Materials Science in Semiconductor Processing 13 (2010) 71–79

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

New insights into acidic wet chemical silicon etching by $HF/H_2O–NOHSO_4–H_2SO_4$ solutions

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ARTICLE INFO

Available online 8 April 2010

Keywords:
Semiconductors
Etching
Chemical techniques

ABSTRACT

Acidic wet chemical etching of crystalline silicon has been examined by utilization of $HF–NOHSO_4–H_2SO_4$ mixtures. In light of our previous studies the effects of nitrosyl ion concentrations on etching rates were studied time- and temperature resolved. The reactivity of crystalline silicon surfaces in HF/H_2SO_4 solutions is determined by NO^+-ion concentrations at the silicon/electrolyte interface, measured by ion chromatography. Quantitative solution analysis proofed accumulation of ammonium ions and indicated the conversion of NO^+ as limiting for the overall etching process. Direct participation in the rate-limiting step was confirmed by calculation of activation energies. Increasing NO^+-ion contents cause transition from reaction ($E_A = 55\,kJ\,mol^{-1}$) to diffusion controlled ($E_A = 10\,kJ\,mol^{-1}$) etching procedures. In combination with time and concentration dependent studies of produced structures a convenient regime for selective texturing or polishing polycrystalline silicon surfaces is reported. Qualitative analysis by ^{19}F-NMR and *Raman* spectroscopy identified SiF_5^-/HF_2^- complexes as well as elementary hydrogen (H_2) as hitherto unknown products of silicon dissolution reactions in $HF–NOHSO_4–H_2SO_4$ mixtures. Based on our findings a strategy for fundamental investigations of relevant reaction pathways is presented and discussed with regard to reported mechanistic concepts.

1. Introduction

Acidic wet chemical etching processes are extensively applied by the electronic and solar industry in order to remove impurities and saw damage, texture surfaces or decorate defects [1]. Though $HF–HNO_3–H_2O$ solutions are widely utilized, fundamental chemical reaction steps are roughly understood and therefore in need of detailed investigation.

Chemical dissolution of silicon includes two general reaction stages: the stepwise silicon oxidation by oxidizing agents and the formation of water soluble silicon complexes. According to *Robbins* and *Schwartz* conventional isotropic silicon etching might produce SiO_2 (Eq. (1)), accompanied by H_2SiF_6 formation (Eq. (2)) [2–5]. The overall reaction can be written as Eq. (3) and is thought to be limited by diffusion or reaction steps of minority reactants (HNO_3 or HF)

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \quad (1)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (2)$$

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \quad (3)$$

Recent fundamental studies of $HF–HNO_3–H_2O$ mixtures agree in the concept of nitrogen–oxygen cations being important species, which are formed as reaction intermediates and are crucially involved in silicon oxidation processes [6–13]. In particular, reactions of nitrosyl ions (NO^+) with hydrogen terminated surface silicon

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doi:10.1016/j.mssp.2010.03.001

atoms are proposed as rate determining steps, illustrated by the simplified Eq. (4)

$$\mathrm{Si}_{4-n}{=}\mathrm{SiH}_n + x\mathrm{NO}^+ \rightarrow \mathrm{Si}_{4-n}{=}\mathrm{H}_n + \mathrm{Si}^{4+} + (x-y-z)\mathrm{NO} + y\mathrm{N_2O} + z\mathrm{NH_4^+} \quad (4)$$

Thus, advanced mixtures based on nitrosyl ion solutions are promising systems for detailed investigations of acidic etching reactions. Due to their instability in aqueous solutions, concentrated sulphuric acid (97% H_2SO_4) has to be added in excess [14]. As reported previously, HF–$NOHSO_4$–H_2SO_4 mixtures exhibit a strong reactivity towards crystalline silicon [9,12,14]. Nitrosyl ions are reduced to various reaction products (NO, N_2O, NH_4^+), while oxidized silicon atoms are dissolved as complex SiF_6^{2-}-ions [12], see Fig. 1.

Supposed intermediates (HNO, NH_3OH^+) are very unstable in highly acidic solutions and proofed analytically elusive so far. Instead of stepwise reduction ammonium ions might be formed by disproportionation reactions.

Etching rates and formed Si(1 0 0) surface structures are controlled by the concentrations of HF- and NO^+-reagents. However, correlations among selective texturing or polishing polycrystalline silicon surfaces in HF-based NO^+-etching solutions are yet unresolved. This work is devoted to fundamental investigations of chemical reactions occurring during crystalline silicon etching by advanced HF–$NOHSO_4$–H_2SO_4 mixtures. Time-dependent correlations among nitrosyl ion concentrations, etching reactivities, resulting etching structures, formed reaction products and activation energies are presented. A mechanistic model is discussed, wherein oxidation of hydrogen terminated silicon surface groups ($\mathrm{Si}_{4-n}{=}\mathrm{SiH}_n$, $n=1\ldots3$) are rate-determining reaction steps.

The etching solution was characterized by IC (ion chromatography) and NMR (nuclear magnetic resonance) spectroscopy, produced gases were investigated by means of *Raman* spectroscopy. The formed polycrystalline silicon surface morphologies were analyzed by scanning electron microscopy (SEM) and DR/FT-IR (diffusive reflectance Fourier transformation infrared spectroscopy) measurements.

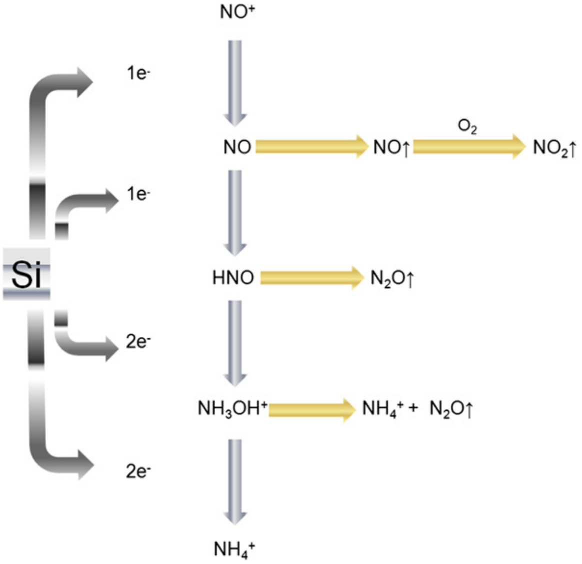

Fig. 1. Potential NO^+-ion redtuction pathways and generated products during wet chemical silicon etching in HF-based solutions.

2. Experimental section

2.1. Preparation of HF–$NOHSO_4$–H_2SO_4 etching solutions

Caution: All manipulations were performed in a HF-proof hood. The concentrations of the solutions are given in weight percent (wt%) in reference to concentrated acids. Analytical grade sulphuric acid (97%, 18.78 mol l^{-1}, *Merck*), hydrofluoric acid (40%, 22.77 mol l^{-1}, *Fluka*) and deionized water (DI) were used. The total volume of a typical etching mixture was 50 ml. For a given solution, 40% HF (10 wt%) means that the used etching solution contains 10 weight percent of 40% hydrofluoric acid.

$NOHSO_4$ was synthesized by bubbling dried SO_2 into HNO_3 (100%, *Fluka*) for several hours, followed by *Schlenk*-filtration and rinsing with CH_3COOH (100%) and CCl_4 under inert gas atmosphere (Ar) Eq. (5) [15]

$$\mathrm{HNO_3} + \mathrm{SO_2} \rightarrow \mathrm{NOHSO_4} \quad (5)$$

The etching solutions were prepared by slowly mixing the components in a high density polyethylene (HDPE) beaker. For inert gas investigations a 250 ml PTFE three necked flask, equipped with PTFE ball valves, a plug and tubes were used under argon atmosphere. The temperature was kept constant during the series of experiments ($T=20\,^\circ C$) using a thermostat (Julabo ECF-12). Differing reaction conditions are mentioned explicitly.

2.2. Silicon materials and etching procedure

Multicrystalline silicon wafers (boron doped, thickness 330 μm, resistivity 0.5–2.0 $\Omega^{-1}\,cm^{-1}$, *Deutsche Solar AG*, Freiberg, Germany) were cut into pieces of about $2\times2\,cm^2$ and immersed into the etching solution after weighing. During the etching procedure the solution was not agitated by a magnetic stirrer, but stirred between the etching experiments. All reactions were quenched by removing the silicon wafer pieces out of the bath with Teflon tweezers and rinsing them with deionized water and acetone. The samples were dried and analyzed. Etching rates (nm s^{-1}) were determined by differential weighing.

2.3. Spectroscopic characterization of etching mixtures, gases and silicon surfaces

NMR spectra of etching solutions were measured using a Bruker DPX 400 spectrometer and Teflon inserts. The resonance frequency and reference standard for the ^{19}F nucleus is $CFCl_3$ (376 MHz).

Raman spectra of the produced gases were recorded with a T64000 (Hariba Jobin Yvon) instrument. The samples were excited by 514.532 nm radiation of an ILA 120 (Carl-Zeiss Jena) Ar-ion laser. The scattered light was collected in 90° geometry.