Nonlinear Etch Rate of Au-Assisted Chemical Etching of Silicon

Keorock Choi,†‡ Yunwon Song,†‡ Bugeun Ki,†‡ and Jungwoo Oh*,†‡

†School of Integrated Technology, Yonsei University, 85 Songdokwahak-ro, Yeonsu-gu, Incheon 21983, Republic of Korea
‡Yonsei Institute of Convergence Technology, 85 Songdokwahak-ro, Yeonsu-gu, Incheon 21983, Republic of Korea

ABSTRACT: We demonstrated time-dependent mass transport mechanisms of Au-assisted chemical etching of Si substrates. Variations in the etch rate and surface topology were correlated with catalyst features and etching duration. Nonlinear etching characteristics were associated with the formation of pinholes and whiskers. Variable rates of mass transport as a function of whisker density accounted for the nonlinear etch rates of Si. Nanopinholes on Au catalysts facilitated the vertical mass transport of reactants and byproducts, which dramatically changed the etch rate, surface topology, and porosity of Si. The suggested transport models describe the transient mass transport and the corresponding chemical reactions.

INTRODUCTION

Three-dimensional (3D) semiconductor architectures are being adapted to multiple electronic and photonic applications to address technical challenges that are associated with performance and power reduction.1–4 To fabricate high-aspect-ratio semiconductors, dry etching is conventionally used to produce anisotropic vertical profiles. Dry etching exposes a semiconductor surface to ion bombardment in vacuum chambers that are equipped with gas supply systems and a radio frequency generator. Plasma ions dislodge the semiconductor and inevitably cause crystal defects.5 Various types of defects frequently occupy the mid-gap level in the bandgap energy and act as recombination and generation sites. Coulombic scattering decreases carrier mobility, and transient charge trapping and detrapping increase, which tends to compromise both device performance and reliability. As the features of Si integrated circuits have been consistently scaled to the nano level over the years in 3D architecture, researchers have noted that crystallographic defects adversely affect the control of electrostatic potential over highly scaled Si devices. For compound semiconductors, process-induced defects are a more challenging issue because of their elemental stoichiometry.6 Moreover, other challenges associated with dry etching are that the achievable etch depth is limited by the etching direction at the interface of metal catalysts and semiconductors. At low temperatures, MACE of GaAs occurred outside of the catalyst; however, at relatively high temperatures, etching occurred directly under the catalyst.7–10 Catalyst characteristics were associated with the formation of pinholes and whiskers. Variable rates of mass transport as a function of whisker density accounted for the nonlinear etch rates of Si. Nanopinholes on Au catalysts facilitated the vertical mass transport of reactants and byproducts, which dramatically changed the etch rate, surface topology, and porosity of Si. The suggested transport models describe the transient mass transport and the corresponding chemical reactions.
The regime was attributed to the excess electronic holes, which were not completely consumed directly under the catalysts. However, one did not attempt to correlate these physical characteristics (i.e., the porous Si regime and the Si whiskers) with mass transport in chemical etching. In this study, variations in the etch rates as a function of catalyst thickness and etch duration were correlated with the formation of a porous Si regime and the localized Si whiskers. Time-dependent mass transport models were used to describe the nonlinear etch rates during MACE.

RESULTS AND DISCUSSION

Figure 1 shows the tilted scanning electron microscopy (SEM) images of Si substrates after MACE for 10 min with various Au thicknesses. Au catalysts were dot-mesh patterns (4 μm diameter opening and 3 μm space covered with metal) with thicknesses of (A) 20, (B) 30, (C) 40, and (D) 50 nm. The insets show the lateral and vertical dimensions in an enlarged image after etching. Chemical etching with dot-mesh patterns occurred under Au catalysts and formed an array of Si pillars. Reverse chemical etching did not occur. Au catalysts with various thicknesses exhibited substantial differences in the etch rate and surface topology. When relatively thin (20 and 30 nm) Au catalysts were used, as shown in Figure 1A,B, high-aspect-ratio Si pillars were fabricated at an etch rate of approximately 1.3 μm/min. Certain Si whiskers were observed on the Si substrates, as shown in the insets. When the catalyst thickness was increased to 40 nm (Figure 1C), relatively short Si pillars were fabricated at a reduced etch rate of 1 μm/min. When the Au catalyst thickness was further increased to 50 nm (Figure 1D), the etch rate was substantially reduced to 0.2 μm/min, the Si pillars were not shaped correctly, and the topology of the Si
was severely deformed. The results show that as the thickness of Au increases, the lateral etch rate increases while the vertical etch rate decreases. In Figure 1AB, with a thin Au catalyst, a conical shape appeared at the top of the Si pillar after etching. During the etching process, initially, lateral etch was more active than vertical etch for a short period of time. Afterward, vertical etching rate increased, surpassing the lateral etching rate, and a Si pillar structure was formed. Figure 1D, in which a thick Au catalyst was used, shows a tapered conical Si shape. This shows that the lateral etch with a thick Au catalyst is more active than the lateral etch with a thin Au catalyst.

Figure 2 shows the SEM images of the cross section of Si substrates after Au-assisted chemical etching with Au catalysts of various thicknesses for 15 min. To compare the etch characteristics more clearly, chemical etching of Si was conducted on solid-stripe-patterned Au catalysts (8 μm wide metal stripes and 6 μm spaces between stripes) with thicknesses of (A) 20, (B) 30, (C) 40, and (D) 50 nm. A cross section was made on the trenches. Note that Si whiskers were grown in the trenches after chemical etching and the density of the whiskers varied with the thickness of the metal catalyst. Dense Si whiskers were formed on a smooth bottom trench when a thin 20 nm Au catalyst was used, as shown in Figure 2A. In the case of the 30 nm Au catalyst, the etch rate was almost identical and the density of Si whiskers was slightly reduced compared with that of the Si whiskers formed with the 20 nm Au catalyst. Porous Si was observed on the top and gradually decreased, where Si whiskers were present. As shown in Figure 2C, when thick 40 nm Au catalysts were used, the Si etch rates substantially decreased and etching did not occur uniformly under the Au catalysts; moreover, the Si whisker formation was negligible. The 50 nm thick Au catalysts severely deformed the Si substrates, as shown in Figure 2D, and resulted in a rough Si surface topology. Thick catalysts tend to cause a rough surface topology, particularly in the case of micron-scale MACE, because of nonuniform etch rates at the edge and center of the metal catalysts.19,30–32 Long diffusion path during the lateral mass transport causes this phenomenon. Therefore, we attribute the dramatic difference in surface topology and etch rates as functions of the Au catalyst thickness to mass transport through the nanopinholes of the Au catalyst. The dominant transport mechanism switched from lateral to vertical mass transport, with decreasing metal catalyst thickness.

Figure 3 shows the etch-rate variation as a function of etching time for Au catalysts of various thicknesses. Etch depths shown in the inset were measured after chemical etching of solid-stripe patterns of Au catalysts.

Figure 3. Etch-rate variation as a function of etch time for Au catalysts of various thicknesses. Etch depths shown in the inset were measured after chemical etching of solid-stripe patterns of Au catalysts.

The variable etch rates observed for the thin Au catalysts are related to the mass transport of reactants and byproducts via the metal catalyst nanopinholes. When only lateral mass transport occurred for thick metal catalysts, undesirable outcomes such as metal catalyst bending, low etch rates, and porous Si were observed. By contrast, when vertical mass transport occurred with lateral mass transport in the case of the thin metal catalysts, high diffusivity of reactants and byproducts dramatically enhanced the etch rates, micron-scale uniformity, and the surface topology of the Si substrates.19,33 The formation of whiskers indicates that vertical mass transport was enhanced through the nanopinholes. The porous Si remaining on the top surface after etching is related to the whisker formation, which will be discussed in detail later.

Figure 4 shows the progress of whisker formation on the recessed Si substrates in the cross-sectional SEM images after 20 min of etching with 30 nm Au catalysts. As shown in Figure 4A, different heights of whiskers were grown on the recessed Si substrates, which suggests that the rate of whisker formation was time-dependent. High-density whiskers were observed on the bottom Si substrates. Because whiskers were formed via locally distributed nanopinholes in the Au catalysts, this phenomenon was more prominent for the thinner Au catalysts. Another notable feature is the porous Si on the top surface. The voids in Si decreased as chemical etching proceeded along the trench depth. Si tends to be porous because of the lateral diffusion of electronic holes to the other regions of catalysts. The formation of porous Si is related to the amount of excessive holes that cannot be used for etching. In this experiment, a solution of high ρ value was used and the amount of holes produced by H2O2 was not very large. However, in the initial stage of etching, mass transport did not occur smoothly and etching did not proceed well. This resulted in the formation of excessive holes and porous Si despite the small amount of holes generated. Figure 4B compares the densities of whiskers calculated from Figure 4A using ImageJ, which is a two-dimensional image-processing software program. The whisker density increased as a function of etch depth, which supports the etch-rate variation, as shown in Figure 3. Initially, the rate of whisker formation was low, but then it increased sharply and finally saturated. At low rate of whisker formation, lateral mass transport was the dominant mechanism for the
diffusion of reactants and byproducts, which resulted in low and nonuniform etching. As chemical etching proceeded, many whiskers were formed through nanopinholes via short-range MACE; moreover, long-range MACE under the catalysts occurred simultaneously.

Figure 5 shows the mass transport models of nonlinear Au-assisted chemical etching and the corresponding whisker and void distributions. At the initial stage of MACE (A, incubation), short-range MACE in the Au catalyst for whisker formation did not occur. Mass transport for chemical reaction occurred only in the lateral direction of the Au−Si interface. The porous Si tended to form because of the limited diffusivity of the reactants and byproducts. After the incubation stage, nanopinholes began to form in the Au catalysts (B, formation). The mass transport path of the reactants and byproducts required for chemical etching became short via nanopinhol sites, which increased the etch rate and uniformity. Si whiskers grew through the pinholes simultaneously. As the number of pinholes continued to increase, the etch rate increased sharply with enhanced mass transport at the interface of the Au catalysts and Si substrates (C, acceleration). When vertical mass transport drove the redox processes under the Au catalysts, the chemical etching rate dramatically increased. Electronic holes were completely consumed during chemical etching under the catalysts, and a porous region did not appear in the Si substrates. After the acceleration, MACE rate was reduced, presumably because the diffusion of reactants and byproducts was limited at the bottom. Another possible explanation is that the pinholes that improved the mass transport have now weakened the durability of the Au catalysts, reducing the catalytic activity for complete chemical reactions (D, saturation).33

■ CONCLUSIONS

We demonstrated the nonlinear characteristics of Au-assisted chemical etching of Si substrates. The variability in the MACE rate was interpreted as four characteristic stages according to the Si whisker formation and mass transport. The incubation stage represented low and nonuniform etch rates of porous Si. In the formation stage, whiskers were generated via nanopinhol sites. Vertical mass transport facilitated the chemical reactions, which substantially increased the etch rate of Si. As the density of whiskers increased sharply, the etch rate reached its highest value in the acceleration stage. After prolonged etching, the Au catalyst was subject to deformation, which eventually reduced its catalytic activity in the saturation stage.

■ EXPERIMENTAL METHODS

Boron-doped p-type Si(100) substrates with a resistivity of 5−10 Ω·cm were used for MACE. The substrates were precleaned with conventional acetone, isopropanol, and deionized (DI)
water. Dot (4 μm diameter and 3 μm spaces) and stripe arrays (8 μm width and 6 μm spaces) were photosist-patterned using image-reversal optical lithography. Organic residues were descummed using a plasma asher after photolithography. Native oxide was removed using a buffered oxide etchant, and Si substrates were rinsed with DI water before metallization. Au catalysts were thermally evaporated onto the Si substrates at a 2 Å/s deposition rate under a 10−6 Torr pressure. Various thicknesses (20, 30, 40, and 50 nm) of Au catalysts were deposited onto the Si substrates after liftoff. 

Etching was stopped by thoroughly rinsing the sample with DI water and drying it in an N2 stream. The height of the etched structure was measured using field-emission SEM, and the etch rate was calculated based on the pillar height.

### REFERENCES

1. Colinge, J.-P. Multiple-gate SOI MOSFETS. Solid-State Electron. 2004, 48, 897−905.
2. Cui, L.-F.; Ruffo, R.; Chan, C. K.; Peng, H.; Cui, Y. Crystalline-amorphous core−shell silicon nanowires for high capacity and high current battery electrodes. Nano Lett. 2009, 9, 491−495.
3. Hallbax, M.; Sarnet, T.; Delaporte, P.; Sentis, M.; Etienne, H.; Torregrosa, F.; Vervisch, V.; Perchaud, I.; Martinuzzi, S. Micro- and nano-structuration of silicon by femtosecond laser: A review of characteristics and applications in photovoltaics. Curr. Opin. Solid State Mater. Sci. 2012, 16, 71−81.
4. Balasundaram, K.; Sadhu, J. S.; Shin, J. J.; Azeredo, B.; Chanda, D.; Malik, M.; Hsu, K.; Rogers, J. A.; Ferreira, P.; Sinha, S.; Li, X. Porosity control in metal-assisted chemical etching of degenerately doped silicon nanowires. Nanotechnology 2012, 23, 305304.
5. Chartier, C.; Bastide, S.; Lévy-Clement, C. Metal-assisted chemical etching of silicon in HF−H2O2. Electrochim. Acta 2008, 53, S509−S516.
6. Tsujino, K.; Matsumura, K. Helical nanoholes bored in silicon by wet chemical etching using platinum nanoparticles as catalyst. Electrochem. Solid-State Lett. 2005, 8, C193−C195.
7. Choi, K.; Song, Y.; Oh, L.; Oh, J. Catalyst feature independent metal-assisted chemical etching of silicon. RSC Adv. 2015, 5, 76128−76132.
8. Geyer, N.; Fuhrmann, B.; Huang, Z.; de Boor, J.; Leipner, H. S.; Werner, P. Model for the mass transport during metal-assisted chemical etching with contiguous metal films as catalysts. J. Phys. Chem. C 2012, 116, 13446−13451.
9. Tsujino, K.; Matsumura, K. Boring deep cylindrical nanoholes in silicon using silver nanoparticles as a catalyst. Adv. Mater. 2005, 17, 1045−1047.
10. Peng, K. Q.; Hu, J. J.; Yan, Y. J.; Wu, Y.; Fang, H.; Xu, Y.; Lee, S. T.; Zhu, J. Fabrication of single-crystalline silicon nanowires by scratching a silicon surface with catalytic metal particles. Adv. Punct. Mater. 2006, 16, 387−394.
11. Lai, C. Q.; Cheng, H.; Choi, W. K.; Thompson, C. V. Mechanics of catalyst motion during metal assisted chemical etching of silicon. J. Phys. Chem. C 2013, 117, 20802−20809.
12. Li, L.; Liu, Y.; Zhao, X.; Lin, Z.; Wong, C.-P. Uniform vertical trench etching on silicon with high aspect ratio by metal-assisted chemical etching using nanoporous catalysts. ACS Appl. Mater. Interfaces 2014, 6, 575−584.
13. Chen, C.-Y.; Liu, Y.-R.; Tseng, J.-C.; Hsu, P.-Y. Uniform trench arrays with controllable tilted profiles using metal-assisted chemical etching. Appl. Surf. Sci. 2015, 333, 152−156.
14. Song, Y.; Oh, J. Thermally driven metal-assisted chemical etching of GaAs with in-position and out-of-position catalyst. J. Mater. Chem. A 2014, 2, 20481−20485.
15. Chen, S. L.; Chung, C. H.; Lee, H. C. A study of the synthesis, characterization, and kinetics of vertical silicon nanowire arrays on (001) Si substrates. J. Elec. Chem. Soc. 2008, 155, D711−D714.
16. Zahedinejad, M.; Farimani, S. D.; Khaje, M.; Mehrara, H.; Erfanian, A.; Zeinali, F. Deep and vertical silicon bulk micromachining using metal assisted chemical etching. J. Microech. Microeng. 2013, 23, 055015.
(29) Um, H.-D.; Kim, N.; Lee, K.; Hwang, I.; Seo, J. H.; Yu, Y. J.; Duane, P.; Wober, M.; Seo, K. Versatile control of metal-assisted chemical etching for vertical silicon microwire arrays and their photovoltaic applications. *Sci. Rep.* 2015, 5, 11277.

(30) Lianto, P.; Yu, S.; Wu, J.; Thompson, C. V.; Choi, W. K. Vertical etching with isolated catalysts in metal-assisted chemical etching of silicon. *Nanoscale* 2012, 4, 7532–7539.

(31) Cheung, H.-Y.; Lin, H.; Xiu, F.; Wang, F.; Yip, S.; Ho, J. C.; Wong, C.-Y. Mechanistic Characteristics of Metal-Assisted Chemical Etching in GaAs. *J. Phys. Chem. C* 2014, 118, 6903–6908.

(32) Asoh, H.; Suzuki, Y.; Ono, S. Metal-assisted chemical etching of GaAs using Au catalyst deposited on the backside of a substrate. *Electrochim. Acta* 2015, 183, 8–14.

(33) Song, Y.; Ki, B.; Choi, K.; Oh, I.; Oh, J. In-plane and out-of-plane mass transport during metal-assisted chemical etching of GaAs. *J. Mater. Chem. A* 2014, 2, 11017–11021.