

Synchrotron-radiation-induced Wet Etching of Germanium

Q. Ma, N. Moldovan, D. C. Mancini, R. A. Rosenberg
Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Etching of germanium (Ge) has been investigated with regard to both substrate preparation for subsequent epitaxial growth and microfabrication for electronics and optics applications. It has been demonstrated that Ge can be etched chemically and thermally by using various agents, including peroxide solutions and water vapor [1-4]. Here, an x-ray-induced chemical wet-etching process for Ge is described. The process employs synchrotron radiation (SR) and uses water or dilute acid solutions as etchants. It produces etched surfaces with a surface roughness of about 5 Å with a moderate etching rate.

Methods and Materials

The samples were intrinsic (i-type), n-type, and p-type Ge wafers (Montco Silicon Tech., Inc.). The resistivity for the p- and n-type samples ranged from 0.05 to 0.4 Ω-cm. The wafers were cut into small rectangular shapes that were then cleaned by using standard degreasing procedures and dried with N₂. Deionized water and four solutions of HNO₃:H₂O with concentrations equal to 2.0%, 3.5%, 5.0%, and 9.0% were used in the etching experiments. Dark etching tests showed that the surface oxide dissolved in water with no indication of H₂O-induced oxidation.

The etching experiments were performed on a bending magnet beamline (2-BM) at the APS. A Pt-coated mirror was employed at an angle of incidence of 0.15°, which attenuates photons with energies above 35 keV. A plastic cell was used to house the etching solutions and samples [5]. It has an opening on one side that can be O-ring-sealed by a 0.125-mm-thick Kapton window by using a flange. The flange can hold both a patterning mask and an entrance slit (2 × 20 mm²). The latter defines the exposed area on the sample. The distance between the sample surface and the mask can be adjusted from 2 to 5 mm. The sample was vertically scanned at 4 mm/s across the x-ray beam to produce a uniform exposure. The x-ray-exposure area on the sample is determined by a horizontal and vertical slit. To check for any possible x-ray beam size effects on etch rate [6], the size and position of the illumination is changed by using the vertical slit while keeping the horizontal slit unchanged. After x-ray transmission through a 3-mm-thick solution, x-ray photons with energies of > 6 keV impinge on Ge wafers [5].

Results

A gold mask for deep x-ray lithography was used to print various sizes of stars on Ge wafers. Figure 1 shows a photograph of a star pattern etched on a p-type Ge wafer by using deionized water as the etchant under x-ray illumination. The feature depth is about 1.1 μm. For an averaged electron current of 85 mA in the storage ring, the etch rate is ~3 nm/min. Note that for these experiments, there were no suitable masks available to demonstrate the lateral resolution. Optical microscopy indicated that the stars on the gold mask were not very well fabricated; in particular, the edges were not sharp and uniform. However, the resolution estimated from the sharpest feature that could be found on the etched pattern was < 1 μm.

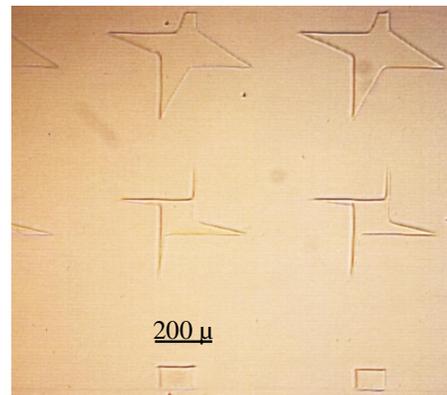


FIG. 1. Optical micrograph of a patterned p-type Ge (100) wafer by using deionized water under x-ray illumination. The etched depth is about 1.1 μm.

Figure 2 compares the atomic force microscope (AFM) images obtained on the etched and unetched surfaces. The images show an 8 × 8-μm area and an rms surface roughness of 5 ± 2 Å for both surfaces. Therefore, this x-ray wet etching technique is capable of obtaining very smoothly etched surfaces by using an inexpensive and environmentally sound agent (i.e., H₂O). Such a surface smoothness could not be achieved by any route other than atomic layer-by-layer peeling or etching, as demonstrated by Ikeda et al. on the etching of Ge by using Cl₂

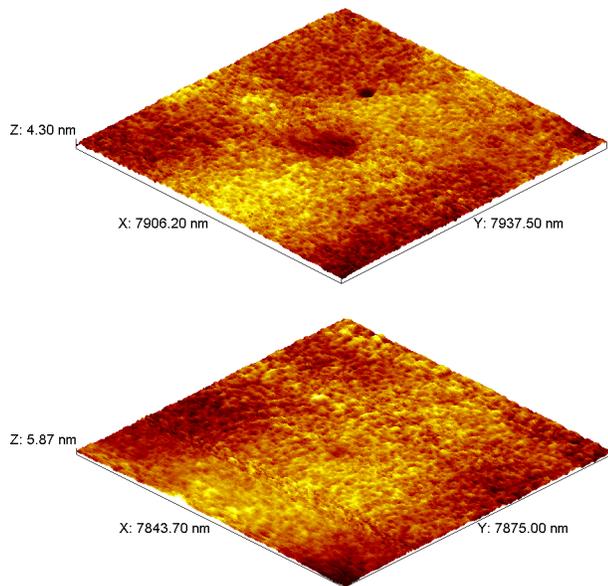


FIG. 2. AFM images taken on an unetched area (upper) and an etched area (bottom) on the sample shown in Fig. 1.

adsorption and thermal desorption in a vacuum environment [7]. This method can etch Ge regardless of its doping levels and type or crystallographic orientation.

By using various solutions, a series of etching experiments was carried out on three types of Ge wafers to examine the dependence of etch rate on solution concentration. The results indicate no obvious relationship with solution concentration. The rate is generally larger for i- and n-type Ge than for p-type Ge. When the electron beam current averages 85 mA, the former is typically in a range of 7-23 nm/min, and the latter is 2-6 nm/min. For an HNO_3 concentration of $\geq 5\%$, the rate drops, and etched surfaces become opaque and rough. AFM analysis indicates an rms roughness as high as 20 nm for p-type Ge surfaces etched by using a 5% HNO_3 solution. By using a step exposure scheme in which the horizontal slit size was programmed to reduce as a function of x-ray exposure, x-ray dose dependence experiments were also carried out. The results show a linear relationship of etch rate with x-ray doses regardless of doping and solution.

The x-ray intensity (100 to 65 mA) could be varied over only a limited range, so it was not practical to perform etching as a function of intensity. Such tests are usually important for understanding the etching mechanism [8-10]. For etching semiconductors, a photoelectrochemical mechanism often governs the etching. Illuminating a semiconductor with a light having

more energy than the bandgap generates electron-hole (e-h) pairs on the surface that enhance the oxidation of the surface in contact with an aqueous solution. In the early 1960s, Haisty [11] showed that the photoilluminated area of a GaAs surface acts as an anode, while the nonilluminated area of the surface acts as a cathode. At the onset of illumination, local current flows between these two electrodes. This was also demonstrated by Ruberto et al. [10]. Incident light creates e-h pairs in the surface. Photogenerated holes assist in the oxidation and subsequent dissolution of the surface into solution [10-12]. For etching by this mechanism, only n-type semiconductors can be etched for whichever holes drift to the sample surfaces. Etch rate is proportional to light intensity. However, it does not seem to govern the Ge etching described in this work, since the etch rate for i-type samples is comparable to that for n-type samples, both of which are only slightly higher than that for p-type samples. Moreover, the etching proceeds with deionized water, which is a *poor* electrolyte.

One of the distinct characteristics associated with photoelectrochemical etching is a *size* effect on the etch rate, as recently demonstrated by Ma et al. on x-ray wet etching of n-GaAs [6]. For a given photon flux density, etch rate increases drastically with a decrease in the illuminated area relative to the sample size. Qualitatively, reducing the irradiated area results in a decrease of the deposited light power and thus induces a smaller photovoltage on the sample. In the case of an n-type semiconductor, it increases the band bending that allows holes to drift toward the sample surface and reduces the hole recombination rate, which, in turn, increases the etch rate. As mentioned previously, size dependence experiments were carried out for etching of n-Ge. Etching depth measurements indicated little evidence of such an effect on etch rate. Therefore, it is very unlikely that photoelectrochemical etching plays any major role in the x-ray wet etching of Ge.

To examine possible changes in surface chemistry as a result of etching, x-ray photoelectron spectroscopy (XPS) analyses were performed on as-received and etched Ge surfaces. Figure 3 shows Ge $2p_{3/2}$ spectra for a p-Ge surface (a) as received, (b) dipped into deionized water for 10 min, and (c) etched in deionized water under x-ray illumination. A roughly 3-nm GeO_2 layer covers the as-received Ge wafer. Interestingly, a 10-min dip into water removes nearly all the oxide, which demonstrates a simple way of cleaning Ge surfaces. On the other hand, this result suggests that the *dark* etching of Ge in water may be limited by oxidation. In contrast, a significant amount of GeO is present on the x-ray-etched surface, which may result from the limited power of water to dissolve GeO. For etching of Ge with water vapor, the

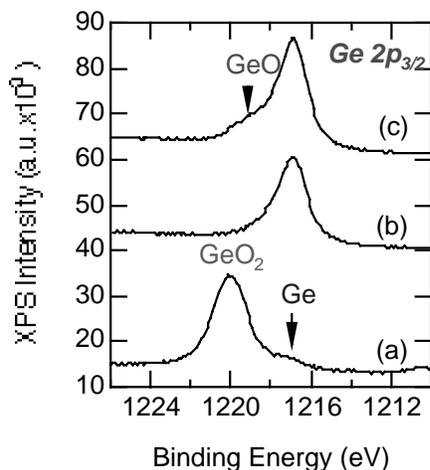
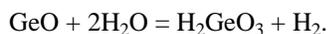
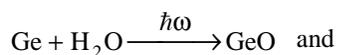


FIG. 3. XPS spectra collected on (a) an as-received p-Ge surface, (b) an as-received p-Ge surface dipped into water for 10 min, and (c) a p-Ge surface etched by using x-rays and water.

chemical reaction is proposed to be $\text{Ge (s)} + \text{H}_2\text{O (g)} = \text{GeO (g)} + \text{H}_2 \text{ (g)}$ [4]. It is likely that at least a two-step process is involved in x-ray etching:



The second step, i.e., dissolution of the oxide, is believed to limit the photostimulated etching of Ge in water. In a study of photostimulated processes in GeO_x films [13], Nazarenkov and Sterligov also concluded that the rate of the photostimulated dissolution for GeO_x films in water is low. However, they also demonstrated that by enriching water with O_2 , the second step is accelerated considerably, which will be investigated in the future.

The enhanced oxidation of Ge is likely associated with a more effective dissociation reaction for water under x-ray illumination to produce more *active* particles such as O^- [13]. In contrast to ultraviolet (UV) light, high-energy x-ray photons may produce water radiolysis typically associated with radiation chemistry [14]. Preliminary tests using either a 1-mW He-Ne laser (633 nm) or UV light (256 nm) to etch Ge in water showed no signs of etching, which underscores a unique role for the x-ray photons in the etching process described here. As reported previously [5], both n- and p-type GaAs were also etched in water under x-ray illumination (at a considerably low rate). In contrast, Yu et al. observed only accelerated oxidation of GaAs in water under UV illumination [15].

Discussion

In summary, at room temperature, an x-ray-induced wet etching process for Ge is presented. It uses deionized water and dilute acid solutions as etchants. When using water, the process produces smoothly etched surfaces with an rms roughness identical to that of the pristine Ge wafer ($\text{rms} = 5 \pm 2 \text{ \AA}$). This result may imply an atomic layer-by-layer etching process for removal of Ge. It differs significantly from the photoelectrochemical processes for etching n-type semiconductors [6, 9, 10, 16]. The photostimulated chemistry, possibly radiolysis as well, is the likely underlying cause of the etching action. Future experiments will focus on increasing the etching rate and examining the x-ray photon-energy dependence and temperature dependence of the process.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] B. Schwartz, *J. Electrochem. Soc.* **114**, 285 (1967).
- [2] S. Kagawa, T. Mikawa, and T. Kaneda, *Jap. J. Appl. Phys.* **21**, 1616 (1982).
- [3] T. L. Chu and R. W. Kelm, *J. Electrochem. Soc.* **116**, 1261 (1969).
- [4] M. Inoue, *Jap. J. Appl. Phys.* **11**, 1147 (1972).
- [5] Q. Ma, N. Moldovan, D. C. Mancini, and R. A. Rosenberg, *J. Appl. Phys.* **89**, 3033 (2001).
- [6] Q. Ma, N. Moldovan, D. C. Mancini, and R. A. Rosenberg, *Appl. Phys. Lett.* **77**, 1319 (2000).
- [7] K. Ikeda, S. Imai, and M. Matsumura, *Appl. Surf. Sci.* **112**, 87 (1997).
- [8] C. Youtsey, I. Adesida, and G. Bulman, *Appl. Phys. Lett.* **71**, 2151 (1997).
- [9] C. Youtsey, I. Adesida, L. T. Romano, and G. Bulman, *Appl. Phys. Lett.* **72**, 560 (1998).
- [10] M. N. Ruberto, X. Zhang, R. Scarmozzino, A. E. Willner, D. V. Podlesnik, and R. M. Osgood, Jr., *J. Electrochem. Soc.* **138**, 1174 (1991).
- [11] R. W. Haisty, *J. Electrochem. Soc.* **108**, 790 (1961).
- [12] R. Khare and H. L. Hu, *J. Electrochem. Soc.* **138**, 1516 (1991).
- [13] F. A. Nazarenkov and V. A. Sterligov, *Thin Solid Films* **254**, 164 (1995).
- [14] N. V. Klassen, in *Radiation Chemistry — Principles and Applications*, edited by Farhataziz and M. A. J. Rodgers (VCH, Weinheim, 1987), p. 57.
- [15] C. F. Yu, M. T. Schmidt, D. V. Podlesnik, and J. R. M. Osgood, *J. Vac. Sci. Technol. B* **5**, 1087 (1987).
- [16] Q. Ma, D. C. Mancini, and R. A. Rosenberg, *Appl. Phys. Lett.* **75**, 2274 (1999).