm were grown on 5 in. Si(100) wafers by ultrahigh vacuum/chemical vapor deposition (UHV/CVD).^{7,8} Chips measuring 1 in. on each side were cut from these wafers and used for the etch rate and surface analysis experiments. Si and Ge single crystals (1 in. diam) were also examined. For RIE the samples were placed in the center of a 300-mm-diam water-cooled quartz electrode of a parallel-plate reactor which has been described previously.⁹ In practical etching processes it has been found that HBr reactive ion etching is only useful in a relatively narrow pressure regime; at low pressure the high ion energies cause excessive sputtering and poor selectivity to the mask while at high pressure the discharge becomes unstable and localized. Consequently all the results presented here were obtained at one set of plasma conditions, which produce a satisfactory plasma. These “standard” conditions are a pressure of 25 mTorr, a rf power density of 0.27 W/cm^2 at the electrode, and a gas flow of 100 sccm. These plasma parameters result in a self bias potential at the substrate electrode of about -150 V . Etch rates were measured using *in situ* ellipsometry. The etch rate of Si and SiGe in HBr plasmas is very sensitive to the surface preparation; indeed the native oxide on as-received samples may be sufficient to inhibit etching. Consequently the sample surfaces were cleaned using a brief (typically 30 s) dip into dilute (1:10) HF immediately before loading into the chamber, and a nitrogen-purged glove box was used to load samples in and out of the reactor, to minimize contamination of the etch-

ing reactor by the atmosphere. Patterned SiGe, Si, and Ge samples employing photoresist or oxide masks were used to examine the profile obtained using HBr RIE.

Figure 1 shows reactive ion etch rates of SiGe alloy and elemental Si and Ge films as a function of the Ge content of the layer. The etch rate of the SiGe alloys is seen to increase as the percentage of Ge in the alloy is raised. The etch rate increase is consistent with the ≈ 3 times greater etch rate of elemental Ge as compared to that of Si. The inset shows the SiGe/Si etch rate ratio which is achieved under these conditions as a function of Ge content. It is seen that for 15% Ge in the SiGe alloy the etch rate is $\approx 40\%$ greater than that of Si. Etching of SiGe alloys under these conditions is highly directional, and near-vertical sidewalls are formed. This is demonstrated by the scanning electron micrograph shown in Fig. 2 which displays a shallow trench etched through a 800-nm-thick $\text{Si}_{85}\text{Ge}_{15}$ alloy film into the Si substrate. An oxide mask [which was removed prior to taking the scanning electron microscopy (SEM) image] and a gas mixture of 98 sccm HBr/2 sccm CF_4 were employed for this experiment. A near-vertical etch profile all the way from the top of the SiGe into the Si substrate is obtained, and no difference in directionality between the $\text{Si}_{85}\text{Ge}_{15}$ alloy and the Si substrate is noticeable.

The width of the SiGe base layer of heterojunction bipolar transistors is of the order of only a few tens of nanometers and a precisely controlled Ge profile is required for optimum electrical performance.¹ If, as a result of reactive ion etching significant enrichment or depletion of Ge at the surface occurred, the device performance could be degraded. The bromides of Ge are less volatile than those of Si¹⁰ and therefore a Ge-rich reaction layer on the surface of the dry-etched SiGe surface may be expected. The composition and extent of the surface reaction layer formed as a result of HBr RIE was examined using x-ray photoelectron spectroscopy (XPS). Blanket (unpatterned) SiGe films etched for 5 min were used for the XPS studies. Immediately after etching they were transferred from the etching chamber to the analysis chamber (at a pressure of about 10^{-10} Torr) using a vacuum transfer mechanism. XPS measurements were made using a Vacuum Generators ESCALAB MkII system, with a non-monochromatized $\text{Al K}\alpha$ x-ray source. Measurements were taken at two different electron emission angles: Nor-

FIG. 1. Reactive ion etch rates of epitaxial SiGe films as a function of the Ge percentage of the alloy. A 25 mTorr, 200 W rf plasma fed with 100 sccm HBr was used. For comparison elemental Si and Ge etch rates are shown. The inset shows the SiGe/Si etch rate ratio vs the Ge percentage of the alloy.

mal to the surface (90°) and at a glancing angle (15°). The XPS peaks of interest in this study are Si $2p$, Ge $2p$, Ge $3p$, and Br $3d$. Peaks corresponding to F $1s$, O $1s$, and C $1s$ (the most likely contaminants) were also examined, but none of the spectra showed any significant surface contamination. Ge $2p$ has been used in previous studies to examine chemical binding energy shifts due to halogen bonds, and is useful for surface studies because it has a high binding energy, and thus a relatively short mean free path (λ) of approximately 0.9 nm.¹¹ For comparison, the mean-free path of photoelectrons due to Si $2p$ and Ge $3p$ electrons is about 2.5 nm.^{11,12}

In Fig. 3 high-resolution silicon $2p$ photoemission spectra are shown for a clean $\text{Si}_{85}\text{Ge}_{15}$ alloy control and after 5 min of reactive ion etching in HBr. The control sample produces a single, asymmetric peak centered at 99.7 eV, which is due to Si—Si and Si—Ge bonding. The main peak from the $\text{Si}_{85}\text{Ge}_{15}$ sample etched using HBr

FIG. 3. Si $2p$ photoelectron spectra of epitaxial SiGe-film (15% Ge) control and after reactive ion etching using HBr.

(also due to Si—Si and Si—Ge) is relatively more intense than that from the control, and contains a pronounced shoulder on the high binding energy (BE) side of the main Si $2p$ peak. This shoulder has been studied previously for Br-based etching of Si and shown to be due to Si bonded to Br.⁵ Figure 4 shows the corresponding germanium $2p$ photoemission spectra. The Ge $2p$ peak from the control sample is centered at a binding energy of 1217.9 eV and is attributed to Ge—Si and possibly Ge—Ge bonding. After RIE the Ge $2p$ peak is reduced in intensity, but there is no evidence of any brominated Ge. This is in contrast to the Ge $2p$ peaks obtained from samples etched in fluorine-based processes, where a distinct chemical shift due to Ge—F bonds is observed.¹¹ The explanation for this appears to be that the residual bromine is all bonded to Si and that the SiGe surface is enriched in Si. This was established by studying Ge $3p$ photoemission.

The Ge $3p$ peak at approximately 122 eV is quite close to the Si $2p$ peak at ≈ 100 eV. Consequently, the inelastic mean free path (λ) of photoelectrons due to Ge $3p$ and Si $2p$ is very similar, Ge $3p$ and Si $2p$ photoelectrons have the same mean free path and the ratio between these two peak intensities should be constant as a function of electron emission angle if the samples are of uniform composition.

FIG. 2. Scanning electron micrograph of the etch profile of SiGe (15% Ge) after reactive ion etching using 98 sccm HBr/2 sccm CF_4 . A ≈ 450 -nm-thick oxide mask was used in this experiment and removed using buffered HF prior to taking the secondary electron micrograph.

FIG. 4. Ge $2p$ photoelectron spectra of epitaxial SiGe-film (15% Ge) control and after reactive ion etching using HBr (see Fig. 3).

FIG. 5. The surface Ge/Si element ratio of SiGe alloys after HBr RIE as obtained by Ge 3*p* and Si 2*p* photoemission as a function of the bulk Ge/Si ratio of the alloy obtained by Rutherford backscattering spectrometry.

The Ge/Si ratios determined from the Ge 3*p* and Si 2*p* peak intensities are plotted in Fig. 5 as a function of the bulk Ge/Si ratio, which was determined by Rutherford backscattering spectrometry. It is seen that the surface Ge/Si ratio determined by XPS is always less than the bulk Ge/Si ratio. Furthermore, the Ge 3*p*/Si 2*p* ratio is consistently higher at 90°, indicating that there is proportionally less Ge at the surface than there is in the bulk. Thus the SiGe surfaces after reactive ion etching using HBr are Si rich.

The thickness of the reaction layer on SiGe surfaces may be estimated by assuming that the reaction layer consists of a layer of brominated Si, which attenuates the Ge 2*p* photoelectrons from the underlying SiGe. In this case the ratio of the Ge 2*p* peak intensity at 15° and 90° may be used to calculate the reaction layer thickness, since the two angles correspond to two different effective path lengths for the photoelectrons. For each of the SiGe alloy samples considered, this calculation yields a value of about 0.2 nm (i.e., about 1 monolayer) for the thickness of the brominated Si layer on the surface. This thickness was tested by using Mg *Kα* excitation instead of Al *Kα* and a 15° emission angle which reduces the inelastic mean free path of the Ge 2*p* photoelectrons to an effective sampling depth of ≈0.3 nm. Under these conditions of Ge 2*p* signal was not detected, but strong Si and Br signals were observed. These results confirm that the surface is SiBr_x-like. The observations of monolayer-like SiBr_x reaction layers and absence of Ge—Br bonds on etched SiGe surface indicate that the removal of Si from the surface is the rate limiting step.

Typically the Br 3*d* peak is less useful than the Ge or Si peaks in quantitative XPS analysis, because BE shifts are not readily observed. However, the Br 3*d* peak intensities may be used to check the consistency of the model that is suggested by the Ge and Si XPS results. If the etched surface is covered with a monolayer of brominated Si, then the Br peak intensity, corrected for the angular dependence of instrument sensitivity, should be essentially independent of angle. This is because the effective depth sampled by the photoelectrons is now irrelevant, and there will be no attenuation if the brominated layer is on the surface. When the corrected Br 3*d* peak intensities are calculated, it is found that indeed there is no difference between the Br 3*d* intensities at 15° and 90°, supporting the model that coverage is monolayer-like.

In conclusion, it is found that RIE of SiGe alloys using HBr results in the formation of a brominated Si layer at the surface which is about a monolayer thick. This result, together with the observation that the etch rate of SiGe increases approximately linearly with the Ge content, indicate that the rate-limiting step in this process is the removal of Si. RIE using HBr offers anisotropic etching, resulting in profiles that are independent of the Ge content of the sample, and appears to result in a very thin surface reaction layer.

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