

Improvements in the modulation amplitude of submicron gratings produced in *n*-InP by direct photoelectrochemical etching

R. M. Lum, F. W. Ostermayer, Jr.,^{a)} P. A. Kohl,^{a)} A. M. Glass,^{a)} and A. A. Ballman
AT&T Bell Laboratories, Holmdel, New Jersey 07733

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The modulation amplitude of gratings produced by maskless etching techniques decreases rapidly at spatial frequencies $> 500 \text{ mm}^{-1}$. This has limited the usefulness of these techniques for producing the submicron gratings required for distributed feedback lasers. We report improvements as large as a factor of 100 in the direct photoelectrochemical (PEC) etching of gratings in *n*-InP which were accomplished by changing the composition and concentration of the electrolyte solutions. Measurements on the PEC etching characteristics of *n*-InP in HF, HCl, HBr, and H₂SO₄ solvents are presented.

Direct holographic recording of submicron gratings in III-V materials by liquid phase photoetching has been demonstrated using both photochemical (PC)¹⁻⁴ and photoelec-

trochemical (PEC)⁵ techniques. Maskless techniques for producing gratings have potential application in the fabrication of distributed feedback (DFB) lasers which are currently made by a multistep photoresist process.^{6,7} However, gratings produced by PC⁴ and PEC⁵ etching exhibit an abrupt

^{a)} AT&T Bell Laboratories, Murray Hill, NJ 07974.

TABLE I. Experimental values of the reaction velocity for surface dissolution of *n*-InP in various electrolytes.

Electrolyte	Volume ratio	Reaction velocity (cm/s) $\times 10^{-2}$
H ₂ SO ₄ :H ₂ O ₂ :H ₂ O	1:1:10	25
H ₂ SO ₄ :H ₂ O ₂ :H ₂ O	1:1:100	0.15
H ₂ SO ₄ :H ₂ O	1:10	15
2M HF/0.5M KOH	...	0.63
2M HCl	...	8.9
2M HBr	...	15

decrease in modulation amplitude (the ratio of the grating amplitude to the average depth etched) for grating spatial frequencies $> 500 \text{ mm}^{-1}$.

Shallow gratings impose inherent limitations on the lasing characteristics of DFB lasers, since both the coupling coefficient for the propagating waves and the threshold gain are strongly dependent on grating depth.⁸ In addition, during laser fabrication using liquid phase epitaxy for grating overgrowth, thermal deformation causes a reduction in the final grating amplitude.⁸⁻¹⁰ To overcome these limitations we have sought to improve the modulation amplitude of gratings produced by laser interference PEC etching.

In the PEC technique the semiconductor is placed in an electrolyte and electrically biased to form a depletion region at the sample surface.^{5,11} For *n*-type materials, etching occurs by an oxidative decomposition reaction induced by photogenerated holes and is controlled by the laser beam intensity incident on the semiconductor. The PEC etching rate is directly proportional to the hole concentration at the crystal-electrolyte interface. The amplitude of the resulting surface relief grating thus is proportional to the amplitude of the spatial modulation of the hole density at the interface.

The dissolution reaction velocity depends upon the detailed solvent-crystal molecular interactions (e.g., formation of reaction intermediates, solution complexes, etc.) and the concentration of the electrolyte. In this letter we investigate the effects on the PEC etching of *n*-InP of changing both the chemistry and the concentration of different electrolyte systems. The data are analyzed in terms of a hole transport model,¹² and values of the overall reaction velocities characteristic of the different electrolyte solutions are reported.

Evaluation of the electrolyte solutions was performed by etching gratings in sulfur-doped *n*-InP ($n = 6 \times 10^{18} \text{ cm}^{-3}$). The samples were mounted as electrodes and electrically biased to 0.3–0.5 V vs a saturated calomel electrode.¹¹ A HeCd laser ($\lambda = 0.4416 \mu\text{m}$) was used as the radiation source. Exposures were performed with a beam intensity of 50 mW/cm^2 . The composition and concentrations of the electrolytes investigated are listed in Table I.

Details of the laser interferometer arrangement used to produce the gratings have been published previously.⁵ For small amplitude sinusoidal phase gratings, the grating depth can be related to the intensity of the first-order diffracted beam by^{5,13}

$$d = (\lambda_0 \cos \Theta_e / \pi n_e) (I_1 / I_0)^{1/2}, \quad (1)$$

where d is the grating depth, I_1 the intensity of the first-order diffracted beam, I_0 the incident beam intensity, λ_0 its free-

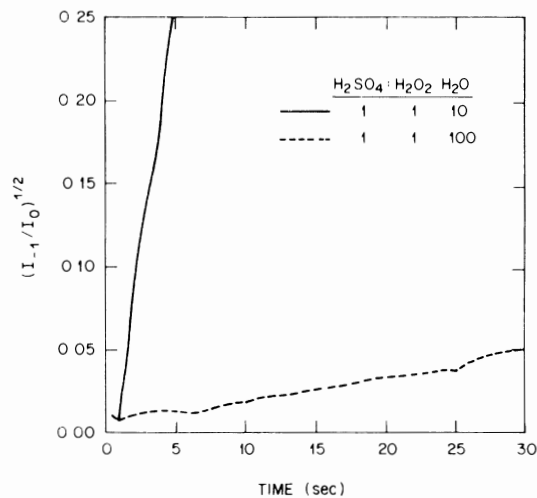


FIG. 1. Effect of H₂SO₄/H₂O₂/H₂O electrolyte concentration on the PEC etch rate of 0.6- μm gratings etched in *n*-InP.

space wavelength, Θ_e the half-angle between the two incident beams in the electrolyte, and n_e the refractive index of the electrolyte. The ratio (I_1/I_0) is defined as the diffraction efficiency of the grating. The first-order ($n = -1$) diffracted beam intensity and the PEC etching current are monitored in real time to provide *in situ* measurements of the etch rate and the grating modulation amplitude. This enables an exposure to be stopped once a given efficiency or grating depth is attained. The data are corrected for the effect of the Gaussian light distribution in the laser beam,¹⁴ and the quantum efficiency of the PEC etching process.¹¹

The effect of electrolyte concentration on the grating modulation amplitude was investigated using H₂SO₄:H₂O₂:H₂O solutions having volume ratios of 1:1:10 and 1:1:100. Measurements of the grating growth, as determined from the diffracted beam intensity, are shown in Fig. 1 for 0.6- μm gratings. From these data, etch rates of 0.32 and 0.009 $\mu\text{m}/\text{min}$ are obtained for the two solutions. Scanning electron microscope analysis of cleaved samples confirms that the gratings have amplitudes in good agreement with those derived from the intensity data.

Figure 2 presents a comparison of the variation in mo-

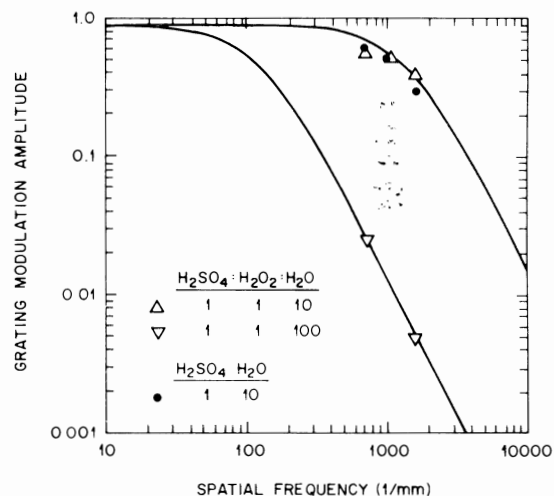


FIG. 2. Spatial frequency response of gratings etched in *n*-InP using H₂SO₄/H₂O₂/H₂O and H₂SO₄/H₂O electrolytes.

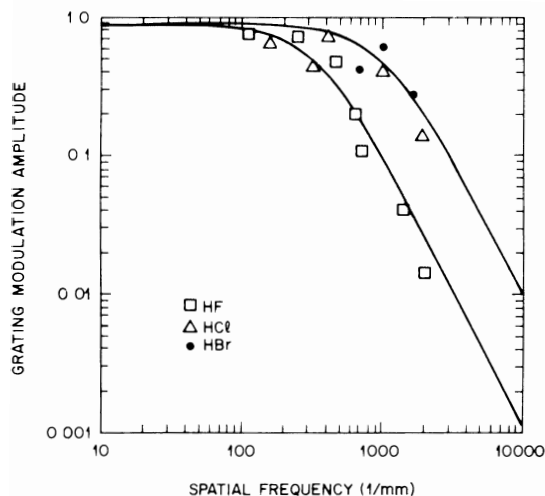


FIG. 3. Spatial frequency response of gratings etched in *n*-InP using HF, HBr, and HCl electrolytes.

duction amplitude as a function of spatial frequency for gratings produced in the two H_2SO_4 solutions. For sub-micron gratings a hundredfold increase is observed in the modulation amplitude for a tenfold increase in H_2SO_4 concentration. This is opposite to the effect reported for similar solutions in the PC etching of *n*-GaAs.⁴ Data for a 1:10 H_2SO_4 : H_2O solution are also shown in Fig. 3. Since PEC etching occurs via a photo-oxidation process, elimination of the H_2O_2 oxidizer is seen to have little effect.

The solid curves in Fig. 2 were fit to the data using a two-dimensional hole-transport model¹² for the hole distribution during exposure. The model determines the amplitude of the modulation of the surface hole concentration relative to its average value taking into account the diffusion, drift, recombination, and reaction at the surface of the photogenerated holes resulting from light absorption within the semiconductor. This model satisfactorily accounts for the decrease in grating modulation amplitude observed at high spatial frequencies. The model also predicts that substantial improvement in the modulation amplitude can be obtained by increasing the reaction velocity of the dissolution reaction (e.g., by increasing the electrolyte concentration). From the fit of our model to the data reaction velocities of 2.5×10^3 and 15 cm/s were determined for the concentrated and dilute H_2SO_4 solutions, respectively.

Since the holographic sensitivity of gratings produced by PEC etching depends on the reaction velocity of the dissolution reaction, HF, HCl, and HBr electrolytes were investigated to study the effects of changing the details of the electrochemistry. Previous studies¹⁵⁻¹⁷ of the electrochemical behavior of these electrolytes found that Cl^- and Br^- were directly involved in the dissolution of In-containing electrodes via formation of an intermediate species. In contrast,

F^- from HF electrolytes does not participate in the dissolution reaction, but rather only forms solution complexes such as InF^{2+} .

The modulation amplitude of gratings etched in HCl, HBr, and HF is compared in Fig. 3. Both HCl and HBr exhibit improved grating modulation characteristics over HF at high spatial frequencies. With the former, the spatial frequency at which the grating modulation amplitude decreases to 0.5 is extended to 1000 mm^{-1} (i.e., to the sub-micron range). The reaction velocities determined from the data of Fig. 3 are listed in Table I, along with the values obtained for the H_2SO_4 electrolytes.

The modulation amplitude of gratings produced in *n*-InP by direct PEC etching was found to depend on the concentration and composition of the electrolyte. A hundredfold improvement in the modulation amplitude of $0.6\text{-}\mu\text{m}$ gratings was achieved with a tenfold increase in the concentration of H_2SO_4 solutions. Improvements of a factor of 10 were accomplished by the use of electrolytes whose ionic species directly participate in the semiconductor dissolution reactions (e.g., HCl and HBr) over those which do not (e.g., HF). These results are in good agreement with predictions from a two-dimensional hole-transport calculation which was used to model our experiments.

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