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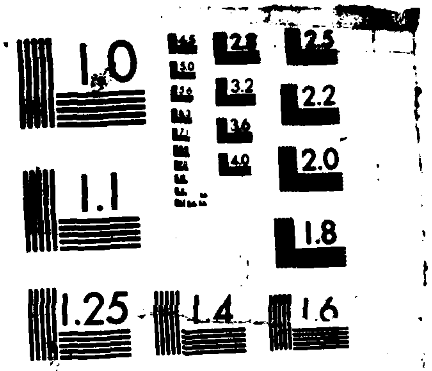

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SPATIALLY SELECTIVE PHOTOELECTROCHEMISTRY

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This program has dealt with applications of photoelectrochemistry to semiconductor technology. Light localized etching and electroplating have been demonstrated for n-GaAs, including imaging with a computer-controlled focused laser light source and crystallographically enhanced photoelectrochemical etching using conventional photoresist masks. These studies have resulted in new processes for high aspect ratio etching in compound semiconductors, and in fabrication of sawtooth Eschelle-type diffraction gratings for spectroscopy and integrated electro-optics.

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SUMMARY

The purpose of this program has been to explore applications of photoelectrochemistry to semiconductor technology. Two general applications have been considered: 1) photoelectrochemistry as a tool for nondestructive evaluation of semiconductor bulk and surface properties, and light-localized electrochemical imaging processes or semiconductors, including etching and metal deposition.

Photoelectrochemical Nondestructive Evaluation. A computer controlled laser spot scanner was developed which allowed the profiling of the photoelectrochemical activity of a semiconductor with $\sim$1 μm spatial resolution [5,9]. Research was conducted to demonstrate stabilizing electrolytes which could be used nondestructively with III-V compounds and Si, e.g., $CH_3CN/I^-/I_3^-$ [1,3] and $CH_3CN/Cu^+/Cu^{+2}$ [4] were used with n-GaAs, and nickelocene in propylene carbonate [1] and methyl viologen in methanol for n-Si. Laser scanning was used to map out defects in thin film electrodes [5,9]. Liquid junctions were also employed for the rapid assessment of minority carrier diffusion lengths in Si [8]. A novel "photoelectrochemical vidicon" imaging device was demonstrated in which a near infrared image was projected onto a Si photoelectrode while a low power He-Ne laser raster scanned the surface. The projected image was replicated on an oscilloscope in real time as photovoltage or photocurrent vs. position due to image induced redox concentration gradients at the electrode surface [3].

Electroplating. Direct photoelectrochemical imaging of microscopic metal film patterns was achieved on p-GaAs and p-Si electrodes in contact with electroplating baths [2,7]. Reductive electroplating was confined to the areas of illumination. Resolution of $\sim$10 μm was achieved, limited primarily by nondirectional growth of the metal nuclei. The photoelectrochemical mechanism of plating various metals was described. Also demonstrated was "negative" photoelectrochemical plating on n-type semiconductors, in which illumination prevented electroplating while it proceeded in dark portions of the electrode surface [7]. In this way, the general applicability of the photoelectrochemical plating process was described.

Additional research was conducted on removing the necessity for an electrochemical cell in the imaging process [6]. This approach relied on complementary oxidation and reduction reactions occurring at the illuminated and dark portions of the semiconductor surface. High quantum yield light localized electroless plating of electropositive metals (Zn, Cd, etc.) was achieved on both p-Si and p-GaAs by using Zn, ohmically contacted to a nonilluminated region of the surface, as an internal bias agent. On illumination of the semiconductor/plating electrolyte junction, an internal cell was set up in which metal was plated onto the illuminated regions and dissolved from the sacrificial Zn source.

Focused Laser Etching [9,10]. The computer controlled laser scanning instrument developed on this project [9] was used in the direct etching of microscopic patterns on semiconductors. During this period, we demonstrated and parameterized the high rate photoassisted etching of n^+-GaAs using a scanning focused laser and 10% aqueous KOH electrolyte [10]. In particular, we were interested in the relationship between intensity and resolution of holes developed using a diffraction limited focused spot of diameter <1 μm. We determined that the hole diameters are a function of total delivered energy rather than intensity, at least in the intensity regime investigated. This limits the depth of features that can be produced using high rate laser etching processes. The process still can be used for lower energy etching of shallow patterns, such as character sets for identification of individual integrated circuits.

High Aspect Ratio Etching. Experiments were carried out to determine the utility of using photoelectrochemistry for etching deep structures in n-GaAs. In one series of experiments, the (100) surfaces of n-GaAs single crystals were lithographically patterned in with 10 μm wide grooves pointed in the [011], [010], and [011] crystallographic direction [11,12]. Photoelectrochemical etching of these channels showed that deep, vertical walled structures could be produced with a great deal of process control [12]. Undercutting of the mask occurred in crystals of low doping, which fosters rapid surface diffusion of photogenerated holes. Marked crystallographic effects were observed as well [11-13]. Photogenerated holes reacted more readily with the nucleophilic (111) As face than the (111) Ga face, an effect which enables the photoelectrochemical etching of sawtooth structures in the GaAs surface. The latter process was shown to be a new technique for fabricating deep low pitch Eschelle diffraction gratings for high performance spectrometers [12].

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