Synchrotron-radiation-induced anisotropic wet etching of GaAs*

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Introduction

The conventional use of x-rays from synchrotron radiation (SR) sources in material science has been for the study of structure-property relationships. Recently, SR has also been utilized for material processing in such areas as lithography [1], micromachining [2], etching [3, 4], deposition [5], phase transitions [6], and x-ray welding [7]. High-energy x-rays can be used at atmospheric pressure, potentially produce very small features, and have elemental specificity.

In this work, an x-ray-enhanced chemical wet etching process for n-type GaAs is described. It produces smoothly etched surfaces with etching rates as high as 80 nm/min. Wet, photoinduced etching of semiconductors has been explored using laser and ultraviolet (UV) light [8, 9]. Illumination of a semiconductor using a light with energy larger 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. High-energy x-rays from a synchrotron are able to excite deep core holes of the semiconductor elements. Relaxation of these core holes generates secondary electrons and thus e-h pairs near the Fermi level. The process induces little surface damage and maintains the surface composition.

Methods and Materials

The etching experiments were performed on beamline 2-BM. The details of the beamline can be found elsewhere [10]. Either a Cr- or Pt-coated mirror was employed at an angle of incidence of 0.15°, which attenuates photons with energies above 20 keV and 35 keV, respectively. For x-ray exposures, a beam size of 2 x 20 mm^2 was used. A plastic cell was used to house the etching solutions and samples. It has an opening on one side that can be O-ring sealed by a 0.125 mm thick Kapton window using a flange. The flange can hold both a patterning mask and an entrance slit (2 x 20 mm^2). 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 beam to produce a uniform exposure. An Au/Si mask for deep x-ray lithography was used for patterning.

The samples were n-type GaAs (100) wafers (ATRAMET, Inc.). The wafers were cut into small rectangular shapes of about 1 x 1 cm^2, which were then cleaned with standard degreasing procedures and dried with N_2. Four solutions of HNO_3:H_2O were prepared with concentrations, c, equal to 2.0%, 3.5%, 5.0%, and 7.0%. Dark etching tests showed that no visible dark etching developed within a few hours. A layer of opaque film was visible for a longer period of time for n- and p-type samples. An atomic force microscope (AFM) was used to measure the depths and hence the etching rate. The etched depths were all < 1 μm. Note that except for intensity-dependent studies, the etching rate values are all scaled to storage ring current of 100 mA.

Results and Discussion

Photoenhanced etching of semiconductors using laser and UV light has been determined to be electrochemical in nature. The photon-illuminated area of a GaAs surface acted as an anode, while the nonilluminated area of the surface acted as a cathode. Local current flows between these two electrodes at the onset of illumination. The chemistry of the etching is oxidative decomposition. Incident light creates e-h pairs in the surface. Photogenerated holes assist in the oxidation and subsequent dissolution of the surface into solution. Electrons participate in the reduction of the oxidizing agent in the electrolyte solution.

Figure 1(a) shows that the etching rate, γ, increases linearly with concentration, c. Photon-intensity-dependent studies also showed a linear relationship with γ. Figure 1(b) illustrates γ vs. photon intensities for two experimental conditions. One set of data was obtained with the mask and the other without the mask. These results clearly demonstrate that the etching rates vary linearly with x-ray intensity and suggest that, for a given light intensity, the reaction rate is proportional to the rate of e-h pair generation at the GaAs surface. This has been proposed previously by workers using other light sources operating in the low-power regime where the etching process is limited by the rate of carrier (e-h pair) generation. For $\gamma = 71$ nm min^{-1} and an etched area of 0.28 cm^2, the number of absorbed photons is 3.5 x 10^{10} sec^{-1}, which gives a power density of 2.7 mW cm^{-2}. This value falls well within the low-power regime for conventional light sources. Therefore, the etching by x-rays delivered from a bending magnet (BM) beamline is a carrier-limited process.

Figure 2 presents an optical micrograph of a pattern-etched GaAs surface produced using a 5.0% HNO_3 solution. The best resolution (δ) achievable under the current conditions is ~2 μm. Mechanical instability may contribute in part to the resolution. For photoetching, δ also depends on the spatial distribution of carriers at the surface, which is predetermined by the magnitude of internal electric fields, the doping levels (affecting recombination rate), and the rate of reaction of holes at the surface. The experiments with the samples doped at two levels show that δ for a doping of 2 x 10^{18} cm^{-3} is better by a factor of two than for a doping of 3-10 x 10^{17} cm^{-3}.

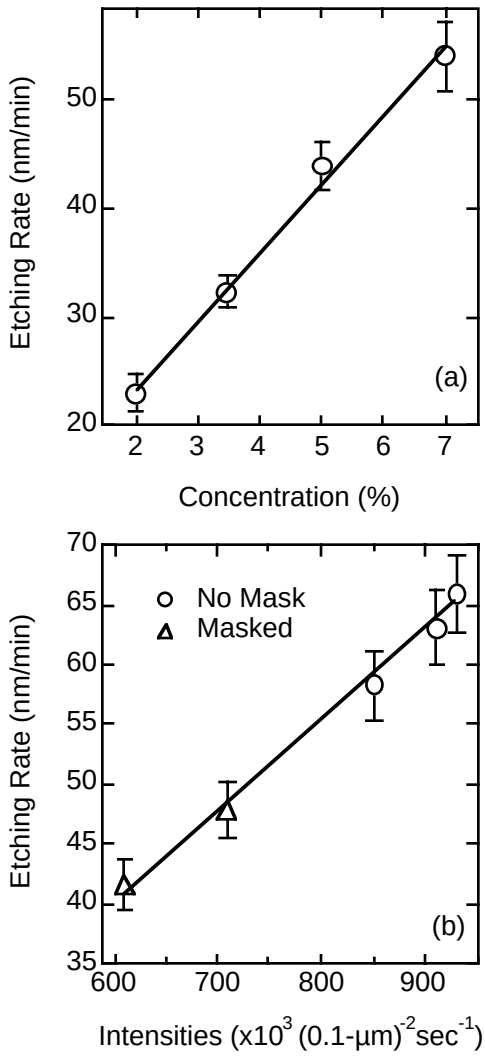

Figure 1: (a) Etching rate vs. nitric acid concentration obtained in the presence of the Au/Si mask. (b) Etching rate vs. x-ray intensity. Data were obtained with and without a mask. The straight line is a linear fit to the data. A Pt-coated mirror was used in both cases.

AFM measurements show that x-ray etching produces smoothly etched surfaces, provided the sample is scanned during exposure. The etched surfaces showed a root-mean-square (rms) value ranging from 0.7 nm to 2.0 nm. These values compare favorably to the unetched surface with rms = 0.4 nm. On the contrary, stationary exposures produce rougher surfaces, for which the rms values ranged from 4 nm to 20 nm. In both scanning and stationary exposures, there was no clear correlation of the surface roughness to light intensity and solution concentration.

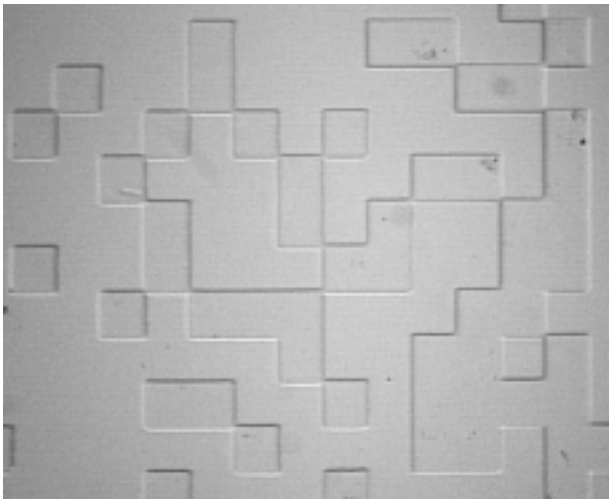

Figure 2: Optical micrograph of a pattern-etched GaAs surface using 5.0% HNO_3. The smallest feature size is 100 μm.

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References

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