Precision plasma etching of Si, Ge, and Ge:P by SF_6 with added O_2

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The impact of the O_2 content in SF_6-O_2 gas mixtures on the etch rate and sidewall profile of silicon (Si), germanium (Ge), and phosphorous doped germanium (Ge:P) in reactive ion etching has been studied. The characteristics of etch rate and sidewall profile are greatly affected by the O_2 content. Below 50% of O_2 content, a large variation in Ge etch rates is found compared to that of Si, but for O_2 content above 50% the etch rates follow relatively the same trend. Lightly doped Ge shows the highest etch rate at a O_2 concentration up to 20%. Sidewall angles range from a minimum of 80° to a maximum of 166°, with O_2 concentration of 20% yielding perfect anisotropic mesa etch. Also at this O_2 concentration, reasonable Si/Ge selectivity is possible. These observations indicate that by adjusting the O_2 concentration, precision plasma etching of Si, Ge, and Ge:P is possible. © *2014 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4868615]

I. INTRODUCTION

Dry etching for micro and nanofabrication has been widely investigated and is used extensively in CMOS processes where arbitrary shapes and complex design are required. SiGe heterostructures are increasingly used in advanced CMOS,[1] bipolar junction transistors,[2] and have gained recent interest as optoelectronic devices.[3] For such devices, dry etching techniques enable selective removal of Si, Ge, or SiGe alloy layers through masking techniques, which give superior dimensional control and process flexibility, relative to wet etching processes.[4] Anisotropy of the dry etch process can be achieved and is useful for mesa definition.[5] Anisotropic dry etching is used in device isolation,[6] in modern DRAM capacitor,[7] and in power device fabrication.[8]

Reactive ion etching (RIE) is most commonly used during semiconductor device fabrication as it allows both physical and plasma etching simultaneously. Physical etching is caused by sputtering effects due to energetic positive ions with energies below 500 eV.[9] Plasma etching involves a chemical reaction using a gas glow discharge to dissociate and ionize radicals, which react chemically with material surface to form volatile products. Because physical etching can result in structural rearrangement of surface, it may affect the chemical reactions. With SF_6 gas, energetic ions are generated that remove material by physical sputtering, and fluorine radicals that etch material by chemical reaction. Adding O_2 in SF_6 influences primarily the chemical reaction processes, allowing control of the etch rate and sidewall profile.

Previous work on SF_6-O_2 plasma etching characteristics has been carried out by several groups. In early work, d'Agostino and Flamm[10] showed that the etch rate in SF_6-O_2 gas mixture is faster than in CF_4-O_2 gas mixture for Si and SiO_2 dry etching. Korzec *et al.*[11] and Syau *et al.*[12] investigated the effect of many SF_6-O_2 plasma parameters such as O_2 content in gas mixture, RF power, and total gas pressure. The results of Syau *et al.* showed that the etch rate of Si declined as O_2 content was increased and found that the anisotropy depended on the substrate temperature when using 25% of O_2 in SF_6-O_2 gas mixture. Another important work is Campo *et al.*[13] concerned with how O_2 content (%O_2) in SF_6-O_2 gas mixtures affected Si and Ge dry etching. They found that Si has some selectivity and up to 2× different etch rates with respect to Ge, with O_2 content below 50%. Legtenberg *et al.*[14] made comparable studies on Si using SF_6-O_2-CHF_3 gas mixtures, the addition of CHF_3 was used to reduce the surface roughness of the etched surface. Zou[15] also found the anisotropy in Si etching depended on the O_2 content and total pressure. Shim *et al.*[16] investigated the characteristics of Ge dry etching by using SF_6 plasma. They found that gas flow, power and total pressure influenced both the etch rate and anisotropy. Recent work in 2013 by Liu *et al.*[17] considered SF_6-O_2 plasma etching on silicon at low temperatures. When the temperature was decreased, the etching indicated more anisotropy. To obtain the perfect anisotropic etching, a low percentage of O_2 is required at low temperature.

We have investigated the RIE of single crystal Ge at low working pressures where the physical etching is more prevalent and investigated whether phosphorus doping affects Ge etching. We also investigate how the %O_2 in the SF_6-O_2 gas mixture influences the side wall orientation and profile for the room temperature SF_6-O_2 dry etching. We use Si as the control.

II. EXPERIMENT

In this experiment, 100 mm diameter, low-doped (1–10 Ω-cm) Si(001) substrates were used and Ge and Ge:P layers grown on the Si substrates. Growth was performed by reduced pressure chemical vapor deposition in an ASM Epsilon 2000 reactor using germane (GeH_4), where the specific growth properties and material properties of these layers have been previously reported.[18] The doping concentrations of the final Ge layer were 1×10^{18} cm^{-3} (herein referred to as "lightly doped," Ge:P[L]) and a 3×10^{19} cm^{-3} (referred to as "heavily doped," Ge:P[H], respectively. Schematic diagrams of the samples are presented in Fig. 1.

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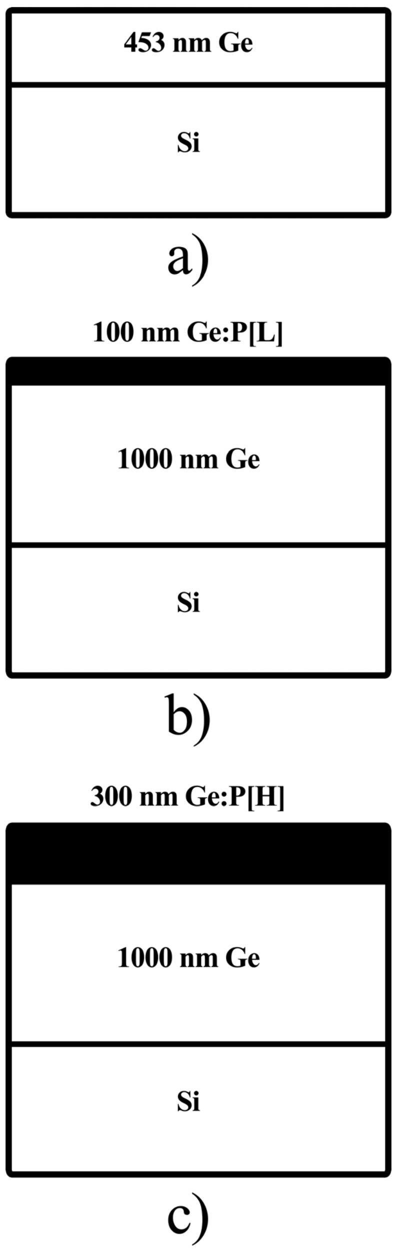

FIG. 1. Schematics of samples: (a) Ge (undoped layer); (b) Ge:P[L] (1×10^{18} cm^{-3}); and (c) Ge:P[H] (3×10^{19} cm^{-3}).

The investigation was performed on small (7 × 7 mm^2) pieces of the grown wafer where photolithography was performed using a 1.8 μm S1813 photoresist, a Karl Suss MJB4 mask aligner, and MF-319 developer to create mesas of photoresist of width 8 μm, and 8 μm spacing, and 2 mm long, alighted along the ⟨1 1 0⟩ direction. Samples were cleaned by deionized water and then dried with nitrogen.

The apparatus for dry etching used in this work was the Corial 200 IL operating at a frequency of 13.6 MHz and using gas sources of SF_6 (99.999%), O_2 (99.9995%), and He (99.999%) as a temperature control gas to a handle wafer, upon which the sample was placed. All fabrication equipment used was housed and operated in a class 100 clean room. The RIE process parameters were: working pressure of 20 mTorr, RF power 100 W, and total gas flow of 30 sccm. A cooling system was used to keep the handle wafer at a constant temperature of 20 °C throughout the etch process.

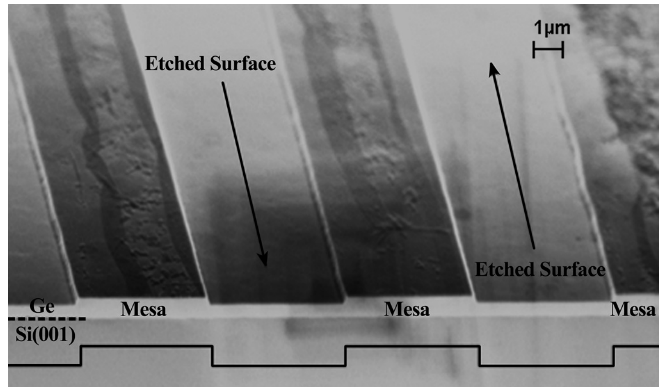

FIG. 2. Ge mesa pattern using RIE, removed photoresist (PR) (still have residual PR).

Surface steps were measured using an Ambios XP-100 step-profilometer. After RIE, the mesa height was measured postresist removal, an example of which is shown in Fig. 2. The mesa step without resist measured the vertical amount of material removed and in conjunction with the etch time this determining the etch rate. To investigate the results of anisotropy, samples were then cleaved along ⟨1 1 0⟩ directions across the mesas so that their cross-sections could be examined by secondary electron microscopy (SEM) using an accelerating voltage of 5 kV and a Zeiss Supra InLens backscattered electron detector.

III. RESULTS AND DISCUSSION

A. Etch rate

Figure 3 shows the measured etch rates versus O_2 dilution (%O_2). A sharp rise in etch rate is observed for all samples when O_2 was introduced into the SF_6 up to%O_2 of 5%, and then fell as the O_2 dilution was increased beyond this value. Specifically, the Si etch rate declines linearly as %O_2 increases from 5% to 50%, and then has a slow linear reduction up to 90%. Ge and Ge:P etch rates rapidly decline as

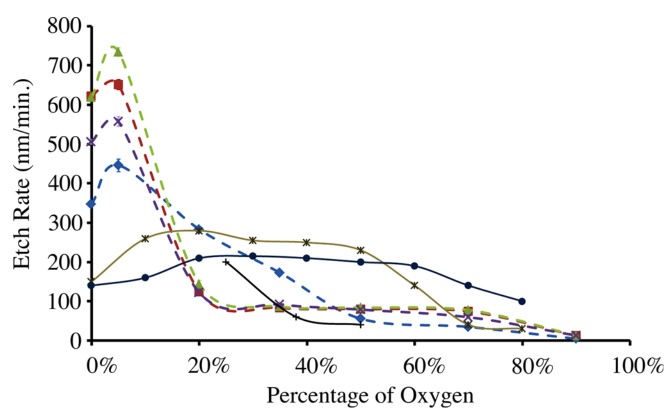

FIG. 3. (Color online) RIE etch rates of Si and Ge as a function of percentage of O_2 in the SF_6-O_2. ◆ Si, Undoped ■ Ge, Undoped ▲ Ge:P[L] (1×10^{18} cm^{-3}) × Ge:P[H] (3×10^{19} cm^{-3}) * Si, Undoped A—Campo *et al.* (Ref. 13). • Undoped A—Campo *et al.* (Ref. 13) + Si, Undoped T—Syau *et al.* (Ref. 12).

$\%O_2$ increases to 20%, above which the etch rate levels off and remains roughly constant up to $70\%O_2$, approaching zero at 90%. The effect of doping level upon the etch rate is more significant at lower $O_2\%$, where the etch rate of the lighter doped Ge:P[L] is higher than the intrinsic Ge (i-Ge), which are both higher than that of heavily doped Ge:P[H]. Where $O_2 > 20\%$, the etch rate of all types of Ge samples are similar and does not show any differences. Overall, the O_2 content has a larger influence on etch rate compared to doping level when O_2 content is more than 20%, whereas doping effects are more prevalent with O_2 content below 20%.

Lee and Chen[19] concluded that doping level does not affect physical etching, but can influence plasma etching. We can assume that the etching mechanism of Ge:P[L] can be explained by the charge transfer mechanism.[20] For an n-type semiconductor, the electron from conduction band tunnels through the potential barrier at the surface and reaches the chemisorbed F atom. The F atom is thus negatively charged to form a surface dipole involving the ionized donor atoms(P) in Ge, giving higher etch rate.[21] We suggest that the lower etch rates as seen in the more highly doped Ge could be a result of suppressing the tunneling process, due to the potential fluctuations of the band edges (band tailing), which occurs at higher n-doping concentrations.

For Si, our results are comparable with Syau *et al.* who used the same total pressure, albeit over a limited $\%O_2$ range and a higher RF power of 200 W. In contrast to our findings, Campo *et al.* found that the etch rate maxima, when introducing O_2 into an SF_6 mixture, occurs at 20% O_2. At 20% O_2, our Si etch rate is three times faster than for Ge, verging on the criteria of reasonable selective etching that is not seen in the work of Campo *et al.* In the same way as we do, they found that the trend of etch rate for silicon drops significantly beyond 50% O_2, allowing the etch to be selective to Ge beyond that. However, comparison with Campo *et al.* is complicated because our etching parameters are different in at least two important respects: the total gas pressure used for our work is 1/5 of that used by Campo *et al.* and the power we use is twice as large, both of which impact on the dynamics of the etching process. This suggests that the mechanism that occurs at that point is mostly chemical as opposed to physical or plasma related.

When a few percent of O_2 is added to SF_6 (up to 5%), the concentration of the etchant species (F atoms) increases causing an increase in the etch rates of Si for low$\%O_2$, because the O_2 in the plasma reduces SF_x/F recombination rates.[13] The maximum etch rate attained in this work occurs at the lowest O_2 examined at $\%O_2 = 5\%$ whereas Campo *et al.* find a maximum etch rate at $\%O_2 = 20\%$, where we observe etch rates 2–3 times larger due to the larger power used in our work. Above 5% of O_2, etch rates decrease because O atoms increasingly compete with F atoms for occupancy of active sites on the surface,[13] we observe a faster decline in etch rates with lower overall values compared to Campo *et al.* due to our lower working pressure. In the range of 5%–20% of O_2, etch rates of all Ge samples dramatically decline, whereas Si etch rates decrease at a lower gradient. This effect can be explained by the superficial layers of SiO_xF_y and GeO_xF_y that form on the surfaces impeding chemical etching,[22] with the Ge-O bond (3.66 eV) more readily breaking than the Si-O bond (4.82 eV).[13] Below 5% O_2, we postulate that the concentrations of SiO_xF_y and GeO_xF_y are not high enough to affect the etch rates.

B. Sidewall profile

Our definition for the etch sidewall profile and the associated measured angle[11] are shown in Fig. 4. The samples are patterned on the ⟨110⟩ directions and are cleaved using standard cleaving techniques perpendicular to the mesa direction. The etched mesas are analyzed by SEM and anisotropic etching is evident for all samples, where images of the sidewalls are shown in Fig. 5 and are presented graphically in Fig. 6. When the Si and Ge sidewall angles are compared, it is observed that there is no significant difference. The perfect anisotropic mesa, where $\theta = 90°$, is achieved with $\%O_2 = 20\%$. This is the critical concentration beyond which the angle changes from acute to obtuse; these observations are consistent with a transition between plasma-to-sputter--dominated etching, the isotropic profile being caused by plasma etching and anisotropic profile through physical etching.[22]

With O_2 content $< 20\%$, the results show evidence of isotropic etching with $\theta \leq 90°$. It is known that if materials are

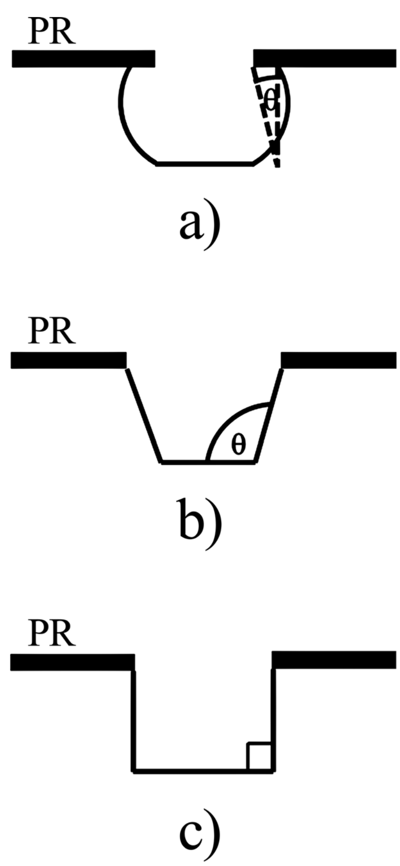

FIG. 4. Mesa profiles produced by anisotropic and isotropic etching (PR = photoresist): (a) Isotropic, (b) partially anisotropic, and (c) perfect anisotropy.

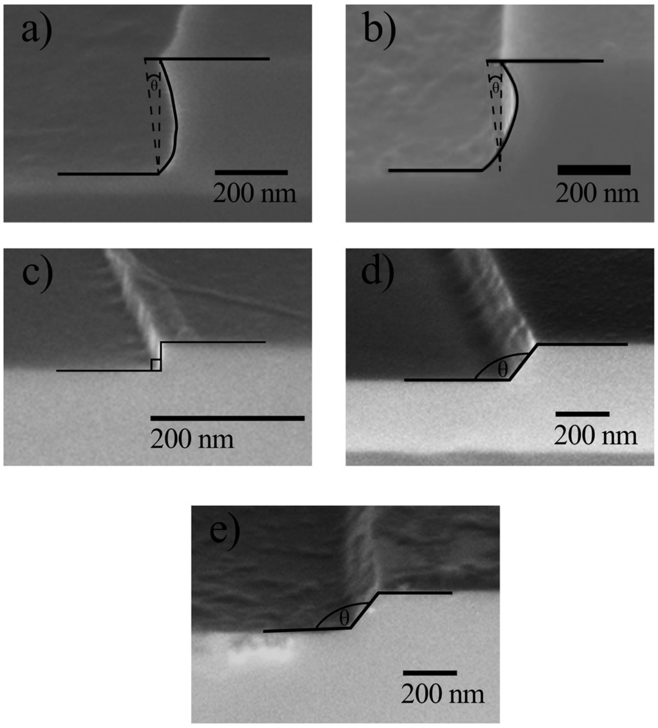

FIG. 5. SEM images of the surface morphology of Ge mesa after dry etching with SF_2-O_2 of various O_2 percentages: (a) 0%, (b) 5%, (c) 20%, (d) 50%, and (e) 70%.

etched by using pure SF_6, the resulting sidewall is perfectly isotropic.[23] With increasing %O_2, plasma etching is suppressed and physical etching becomes more prominent, ultimately yielding a maximum sidewall angle of 166° to the surface. Since the threshold for reduction of etch rate and the critical concentration for etching angle coincides at a %O_2 of 20%, we propose that the mechanism is due to sidewall oxide formation at higher %O_2 and redeposition of SiO_xF_y and GeO_xF_y etched products, which have been reported to help in promoting an anisotropic etch profile.[22] When the O_2 concentration is below 20%, these oxides are not so prevalent. In this case, F^+ ions created in the plasma would be absorbed in the etched surface and move until they reach sites of lowest potential energy at the bottom of the mesa,

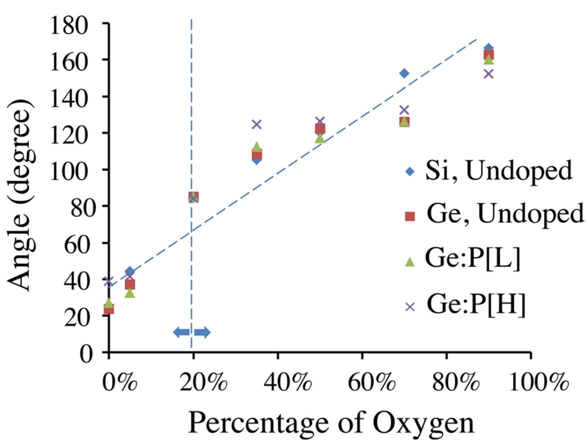

FIG. 6. (Color online) Anisotropic angle as a function of percentage of oxygen.

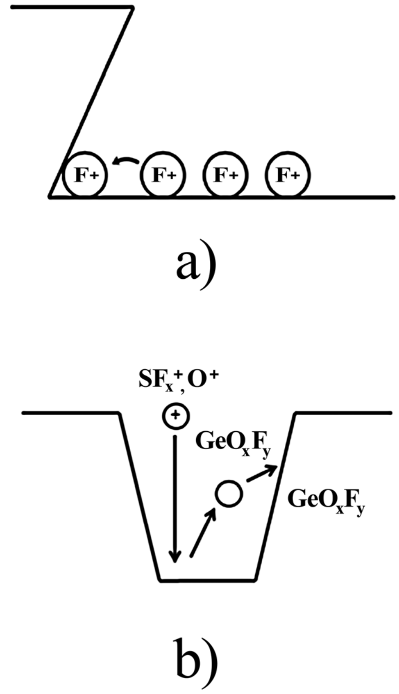

FIG. 7. Proposed etch mechanism: (a) the F+ ions find the site of least potential energy, the step and therefore etch slightly laterally. (b) GeO_xF_y is sputtered from the bottom surface and redeposited onto the sidewall.

which would cause lateral etching of the mesa. By contrast, when the O_2 content is above 20%, O^+ ions would be increasingly absorbed in the etched surface. This would create SiO_2 or GeO_2 on the sidewall, effectively impeding chemical etching. Hence, physical sputtering would tend to be dominant and some of sputtering products would redeposit on the sidewall, creating a partially anisotropic profile. This postulated process is depicted in Fig. 7.

IV. SUMMARY AND CONCLUSIONS

Reactive ion etching of Si, Ge, and Ge:P has been studied, using an SF_6-O_2 gas mixture. The etch rate rises sharply as small amounts of O_2 (up to 5%) are added to a pure SF_6 etch and then decreases when the O_2 content is increased further. The etch rate of Ge and Ge:P is significantly increased over Si for O_2 content in the ranges 0% to 12% and >46%, indicating that well-controlled selective etching is achievable simply by varying O_2 flow rates. Perfectly perpendicular sidewalls are also clearly evident close to 20% O_2 content, again allowing excellent etching control. Future work could usefully investigate the depth of trenches with vertical sidewalls that could be made using this processing condition. In summary, adding O_2 to SF_6 for RIE applications enables significant advantageous and well controllable variations in the process.

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