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Communication—Controlling Etching of Germanium through Surface Charge Manipulation

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Potassium hydroxide (KOH) aqueous solutions can effectively etch germanium. Etch rates were determined in an electrolytic etch cell. Electrically isolated Ge wafers were subject to an etch rate of 1.45 ± 0.07 nm min^{-1}, increasing to 12.6 ± 0.2 nm min^{-1} when grounded, 97 ± 2 nm min^{-1} when biased at −0.9 V, and 138 ± 2 nm min^{-1} with periodic biasing. Results suggest that the previously reported limited etching in KOH is associated with the recombination of holes with electrons injected from the surface reaction. The results of this study demonstrate that changing the hole concentration through biasing is an effective tool to control electrolytic etch rates, enabling future selective etching processes for germanium.

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Germanium is a promising alternative for next-generation backside imagers since recent homoepitaxial growth has yielded extraordinarily low defect densities.[1–4] The intrinsic properties of germanium enable high-speed hard X-ray detection, and absorption in the near-infrared regime where silicon is essentially transparent.[1,5] Furthermore, germanium is suited as a potential foundational material in the growing field of quantum computing.[6,7] The manufacturing of ultra-thin diode devices necessitates the removal of the substrate employed for homoepitaxial growth. For silicon this task is commonly achieved through selective etching. For germanium, however, new etching techniques are required due to the fundamental differences in chemistry and oxidation behavior compared to silicon. Etching is initiated by an oxidizing agent, typically hydrogen peroxide or nitric acid, to form a germanium oxide complex. The subsequent dissolution of the oxide is commonly performed by acids such as HF, H_3PO_4, H_2SO_4, and HCl. Bases like NaOH and tetramethylammonium hydroxide have also been employed. Potassium hydroxide (KOH) is a common selective etchant for silicon capable of achieving etch selectivity over 100 between intrinsic and p-type silicon.[8,9] While used as the dissolution agent in multicomponent etchants for germanium,[10,11] KOH alone is considered ineffective to etch germanium[10–12] since the electronegativity of the hydroxide ions is insufficient to break Ge-Ge back bonds.[12,13] Despite the large disparity between etch rates of germanium and silicon in KOH, Ge-doped silicon has proven ineffective as an etch stop. A detailed mechanistic explanation for this observations has not yet been reported.[9,13]

Experimental

Etching of the (100) surface of single crystal n-type undoped germanium wafers (>50 ohm-cm) was carried out in five different etch solutions. Each sample was cleaned before and after etching in sonication baths of acetone, deionized (DI) water, and methanol, and blow-dried to a specular finish. For electric contact, 300 nm of silver was thermally evaporated onto the back and side surfaces of the germanium wafers. Potassium hydroxide-based etchant solutions were composed of a 45 wt% KOH solution (electronic grade), DI water (∼16 MΩ-cm), and tertbutyl alcohol (TBA) with a volumetric composition ratio of 5:14:1, respectively. Hydrogen peroxide-based solutions were composed of 30% H_2O_2 (electronic grade), DI water, and TBA with a ratio of 6:11:1 by volume with 5 g of sodium phosphate monobasic monohydrate added to stabilize the peroxide. Phosphoric acid solutions consisted of equal volumes of 85% H_3PO_4 (electronic grade), H_2O_2, and DI water. Sodium hydroxide-based solutions contained a concentration of 2 N NaOH dissolved in 2:1 by volume mixture of DI water and 30% H_2O_2. Etching was also carried out in pure DI water.

NaOH- and H_3PO_4-based etch experiments were carried out at 25 °C by dipping Ge wafers halfway into beakers filled with the respective etchant solution. Etch experiments with H_2O_2- and KOH-based solutions were performed at 25 °C in a previously described custom-built electrolytic etch cell[2] under continuous stirring at 1800 rpm. During experiments labeled as "isolated" Ge wafers were electrically insulated and no reference electrode (RE) or counter electrode (CE) was used. Experiments labeled as "grounded" employed a platinum CE with the Ge wafer acting as the working electrode (WE). For cyclic voltammetry and biased etch experiments a Mercury/Mercury oxide RE was utilized.

A differential step-height contact profilometer (Bruker Dektak XT 2D) was used to determine topographic profiles of the etched surfaces. Topography profiles were extended over unetched regions for calibration, and effective etch depths and rates were determined from acquired profiles.

Results and Discussion

Figure 1 compares the experimentally determined etch rates for the five different etchants. Isolated etching with H_3PO_4 and NaOH resulted in similar etch rates of approximately 300 ± 7 nm min^{-1}. Etch rates observed for H_2O_2 were 30.4 ± 0.4 nm min^{-1}. Significantly smaller rates of 1.45 ± 0.07 nm min^{-1} and 0.47 ± 0.06 nm min^{-1} were observed for isolated KOH and DI water, respectively. Establishing an electric circuit by grounding the Ge wafer resulted in an increased etch rate of 12.6 ± 0.2 nm min^{-1} in KOH.

The nearly 10-fold increase in etch rate between grounded and isolated germanium in KOH-based etchant demonstrates the ability to etch germanium at a rate comparable to hydrogen peroxide. The previously reported inability of KOH to etch germanium[9,13] must therefore be related to limitations of surface charge dissipation. Completing the electrochemical circuit enables charge transfer and sustains the surface oxidation reaction. An electric potential difference of 0.526 ± 0.004 V is detected by the RE during the grounded etch experiment. For isolated experiments, the galvanic reaction leads to a negatively charged surface due to the injection of electrons. In this case hydroxyl ions in the etchant are repelled

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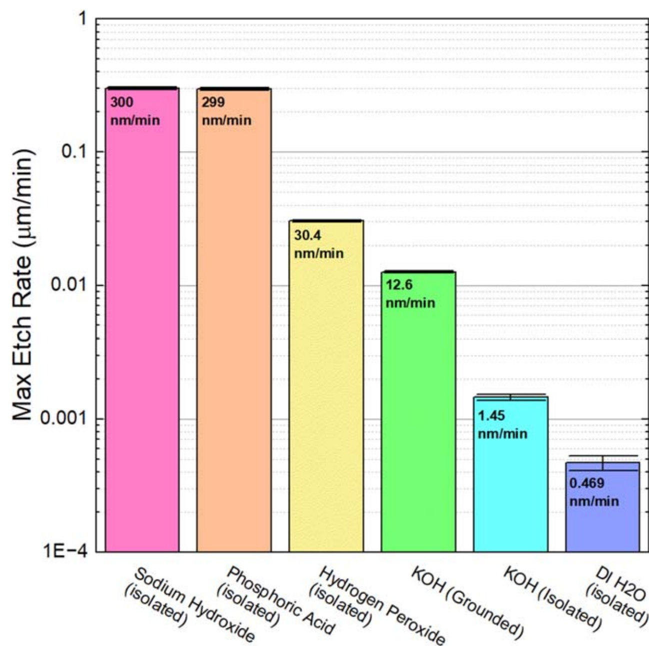

Figure 1. Maximum etch rates for (100) germanium surfaces in different etch environments. "Isolated" denotes an electrically isolated sample.

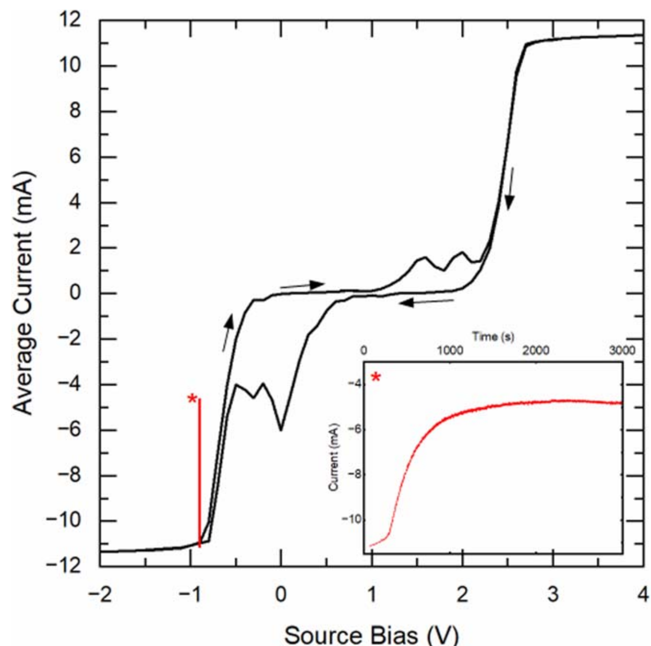

Figure 2. Current as a function of applied bias recorded during cyclic voltammetry in KOH-based etch solution. Arrows indicate the direction of voltage sweeping. Inset: current recorded as a function of time for a static bias of −0.9 V (also included in CV marked by asterisk).

from the surface and can no longer sustain the etch process, i.e., oxide formation and subsequent dissolution.

Seidel showed for etching of silicon in KOH that the presence of holes at the surface allows for the breaking of back-bonds of surface atoms.[8,9,14] Etch selectivity was obtained by controlling the presence of holes through doping. Myamlin and Pleskov[15] derived a model in which the etch rate is dependent on the concentration of holes at the surface. Their equation relates the current of dissolution i_{diss} to the exchange current i_0, surface hole concentration p_s, transfer coefficient β, and the potential drop across the electric double layer (EDL), which was calculated as the difference between the potential across the cell φ_0^0, and the potential at the surface of the wafer φ_0:

$$i_{diss} = -i^0 \frac{p_s}{p_s^0} e^{\frac{\beta F(\varphi_0 - \varphi_0^0)}{RT}}, \tag{1}$$

R is the gas constant, and ***F*** is the Faraday constant. Hole assisted etching was previously observed experimentally in the vicinity of metal particles located on the surface of germanium.[16]

Figure 2 is a cyclic voltammogram (CV) recorded for germanium in the KOH-based etchant by rapidly scanning biases and collecting instantaneous current. The polarity of the sample surface switches during CV acquisition, leading to the observed hysteresis behavior. CVs were collected at a polling rate of 5.6 steps/s in increments of 0.1 V. A negative current represents the anodic dissolution of germanium. Current plateaus are observed at −11.5 mA for negative biases at −0.9 V, and 11 mA for positive biases at +2.7 V. Between −0.5 V and +0.8 V, distinct peaks indicate the oxidation of the germanium surface, and reduction reactions occur between +1 V and +2.2 V. The data marked with an asterisk was recorded during an etch experiment with a static bias of −0.9 V. The onset current of −11 mA decreased within the first 1500 seconds of the experiment and reached a steady current around −4.7 mA (see inset of Fig. 2). The decrease of current during the static bias etch experiment results from the formation of an electric double layer (EDL) that impedes charge transport towards the sample surface[8,9,15,17] and limits the total reaction rate to the rate of diffusion. During CV acquisition there is insufficient time to establish a stable EDL. Consequently, etch currents observed in CV experiments are similar to those initially observed at the onset of static bias etching. However, as the EDL forms, the potential drop through the etchant increases resulting in current decreasing (cf Eq. 1). This interpretation is supported by the inset in Fig. 2 displaying that the current recorded in the first 200 s reproduces that observed during CV acquisition.

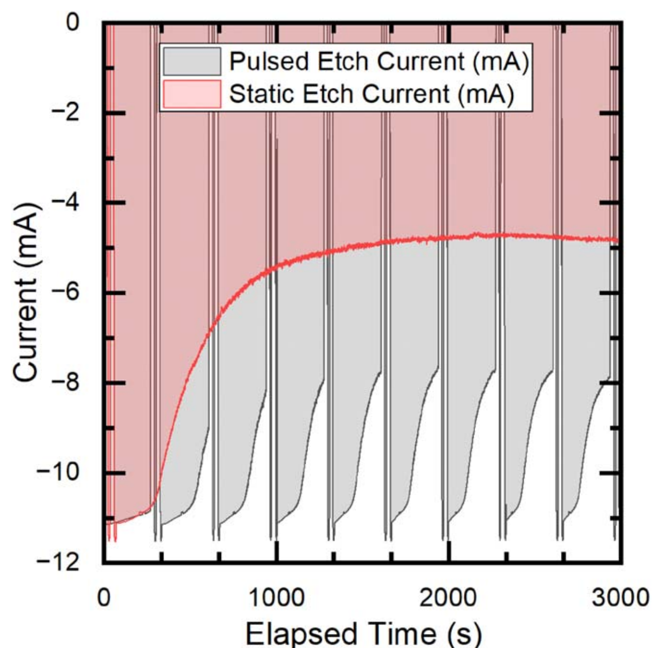

Figure 3. Current as a function of elapsed etch time in KOH for etching at a static bias of −0.9 V and for etching at −0.9 V with intermittent CV acquisition every 5 min. Areas under the curves are shaded to highlight the difference in total charge transfer.

To prevent EDL formation and maintain higher dissolution currents etch experiments were carried out at −0.9 V and interrupted every 5 min to acquire intermittent CVs. The currents recorded during the static and intermittent etch experiments are plotted in Fig. 3. During each interval of constant bias the decline in current is

identical to that of the static etch experiment. After each intermittent CV acquisition the observed current resets to its peak value of approximately −11 mA. We have previously shown that the integrated current is directly correlated to the total mass of etched germanium[2]. Hence, the difference in the shaded areas underneath the curves in Fig. 3 represents the additionally etched germanium due to the disruption of EDL formation.

Static etching resulted in an effective etch rate of 97 ± 2 nm min^{-1}, while intermittent etching increased the rate to 138 ± 2 nm min^{-1}. Imaging and topography characterization revealed no degradation in etched surface quality (see Fig. S1 in supplemental materials). The availability of updated CVs during the etch process has the additional advantage of providing enhanced monitoring of the etch process. The relatively abrupt change in slope of the current recorded during intervals of constant bias (see Fig. 3) identifies the onset of EDL formation, indicating the ideal duration of constant bias application. Shorter periods at constant bias will limit etching. Longer periods of constant bias will limit effective etch rates by decreasing the total current.

Conclusions

This study demonstrates the two order of magnitude enhancement of etch rates for germanium in KOH-based etchant solutions under electrolytic conditions. Oxidation reactions inject electrons into the germanium surface which retards the etch process. Charge transfer in an electrolytic etch cell sustains surface etching and increases the etch rate by more than a factor of 8. Manipulation of the surface charge by biasing was discovered to further increase etch rates by an order of magnitude. Surface charges promote the formation of EDLs in the etchant solution and inhibit diffusion of reacting species. Periodic disruptions of EDL formation by cycling the applied bias sustained higher etch currents and enhanced etch rates. The manipulation of surface charges provides a new avenue towards etch selectivity either through intentional biasing of the surface, or the moderation of hole concentration through doping.

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