The influence of aluminum concentration on photoelectrochemical etching of first order gratings in GaAs/AlGaAs

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We present a set of experiments which systematically clarifies the enhancement of photoelectrochemical (PEC) etching due to the mole fraction of aluminum in AlxGa1-xAs. The spatial resolution of gratings etched in Al0.3Ga0.7As is as much as three times greater than the spatial resolution of gratings etched in GaAs, so that the smallest practical grating period is about 0.3 μm, as compared with about 0.7 μm using previous techniques. This technique enabled PEC fabrication of first order gratings for waveguide outcouplers. The lower hole mobility of AlxGa1-xAs is proposed as a possible explanation for this grating resolution improvement. © 1995 American Institute of Physics.

Photoelectrochemical (PEC) etching allows direct, light-assisted patterning of etched features into n-type III-V semiconductors. By interfering two coherent laser light beams at the surface of a semiconductor sample, submicron diffraction gratings can be etched. It is recognized that PEC etching of gratings offers advantages over conventional phototransfer/mask fabrication of gratings, however, the technique has been used infrequently for device fabrication in the field of semiconductor waveguide optics. When gratings are PEC etched, some etching takes place in nonilluminated areas, due to photogenerated carrier diffusion. This effect becomes increasingly pronounced at shorter grating periods, so that the ratio of grating etch depth to total etch depth (grating resolution) becomes very small. While very short period gratings (<0.4 μm) can be etched in GaAs, the total etch depth necessary to achieve a modest surface relief height is unacceptably large for most optical device applications. On the other hand, the longer period gratings (>0.8 μm) which can effectively be formed in GaAs are of limited interest for semiconductor waveguide optics devices.

A variety of investigations have focused on improving the spatial resolution of the PEC grating etching process by increasing the chemical reaction rate of the etching process.1–5 We present a contrasting approach which exploits differences in material parameters between GaAs and AlGaAs. We show that the resolution of gratings etched in Al0.3Ga0.7As is as much as three times greater than the resolution of gratings etched in GaAs, and suggest that this effect is a consequence of the difference in hole mobility between GaAs and AlGaAs. Using an aluminum enhanced etching approach, we demonstrate an effective way to fabricate first order gratings (A=0.3 μm) for outcoupling from GaAs/AlGaAs waveguides (at λ = 1.06 μm).

The striking differences in grating resolution between gratings formed in AlGaAs and GaAs are exhibited in Fig. 1. Here, a 0.575 μm grating has been simultaneously etched into the cleaved face of a double heterostructure, consisting of a GaAs substrate, top and bottom layers of Al0.3Ga0.7As, and a middle layer of Al0.15Ga0.85As, demonstrating that gratings form increasingly better as a function of x in AlxGa1-xAs than in GaAs. Experimental uncertainty is minimized because the different materials were grown in a single sample, and with the same doping.

Here we present a series of experiments which systematically clarifies the advantages of an etching approach which is enhanced by the mole fraction of aluminum in AlxGa1-xAs (aluminum enhancement). To reduce scatter and uncertainty in the experimental data, we introduce a measurement technique which provides a direct measure of both the total etch depth and of the grating depth, allowing a precise calculation of the grating resolution (ratio of grating etch to total etch). This direct measurement technique reduces scatter in the data and eliminates the need for assumptions which are inherent in a hybrid measurement/calibration approach. Previous measurement techniques relied upon a calculation of the total etch depth from etch current, etch time, and sample size data.1–7 and upon an estimation of the grating depth, determined from measurements of the diffraction efficiency of the grating.

FIG. 1. A 0.575 μm period grating has been etched on the cleaved face of a double heterostructure, consisting of a GaAs substrate, top and bottom layers of Al0.3Ga0.7As, and a middle layer of Al0.15Ga0.85As, demonstrating that gratings form increasingly better as a function of x in AlxGa1-xAs.
FIG. 2. (a) Masked stripes thwart etching to allow a direct measurement of total etch depth and grating depth. SEM of (b) 0.7 μm period grating in Al0.5Ga0.5As, illustrating high grating resolution, and (c) 0.7 μm period grating in Al0.1Ga0.8As, illustrating lower grating resolution.

To allow a direct comparison of the grating depth to the total etched depth (relative to the unetched surface), we create alternating stripes of unetched material and material etched into gratings by PEC (Fig. 2). These alternating stripes are defined by masking the surface of the semiconductor sample with 10 μm wide stripes of a thin opaque layer of Ti/Au. Then, gratings are PEC etched in the exposed stripes, with the grating grooves parallel to the masking stripes. An optical interferometer was used to create a sinusoidal variation in intensity across the semiconductor surface using the 488 nm line of an Ar+ laser. An optical intensity of 50 mW/cm² was incident on the sample, which was (100) oriented n-type GaAs, Al0.15Ga0.85As, or Al0.3Ga0.7As, producing gratings oriented along the [011] direction. All of the samples were doped with silicon to the same level, n₀ = 5 × 10¹⁷ 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 in a 1 M H₂SO₄ electrolyte. One 0.33 μm grating was etched on an Al0.3Ga0.7As sample using a HCl:HNO₃:H₂O (4:1:50) electrolyte. Any movement of the optical table or any fluctuations in air temperature causes the optical interference pattern to shift, causing the gratings to be malformed. For this reason, several samples were etched at each grating period, and the one with the greatest grating height was selected for measurement, under the assumption that these represent gratings etched under the most favorable conditions. Finally, the masking layer was removed. To characterize the resultant etch, the samples were cleaved perpendicular to the grating grooves and masked areas, and the cross-sectional cleaved profile was imaged and measured with a SEM. The error in these measurements is a few percent. Figures 2(b) and 2(c) show photos typical of those used for measurement.

A series of etches on GaAs, Al0.15Ga0.85As, and Al0.3Ga0.7As were performed over a range of grating periods (Fig. 3). From these experiments, we conclude that gratings form with higher resolution in Al0.3Ga0.7As than in Al0.15Ga0.85As or GaAs. As the grating period becomes smaller, the grating resolution decreases, but at each grating period, the material which has higher aluminum content consistently produces gratings with greater spatial resolution.

There are several possible explanations for the aluminum enhancement effect. A systematic investigation of these possible explanations suggests that chemical reaction enhancements (increases in the velocity of the chemical reaction) play a small role, while carrier transport effects predominate. In PEC etching, an n-type semiconductor is immersed in an electrolyte and a depletion region is formed within the semiconductor at the solid–liquid junction. Photogenerated holes migrate to the semiconductor-electrolyte interface where they participate in the oxidative decomposition of the semiconductor. At submicron grating periods, the spatial resolution of the PEC etching decreases because this oxidative decomposition and dissolution process is slow enough to allow the photogenerated holes in the semiconductor to diffuse away from the illuminated regions of the laser interference pattern, to the dark regions. The resolution of the gratings etched by PEC depends, therefore, on both carrier movement within the semiconductor, as well as on the rate of the chemical reaction at the semiconductor-electrolyte interface.

First, we consider possible grating resolution differences which could be attributed to differences in the chemical reactions between GaAs and AlGaAs at the semiconductor-electrolyte interface. One possible explanation is that there is initially a native oxide present on the material surface which is more robust and slower to dissolve on GaAs than on AlGaAs. To evaluate this possibility, native oxides were removed by a pre-etch in H₂SO₄:H₂O₂:H₂O 1:1:10 (by volume) for time intervals ranging between 5 and 120 s. After
oxide removal, the AlGaAs still produced higher spatial resolution gratings than the GaAs. In another experiment, gratings were etched using two different electrolytes, to investigate if chemical reaction effects were the root cause of the aluminum-enhanced etching. Gratings were etched in a citric acid electrolyte (0.25 M citric acid: 0.25 M sodium citrate, pH 2.9), and in a HCl:HO3:H2O 4:1:50 (by volume) electrolyte. In both cases, we observed that gratings etched significantly better in AlGaAs than in GaAs. These experiments suggest that the aluminum enhancement is not an effect of a chemical process, but rather an effect of hole transport properties of the material.

To evaluate the possibility of enhanced etching due to differences in the valence band bending or electric field within the semiconductor between AlGaAs and GaAs, we performed a series of etches at different bias voltages. The aluminum enhancement effect was observed over a range of biases. This confirmed that differences in flatband potentials were not responsible for etching differences.

The best explanation of the aluminum enhancement effects is related to differences in carrier transport properties between GaAs and AlGaAs. As the semiconductor is etched, the photogenerated holes drift to the surface under the effect of an electric field induced by the applied bias. While awaiting the chemical reaction process, the holes diffuse laterally, thereby decreasing the grating resolution. We hypothesized that the grating resolution is dramatically better for AlGaAs because the holes diffuse a shorter distance in AlGaAs than in GaAs for the same time interval. The distance which holes diffuse before being consumed in the etching reaction is given by the well-known diffusion length equation

\[ L_p = \sqrt{D_p \tau} \]  

(1)

where \( L_p \) is the hole diffusion length, \( D_p \) is the hole diffusion coefficient, and \( \tau \) is the hole lifetime. It is necessary to consider both \( D_p \) and \( \tau \) in order to understand why the diffusion lengths of holes in AlGaAs and GaAs are different.

The most important factor for hole lifetime, \( \tau \), is the reaction velocity. The expression for the hole lifetime incorporates several terms, and is given by

\[ \frac{1}{\tau} = \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{band-to-band}} + \frac{1}{\tau_{surface}} + \frac{1}{\tau_{PEC}} \]  

(2)

For the semiconductor electrolyte system under consideration a number of these terms are small and may be neglected. Auger recombination will be negligible because the sample is not highly doped and there is low-level injection from photogenerated carriers. Shockley–Read–Hall and band-to-band recombination are small since there are few majority carriers in the space charge region. Neglecting the effect of surface recombination velocity on hole lifetime is appropriate for two reasons. First, previous studies demonstrate that the quantum efficiency of the PEC etching process is close to 100% (that is, most photogenerated holes contribute to the etching reaction), indicating that the surface recombination velocity is much less than the surface reaction velocity. A second, and independent reason, is that surface recombination is typically an order of magnitude higher for AlGaAs than for GaAs. If surface recombination velocity was much larger than the PEC reaction velocity, then \( L_p \) (GaAs) < \( L_p \) (AlGaAs), which is in opposition to the experimental results, which indicate that \( L_p \) (GaAs) > \( L_p \) (AlGaAs). Thus, 1/\( \tau_{PEC} \) is the most important factor in the hole lifetime equation, so that other recombination processes, including surface recombination velocity, are negligible.

Although \( \tau_{PEC} \) has a large influence on the hole lifetime, the diffusion length \( L_p \), is the quantity of interest, thus \( D_p \) must also be considered. We suggest that the dramatic differences in the diffusion length be ascribed to \( D_p \), the diffusion coefficient, which is related to mobility by \( D_p / \mu_p = constant \), where \( \mu_p \) is the hole mobility. Published values for the hole mobility of GaAs range from 230 to 400 \( \text{cm}^2/\text{Vs} \) whereas those of \( \text{Al}_{0.3}\text{Ga}_{0.7} \text{As} \) range from 120 to 300 \( \text{cm}^2/\text{Vs} \). The higher hole mobility of GaAs indicates that holes in GaAs should diffuse twice as far as those in AlGaAs in the same time interval before the etching reaction takes place, causing a lower ratio of grating etch depth to total etch in GaAs than in AlGaAs, as experimentally observed. In conclusion, one must consider the \( \tau_{PEC} \) \( D_p \) product (\( L_p \)) and not \( \tau_{PEC} \) or \( D_p \) independently.

To summarize, we have shown that etching gratings into an epitaxial AlGaAs layer, as compared to a GaAs layer, is a simple and effective technique for PEC etching 0.3 \( \mu \text{m} \) period gratings. This technique enabled first order gratings for a waveguide coupler to be made. We have shown that gratings with about three times the ratio of grating depth to total etch when etched in \( \text{Al}_{0.3}\text{Ga}_{0.7} \text{As} \) rather than GaAs. The lower hole mobility of AlGaAs was proposed as a possible explanation for this grating resolution improvement.

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