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A Wet Etching Technique to Reveal Threading Dislocations in Thin Germanium Layers

L. Souriau[1,a], V. Terzieva[1], M. Meuris[1] and M. Caymax[1]

[1] Imec, kapeldreef 75, B-3001 Heverlee, Belgium

[a]Laurent.Souriau@imec.be

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A defect selective *wet chemical etching* technique that allows accurate determination of etch pit density (EPD) in *thin Germanium* (Ge) layers is described. The effect is achieved by using chromium (Cr^{VI}) based solution. Such a solution, in combination with other chemicals, exhibits mild oxidation power which provides low etch rates (ER) and excellent selectivity towards *threading dislocations*. The etching technique is able to delineate threading dislocations in layers with thickness in the range of 80 – 1500 nm within the resolution of scanning electron microscopy (SEM). Different types of Ge layers were analyzed (doping levels, defect density, degree of relaxation). The ER is shown to depend on several characteristics of the layer and is in the range of 7 to 100 nm/min.

Introduction

As the scaling of Silicon CMOS structure reaches its fundamental limits, new materials with high carrier mobility like Ge are needed to continue improving the device performance. The successful integration of Ge in device manufacturing is determined to high extent by its surface properties and crystal quality. Although bulk Ge substrate of high quality can be grown, from a viewpoint of material cost and supply it is clear that Ge CMOS technology will be developed on thin Ge layers. As a result of the large 4% lattice mismatch between Si and Ge, the growth of epitaxial Ge on Si is limited by a critical thickness [1] above which too much energy is required to strain the layer coherently with the substrate. Misfit dislocations are thus generated and they are connected to the surface by the so-called threading dislocation. As a general rule, all defects in the electronically active part of an integrated circuits (IC) are deadly for the device. They have to be avoided and that means that they have to be monitored first. To achieve such monitoring, a method of choice is defect etching. Most popular etchants used in micro-defect decoration are mixtures of an oxidant, a chemical dissolving agent (generally hydrofluoric acid) and inert diluents.

In order to reveal the defects, the etchant must exhibit sensitivity to the local stress level or composition difference so that the ER is different between the perfect crystal lattice and the defect sites. The pits or hillocks produced in that way can then be identified and counted under microscope (Optical, SEM or Atomic Force Microscopy (AFM)).

As can be seen in the literature [2-5], there are already defect etching solutions for Ge but the etch rates are too high (order of μm/min) to be used for thin Ge layers. The goal of the present work is to find an etchant exhibiting a low ER as well as a good selectivity toward defects.

Experimental

The defect etching was performed in a chromium based solution which consists of Cr^{IV} / HF / H_2O. Different substrate types were investigated in our study: Ge epitaxial layers on Si and bulk Ge (100) wafers. The Ge epitaxial layers were of two different types: thick (1.6μm) relaxed epitaxial Ge layers (ASM) grown on Si (100) and a set of thin (100, 200 and 300nm) partially relaxed epitaxial Ge layers (IMEC) grown on Si (100). The bulk Ge (100) wafers, which were supplied by Umicore, were also of two types: grown dislocation free or not. In addition, the dislocation free bulk Ge wafers had different doping type (Sb and Ga for N and P type respectively) and doping level (10^{14} and 10^{16} at/cm^3). The samples were cut into pieces of 2 x 2 cm. They were etched by dipping them

into the etchant for various times without stirring. The samples were then thoroughly rinsed with DI-water and dried under N_2 flow. Before and after etching, the sample surfaces were characterized using Normaski microscopy, SEM (45° tilted) and AFM. Etch rates were determined either by step measurements using Step Height Profiler (for bulk Ge) or cross-section SEM (for epi-layers).

Results and discussion

Etch rate: The dependence of the ER on the doping level has been determined on N and P- type bulk Ge wafers with two different doping levels (10^{14} and 10^{16} at/cm^3) etched for various time up to 20 min. Results are given in Figure1a. As a next step, the ER of thick relaxed epitaxial Ge layers has also been measured for various times (up to 30 min) and it was found to be increasing (from 7 nm.min^{-1} to 33 nm.min^{-1}) with etching time as indicated in Figureb.

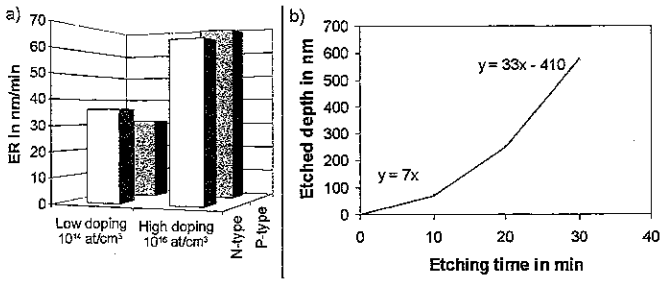


Figure1: a) ER of bulk Ge with different doping level b) Etch depth of thick epitaxial Ge layers as a function of etching time

Furthermore, the ER of thin partially relaxed epitaxial Ge layer has been measured for various times (up to 3 min) and was found to be in the order of 100 nm.min^{-1}.

It is obvious that the ER of Ge depends on several characteristics of the layer. It increases with the doping level: ranging from 7 nm.min^{-1} for un-doped layer to 68 nm.min^{-1} for highly doped layers. It also depends on the degree of relaxation of the layer: although the investigated epitaxial layers were all intrinsic, the determined ER range from 7 nm.min^{-1} for thick relaxed layer to about 100 nm.min^{-1} for thin partially relaxed layers

Defect delineation: In order to verify the defect delineation capability of the solution, bulk N-type ([Sb]=10^{16} at/cm^3) Ge samples were first investigated. The etching revealed no etch pits but few etch artifacts on dislocation free samples etched for 5 min. On the other hand, the delineation of threading dislocations was achieved on samples grown with dislocations. As the EPD of samples grown with dislocations provided by the supplier was quite low (1-2×10^4 /cm^2), samples were etched for 30 min so as to produce etch pits big enough to be found with SEM inspection as well as Normaski optical microscope. As can be seen on Figure, the etching resulted in well defined, pyramidal pits. These pits indicate the places where the dislocations cross the surface. They are not perfect squares because of the miscut of the wafer. The determined EPD (10^4 /cm^2) was in accordance with supplier specifications.

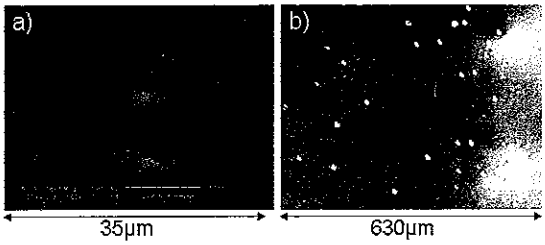


Figure2: Dislocation pits on bulk Ge n-type heavily doped observed under: a) SEM b) Normaski microscope

In the next step, thick epitaxial Ge layers were etched for different times (up to 10 min) in order to: (i) identify the defects, (ii) follow the kinetic of etch pit formation and growth. SEM surface characterization revealed pyramidal etch pits with EPD around 8-9×10^7 /cm^2, which was constant as function of etching time (Figure3a,b,c). This result was in accordance with cross-section TEM inspection (not given here) that had shown threading dislocation density of approximately 7×10^7-10^8 /cm^2 in the top first micron of the layer. The etch pit width (measured on isolated pits), increased linearly as a function of etching time (Figure3d).

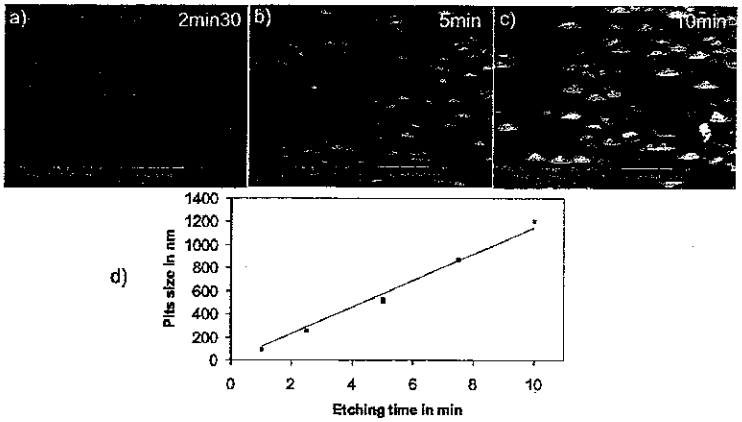


Figure 3: a), b) and c) Morphology of the etched surfaces
d) Kinetic of pit formation on thick relaxed epitaxial Ge layers

To further characterize the pits, AFM was used. It has revealed that the side-walls of the pits were, independently of etching time, approximately 16° inclined from the (100) surface indicating the presence of (511) planes.

The thin epitaxial Ge layers were all etched for 20 s. The determined EPD (approx. 10^{10} /cm^2) was in accordance with cross-section TEM. As presented in Figure4a, a slight decrease in the EPD was observed as the starting thickness of the Ge layer increased which can be explained by the fact that some dislocations cancel each other as growth proceeds. Detailed SEM characterization revealed that about 1% of the etch pits were bigger than the others (Figure4b). We found out using AFM that these pits were actually the intersection of several pits corresponding to threading dislocations crossing the surface very closely (Figure4c).

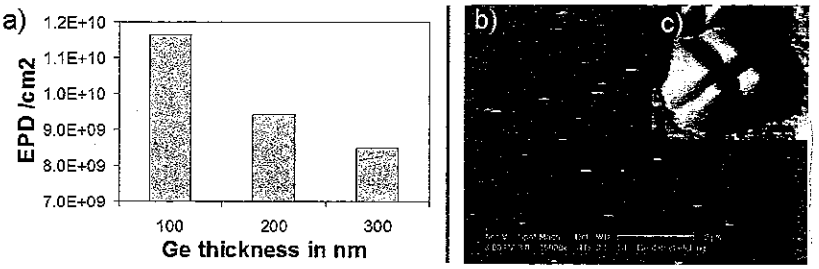
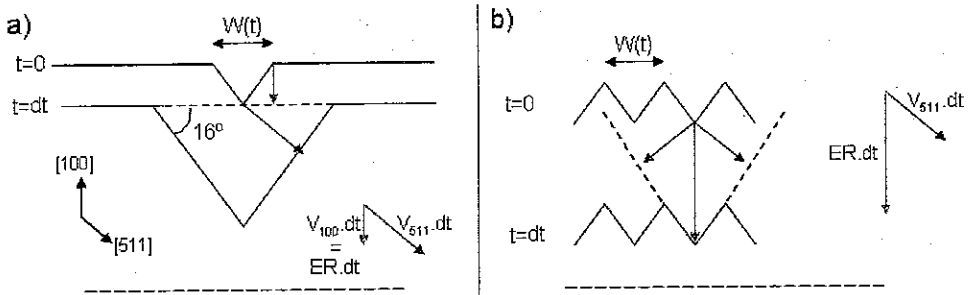


Figure 4: a) EPD as a function of epitaxial Ge thickness b) SEM image of dislocation pits on thin epitaxial Ge layers; c) AFM of the bigger pits

In order to understand the changes in surface morphology as well as etch pit size while etching proceeds, we suggest the following model. As (511) planes are revealed around threading dislocations, we can define two removal rates: V_{100} is the removal rate in the [100] direction and V_{511} in the [511] direction (Figure5a).



$$ER = V_{100}$$

$$W(t+dt) = W(t) + \left(\frac{V_{511}dt}{\sin 16} - \frac{V_{100}dt}{\tan 16} \right)$$

$$ER = \frac{V_{511}}{\sin 74}$$

$$W(t+dt) = W(t)$$

Figure 5: a) Pit formation and growth according to the suggested model
b) Kinetic when pits are intersecting at the surface according to the suggested model

At the beginning of the etching, isolated etch pits start to form (Figure3a, Figure5a). The surface of the sample in that moment is mainly composed of (100) planes. In that case, the etch rate is defined by the removal rate of (100) planes V_{100} and the etch pits width W is increasing linearly with time.

When etching proceeds, the pit lateral sizes increase and the pits intersect at the surface (Figure3c and Figure5b). The surface of the sample is now mainly composed of (511) planes. The etch rate is not anymore defined by the removal rate of (100) planes but (511) planes V_{511} and the etch pits width W is not changing anymore.

This model helps understanding why for the thick epitaxial Ge layer, the ER increased from 7 $nm.min^{-1}$ at the beginning to 33 $nm.min^{-1}$: we actually have observed the change from the regime determined by the removal rate V_{100} to the one determined by V_{511}.

Summary

We have demonstrated that a chromium containing solution (Cr^{IV} / HF / H_2O) is a suitable etchant for delineating *threading dislocation in thin Ge layers*. The ER is sensitive to the doping level and the degree of relaxation of the layer but is low enough for thin layer characterization ($100nm.min^{-1}$ and less). A model has been proposed to describe the kinetic of etch pit formation and growth.

References

[1] R. Hull and J.C Bean, J. Vac. Sci. Technol. A 7 (4), (1988), p2580

[2] A.W. Laubengayer and D.S. Morton, J. Am. Chem. Soc. **54**, (1932), p2303

[3] M. Schweizer, S.D. Cobb, M.P. Volz et al.; J. Cryst. Growth **235-1-4**, (Feb. 2002), p161-166

[4] IEEE Std 1160-1993; IEEE St. test procedure for high-purity Germanium crystals for radiation detectors

[5] P. Wang; The Sylvania technologist, **XI-2**, (Apr. 1958), p50-58