Studies of the reactive ion etching of silicon-germanium alloys

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Studies of the reactive ion etching of SiGe alloys

G. S. Oehrlein, G. M. W. Kroesen, E. de Frésart, Y. Zhang, and T. D. Bestwick

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

Reactive-ion etching (RIE) of epitaxial, strained $Si_{1-x}Ge_x$ alloys, $x \leqslant 0.20$, in fluorine-chlorine-, and bromine-based low-pressure plasmas has been investigated. The reactive-ion etch rates of the $Si_{1-x}Ge_x$ alloys increase with the Ge content of the alloy for most etching gases. This effect is most pronounced for fluorine (CF_4 and SF_6) plasmas where the etch rate of a $Si_{80}Ge_{20}$ alloy is increased by a factor of $\simeq 2$ over that of Si. The etch rate enhancement is of reduced importance for chlorine (CF_2Cl_2) and bromine (HBr) plasmas, where the etch rate increases by less than 50% for a $Si_{80}Ge_{20}$ alloy relative to that of elemental Si. Analysis shows that the etch rate increase is not accounted for by the greater rate of gasification of Ge atoms alone but that the presence of Ge atoms in the SiGe alloy increases the Si etch product formation rate. Directional SiGe profiles are observed for CF_2Cl_2 and HBr plasmas which are identical to those obtained with Si. After etching in CF_4 or SF_6 plasmas the Ge surface concentration of the SiGe alloy is increased relative to its bulk value and both fluorinated Si and Ge are observed by *in situ* x-ray photoemission spectroscopy. On the other hand, for CF_2Cl_2 and HBr plasmas the SiGe surface is Si rich. The effect of band-gap narrowing, strain and plasma-induced surface modifications on the etching of the SiGe alloys is discussed.

I. INTRODUCTION

The study and application of silicon-germanium alloys has recently become important because of progress in thin film growth techniques and the ability to tailor the band gap and electronic properties of the SiGe alloy according to the requirements of the specific desired electronic device.[1,2] Because of the lattice mismatch between Si and Ge, epitaxial $Si_{1-x}Ge_x$ alloys grown on Si are strained.[1] Therefore only thin layers of $Si_{1-x}Ge_x$ with good crystallinity can be grown. For many applications, e.g. for heterojunction bipolar transistors, $Si_{1-x}Ge_x$ films with a low percentage of $Ge(x \leqslant 20\%)$ are of primary interest and fairly thick films ($\simeq 1~\mu m$) may be grown in that case. The fabrication of heterojunction structures often requires to make contact to a buried SiGe or Si layer, e.g. Si/SiGe/Si heterostructures are used to form Si-based heterojunction bipolar transistors where the base region consists of the SiGe alloy whereas the emitter and collector regions are made of Si.[2] Making contact to the SiGe base region requires etching of Si and stopping on the SiGe base. In other applications etching of SiGe and stopping on a Si underlayer is required. So far little is known about the dry etching behavior of SiGe alloys and how it differs from that of silicon. From the point of view of technological applications of dry etching $Si_{1-x}Ge_x$ films with a low percentage of $Ge(x \leqslant 20\%)$ the following issues need to be addressed: Are there any significant differences between dry etching of SiGe with a low percentage of Ge relative to etching Si? Is it possible to etch selectively SiGe over Si or vice versa? Does the etching process introduce surface modifications, e.g. Ge or Si enrichment? How do the surface modifications differ for F-, Cl-, and Br-based etching chemistries? Scientifically the study of halogen-based plasma etching of epitaxial $Si_{1-x}Ge_x$ on Si is interesting since it can be viewed as a model system for the interaction of a multi-component substrate with an etching plasma with the attraction of flexible composition without change in crystal structure and the availability of a great deal of data on strain, band gap, etc.

This paper presents a survey of the reactive ion etching (RIE) of epitaxial, strained SiGe thin films on Si (100) with a Ge content of up to $\simeq 20\%$. The etch rate, degree of etch directionality and surface chemistry of SiGe alloys were studied as a function of the Ge concentration using *in situ* ellipsometry, secondary electron microscopy of etched profiles in patterned wafers, and x-ray photoemission spectroscopy (XPS), respectively. The results are compared to data obtained with single-crystal Si and Ge. The following gases were used in this work: CF_4 and SF_6 for which atomic fluorine is the primary etching species; CF_2Cl_2 for which etching is due to atomic Cl^3 and HBr where etching is due to attack of Br atoms. Atomic fluorine attacks Si and Ge spontaneously and produces mask undercutting.For Cl and Br the etching of undoped Si is ion initiated[3] and both CF_2Cl_2 (Ref. 4) and HBr (Refs. 5 and 6) plasmas produce highly directional etch profiles in Si. For all of the aforementioned halogens it has been shown that Ge etches at a greater rate than Si.[7] On the other hand, silicon can be etched with high selectivity over Ge in $SF_6/H_2/CF_4$ gas mixtures, e.g. a Si/Ge etch rate ratio of greater than 80 with negligible etching of Ge has been demonstrated.[8] We therefore also investigated the etch rate of SiGe alloys in $SF_6/H_2/CF_4$ gas mixtures.

II. EXPERIMENTAL PROCEDURES

Strained, undoped, epitaxial SiGe-alloy films with a Ge content of up to $\simeq 20\%$ and a film thickness of up to 800 nm were grown on 5-in Si (100) substrates by ultrahigh vacuum/chemical vapor deposition (UHV/CVD).[9,10] Unpatterned $1.5 \times 1.5~cm^2$ chips of these wafers were used for the etch rate and surface analysis measurements. The samples were placed in the center of a rf powered,water-cooled (15 °C) electrode (30 cm diam) made of Cu with an Al cover. This 13.56-MHz-powered diode reactor and the asso-

ciated experimental apparatus have been described be-fore[11,12] and only a brief summary of the experimental con-ditions relevant to the present etching studies is provided here. For most of the work the bottom electrode was covered with a 2-mm-thick quartz plate, but for some studies the quartz plate was additionally covered with a sheet of Ardel. The applied rf power was varied between 50 and 200 W. Flow rates of 100 sccm of either CF_4, SF_6, CF_2Cl_2, or HBr at a pressure of 25 mTorr were used for part of the experiments. The $SF_6/H_2/CF_4$ etching experiments used relative gas flows of 35 sccm/65 sccm/80 sccm and were performed at a pressure of 150 mTorr and an rf power of 50–150 W.[8] For improved thermal contact the samples were glued to the sur-face of the water-cooled electrode employing high-vacuum grease; temperature measurements using a fluoroptic probe have shown that in this case a wafer temperature of $\simeq 50$ °C is typical for the 200-W 25-mTorr conditions used for most of the work. The etch rate of the SiGe films was determined *in situ* using HeNe laser ellipsometry. These measurements used the recently established[13] relationship between the frac-tion x of Ge of the $Si_{1-x}Ge_x$ alloy and its complex refractive index (at 632.8 nm). For etch profile analysis both photore-sist and oxide masks were examined. Approximately 1.5 μm photoresist was spun either directly onto the SiGe layers or after first depositing $\simeq 450$ nm of SiO_2 using a low-tempera-ture CVD process (<300 °C). After patterning of the photo-resist using standard lithographic techniques, the photore-sist pattern was either used directly as an etch mask or, for the wafers with the oxide interlayer, transferred into the ox-ide layer using CF_4/H_2 reactive ion etching followed by O_2 plasma removal of the photoresist mask. Surfaces of SiGe-alloy films after 5 min of reactive ion etching, i.e. for steady-state etching conditions, were examined using Al $K\alpha$ x-ray photoemission after vacuum transfer into a UHV surface analysis system.

III. EXPERIMENTAL RESULTS

A. Etch rates and profiles of SiGe alloys

In Fig. 1 etch rates of SiGe alloys are shown as a function of Ge concentration in CF_4, HBr, and $SF_6/H_2/CF_4$ plasmas. Elemental Si and Ge etch rates are shown for comparison. For CF_4 and HBr plasmas the etch rate of SiGe increases as the percentage of Ge is raised. This behavior is consistent with the greater etch rate of elemental Ge as compared to that of Si in these plasmas.[7] (The purpose of the dashed lines connecting the SiGe alloy data with the elemental Ge etch rate data is to aid in the comparison of SiGe and Ge etch rates. We do not wish to imply that the actual etch rates would follow the dashed lines.) The SiGe etch rates in CF_2Cl_2 show a behavior intermediate to that seen for CF_4 and HBr plasmas and have been omitted from the figure for the sake of clarity. For $SF_6/H_2/CF_4$ RIE a very different behavior of the SiGe etch rate as a function of Ge content is shown. In this case a drop in the etch rate of the SiGe alloys with increasing Ge concentration is seen. This behavior is also consistent with the etch rate ratio (ERR) of elemental Si and Ge since for this gas mixture and the particular RIE conditions employed here no etching of Ge takes place whereas Si continues to etch at a finite rate.[8]
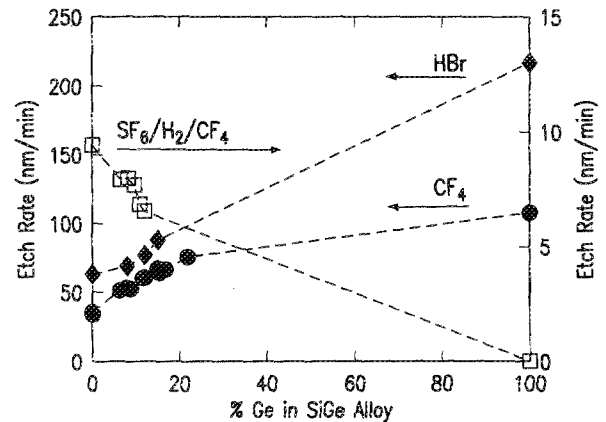
FIG. 1. Reactive ion etch rates of epitaxial SiGe films as a function of the Ge percentage of the alloy. The following plasma conditions were used: 100 sccm CF_4, 25 mTorr, 200 W, quartz electrode; 100 sccm HBr, 25 mTorr, 200 W, quartz electrode; 35 sccm SF_6/65 sccm H_2/80 sccm CF_4,150 mTorr, 50 W, Teflon cathode.

The ratios of the SiGe and Si etch rates for all etching gases investigated is shown as a function of the Ge concen-tration in Fig. 2. For the fluorine etchants, CF_4 and SF_6, the SiGe/Si etch rate ratio reaches $\simeq 2$ for 20% Ge. The SiGe/Si etch rate ratios obtained in CF_4 and SF_6 plasmas are remark-ably similar, although the absolute etch rates differ by about an order of magnitude. For HBr and CF_2Cl_2 the increase of the SiGe/Si ERR with the Ge content is less pronounced. Only for $SF_6/H_2/CF_4$ the SiGe/Si ERR drops below 1 as the Ge content is increased. The etch rate decrease of SiGe alloys in $SF_6/H_2/CF_4$ plasmas with increasing Ge concentration is explained by the formation of increasingly more involatile Ge sulfide at the surface of the alloy. For SiGe alloys with a high Ge concentration, e.g., $Si_{50}Ge_{50}$, a Si/SiGe ERR of $\simeq 10$ has been demonstrated in $SF_6/H_2/CF_4$ plasmas.[7] Sur-face analysis using XPS has shown that the surface of the SiGe alloy becomes very similar to that of elemental Ge reac-tive ion etched using the same conditions.

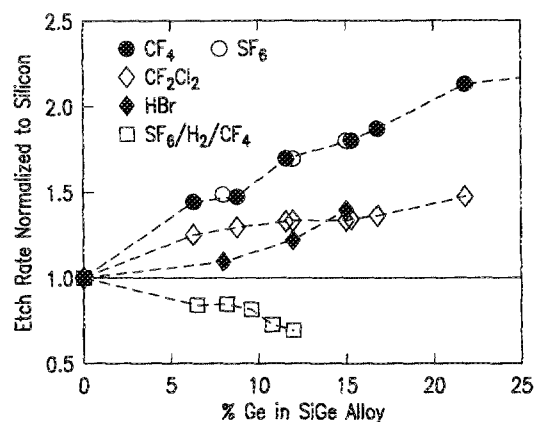Etch profiles obtained with $Si_{1-x}Ge_x$ films with a low

FIG. 2. The SiGe/Si etch rate ratio for various SiGe alloys and different reactive ion etch conditions.
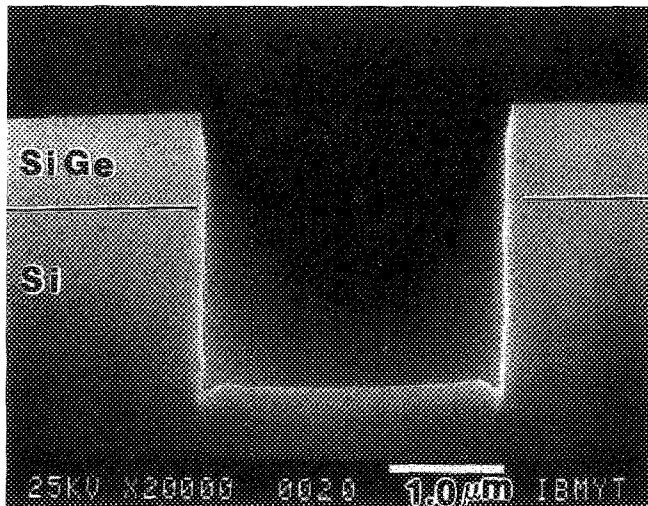
FIG. 3. Secondary electron micrographs of the etch profiles SiGe (15% Ge) after reactive ion etching using 98 sccm HBr/2 sccm CF$_4$. A 450-nm-thick oxide mask was used in this experiment and removed using buffered HF prior to taking the secondary electron micrograph.

percentage of Ge ($\leqslant 20\%$) were similar to profiles observed in the etching of single-crystal Si. For fluorine-rich discharges, e.g. SF$_6$, and oxide-masked SiGe, nearly isotropic etch profiles were observed. For fluorine-deficient plasmas, e.g. a CF$_4$ discharge using an Ardel electrode, and a photoresist mask, more directional profiles were seen. However, the width of the trench narrowed in this case as a function of etch depth, indicating the importance of the deposition of carbonaceous sidewall passivation material. For CF$_2$Cl$_2$ directional etch profiles were obtained for both photoresist and oxide masks, but the etch selectivity with respect to the mask was low ($\simeq 4{:}1$). The most encouraging results were obtained with HBr plasmas. In Fig. 3 the profile of a shallow trench etched through a 800-nm-thick SiGe film (15% Ge) into the Si substrate using 98-sccm HBr/2-sccm CF$_4$ is shown. The oxide mask had been removed prior to taking the scanning electron microscopy image. We see a highly directional etch profile all the way from the top of the SiGe film into the Si substrate. No difference in directionality between the SiGe and the Si is noticeable. Some trenching at the sidewalls at the bottom of the trench is evident.

If oxide-masked epitaxial SiGe was etched in pure HBr we observed frequently the introduction of rough features in the etched areas. Introduction of SiGe surface roughness was not observed if unpatterned SiGe films were etched using the same procedures of initial surface cleaning, *in situ* etch initiation (native oxide removal) and identical conditions for the main etch. We were unable to pinpoint the source of oxygen which caused the rough features of oxide-patterned substrates, but it may be due to sputtering of the oxide mask during the initial period of the etch. It is possible to avoid the introduction of surface roughness on the trench bottoms for oxide-masked SiGe specimens by adding a small amount of CF$_4$ ($\simeq 2\%$ of total flow) to HBr and reducing the Si$_{85}$Ge$_{15}$-to-SiO$_2$ etch selectivity from $\simeq 250$ obtained in pure HBr to
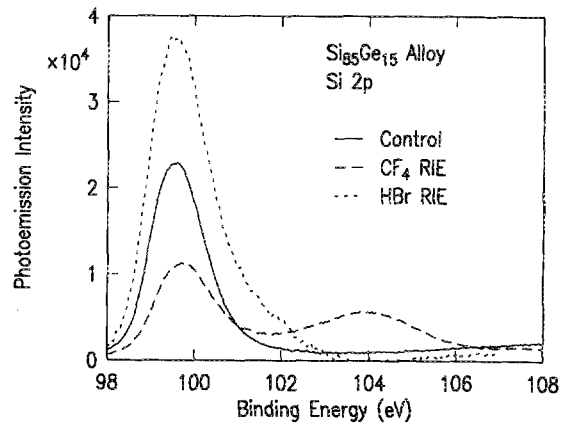
FIG. 4. Si 2p photoelectron spectra of epitaxial SiGe film (15% Ge) control and after reactive ion etching using CF$_4$ and HBr.

$\simeq 19$ for 98% HBr/2% CF$_4$ during the initial period of the main etch.

B. Surface analysis

Surfaces of reactive-ion-etched SiGe specimens were examined using XPS after vacuum transfer. X-ray photoelectron spectroscopy survey scans from 0 to 1100 eV binding energy of SiGe alloys after CF$_4$ reactive-ion etching showed in addition to the expected Si, Ge, and F features weak peaks due to O and C. The source of the oxygen is the etching of the quartz electrode cover in CF$_4$ plasmas which causes the equivalent of $\simeq 4$ sccm O$_2$ to be added to the 100 sccm CF$_4$. The amount of oxygen measured for the SiGe surfaces increased slightly as the percentage of Ge in the SiGe alloy was increased. For HBr RIE the etching of the quartz electrode cover is negligible and the SiGe samples showed in that case only Si-, Ge-, and Br-related photoemission features.

In Fig. 4 high-resolution silicon 2p photoemission spectra are shown for a Si$_{85}$Ge$_{15}$ alloy control and a similar sample after 5 min of reactive-ion etching in either CF$_4$ or HBr. The RIE conditions were 200 W rf power, 25 mTorr pressure, and 100 sccm total gas flow. The spectra were acquired at grazing emission (15° from the surface) for high surface sensitivity. For the control a single, asymmetric peak centered at 99.7 eV is observed which is due to Si–Si and Si–Ge bonding. For the sample etched in CF$_4$ the main peak due to Si–Si and Si–Ge bonding is reduced relative to the control and an additional broad peak near 104 eV is seen. This latter feature is caused by silicon bonded to fluorine and a small amount of oxygen.[12] As judged from the relative intensities of F 1s and O 1s photoemission, the F/O ratio in the reacted surface layer is greater than 10. For the Si$_{85}$Ge$_{15}$ sample etched in HBr the Si–Si/Si–Ge peak is increased in intensity relative to the control and a pronounced shoulder is seen on the high-binding-energy side of the main Si 2p peak. This shoulder has been studied previously and been shown to be due to Si bonded to Br.[6]

In Fig. 5 the germanium 2$p_{3/2}$ photoemission spectra corresponding to the samples of Fig. 4 are displayed. For the
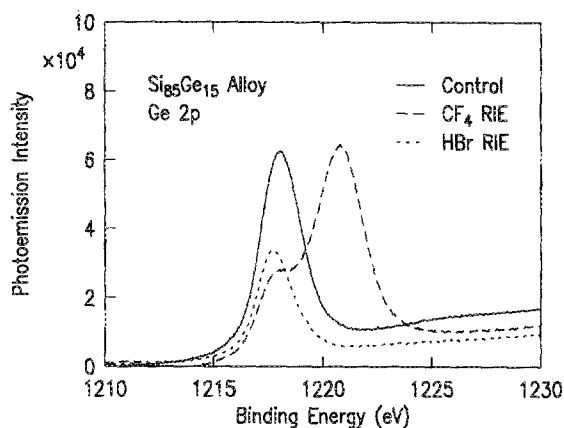
FIG. 5. Ge $2p_{3/2}$ photoelectron spectra of epitaxial SiGe film (15% Ge) control and after reactive ion etching using CF_4 and HBr (see Fig. 4).

FIG. 6. The surface Ge/Si element ratio of SiGe alloys after CF_4 and HBr RIE as obtained by Ge $3p$ and Si $2p$ photoemission as a function of the bulk Ge/Si ratio of the alloy obtained by Rutherford backscattering spectrometry.

control the Ge $2p_{3/2}$ peak is centered at a binding energy of 1217.9 eV and attributed to Ge–Si/Ge–Ge bonding. For a similar sample after CF_4 RIE two distinct peaks are visible, the smaller peak at 1217.9 eV and the dominant peak at 1220.80 eV. The higher binding energy peak is attributed to fluorinated Ge and occurs at the same energy position as that of fluorinated Ge reported previously for single-crystal Ge after reactive-ion etching using CF_4.[14] This agreement appears somewhat fortuitous, since (1) the fluorinated Ge peak results from a superposition of GeF, GeF_2, GeF_3,and GeF_4 groups and the peak position will change with the degree of fluorination of the Ge surface and (2) because of the presence of surface oxygen in the present case there should also be some Ge–O bonding. In the previous study a Teflon electrode cover was used and there was no source of surface oxygen.[14] After RIE using HBr there is no evidence of any brominated Ge although the shift expected in this case should be large enough to be observable for our experimental conditions. The explanation for the lack of brominated Ge in the XPS data appears to be that the SiGe surface is enriched in Si and the residual bromine is all bonded to Si. Figure 5 shows that after HBr RIE the integrated Ge $2p$ intensity of the SiGe alloy is greatly reduced as compared to the control. At the same time a large enhancement of the Si $2p$ intensity is seen in Fig. 4. Therefore RIE using HBr enriches the SiGe surface in Si. On the other hand, for CF_4 RIE the surface of the SiGe alloy is enriched in Ge. This is evident from Fig. 5 which shows that the total integrated Ge $2p$ area after CF_4 etching is greater than that of the control. This result is also borne out by the more quantitative analysis to be described next.

Germanium $2p_{3/2}$ and Si $2p$ photoelectrons have very different kinetic energies and their escape depths are $\simeq 0.8$ and $\simeq 2.5$ nm, respectively.[14] Therefore, the Ge $2p$ and Si $2p$ signals originate from different depths of the SiGe sample and the comparison of their relative intensities for the purpose of element ratio determination is made difficult by these characteristics. On the other hand, the Ge $3p$ and Si $2p$ photoelectrons have very similar energies and escape depths and are well suited to determine the Ge/Si element ratio in the sur-
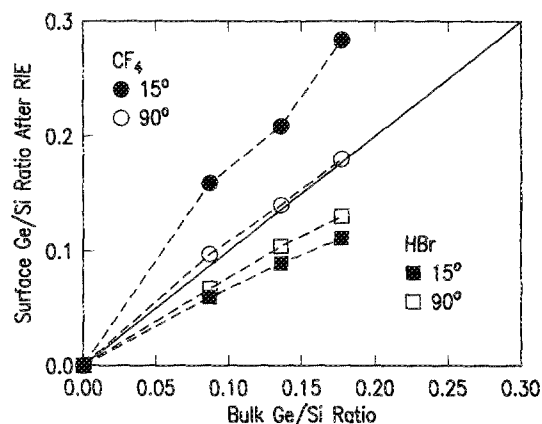
face region of the alloys (after correcting for the different photoionization cross sections[15]). The results of this analysis are shown in Fig. 6. The surface Ge/Si element ratio of SiGe alloys after RIE using CF_4 or HBr is displayed as a function of the bulk Ge/Si ratio which was obtained by Rutherford backscattering spectrometry. Electron emission angles of 15° (high surface sensitivity) and 90° ($\simeq 4\times$ more bulk sensitive) were used. After CF_4 RIE the Ge/Si ratios obtained at 15° are greater than the bulk Ge/Si values showing that the surface is Ge rich in this case. The Ge/Si data obtained at 90° electron emission are close to the bulk values. For HBr the surface Ge/Si ratio is less than the bulk Ge/Si ratio for both photoemission geometries showing that the Si/Ge surface is in this case Si rich. Not shown are results obtained with SiGe alloys after CF_2Cl_2 RIE where also a Si-rich surface layer was found.

IV. DISCUSSION

The reactive ion etch rates of $Si_{1-x}Ge_x$ alloys with $x \leqslant 0.20$ in CF_4, SF_6, CF_2Cl_2, and HBr plasmas all increase with the Ge content of the alloy but they are smaller than etch rates of elemental Ge. The surface analysis data show that for these etching gases the formation of involatile surface films is negligible and transport processes through thick passivation films need not be considered in the understanding of the overall etching reaction. The etch rates are therefore determined by the arrival rate of the F-, Cl-, and Br-etchant species at the surface of the $Si_{1-x}Ge_x$ alloy and the effect of ion bombardment on the surface reactions leading to etching. The etch profiles show that etching of $Si_{1-x}Ge_x$ by atomic F does not require ion bombardment (undercut of mask) but that Cl and Br etching are initiated by ion bombardment (no mask undercutting and vertical profiles), i.e. these etch characteristics are essentially silicon like.[3] In the following we will address (1) possible mechanisms for the etch rate increase of SiGe alloys with Ge content and (2) reasons for the difference in Ge surface concentration of SiGe alloys for F-based plasmas on the one hand and Cl- and Br-based plasmas on the other hand.
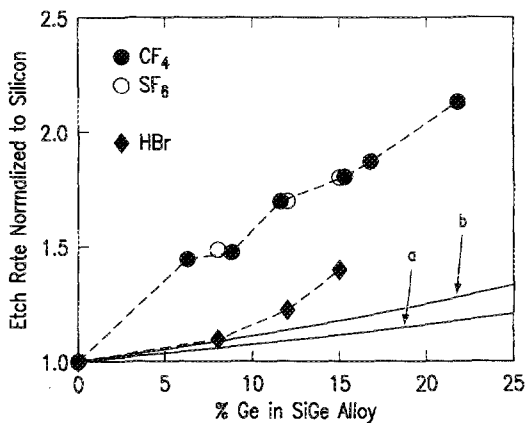
FIG. 7. The SiGe/Si etch rate ratio for various SiGe alloys in CF_4, SF_6, and HBr plasmas. The solid lines are results of model calculations in which the volatilization of Si and Ge atoms is independent. The measured Si etch rate is used and for case (a) the elemental Ge etch rate in CF_4 is used, whereas for (b) the volatilization rate of Ge is assumed to be infinitely fast.

The simplest picture of the etching of SiGe is independent removal of Si and Ge atoms by the etchant atoms from the SiGe surface at rates measured for the pure elements for the same experimental conditions. The etch rate is then primarily determined by the removal of the species which is more slowly volatilized, i.e. Si in the present case. In Fig. 7 the predictions of this kind of "linear combination of elemental etch rates" SiGe etching model are compared with the experimental data obtained for CF_4, SF_6, and HBr RIE. For model a the measured Ge etch rate in CF_4 was used in the calculation. In model b the removal rate of Ge atoms was assumed to be infinitely fast. Figure 7 shows that no matter what Ge etch rate we choose the simple model of independent etching of Si and Ge significantly underestimates the etch rate of SiGe in fluorine-based plasmas. The agreement is better in the case of Br-based RIE for Ge levels lower than 10%, but for higher Ge concentrations the actual SiGe etch rate is again significantly greater than the predictions of the independent species etching model b (Ge etch rate infinitely fast). We conclude that the presence of several percent Ge in a SiGe alloy significantly increases the rate of Si atom volatilization of the alloy. For Ge concentrations of less than 15% a systematic trend in the magnitude of the enhancement is suggested by Fig. 2 as the etchant is changed from F to Cl to Br: The etch rate enhancement is most pronounced for fluorine-based plasmas, less for chlorine plasmas and least important for bromine plasmas. This trend appears intuitively understandable: Fluorine-based etching of Si has a high spontaneous, chemical etching component and an increase in the Si atom reactivity caused by the addition of Ge atoms will have a large effect on the etch rate. On the other hand, chlorine- and bromine-based etching of Si and SiGe is primarily ion driven and a change in the reactivity of the substrate will have a smaller effect on the etch rate.

There are several mechanisms which can explain why the SiGe alloy etch rate increases with Ge content. Some of these effects are interdependent and, in reality, can not be separated.

(1) Presence of Si–Ge bonds in the SiGe alloy with lower bond strength than Si–Si bonds: Since all stoichiometrically complete germanium-halogen products are less volatile than the corresponding silicon-halogen products the smaller strength of the Ge–Ge bond (2.84 eV is the bond strength of the diatomic molecule[16]) as compared to the Si–Si bond (3.25 eV diatomic[16]) has been suggested as a possible explanation for the greater (as compared to Si) etch rate of elemental Ge in various halogen plasmas.[7] Silicon-germanium bonds (3.12 eV diatomic[16]) are also of lower strength than Si–Si bonds and should make the SiGe alloy more susceptible to halogen attack.[7] However, for low Ge concentrations in the alloy the reactivity of only a fraction of the Si atoms is increased by this mechanism and model calculations show that the possible etch-rate enhancement is smaller than what is experimentally observed in the case of fluorine-based RIE.

(2) Surface modifications: A small Ge concentration in the SiGe bulk could affect the etching of the whole substrate if it would be enriched on the SiGe surface. At the surface it could facilitate by an (unknown) catalytic mechanism gasification of Si atoms but remain itself concentrated on the surface. In the growth of SiGe alloys a strong enhancement of growth rates is seen for mixtures of silane or dichlorosilane with germane relative to Si growth rates measured without germane.[10,17] The presence of Ge on the SiGe surface is thought to catalyze silicon growth by enabling increased hydrogen desorption from Ge sites and enabling increased adsorption of film precursors on the growth surface. The Ge enrichment of the SiGe surface after CF_4 and SF_6 RIE seen in this work is consistent with this kind of catalytically enhanced surface mechanism. However, if this mechanism would be solely responsible for the etch-rate enhancement one should observe a maximum enhancement coinciding with the point where the Ge surface concentration has reached the maximum value. Raising the bulk Ge concentration past this value would no longer increase the Ge surface concentration. Instead a linear dependence on the Ge mole fraction is seen experimentally in the case of F-based plasmas. We also find after etching in Cl- and Br-based plasmas the SiGe alloy surfaces to be Si rich. Since for these halogens the SiGe etch rates are also enhanced over the independent species volatilization model the importance of other effects is indicated.

(3) Effect of changes in the electronic properties of the SiGe film with Ge content: The "doping effect", i.e., the dependence of Si etch rate on the type and concentration of electronically active substitutional impurities in the Si lattice, e.g., group III and group VI dopants, has been studied in considerable detail.[3,18–20] Schwartz and Schaible observe a 300% increase in the etch rate of Si doped with 3% As in a Cl_2 plasma.[18] Doping of the Si substrate increases the chemical etching of Si until for high As concentrations significant mask undercutting in Cl_2 RIE is seen.[18] The magnitude of the doping effect depends on temperature, reactant concentration, and ion bombardment. All studies are qualitatively

consistent with a mechanism where the availability and the transfer of electrons from the semiconductor surface to chemisorbed halogens increases the rate of etchant penetration of the substrate followed by etch product formation.

Changes in the electronic properties of the SiGe substrate could enhance the SiGe etch rate by a mechanism similar to the doping effect of Si by increasing the availability of electrons at the substrate surface.[3,19] Since Ge in a Si lattice is an isoelectronic impurity it has even for concentrations in the percent range a much smaller effect on the electronic properties of Si than electronic dopants. The band gap of $Si_{1-x}Ge_x$ alloys with $x \leqslant 0.20$ depends greatly on strain and more weakly on the mole fraction of Ge; for the SiGe films with the highest Ge concentration studied in this work the minimum band gap is $\simeq 1$ eV as compared to 1.17 eV for unstrained Si.[1] The band alignment and band offsets of SiGe with the Si substrate depend additionally on the presence of strain in the Si substrate.[1] These changes of the electronic properties of the SiGe alloy with Ge content make electron transfer from the semiconductor to chemisorbed halogens easier and are qualitatively consistent with the observed etch rate increase. The magnitude of the etch rate increase with impurity concentration seen here is smaller than etch rate effects seen for the electronic dopants, e.g. the etch rate increase of a SiGe alloy containing $\simeq 20\%$ of Ge over that of Si is only a factor of 2 for F and less than that in the case of Br. The smaller changes in the etch rates are qualitatively consistent with the more subtle changes of the electronic properties of SiGe alloys with increasing Ge content (as compared to changes introduced by the addition of group III and group VI dopants).

(4) Strain effects: Silicon and Ge in the pseudomorphic SiGe alloy on a Si substrate are highly strained which could increase the rate of formation of a volatile, strain-reducing phase. The effect of strain alone on the etch rate is difficult to separate from electronic effects since the electronic properties of SiGe depend strongly on strain.[1]

The changes in stoichiometry of the SiGe alloys after RIE using different halogens are surprising and at this time unexplained. For CF_4 RIE the SiGe etch rate increases with Ge content, but the surface is Ge rich. Germanium surface enrichment has already previously been reported for fluorine-based etching of SiGe.[7,14] This result is more plausible if it is assumed that physical sputtering effects play an important role in the overall etching reaction and determine the stoichiometry of the etching SiGe surface. Germanium, being the heavier atom, is concentrated on the surface. This change in surface composition of SiGe alloys is consistent with data obtained on sputtering of compound targets where surface enrichment of the heavier species is often observed.[21] However, ion-induced sputtering effects are even more important for Cl- and Br-based RIE than for F-based RIE but the SiGe surface is found to be Si-rich after Cl and Br plasma etching. It appears that there is no simple explanation for the changes in stoichiometry of the SiGe alloy surfaces as a result of RIE using different halogens and it is likely that the dominant etch product, its volatility, surface binding energy, the extent of the reaction layer, etc. need to be determined in each case before this question can be answered satisfactorily.[22]

V. CONCLUSIONS

For the reactive ion etching conditions examined in this work the dependence of the etch rates of $Si_{1-x}Ge_x$ alloys ($x \leqslant 0.20$) on Ge content is consistent with the relative etch rate ratios of elemental Si and Ge measured for the same etching gases, i.e. if Ge etches faster than Si in a particular gas the SiGe etch rate goes up with Ge content and vice versa. The dry etch characteristics (rate and profile) are similar to those of single-crystal Si; in particular the etch rate ratio of Si over $Si_{1-x}Ge_x$ and $Si_{1-x}Ge_x$ over $Si(x \leqslant 0.20)$ is limited to $\simeq 2$. Reactive ion etching of SiGe using HBr is a promising approach since SiGe alloys can be patterned with a high degree of directionality, high etch selectivity against oxide and photoresist is easily achieved and only relatively minor surface modifications are introduced. The lack of SiGe-to-Si and Si-to-SiGe etch selectivity emphasizes the need for a sensitive and accurate etch endpoint detection method. *In-situ* ellipsometry is useful for this application since it not only will signal the encounter of a SiGe/Se or Si/SiGe interface but also enables the monitoring of the removal of Si or $Si_{1-x}Ge_x$ alloys in real time.

ACKNOWLEDGMENTS

[1] G. L. Patton, J. H. Comfort, B. S. Meyerson, E. F. Crabbe, G. J. Scilla, E. de Fresart, J. M. Stork, J. Y. Sun, D. L. Harame, and J. N. Burghartz, IEEE Electron Dev. Lett. **11**, 171 (1990).

[2] R. People, IEEE J. Quantum Electron. **QE-22**, 1696 (1986).

[3] D. L. Flamm and V. M. Donnelly, Plasma Chem. Plasma Process. **1**, 317 (1981).

[4] D. Chin, S. H. Dhong, and G. J. Long, J. Electrochem. Soc. **132**, 1705 (1985).

[5] M. Nakamura, K. Iizuka, and H. Yano, in *Proceedings of the Tenth Symposium on Dry Process*, edited by Jun-ichi Nishizawa (Inst. Elect. Engineers Japan, Tokyo, 1988), p. 58.

[6] T. D. Bestwick and G. S. Oehrlein, J. Vac. Sci. Technol. A **8**, 1696 (1990).

[7] G. S. Oehrlein, T. D. Bestwick, P. L. Jones, M. A. Jaso, and J. L. Lindström, in *Proceedings of the Eighth Symposium on Plasma Processing*, edited by G. S. Mathad and D. W. Hess (Electrochem. Soc., Pennington, 1990), p. 661.

[8] G. S. Oehrlein, T. D. Bestwick, P. L. Jones, and J. W. Corbett, Appl. Phys. Lett. **56**, 1436 (1990).

[9] B. S. Meyerson, Appl. Phys. Lett. **48**, 797 (1986).

[10] B. S. Meyerson, K. J. Uram, and F. K. LeGoues, Appl. Phys. Lett. **53**, 2555 (1988).

[11] G. S. Oehrlein and H. L. Williams, J. Appl. Phys. **62**, 662 (1987).

[12] G. S. Oehrlein, S. W. Robey, and J. L. Lindström, Appl. Phys. Lett. **52**, 1170 (1988).

[13] G. M. Kroesen, G. S. Oehrlein, E. de Frésart, and G. J. Scilla (to be published).

[14] S. W. Robey, A. A. Bright, G. S. Oehrlein, S. S. Iyer, and S. L. Delage, J. Vac. Sci. Technol. B **6**, 1650 (1988).

[15] C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1979).

[16] *Handbook of Chemistry and Physics*, 57th ed., edited by R. C. Weast (CRC, Cleveland, 1976).

[17] P. M. Garone, J. C. Sturm, P. V. Schwartz, S. A. Schwarz, and B. J. Wilkens, Appl. Phys. Lett. **56**, 1275 (1990).

[18] G. C. Schwartz and P. M. Schaible, J. Electrochem. Soc. **130**, 1898 (1983).

[19] H. F. Winters and D. Haarer, Phys. Rev. B **36**, 6613 (1987).

[20] E. A. Ogryzlo, D. E. Ibbotson, D. L. Flamm, and J. A. Mucha, J. Appl. Phys. **67**, 3115 (1990).

[21] R. Kelly, in *Handbook of Plasma Processing Technology*, edited by S. M. Rossnagel, J. J. Cuomo, and W. D. Westwook (Noyes, Park Ridge, 1990), p. 91.

[22] We cannot rule out the possibility that the SiGe surface under actual plasma etching conditions is Si rich for all halogens and that the differences in surface characteristics are due to different post-plasma processes for F, Cl, and Br once the plasma has been extinguished for the surface analysis. However, a comparison of the fluorine-based etching characteristics of $Si_{50}Ge_{50}$ with those of Ge and Si shows that the etch characteristics of the alloy are Ge like (see Ref. 7). This indicates that the surface of a $Si_{50}Ge_{50}$ alloy under actual etching conditions should be Ge rich.