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High Resolution Photoelectrochemical Etching of n-GaAs with the Scanning Electrochemical and Tunneling Microscope

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We describe here a novel electrochemical device for direct micromachining of a semiconductor substrate by guiding an ultramicroelectrode tip in a predefined pattern above the surface. Currently, the technology for the fabrication of electronic devices is based on microlithography, and the sizes of the pattern are limited by the wavelengths of the optical source used in irradiation. More recently, some laser-induced direct etching techniques in both the gas and liquid phase have also been investigated (1-3). An alternative technique to form a preferential etched pattern in solution was initiated in this laboratory by utilization of a scanning electrochemical and tunneling microscope (SETM), which previously has been used to examine electrode surfaces in solution while maintaining interelectrode spacings with A-resolution (4). This instrument is largely patterned after the scanning tunneling microscope (STM) (5). However, while with the STM the ultramicroelectrode tip is held within ca. 10 Å of the surface and a nonfaradaic tunneling current is measured, with the SETM the tip can be held with larger spacings and faradaic processes to produce modification of the electrode surface are possible. In this method a fine metal tip enclosed in a glass sheath is held in close proximity to the substrate (< 1 μm) under conditions where the application of potential between tip and substrate and simultaneous irradiation by light promote photoelectrochemical reactions at the substrate immersed in an electrolyte solution (Figure 1). The nature of these reactions depends upon the potential applied, the nature of the solution and the light intensity. The ratio of the local reaction rate across the substrate to that immediately under the tip is controlled by the current density distribution at the substrate surface. By adjusting the tip to substrate spacing and minimizing exposed tip diameter, an extremely nonuniform spatial current distribtuion can be expected. For a semiconductor substrate like GaAs, localized photoanodic dissolution will occur, thus forming a selective etched pattern as the tip travels laterally in a defined pattern above the surface. In the work described here, the photoanodic etching of GaAs by photogenerated holes at the semiconductor/solution interface is described (3). The rate of this process and the solvated products depend upon the surface conditions, solvent, electrolyte and pH.

The apparatus for distance adjustment and lateral movement used in the present study has been described previously (4). A 25 μm platinum wire used for the tip was first trimmed by electrochemical etching (4) to less than 0.1 μm diameter. This etched wire was then carefully inserted and sealed by heating in a fine glass capillary. The exposed electrode in this sealed assembly was further trimmed until the tip length exposed was about 1 to 2 μm. The GaAs wafers were degreased in trichloroethylene, then 2-propanol followed by rinsing with deionized water before mounting on the sample holder. Before the photoetching experiment, it is necessary to gauge the roughness and any tilt of the substrate material to avoid crashing the tip into surface features when it is scanned at close spacing from the substrate. Therefore, a bias voltage of 1.2 V was applied and the tip lowered in air until a tunneling current flowed. The substrate was first scanned via the tunneling mode with the tip moved along a predefined path and the positional data, including roughness and tilt, were stored on a floppy disk. The tip was then backed away to ca. 1 μm and electrolyte solution (5 mM NaOH, 1 mM EDTA) was introduced. A bias voltage of 4 V (tip negative) was applied during the etching process with simultaneous irradiation by a tungsten-halogen lamp. The spacing between tip and substrate was about 1 μm and this adjustment was maintained by the computer based on the data found in the preliminary scan. The pattern to be etched is predefined through the computer and is generated by movement of the X-Y translation stage. To avoid bubble formation, it is useful to add a substance that is preferentially reduced at the tip (i.e., a cathodic depolarizer) without gas evolution. Because of the high current densities at the tip, reasonably high concentrations of this substance are required. However, the small tip behaves as an ultramicroelectrode, and mass transport to it is very efficient. For

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example, for a tip of radius, r, of 0.1 μm, the effect mass transfer coefficient, $m_o \approx 0.5$ D/r ≈ 0.25 cm/s; this is equivalent to a rotating disk electrode rotating at 4×10^6 rev/min (where D is the diffusion coefficient). We also performed similar etching processes in organic solvents, e.g., wet acetonitrile. In this case, the reduction process was provided by an added species, such as nitrobenzene or an alkyl halide.

Two examples of fine line etching of n-GaAs are shown in Figure 2. The SEM photographs agree with the predetermined location and patterns with line widths of about 2 μm and 0.3 μm. The difference in line width in these two experiments was caused mainly by different tip sizes. The somewhat noncontinuous nature of the line in Figure 2a probably is caused by some bubble formation and also by the pulsed nature of the applied voltage and illumination. Broadening of the line profiles may also be caused by the lateral diffusion of the photogenerated holes at the semiconductor/electrolyte interface (3). Microscopic examination of the surface revealed that although etching was uniform and well confined to the region where the tip traveled, some etching occurred across the whole GaAs surface. Note that the whole surface was illuminated with no attempt to concentrate the light in the vicinity of the tip.

We are currently investigating, experimentally and through simulation, how the etching resolution is affected by such factors as the etching rate, nature of the reactions at the tip and substrate, and tip to substrate spacing. These results illustrate, however, the potential of this new technique in ultramicromachining. Further experiments on metal deposition and etching, the use of multiple tips, and polymer deposition are in progress in this laboratory.

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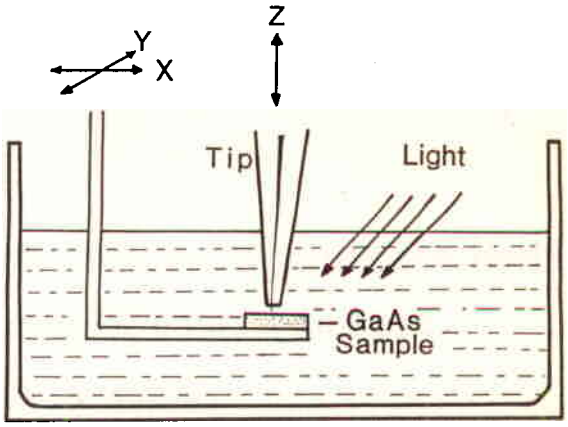

Figure 1: Schematic diagram of the ultramicroelectrode photoelectrochemical etching experiment.

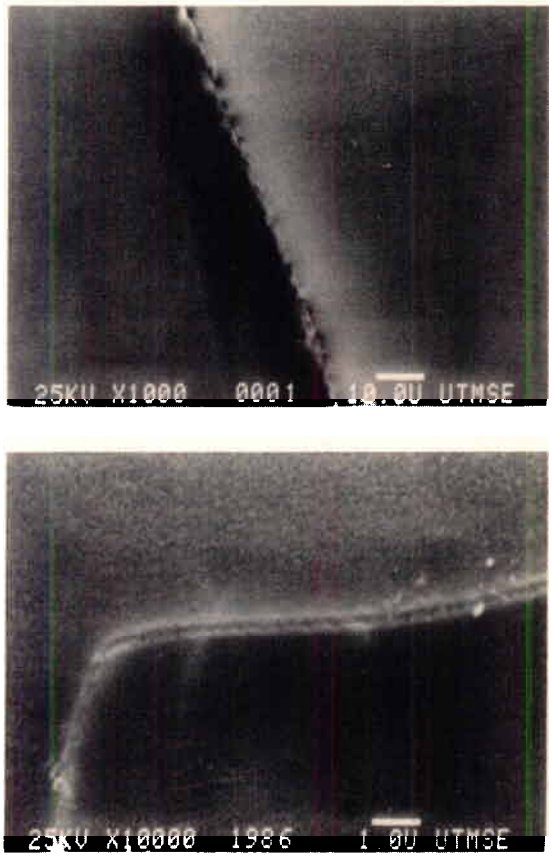

Figure 2: Scanning electron micrographs of n-GaAs electrochemically etched in an aqueous solution containing 5 mM NaOH and 1 mM EDTA. Irradiation with tungsten-halogen lamp. (a) Photoelectrochemical current, 3.2 μA; Tip scan rate, 150 Å/sec; Bias voltage, 4 V; Light and voltage pulsed, 5 sec on, 5 sec off. (b) Photoelectrochemical current, 0.7 μA; Tip scan rate, 0.1 μm/sec; Bias voltage 4 V; Light and voltage applied continuously and the tip was moved in an L-pattern.

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