Wet Chemical Etching of GaAs Using a Novel Rotating-Cell Reactor

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ABSTRACT

A novel rotating-cell reactor was used to study natural-convection-enhanced etching of GaAs. The etch rate of unpatterned samples increased with the square root of the rotation speed. The etch factor of patterned samples was much higher than that expected for pure diffusion and increased with rotation speed.

Wet chemical etching is used extensively for patterning thin and thick films of semiconductors, insulators, and metals (1). For example, wet etching of GaAs is important in the fabrication of optoelectronic devices (2), and etching of copper is used in printed-circuit-board fabrication (3).

Mass transfer of the etchant from the solution bulk to the surface or removal of the reaction product from the vicinity of the surface is often the limiting step in achieving a high etch rate. Different methods have therefore been used to enhance mass transport, most noticeably an impinging jet or cross flow over the cavity (4). At the initial stages of the process, when the cavity is still shallow, such methods can be effective since the external flow can invade the cavity bringing "fresh" solution into the cavity and washing the dissolution products away. As the cavity deepens, however, recirculating flow patterns develop within the cavity, and after a certain aspect ratio (depth:width) has been reached (about 1:2), the external flow can no longer penetrate the cavity. In such a case, communication of the "contaminated" solution trapped in the cavity with the external flow occurs only through a boundary layer along the cavity mouth. Since the recirculating eddy motion is weak, mass transfer is drastically reduced.

A unique method to enhance mass transport in deep cavities makes use of density-gradient-induced natural convection (5). In a typical etching situation, the solution density adjacent to the dissolving solid surface is different from the bulk solution density. Such density gradients can induce fluid motion by natural convection which can be further enhanced in an artificial-gravity environment, *e.g.*, by rotating the substrate. The natural convection flow patterns disrupt the mass-transfer boundary layer which would otherwise exist along the cavity mouth. Fresh solution can now penetrate deep into the cavity, and reaction products can be swept away, *i.e.*, the communication between the external solution and that inside the cavity is greatly improved. The result is an improved mass-transfer rate and, if the process is mass-transfer controlled, an improved etch rate.

Recently we developed a mathematical model to study the effect of mass transport and chemical reaction on the shape evolution of two-dimensional cavities undergoing etching. Finite-element methods were employed to solve for the fluid velocity and reactant concentration distributions in cavities of arbitrary shape. A moving boundary scheme was developed to track the shape evolution of the cavity. The case of cross flow over the cavity in the absence of natural convection was considered first (6). The benefits of forced convection on etch rate and etch factor were reduced as the cavity became deeper and an eddy formed which prevented effective communication between the external flow and the interior of the cavity. In the presence of natural convection, however, both the etch rate and the etch factor remained at relatively high values throughout etching even at later times when the cavity became deeper (7).

In the present work, a novel rotating-cell reactor was used to study experimentally the effect of natural convection on the etch rate and anisotropy. Etching of GaAs using a $K_3Fe(CN)_6$/KOH solution was chosen as a model experimental system.

Experimental

A cross section of the novel rotating-cell reactor used is shown in Fig. 1. The polypropylene cell had an inner "cylin-

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der," in the form of a right hexagonal prism (1.5 cm side), surrounded by an outer hollow cylinder (5.1 cm ID). GaAs samples were attached in a pocket on one side of the inner cylinder. Ports were provided for filling the cell with etching solution and for deaerating any bubbles trapped in the filled cell. The entire cell was mounted onto an aluminum shaft which was machined to fit into a rotator (Pine Instruments) capable of rotating the cell with a speed of up to 10,000 rpm.

The 0.019 in. thick (0.483 mm) samples were p-type GaAs (0.014 Ω-cm) with dimensions of approximately 1.0 × 1.0 cm². The chemomechanically polished samples were attached on the sample holder by using wax (Loc-Wax 10, Rodel Inc.), making sure that only the polished surface of the sample was exposed to the etching solution (edges covered). The etch rate was found by etching the samples for a certain time and measuring the resulting weight change using an electronic microbalance (AND Company). The etchant solution was prepared just before each set of experiments (a set lasting for about 6 h) and was composed of $K_3Fe(CN)_6$ (Fisher Scientific, reagent grade) in KOH (J. T. Baker, reagent grade). The solution pH was varied by varying the concentration of KOH. Experiments were first conducted using unpatterned (plain) samples to assess the effect of operating conditions on the etching rate. Then experiments with patterned samples were performed. The latter samples were masked using negative photoresist (Waycoat SC), and long channels (100-150 μm width, 5 mm long) were developed in the resist to uncover the underlying GaAs. After etching, samples were cleaved normal to the long direction of the channels and were observed under an optical microscope to obtain the cavity shape and size. The etched cavity dimensions were compared to the initial cavity dimensions (measured before etching), and the etch factor was calculated (see below).

Results and Discussion

The basic ferricyanide solution chosen for study etches GaAs without dependence on the crystallographic orientation (8). Hence the capability of the proposed reactor to achieve a
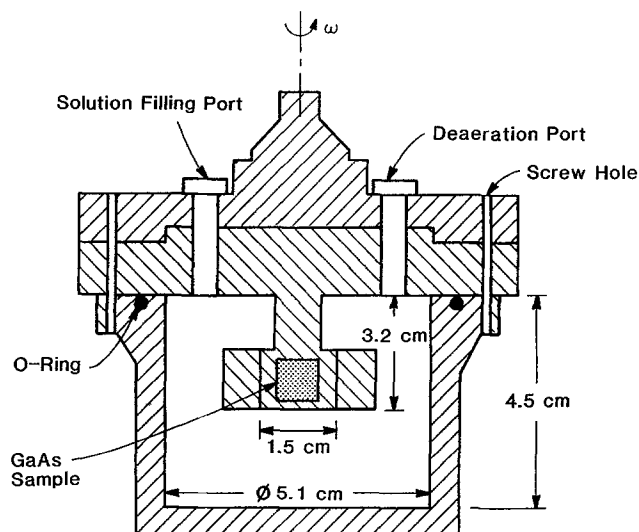

Fig. 1. Cross-sectional view of the rotating-cell reactor.

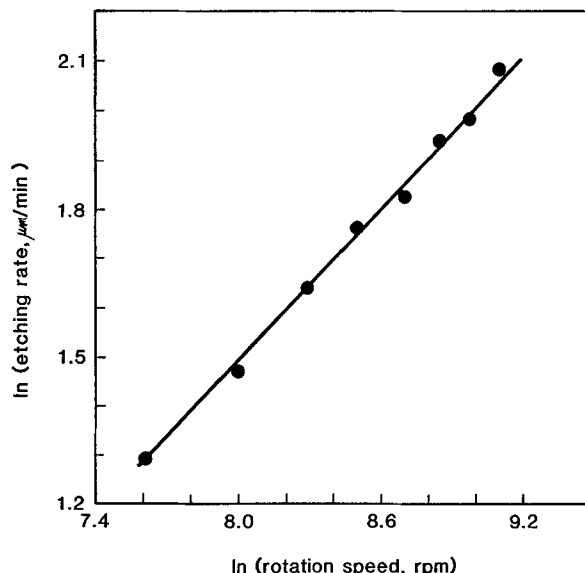**Fig. 2. Etch rate of GaAs *vs.* rotation speed of the rotating-cell reactor.**

Fig. 3. Etch factor *vs.* rotation speed of the rotating-cell reactor.

high etch factor could be tested. The etching reaction can be represented schematically as

$$GaAs + 6\ Fe(CN)_6^{3-} \rightarrow Ga^{III} + As^{III} + 6\ Fe(CN)_6^{4-}$$

where the solid is oxidized by ferricyanide and Ga and As are then being dissolved in the solution. A ferricyanide concentration of $0.5M$ with pH = 13.5 was used, and the solution temperature was 298 K, unless noted otherwise.

Figure 2 shows the etch rate as a function of rotation speed of the rotating-cell reactor. In this reactor, the etching solution rotates with the sample as a solid body. Hence, there is no relative forced-convective motion between the sample and the solution. However, rotation of the sample induces a centrifugal force which is proportional to the square of the rotation speed and to the radial position of the sample. One may calculate the equivalent acceleration at the sample position as α = 420 g (using $\alpha = \omega^2 r$, g is earth's gravitational acceleration) for a speed of 5000 rpm. The acceleration vector is pointing away from the etching surface. The slope of the straight line obtained from the plot of Fig. 2 is 0.5. Hence the etch rate depends on the square root of the rotation speed, for the conditions examined. The fact that the rate increases with rotation speed implies that the solution density near the dissolving surface is higher than the bulk density. Otherwise no instability with concomitant natural convection is expected to set in, since the acceleration vector points away from the surface. From the result of Fig. 2, it may be conjectured that the etch rate depends on the Grashof number as, Etch Rate $\sim (Gr)^{0.25}$. The Grashof number is defined as

$$Gr = \frac{\alpha \Delta \rho L^3}{\nu^2 \rho}$$

where $\Delta \rho$ is the difference in solution density between the surface and the bulk, L is a characteristic length (*e.g.*, size of sample for unpatterned samples), ρ is the solution density, and ν is the solution kinematic viscosity. The present physical system is equivalent to natural convection from horizontal plates facing downwards. The above dependence on Gr is characteristic of mass transfer by laminar natural convection from horizontal plates facing downward (9). For a pH = 13, the rotating-cell etch rate was found to be very low (0.8 μm/min) and independent of the rotation speed, up to a speed of 3000 rpm (etching was carried out for 20 min). Because of the low etch rate, the change in solution density near the dissolving surface was not high enough to yield a value of Gr beyond the critical value (10) for natural convection to set in. Hence, under those conditions, the rate was governed by pure diffusion. Beyond
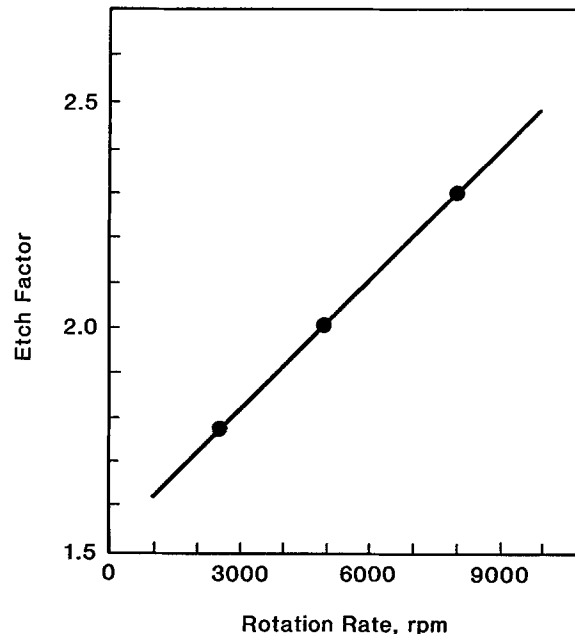
3000 rpm, the etch rate increased with rotation speed, indicating that the critical Gr was then exceeded.

The etch factor was defined as EF = (etched depth)/(average mask undercut). Thus, for an isotropic etch, EF = 1. Patterned samples were etched for different periods of time to determine the EF achieved. The etch factor obtained with the rotating-cell reactor is shown in Fig. 3. The EF was time-independent (10-30 min), and the cavity wall profiles were symmetric or nearly symmetric. The EF is much higher than the value expected for pure diffusion using a thin mask (6) and improves with increasing rotation speed.

In summary, natural-convection-enhanced etching of GaAs was studied using a novel rotating-cell reactor. The etch rate of unpatterned samples increased with the square root of the rotation speed. The etch factor of patterned samples was much higher than that expected for pure diffusion and increased with rotation speed. Natural-convection-enhanced etching may be a viable process from the industrial point of view as well. One may envision a reactor configuration similar to the "hexode" reactor used industrially for dry etching of thin films.

Acknowledgments

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