Increased modulation depth of submicron gratings produced by photoelectrochemical etching of GaAs

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Submicron optical diffraction gratings with improved modulation depth were photoelectrochemically etched on *n*-GaAs. This etching technique uses an elevated etchant temperature to exceed the spatial resolution limits imposed by etching at room temperature, and provides a method of photoelectrochemical etching of gratings whose period is shorter than those of previously reported photoelectrochemically etched gratings. The improved grating modulation depth, the result of an increase in electrolyte temperature, was experimentally measured by etching 0.28 μm period gratings at five different temperatures. These results are compared with theoretical predictions based on analytical expressions for the reaction rate at the etched surface. Experimentally, a 25 °C increase in the etching temperature improved the grating amplitude by a factor of 1.7, which is in agreement with the theoretical predictions.

Diffraction gratings are an important component in many semiconductor optical devices, such as distributed feedback and distributed Bragg reflector (DFB) lasers,[1] wavelength demultiplexers,[2] and input/output couplers.[3] The most efficient gratings for these devices are first-order gratings. Photoelectrochemical (PEC) etching provides a high yield, low cost means of directly etching a surface relief diffraction grating into *n*-GaAs or *n*-InP based compounds.[4] This manufacturable etching process does not use photoresist as an intermediate step, so PEC etching is simple because there are few process steps, and clean because no photoresist residues are produced, enabling regrowth of high quality epitaxial layers. However, high efficiency first order gratings for 0.85 and 1.3 μm lasers have not yet been demonstrated using PEC. This letter shows that very short period gratings, such as those needed for DFB lasers, can be etched more deeply, and with a shorter period, when the temperature of the etchant is elevated.

In PEC etching, an *n*-type semiconductor is immersed in an electrolyte and a depletion region is formed at the surface of the semiconductor. Photogenerated holes migrate to the semiconductor–electroyte interface where they participate in the oxidative decomposition of the semiconductor,[5] given by

$$\mathrm{GaAs}+6h^{+}\rightarrow \mathrm{Ga(III)}+\mathrm{As(III)}. \quad (1)$$

At submicron grating periods, the modulation depth of the grating decreases as the grating period decreases because the slow rate of the PEC reaction allows the photogenerated holes in the semiconductor to undergo surface diffusion.[4–7] At submicron grating periods, the spatial distribution of the photogenerated carriers does not correspond to the spatial distribution of the incident light because carrier diffusion diminishes the carrier modulation which would exist in the absence of diffusion. In this letter, we demonstrate that the temperature of the etchant affects the rate of the reaction, thereby affecting the grating modulation depth and period.

An interferometer was used to create a sinusoidal variation in intensity across the semiconductor surface using the 514 nm line of an Ar^{+} laser. A 0.28 μm optical interference period, and thus etched grating period, was used to observe the effect of etching temperature. An optical intensity of 90 mW/cm^2 was incident on the sample, which was (100) oriented *n*-type GaAs, doped with silicon to 3×10^{18} cm^{-3}. A three electrode electrochemical cell was used to bias the sample at 0.3 V with respect to a saturated calomel reference electrode. The etching duration was 45 s in a 1*M* H_2SO_4 electrolyte, producing gratings oriented along the $[01\bar{1}]$ direction for highest modulation depth.[7]

The modulation depth of the diffraction gratings was measured by comparing grating diffraction efficiencies. High modulation depth gratings are produced through etching only in photoexcited regions, which creates gratings with larger amplitudes than gratings etched at a slow reaction rate, which are isotropically etched. The diffraction efficiency is a function of this grating amplitude and is given by the ratio of the intensity of the first diffracted order (I_{-1}), to the intensity of the zeroth order reflection (I_r). These gratings are etched and evaluated with the same Gaussian laser beam. For the type of sinusoidal gratings which results from PEC etching with a Gaussian beam, the diffraction efficiency is related to the grating amplitude d by[8]

$$d=\left(\frac{\lambda_0\sqrt{3}}{\pi}\right)\cdot\left(\frac{I_{-1}}{I_r}\right)^{1/2}, \quad (2)$$

where λ_0 is the free space wavelength of the incident beam.

Ten gratings were made at each of five temperatures: 15, 21, 28, 33, and 40 °C. A water-jacketed etching container was used to control the temperature of the electrolyte. The diffraction efficiencies of the gratings made at higher temperature are larger than those at lower temperatures since a deeper grating [Eq. (2)] results from PEC etching at a higher reaction rate. These grating efficiencies as a function of temperature are shown in Fig. 1.

A model of the etching process in the semiconductor combined with the limited solubility of the reaction products in the electrolyte closely predicts the observed increase in grating amplitude at elevated etching temperatures. The

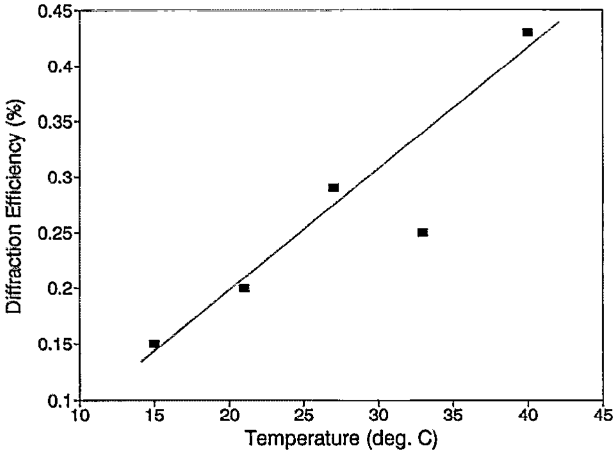

FIG. 1. The experimentally measured diffraction efficiency of gratings increases with fabrication temperature.

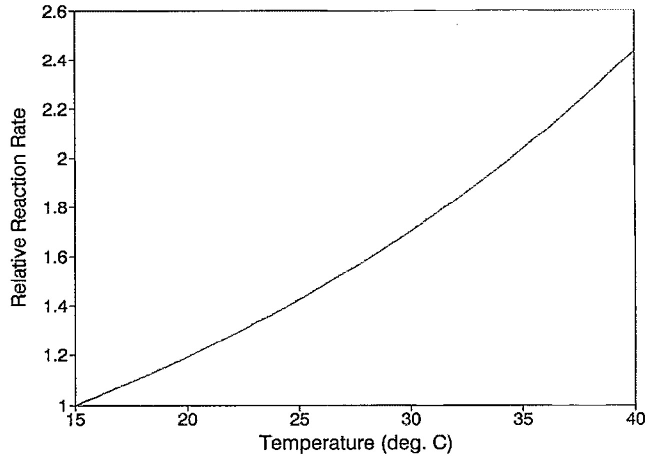

FIG. 2. The theoretical maximum reaction rate increases with temperature, which predicts higher grating resolution and higher diffraction efficiency with increasing temperature.

PEC etching process is directly proportional to the hole concentration at the semiconductor–electrolyte interface.[5] The spatial distribution of the holes at the semiconductor–electrolyte interface is affected by the reaction rate. A slow reaction rate gives the holes time to diffuse along the semiconductor surface, thereby decreasing the modulation depth. The adverse effects of hole diffusion are more pronounced for smaller period gratings since the holes diffuse a correspondingly shorter distance, entering an unilluminated region, thereby decreasing the modulation depth of the grating. For this reason, a fast reaction rate is essential in order to PEC etch very short period gratings. The reaction rate is limited by the solubility and diffusion of the reaction products from the semiconductor interface. The effect of altering the reaction temperature can be evaluated by combining the model of the reaction products in the electrolyte and of the holes in the semiconductor.

The chemical reaction is composed of six one-electron transfer steps [Eq. (1)], and chemical reactions where the Ga(III) and As(III) products are complexed, solvated, and dissolved. The Ga(III) dissolves as Ga^{3+}, whereas the As(III) is complexed by water and dissolves as $HAsO_2$ and As_2O_3, given by[9]

$$\mathrm{As(III)}+2\mathrm{H_2O}\rightarrow\mathrm{HAsO_2}+3\mathrm{H}^+, \quad (3)$$

$$2\mathrm{As(III)}+3\mathrm{H_2O}\rightarrow\mathrm{As_2O_3}+6\mathrm{H}^+. \quad (4)$$

If the concentration of As(III) at the semiconductor surface exceeds the solubility limit, as given by the solubility product K_{sp}, then precipitation occurs and the reaction rate slows. The solubility of As_2O_3 increases with temperature,[10] as does the diffusion of the reaction products away from the semiconductor.[11] These two effects lead to an increase in the grating amplitude with increasing temperature.

The diffusion of the reaction products from the semiconductor is directly related to the hole current density across the semiconductor-electrolyte interface, which is directly proportional to the etch rate. An expression for the maximum current before precipitation is derived from Fick's laws, showing that the etch rate increases as the square root of the diffusion constant[11]

$$\frac{I}{A}=\frac{n\sqrt{D_0}\,FC^*_{x=0}}{\sqrt{\pi}\sqrt{t}}, \quad (5)$$

where D_0 is the diffusion constant, $C^*_{x=0}$ is the concentration of reaction products at the semiconductor-electrolyte interface, I is the current, A is the area, t is time, and F is Faraday's constant. Both $C^*_{x=0}$ and D_0 increase with temperature,[10] thereby increasing the hole etching current. The diffusion constant increases with temperature as $D_0 \approx T/\eta_e$, where T is the temperature in K and η_e is the viscosity of the electrolyte.[11] The viscosity of the electrolyte is also temperature dependent: $\ln \eta_e=A+B/T+CT+DT^2$, where A, B, C, and D are experimentally determined constants. Increasing the temperature by 25 °C decreases the viscosity of the electrolyte by 40%. Raising the temperature from 15 to 40 °C increases the diffusion constant by a factor of 1.9 and increases the solubility of the reaction product As_2O_3 by 1.8 times, leading to a factor of 2.4 increase in the maximum current density [Eq. (5)] as a function of temperature, shown in Fig. 2. Likewise, the predicted grating amplitude increases by a factor of 2.4 [Eq. (2)]. Experimentally, the variation in the results increases as the temperature deviates from ambient conditions because of changes in the refractive index of the electrolyte and water jacket.

In a competing process, the mobility of the holes increases as the semiconductor is heated. Greater hole mobility leads to reduced PEC etching resolution. For high purity polar semiconductors, the mobility varies as $T^{3/2}$.[12] The effect of changing the temperature 25 °C near room temperature in GaAs is small in comparison to the effect of temperature on the reaction rate.

In conclusion, submicron diffraction gratings PEC etched at elevated electrolyte temperatures demonstrate larger amplitudes than those etched at room temperature. The solubility of the reaction products and the rate of diffusion of the reaction products limits the reaction rate, and hence the grating amplitude. The increased solubility of As_2O_3 increases the maximum current 1.8 times and increasing the diffusion of the reaction products increases the maximum current another 1.4 times for a temperature increase from 15 to 40 °C. By combining these two effects, the net effect of raising the temperature from 15 to 40 °C on the reaction rate is to increase the maximum current prior to precipitation by a factor of 2.4. This increase in temperature theoretically predicts an increase in the grating depth by a factor of 2.4. Experimentally, the gratings fabricated at 40 °C showed a 1.7 times greater grating amplitude in comparison to those fabricated at 15 °C.

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