Surface chemistry and nanoscale wet etching of group IV semiconductors in acidic H_2O_2 solutions

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Introduction

Due to physical complications, such as gate leakage, parasitic resistance/capacitance and size channel effects, further downscaling of Si CMOS is impeded [1]. Hence, the semiconductor industry is searching for potential candidates that can replace Si as the material of choice. Recently, Ge is being hailed as a substitute of Si due to its higher electron and hole mobilities, critical for 3 nm technology nodes and beyond [2, 3]. In addition to its nanoelectronics applications, Ge has also found niche in the fields of battery [4], biomedicine [5], solar cells [6], and photodetectors [7].

For device manufacturing a large number of wet-chemical processing and etching steps are required (e.g. rinsing steps, layer selective etching, trimming, recess etching, smoothening, oxide and (sub)surface damage removal). Due to the aggressive scaling, an etching control up to the atomic-layer-scale is necessary. The high reactivity of Ge as compared to Si, makes the design of suitable wet chemical etchants challenging. In order to meet the technological milestone in the near future, a thorough insight in the basic etching kinetics and surface chemical mechanisms is required.

In this work we report on the wet-chemical etching kinetics of Ge (100) in acidic H_2O_2 solutions. Kinetic studies were performed using inductively coupled plasma mass spectrometry (ICP-MS). Dissolution of the group IV semiconductor is mainly controlled by the hydrodynamics of the system and the concentration of the oxidizing. Electrochemical measurements indicate that chemical mechanism control the dissolution process of Ge. These results served as a starting point for the comparison Ge versus SiGe, relevant for device integration schemes. The presence of Si has a profound impact on the etching kinetics. While $Si_{0.25}Ge_{0.75}$ showed a low but continuous etch rate, $Si_{0.49}Ge_{0.51}$ passivates due to the formation of a self-liming oxide. We show synchrotron XPS results and discuss the surface chemistry underlying the wet etching process.

Experimental

Sample preparation. Chemicals were purchased from Sigma Aldrich and were of p.a. quality: 37% HCl (12.0M) and H_2O_2 (9.7M). Bulk p-type 2" (100) Ge wafers (Umicore) were used with a dopant density of ~1E17 cm^{-3}). The $Si_{0.49}Ge_{0.51}$ and p-$Si_{0.28}Ge_{0.72}$ (100) layers were 500 nm thick and unintentionally p-doped. Etching experiments were performed at room temperature in a clean room environment using dedicated polyvinylidene fluoride (PVDF) etching cell. Etch rates were determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS, Agilent 7500cs) [5].
Surface Characterization. Three- electrode system was used for the electrochemical measurements using Ge as the working electrode (WE), a platinum (Pt) sheet as the counter electrode (CE), and a saturated calomel electrode (SCE/ V= 0.242V vs NHE) as the reference electrode (RE). All experiments were conducted in a cleanroom environment at room temperature using a potentiostat

(PARSTAT 4000, Princeton Applied Research). Surface morphology of etched Ge samples was obtained by field-emission scanning electron microscope (SEM, Omicron) and atomic force microscope (AFM, Nanoscope Iva Dimension 3100 in tapping mode). Surface chemical properties were studied by synchrotron X-ray photoelectron spectroscopy (XPS). Photoemission studies were carried out at the undulator beamline UE56/2 PGM1 of the BESSY II storage ring, which provides photons in the energy (hν) range of 100 - 1100 eV.

Results and Discussion

Etching kinetics. The etch rate of Ge (100) was studied as a function of sample rotation rate by ICP-MS for different H_2O_2 concentrations in 1 M HCl (Figure 1a). At 0.5 mM H_2O_2, etching of the group IV semiconductor is already significant with a v_{etch} of about 1 nm min^{-1}. Due to the reactive nature a marked influence of the sample rotation rate is observed at higher H_2O_2 concentrations. Such diffusion-controlled dissolution (<500 rpm) is related to depletion of oxidizing species at the surface (the oxide solubility is high) [8]. At higher rotation rates (≥500 rpm), the hydrodynamics of the system is no longer important and the etching is determined by the kinetics of the system, a condition generally preferred for device fabrication.[9]

Figure 1(b) shows electrochemical data for p-type Ge at 500 rpm in 1 M HCl/10 Mm H_2O_2 solution. When the electrode was illuminated with supra-bandgap light at potentials negative of the flatband potential, the photo generated minority carriers are transferred to surface by the electric field where they subsequently reduce the oxidizing agent. The reduction reaction is characterized by a distinct peak at -0.4 V. The disappearance of the peak under dark conditions, indicates that H_2O_2 decomposition is a conduction band process. This points to a mechanism that is most likely chemical by nature: electroless processes involving hole injection can, most likely, be excluded. However, the dark current plateau feature that is observed, indicates that surface states are formed during etching. The favourable energetic position of these states allows for H_2O_2 reduction by thermally injected electrons. As the injection current is absent for the H_2O_2-free case, surface states directly relate to the presence of the oxidant.

Figure 2 shows the etch rate data for Ge versus SiGe (100) in 0.1 M HCl/10 mM H_2O_2 solution. The presence of some Si in the (100) crystal lattice has a marked influence on the etching behaviour. The etch rate for $Si_{0.28}Ge_{0.72}$ decreased by one order of magnitude to about 1.1 nm min^{-1} (Figure 2(a)). A time-dependent etching experiment points to a stable dissolution kinetics up to 60 min for $Si_{0.28}Ge_{0.72}$ confirming that this SiGe is etched continuously at a given rate. The formed oxide layer must be sufficiently soluble to maintain the surface oxidation reactions. For higher Si content ($Si_{0.49}Ge_{0.51}$), the etch rate lowered by an additional order of magnitude to a value below 0.1 nm min^{-1}. The time-dependent v_{etch} plot showed that the etch rate decreased from 0.08 nm min^{-1} to about 0.01 nm min^{-1} after 60 minutes of etching indicating that a self-limiting oxide layer is formed (Figure 2(b)).

Surface chemistry. Surface sensitive synchrotron XPS spectra were recorded for the Ge3d and Si 2p core levels in 0.1M HCl/10 mM H_2O_2 solution Figure 3. The reference is a sample with native oxide grown in O_3/H_2O. Deconvolution of the 100 eV surface sensitive Ge 3d core level spectra showed distinct Ge 3d5/2 and Ge 3d3/2 doublet peaks with additional Ge^{1+}, Ge^{3+}, and Ge^{4+} oxidation states. Ge^{2+} was not detected. The etched samples showed an overall reduction of Ge (sub)oxides. The Ge^{1+} coverage decreased by almost half for Ge and SiGe while a complete absence of the Ge^{4+} feature could be noted for Ge and $Si_{0.28}Ge_{0.72}$. However, Ge^{2+} and Ge^{4+} species exhibited an apparent stronger bonding on the $Si_{0.49}Ge_{0.51}$ surface. In addition, the existence of Ge-Cl could also be assigned to all the samples.[8] Interestingly, the spectra suggest that surface chlorides are stabilized as the Si content increases from 27% to 49% resulting in higher amounts of Ge-Cl.

The surface sensitive Si 2p SXPS spectra (245 eV) for $Si_{0.28}Ge_{0.72}$ and $Si_{0.49}Ge_{0.51}$ could be well separated into four additional components next to the Si 2p3/2 bulk emission peak labeled as Si^{1+}, Si^{3+} and Si^{4+}. Similar to the Ge 3d measurements, no evidence was found for species with a 2+ oxidation state. The etched $Si_{0.28}Ge_{0.72}$ showed a significant increase for the Si^{1+} component as compared to the reference sample with native oxide. We attribute this to the formation of overlapping species such Si-OH. Furthermore, the amount of Si^{3+} and Si^{4+} was reduced to almost half. Clearly at 28% Si the solubility is sufficient to maintain the etching process in HCl/H_2O_2 solution (see also Figure 1). By contrast, a small increase of the Si^{3+} and Si^{4+} components was seen after etching for $Si_{0.49}Ge_{0.51}$ as compared to the reference oxide grown in O_3/H_2O. Evidently, the build-up of pristine silicon oxides, insoluble in HCl (i.e. SiO_2), induces the growth of a self-limiting passivating oxide; hence, etching ceases. These data provide a link between the silicon bulk concentration and the oxide solubility: at least 50% Si is needed to passivate the surface by the formation of typical Si-O-Si oxide bridges.

Summary

Wet etching of Ge is characterized by the use of low H_2O_2 concentrations. As the reactivity is high, the oxidant is depleted at the surface. Sample rotation is required to obtain stable kinetics. The kinetics of SiGe wet etching were found to be less favorable as indicated by the decrease in v_{etch} by one and two orders of magnitude for $Si_{0.28}Ge_{0.72}$ and $Si_{0.49}Ge_{0.51}$, respectively. $Si_{0.28}Ge_{0.72}$ could be etched actively. By contrast, when the Si bulk concentration was 51%, surface passivation occurred. A comparative synchrotron XPS study suggested that the Ge surface chemistry was mainly dominated by Ge^{1+} and Ge^{3+} species for both Ge and $Si_{0.28}Ge_{0.72}$, while Ge^{2+} and Ge^{4+} components were also important for $Si_{0.49}Ge_{0.51}$. Si 2p analysis indicated that the two investigated SiGe alloys had similar surface chemical species after etching. However, a thicker oxide was noted for $Si_{0.49}$ $Ge_{0.51}$. The presented data provide starting point for understanding the link between Si surface chemistry and the etching kinetics of SiGe.

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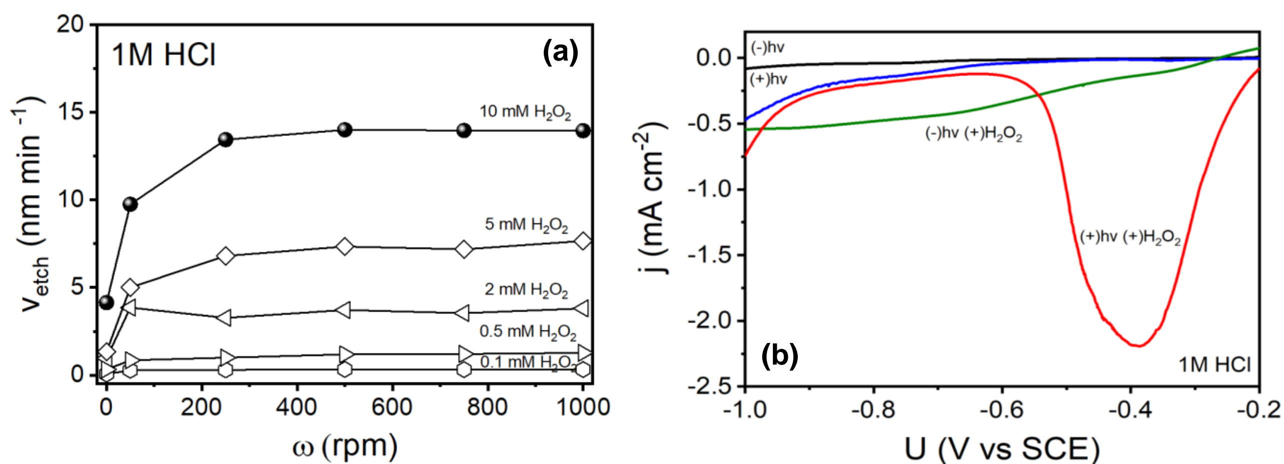

Figure 1: Etch rate of p-type Ge (100) as a function of rotation rate for various H_2O_2 concentrations in 1 M HCl solution (a). Cathodic j-V curves of p-type Ge in 1 M HCl in the presence and absence of 10 mM H_2O_2 with 0.01 V s-1 scan rate at 500 rpm under illumination and dark conditions (b).

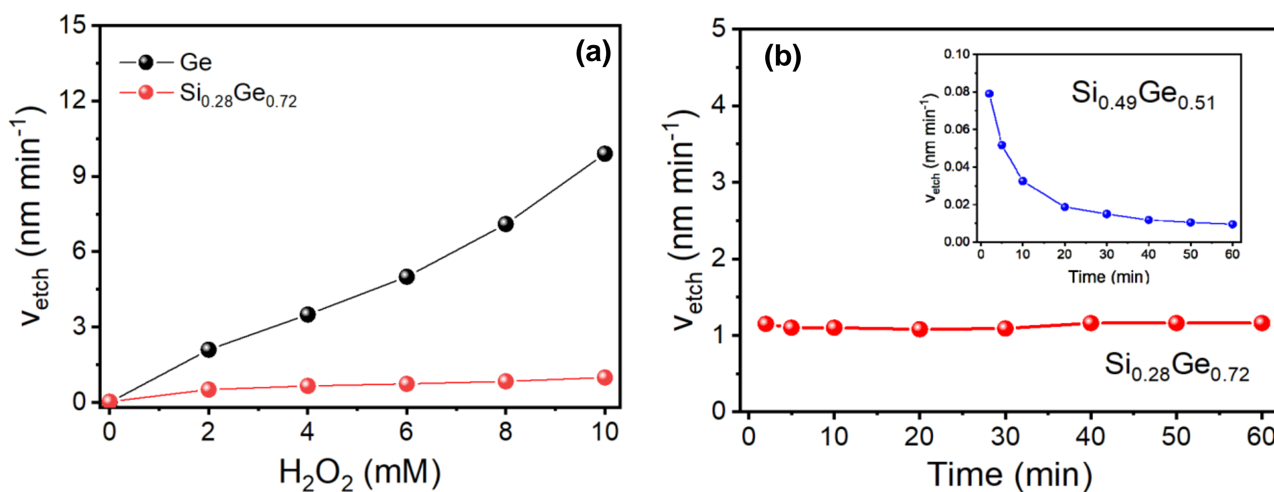

Figure 2: Etch rate of Ge versus $Si_{0.28}Ge_{0.72}$ as a function of H_2O_2 concentration in 0.1 M HCl (a). Time-dependent etching of $Si_{0.28}Ge_{0.72}$ and inset: $Si_{0.49}Ge_{0.51}$ in 0.1 M HCl/10 mM H_2O_2.

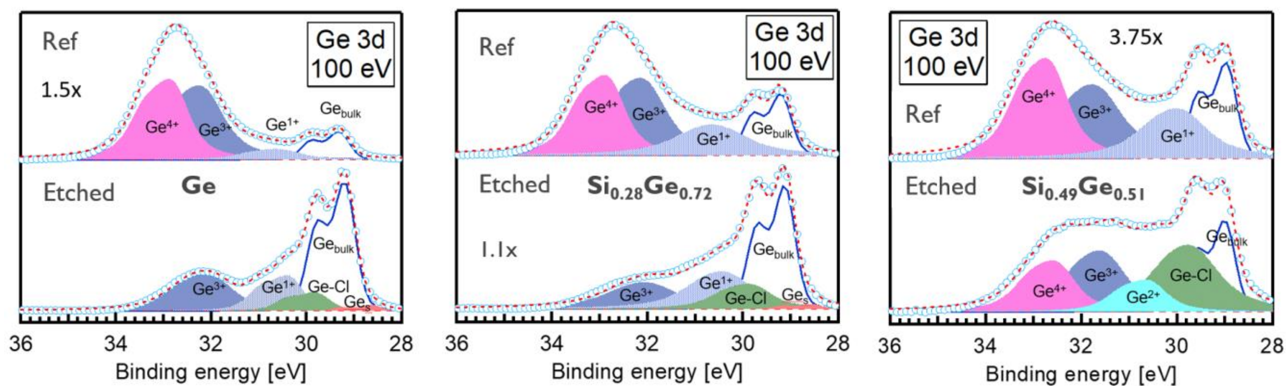

Figure 3: Surface sensitive Ge 3d synchrotron XPS spectra for Ge versus SiGe etched in 1M HCl/10 mM H_2O_2 solution. The reference spectra were samples with native oxide grown in O_3/H_2O solution.

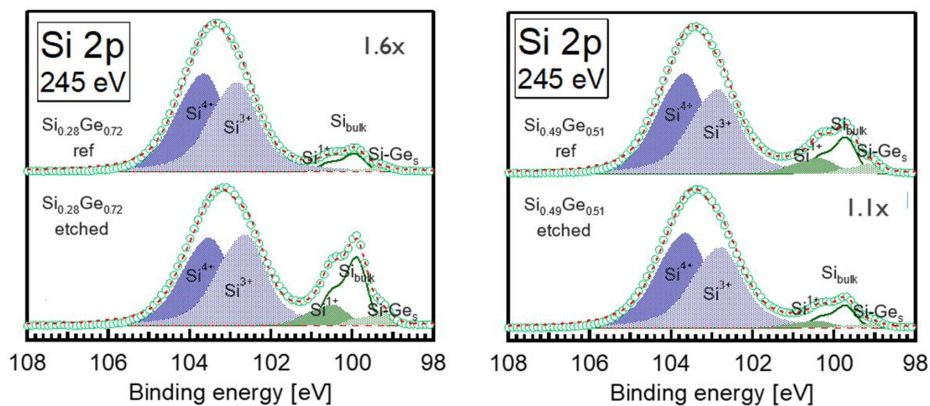

Figure 4: Surface sensitive Si 2p synchrotron XPS spectra for SiGe etched in 1M HCl/10 mM H_2O_2 solution with the O_3/H_2O references spectra shown above.