

Characterization of Threading Dislocations in Thin Germanium Layers by Defect Etching: Toward Chromium and HF-Free Solution

L. Souriau,^{a,b,z} T. Atanasova,^c V. Terzieva,^a A. Moussa,^{a,*} M. Caymax,^{a,*} R. Loo,^{a,*} M. Meuris,^a and W. Vandervorst^{a,b}

^aIMEC vzw, Kapeldreef 75, B-3001 Leuven, Belgium

^bDepartment of Physics and Astronomy, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium ^cFaculty of Chemistry, Sofia University St. Kliment Ohridski, 1400 Sofia, Bulgaria

Defect etching is a fast and simple technique for the revelation of defects in single-crystalline materials. We propose here three different chemistries that allow accurate monitoring of the density of threading dislocations in germanium. This work especially focuses on solutions that have low etch rates and high selectivity in order to work on thin layers. Moreover, solutions that do not contain any carcinogenic Cr^{VI} nor HF acid are proposed in order to reduce the impact on environment and the risks for the user. A comparison of the etch rate and the selectivity toward defects is given as a function of the composition of the etching solutions (components and concentrations). A complete procedure for the proper determination of threading dislocation densities is also presented.

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For decades, performance enhancement of microelectronic chips has been obtained by scaling down the feature size of single silicon (Si) devices, resulting in a concomitant improvement of the drive current and an increase of device density. However, because this strategy is expected to find its limits around the 22 nm node, new channel materials, like germanium (Ge), with intrinsically higher mobility than Si, have to be introduced to further improve efficiency of circuits. Because of the low availability of Ge on earth, it is most likely that mass production will occur on hybrid substrates where only a thin Ge layer is present on a Si substrate serving as mechanical support. For example, Ge can be deposited epitaxially on Si by chemical vapor deposition (CVD).¹ This approach has the additional advantage to offer a platform for cointegration of Si and Ge devices on the same wafer. However because of the large 4% lattice mismatch between the two materials, coherent growth is only limited to less than 1 nm. Convenient layers are always thicker and thus present strain relaxation which mainly occurs via the formation of misfit dislocations at the interface between Si and Ge. These misfit dislocations can terminate at the edge of the wafer but often penetrate through the Ge film and end at the surface as a threading dislocation. The introduction of a SiGe strain relaxed buffer can help decrease the density of threading dislocations in the top electrical active Ge layer.² It is crucial to avoid these defects because of their adverse effects on the electrical performance of devices (reduce mobility, higher junction leakage...) but also on their reliability. Therefore characterization techniques are needed to monitor their density and distribution so as to develop growth techniques minimizing the occurrence of such defects. Unlike transmission electron microscopy (TEM) or electron-beam-induced current, for instance, defect etching is a simple, fast, and low-cost technique to assess the crystal quality of materials.

Wet etching of semiconductors is usually conducted in a threecomponent chemical mixture: an oxidizing agent that oxidizes the semiconductor surface atoms (e.g., HNO₃, H₂O₂, O₃, Br₂, CrO₃, K₂Cr₂O₇...), a complexing agent that dissolves the oxide that is formed on the surface (e.g., HF...), and a solvent for dilution (e.g., H₂O, CH₃COOH...).^{3,4} In the case of defect etching the overall reaction has to be sensitive to the presence of defects at the surface, i.e., sensitive to the difference in stress level and/or composition variation so that the etching proceeds faster or slower at the defect site than in the perfect crystal. As a consequence, because the surface is originally relatively smooth before etching, some topography

^z E-mail: souri@imec.be

(pits and/or hillocks) is created on the etched surface and the defects are rendered visible. Microscopy techniques [optical, scanning electron microscopy (SEM), atomic force microscopy (AFM)...] allow the observation of the etched features and the determination of the nature of the defects and their density.

For Ge, depending on the surface orientation of the substrates (100), (110), and (111), some solutions are already available to reveal threading dislocations.^{5,6} However the etch rates (ERs) of these solutions are on the order of a few $\mu m min^{-1}$, which renders the revelation impossible in thin layers. By dilution, the ER of these solutions can be decreased but the selectivity toward defects is drastically decreased. The overall process shifts from a surface-reactioncontrolled regime to a mass-transfer-controlled regime, that is to say, from a defect preferential etching to a polishing etching. We have studied a solution suited for the revelation of threading dislocations in thin Ge based on the $CrO_3/HF/H_2O$ system,⁷ which was also extensively used for Si^{8,9} and GaAs.¹⁰ It exhibits a very low ER (ranging from 7 to 100 nm min⁻¹ depending on the doping, strain state, and the surface orientation of the layer), and it has very good selectivity toward defects. Revelation of threading dislocations is possible on (100)- and (111)-oriented Ge with such solution. However, it makes use of carcinogenic CrVI and also HF acid, which does not make it environmentally nor user friendly. In the case of Si, fluoride anions are needed in order to dissolve the silicon dioxide that is formed by oxidation according to the reaction $SiO_2 + 6HF$ $\rightarrow 2H^+ + SiF_6^{2-} + 2H_2O$. Whereas authors have usually tried to adapt the HF-containing defect etching solutions used for Si on Ge, it is important to notice that germanium dioxide is water-soluble (the hexagonal form of GeO₂ leads to the formation of metagermanic acid H2GeO3 in water) so that there is no need for HF as compared to the silicon case.

Hence, this paper deals with the development of defect etching solutions for Ge to reveal threading dislocations which do not contain Cr^{VI} nor HF or a low HF concentration. We especially focus on low ER for applicability on thin Ge layers.

Experimental

Two sets of thin, epitaxial intrinsic Ge(100) layers grown on Czochralski (CZ) p-Si substrate by CVD were investigated in this study. The first set of samples, hereafter referred as "standard Ge on Si(100)," consisted of approximately 1.5 μ m Ge layers deposited in a two-step process: a relatively thin, low-temperature Ge buffer followed by a high-temperature Ge thick layer. These layers were provided by ASM America. The samples of the second set, hereafter referred as "annealed Ge on Si(100)," were exactly the same layers to which a high-temperature annealing in H₂ was applied in order to

^{*} Electrochemical Society Active Member.



Figure 1. SEM image of the surface of a standard Ge on Si(100) (a) before defect etching; (b, c, d) after defect etching in $Cr^{VI}/HF/H_2O$ for different times.

efficiently decrease the density of threading dislocations.¹¹ Additionally, few samples consisting of a thin 1.6 μ m (111)-oriented intrinsic Ge grown on CZ p-Si substrate were also studied. All the thin Ge layers used in this study were nearly fully relaxed, as verified by high-resolution X-ray diffraction. Three chemistries were investigated in this study: the standard chromium-based etchant consisting of Cr^{VI}/HF/H₂O, a cerium-based solution consisting of Ce^{IV}/H₂O, and a permanganate based solution consisting of MnO₄/HF/H₂O. The reactants were all analytical grade, and the source of oxidant were CrO₃, (NH₄)₂Ce(NO₃)₆, and KMnO₄, respectively. Other sources of Ce^{IV} have been used and lead to the same results, but the ammonium nitrate form has the best solubility in water which enabled high-concentration solutions to be prepared. The etching was carried out by dipping 2×2 cm² samples in a beaker containing the different solutions. The solutions were always freshly prepared unless mentioned. The samples were partially immersed in the solutions so as to produce a step which was used for the determination of the ER. No stirring was applied to the solutions during etching in order to minimize the ER, and all experiments were done at room temperature. After etching, the samples were thoroughly rinsed in deionized water in order to immediately stop all reactions and also to clean the surface before further characterization; they were dried under N₂ flow. SEM was the main characterization technique. The imaging of the surfaces before and after etching was done in a 45° tilted geometry (for a better etch feature delineation as compared to plain-view geometry), whereas the ER measurement was achieved by doing cross-section measurements in the etched and nonetched region. The threading dislocation densities (TDDs) were determined by counting the number of etch features on a large enough area (several SEM pictures required for a good statistical determination) and dividing it by the area (corrected because of the 45° geometry). AFM was also used to precisely determine the geometry of the etched features. The selectivity S toward defects of all the solutions was assessed by looking at the ratio of the lateral size of the etched features by the etch depth: S = Width of etch feature/Etch depth.

Results and Discussion

Chromium etchant.— The results presented here were obtained with a solution having the following composition: CrO_3 0.6 mol L^{-1}/HF 12 mol L^{-1}/H_2O . As can be observed in Fig. 1, starting from a smooth surface before etching, good revelation of the threading dislocations was obtained for times ranging between 2 min 30 s and 10 min on standard Ge on Si(100). Square pyramidal etch pits



Figure 2. Cross-sectional TEM image of a standard Ge on Si(100) substrate showing the dense network dislocation at the interface and the lower TDDs.

were obtained [as expected for (100)-oriented crystals³], and even though their size increased with etching time, their density remained invariable at a level of $8-9 \times 10^7$ /cm². This was in accordance with cross-sectional TEM which showed a constant TDD of approximately 10^8 /cm² in the top first micrometers of the layer (Fig. 2). It is worth noting that defect etching is much more accurate than TEM for the determination of a TDD lower than 10⁹/cm² because of the larger area probed. The correlation between the etch depth and the etching time is shown in Fig. 3. It reveals two regimes that have been attributed to the fact that for etching times shorter than 10 min, the removal rate of the layer is mainly determined by the ER of (100) planes, whereas for etching times longer than 10 min, the surface is mainly composed of the sidewall of the etch pits, which are (511) planes, and thus the ER is determined by the removal rate of those planes. More details on this model can be found in Ref. 7. The ER for times shorter than 10 min is 7 nm min⁻¹, and good revelation of the threading dislocations is obtained for such time. As a consequence, less than 50 nm material removal is enough in order to determine the TDD, which makes this technique applicable to very thin Ge films. The evolution of the etch pit size (nonoverlapping pits) is illustrated in Fig. 4. It shows a linear behavior with a lateral growth speed of 116 nm min⁻¹ for etching times inferior to 10 min. The selectivity of the solution toward threading dislocations is thus more than 16.

Similar results were obtained on the annealed Ge on Si(100) samples, but a TDD of $1-2 \times 10^7/\text{cm}^2$ was observed, which shows the efficiency of high-temperature H₂ annealing to reduce TDD by an annihilation mechanism.¹¹



Figure 3. Etch depth as a function of time for a standard Ge on Si(100) in $Cr^{VI}/HF/H_2O$.



Figure 4. Width of the pits as a function of the etching time in $\rm Cr^{VI}/\rm HF/\rm H_2O.$

Good revelation of the threading dislocations was also observed on (111)-oriented epitaxial Ge grown on Si(111) (see Fig. 5). Triangular-base pyramidal pits are obtained in this case, as expected for such crystal orientation,³ and a TDD of $6 \times 10^8/\text{cm}^2$ was determined in the studied sample. Some triangular terraces with edges running along the (100) directions are also visible at the surface after defect etching but do not jeopardize the defect density determination.

Cerium etchant.— The defect etching capability of the Ce^{IV} /H₂O solution was evaluated for Ce^{IV} concentrations ranging from 0.01 to 1 mol L⁻¹. Typical examples of surface images after etching are reproduced in Fig. 6, showing the possibility to reveal the threading dislocations with such solution. An interesting point is that depending on the concentration of Ce^{IV} ions in the solution, the morphology of the Ge surface after etching is different. As illustrated in Fig. 7 by the tip trace of the AFM image through etch features, for concentrations inferior to 0.3 mol L⁻¹, some square pyramidal etch pits are produced on the surface. For concentrations between 0.4 and 1 mol L⁻¹, square pyramidal hillocks are present on the surface after etching. We think that in the case of high Ce^{IV}



6µm

Figure 5. SEM image of (111)-oriented epitaxial Ge on Si after defect etching for 120 s in $Cr^{VI}/HF/H_2O$.



Figure 6. SEM image of standard Ge on Si(100) after etching (a) 600 s in 0.1 mol L^{-1} Ce^{IV} and (b) 90 s in 1 mol L^{-1} Ce^{IV}.

concentrations, some insoluble tetragonal GeO₂ oxide is produced on the threading dislocation core which prevents further etching at that point and leads to the formation of the hillocks. The TDDs were determined for all Ce^{IV} concentrations in the studied range and were shown to be independent of the Ce^{IV} concentration (Fig. 8). The etching time was adapted for the different concentrations in order to produce etch features without removing the entire Ge layer: 10 min for concentrations between 0.01 and 0.3 J cm⁻², 3 min between 0.4 and 0.75 mol L⁻¹, and 1 min 30 s in the case of 1 mol L⁻¹. The TDD of approximately $10^8/\text{cm}^2$ was relatively independent of the solution concentration and agreed well within the experimental error with the values determined by defect etching with the chromium



Figure 7. AFM image of standard Ge on Si(100) after etching in Ce^{IV}/H_2O with concentration of 0.1 and 0.6 mol L^{-1} and their respective tip trace through an etch feature (pit/hillock).



Figure 8. TDD on standard Ge on Si(100) determined for the different Ce^{IV} concentrations.



Figure 9. ER measured on standard Ge on Si(100) as a function of the Ce^{IV} concentration.

etchant $(8-9 \times 10^7/\text{cm}^2)$ and by cross-sectional TEM (Fig. 8). These results demonstrate that it is indeed possible to perform defect etching of Ge without using HF acid and take advantage of the solubility of GeO₂ oxide in water. In order to characterize thin Ge layers, it is important to work with an etchant exhibiting a relatively low ER. As can be observed in Fig. 9, the ER of Ge layers in the Ce^{IV}/H₂O solution shows a linear behavior as a function of the Ce^{IV} concentration. This demonstrates that the rate-limiting step in the etching reaction is the oxidation of the Ge surface atoms, which is essential for etching with a preferential behavior (anisotropic etching, defect etching...). Moreover, it shows that the oxidation kinetic of Ge atoms by Ce^{IV} ions is of the first order. The results presented here indicate that it is preferable to work with Ce^{IV} concentrations lower than 0.4 mol L^{-1} in order to have better control of the etched depth. For a Ce^{IV} concentration of 0.01 mol L⁻¹, the ER is only 4 nm min⁻¹. The selectivity of the Ce^{IV}/H_2O solution toward threading dislocation is independent of the Ce^{IV} concentration and is approximately 1. However when the solution is aged, the selectivity is reduced and the etch features become rounded. Similar tests were carried out on the annealed Ge on Si(100) samples. A TDD of $2-3 \times 10^7$ /cm², which is very close to the TDD of 1-2 \times 10⁷/cm² that was determined with the chromium-based etchant, was measured on the annealed Ge on Si(100) samples.

As can be observed in Fig. 10a, the Ce^{IV}/H₂O etching solution is also able to reveal threading dislocations in (111)-oriented Ge on Si. A density of threading dislocations of 2×10^8 /cm² was determined in the studied sample, which is quite in accordance with results obtained with the chromium etchant (6×10^8 /cm²). Similar to the case of the chromium-containing solution, etch lines running in the (100) directions are observed after etching.



Figure 11. (a) SEM and (b) AFM images after etching of standard Ge on Si(100) in $MnO_4^-/HF/H_2O$ for 3 min.

Permanganate etchant. Different compositions of the MnO₄^{-/} (HF)/H₂O solution were also evaluated for the revelation of threading dislocations in thin Ge layers. In general, MnO_4^- concentrations up to 0.6 mol L^{-1} allowed the revelation of defects, but the best results were obtained for low concentrations on the order of 0.01 mol L⁻¹. In all cases square pyramidal etch pits were obtained, but for high MnO₄⁻ concentrations, the etch pits were rounded. Surface imaging (SEM and AFM) of the Ge surface after etching in a solution containing 0.01 mol $L^{-1}\ MnO_4^-$ and 12.5 mol L^{-1} HF for 3 min is given as an illustration in Fig. 11. A 0.01 mol L⁻¹ concentration of MnO₄⁻ anions was selected to evaluate the influence of the concentration of HF acid in the solution on the defect revelation and ER. As can be observed in Fig. 12, the determined TDD of approximately 10⁸/cm² is independent of the HF concentration in the solution and is in accordance with the results obtained with the other defect etching chemistries and also with TEM characterization. The ER of these solutions was measured and is reproduced in Fig. 13. As in the case of the cerium etchant, we can notice that no HF acid is needed to etch the Ge layer and to reveal the defects. The introduction of HF in the etching solution increases the ER. This can be explained by two effects: HF might be more efficient in the dissolution of GeO2 oxide, but also the increase of the acidity of the solution increases the oxidation potential of MnO_4^- anions. However, there is no obvious explanation for the higher ER obtained with 5 mol L^{-1} HF than for 12.5 mol L^{-1} . ERs between 20 and 50 nm min⁻¹ are obtained depending on the HF concentration, which allows working on thin Ge layers easily. The selectivity toward threading dislocations of the MnO_{4}^{-} (HF)/H₂O solution with a MnO₄⁻ concentration of 0.01 mol L⁻¹ is



Figure 10. SEM image of (111)-oriented epitaxial Ge on Si after etching in (a) Ce^{IV}/H_2O and (b) MnO_4^-/H_2O .



Figure 12. TDD of standard Ge on Si(100) etched in $MnO_4^-/HF/H_2O$ as a function of [HF] concentration for a [MnO_4^-] concentration of 0.01 mol L^{-1} .

H680



Figure 13. Etch depth as a function of etching time and the [HF] concentration for standard Ge on Si(100) etched in $MnO_4^-/HF/H_2O$.

approximately 1, regardless of the HF concentration, which is comparable to the results obtained with the cerium etchant.

The surface of a (111)-oriented Ge on Si layer after defect etching with the MnO_4^-/H_2O solution is reproduced in Fig. 10b. Good revelation of the threading dislocation was obtained, and a threading dislocation density of 4×10^8 /cm² was found in the studied sample, which is in accordance with previous results with the $Cr^{VI}/HF/H_2O$ $(6\times 10^8/cm^2)$ and Ce^IV/H2O (2 $\times 10^8/cm^2)$ solutions. Likewise, the two other etching solutions, etch lines running in the (100) directions, are observed after etching but do not compromise etch pit counting.

Conclusions

We studied three different chemistries for the defect etching of thin Ge layers based on the Cr^{VI} , Ce^{VI} , and MnO_4^- oxidants. The

desired very low ERs can be obtained with such etchants, and good revelation of the threading dislocations is achieved on (100)- as well as on (111)-oriented Ge thin layers. A comparison of the different chemistries was carried out. Whereas the chromium etchant shows the best selectivity toward defects with a very low ER, the proposed cerium and permanganate solutions provide good defect delineation performance and allow work to be accomplished without carcinogenous Cr^{VI} nor toxic HF.

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