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# Influence of metallic catalyst and doping level on the metal assisted chemical etching of silicon

A. Backes [*], A. Bittner, M. Leitgeb, U. Schmid

*Institute of Sensor and Actuator Systems, Vienna University of Technology, Floragasse 7, 1040 Vienna, Austria*

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ABSTRACT

The presented work shows a study of the boundary condition between metal and silicon, in metal assisted chemical etching. This is achieved by varying silicon doping type and concentration as well as metal type and oxidation agent concentration. First, the etch rate dependence of silver particles, on n- and on p-doped samples is investigated revealing different etch rates depending on doping concentration. Additional experiments using an etch solution containing no oxidation agent show an impact of the metal–semiconductor combination on the etch process. In this case the higher work function of Pt particles compared to Ag leads to an etching independent of silicon doping.

In the widely accepted model for metal assisted chemical (MAC) etching described by Chartier et al. [1], a positive charge is injected via the metal (catalyst)–semiconductor contact into the silicon surface. To understand the influence of different metals, the Fermi level $E_f$ of the semiconductor has often been compared with the redox potentials of the etch solution [2,3]. Within this work, we vary systematically the metal–semiconductor junction properties in order to clarify the impact on the MAC etching performance. Typical metals used for MAC offer work functions $\varphi_m$ towards vacuum that are either located in the band diagram above the conduction band edge of silicon like Pt, Pd and Au or between the valence and the conduction band edge like Ag [4–8]. The difference $\Delta_{if}$ between the metal ionization Energy $\varphi_m$ and the Fermi level $E_f$ varies for a given metal–semiconductor combination, if the position of $E_f$ is changed. For Pt–Si, only negative values are possible while for Ag–Si the contact potential (CP) can be either positive or negative, as $E_f$ changes with doping concentration and temperature [9]. For the combination of intrinsic silicon and silver at 300 K, the value of $\Delta_{if}$ is about $+0.3^{\circ}$eV. This value increases with p-doping, as the Fermi level is lowered, and decreases with n-doping, turning even into negative values. Therefore, the accumulated charges at the interface are either positive or negative depending on the pre-sign of $\Delta_{if}$. As a consequence, locally different space-charge regions build up at the silicon surface with different boundary conditions, since the redox potential of the etch solution presents a condition different from the metal covered regions. To investigate the influence of the Schottky contact on the etching it is desirable to limit the overall reaction by the charge transition between catalyst and silicon. For this reason an etchant with a low $H_2O_2$ concentration was chosen governing the etch rate by the proton supply, which originates from the $H_2O_2$ decay [1]. Those etchants produce straight pores penetrating perpendicular into the silicon surface with high aspect ratios [10]. Additionally experiments without $H_2O_2$ were carried out to eliminate the influence of the additional proton source to reveal the influence of the contact potential. Furthermore, a clean semiconductor surface is important to exclude parasitic effects on the barrier height, like residual oxides or any other contaminations [9]. The most common deposition techniques for the catalyst are sputtering [1] and evaporation [11], particle deposition through metal salt reduction [12] or sedimentation of dispensed particles [5], respectively. In this study, sputter deposition is applied followed by a thermal dewetting step. This is for two reasons: Sputtering offers the possibility for an in-situ cleaning of the substrate surface and thermal dewetting allows creating particles on the substrate without any additional chemical treatment.

For this study, eleven single-side polished, (100)-oriented silicon wafers were used having different properties. Five of these samples were boron doped with a concentration ranging from $10^{12}$ to $10^{19}\,cm^{-3}$. The six n-doped samples offer a phosphorous concentration between $10^{13}$ and $10^{19}\,cm^{-3}$. Table 1 gives a detailed summary of the sample details as provided by the silicon manufacturer. The Fermi level $E_f$, depending on doping concentration $N_D$ ($N_A$) and type, was calculated using a full ionization approximation. The corresponding values for the intrinsic carrier concentration $n_i$ and intrinsic Fermi level $E_i$ were taken from [9].

Prior to further processing the samples were cleaved into pieces of $10 \times 10^{\circ}mm^2$ and rinsed with acetone and 2-propanol, followed by

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[*] Corresponding author.

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**Table 1**
Properties of the used silicon wafers, ordered according their calculated contact potential values.

| $\Delta_{if}$ to silver [eV] | 0.795 | 0.768 | 0.593 | 0.517 | 0.398 | 0.052 | 0.013 | $-0.024$ | $-0.084$ | $-0.126$ | $-0.315$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Resistivity [Ω cm] | <0.005 | <0.014 | 2.75 | 52.5 | >5000 | 200 | 52.5 | 10 | 1.5 | 0.3 | <0.002 |
| Doping level [$cm^{-3}$]/type | $>1.5 \cdot 10^{19}$/p | $>4 \cdot 10^{18}$/p | $3.9 \cdot 10^{15}$/p | $2.6 \cdot 10^{14}$/p | $<2.3 \cdot 10^{12}$/p | $2 \cdot 10^{13}$/n | $9 \cdot 10^{13}$/n | $4 \cdot 10^{14}$/n | $3.1 \cdot 10^{15}$/n | $1.8 \cdot 10^{16}$/n | $<3.1 \cdot 10^{19}$/n |

chemical cleaning within a $H_2SO_4$:$H_2O_2$ solution for 10 min at 82 °C. Next, a 30 second etch in hydrofluoric acid (HF) is applied. After rinsing with deionized water, the samples were directly transferred into high vacuum “LS 730 Von Ardenne” sputter deposition equipment. After in-situ substrate cleaning in an argon (Ar) plasma for 60°s at 1000°W, a 15°nm silver (Ag) film was deposited at an electrode distance, a plasma power, a back pressure and an Ar gas flow rate of 88°mm, 100°W, 6°μbar and 60°sccm, respectively. Slightly modified parameters (i.e. 88°mm, 150°W, 3°μbar and 60°sccm Ar) were used for the deposition of the corresponding platinum layers having again a thickness of 15°nm. In both cases film thickness was controlled via the sputter time with a prior determined deposition rate for the parameter set used. After the deposition, the Ag (Pt) films were exposed to a peak temperature of 523 K (1173 K) for 600°s (120°s) under atmospheric conditions. Both films agglomerate into a homogenous distribution of particles on the sub-μm scale length, verified with a scanning electron microscope (SEM). To ensure identical conditions for all samples, the surfaces were investigated after dewetting using the open source image processing software “ImageJ V1.45”. The surface fraction covered by metal particles was calculated through the detection of closed contours with similar grey scale. Further details with respect to the particle formation can be found elsewhere [13]. Before all etching experiments, the degree of metal coverage on the silicon surface was measured. Silver particles with diameters between 100 and 800 nm cover the surface by 43% (±2%). In contrast, two types of particles form when dewetting platinum: particles with a size from about 100 to 500°nm that resembled the pattern resulting from silver dewetting, and spherically-shaped particles with diameters between 10 and 50°nm. The surface coverage of silicon by the large particles was determined to 32% (±5%), whereas the smaller particles exhibit a value of about 8% (±15%).

After the sample preparation two sets of experiments were carried out: the first sample set comprising the 11 wafer modifications was loaded with silver particles and immersed in a solution consisting of 5.4°M/l HF and 0.18°M/l $H_2O_2$ at room temperature. The samples were etched simultaneously under stirring conditions in 200°ml solution for 10 min. Prior to the etching experiments the redox potential of the etch solution was determined to be 650 mV, compared to standard Hydrogen Potential, using a Mercury–mercurous sulfate reference electrode.

In the second experiment four selected samples prepared with Ag as well with Pt particles were exposed to 200°ml HF solution with 5.4°M/l for 30°min under stirring conditions.

After etching, the samples were rinsed with DI water, dried and the surface-near porosified samples were cleaved. A Hitachi SU8020 scanning electron microscope is applied to determine the etch depth, the morphology of the pores and the microstructure of the adjacent regions.

Fig. 1 shows cross-sectional SEM images after etching of silicon in a HF/$H_2O_2$ with silver particles. All samples show a front of particles penetrating into the substrate, thus generating macro-pores with low depth deviation. The straight-lined pores are arranged perpendicular to the silicon surface, following the (100) direction. The initially silver-free surface appears roughened due to the isotropic silicon etching of the HF/$H_2O_2$ solution [14]. For high doping levels $>10^{17}$ $cm^{-3}$ meso-porous silicon is generated in the areas adjacent to the pores, whereas moderately doped samples exhibit solid silicon in combination with a straight pore geometry. These results are in good agreement with observations reported in previous studies for highly doped samples [8,15].

In Fig. 2, the etch depths are shown as a function of the contact potential between silver and silicon. In a wide range between −0.2 and +0.6°eV, the etch rate is within the measurement accuracy independent of doping level and dopant type. In the case of p-doped samples (>0.4 eV) the results match previously reported findings [13].

In the experiments without hydrogen peroxide only four samples with the highest and lowest doping representing the maximum and minimum $\Delta_{if}$ values for each dopant type were used. In the case of silver particles the corresponding $\Delta_{if}$ values are as follows: 0.35°eV which is close to the undoped (i.e. intrinsic) case, −0.07°eV which is closest to zero, and −0.3°eV and +0.8°eV representing the minimum and maximum values. The p-doped samples were etched with 10°nm/min resulting in straight pores. The moderate n-doped sample ($\Delta_{if}$ = 0.07°eV) shows also an etch attack, but as the particles inclined during the penetration into the silicon only an estimation on the etch rate can be given. As no particles were found to have etched deeper than 300°nm, the etch rate is assumed to be lower than 10°nm/min. On the highly n-doped sample ($\Delta_{if}$ = −0.3°eV) the silver particles did not penetrate into the surface, but meso-porous silicon formed surface-near in the vicinity of the particles, the meso-porous silicon also formed for high p-doped samples ($\Delta_{if}$ = 0.8°eV). As illustrated in Fig. 3, high p-doped samples even show etching with a rate of about 10°nm/min.

The MAC experiments without hydrogen peroxide were also performed using platinum (Pt) particles, as shown in Fig. 4. The etch rates range from ~5°nm/min for highly p-doped to ~1.5°nm/min for highly n-doped samples. Only this fraction of particles having a size larger than 100°nm penetrates into the silicon, while the rest remains on the

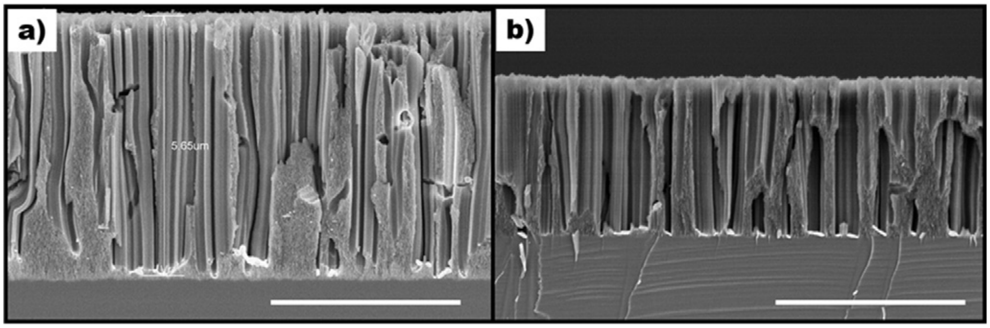

**Fig. 1.** N-doped silicon samples CP = −0.3 eV (a), p-doped silicon samples (CV = +0.8°eV) (b). All samples were exposed for 10 min to a $H_2O_2$/HF mixture. The white scale bars correspond to 4 μm.