Numerical Simulation of a Directional Selectivity Model for Anodic Formation of Porous InP.

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Porosity in electrochemically etched semiconductors has been extensively investigated in the case of silicon and to a lesser degree in the case of III-V compounds such as GaAs[1,2] and InP[3-6]. It has been suggested that controlled modulation of the pore diameter and pore growth direction in semiconductors could allow for the fabrication of devices based on photonic crystal structures.

In previous work by our group, the growth mechanism leading to sub-surface porosity in n-type InP, anodically etched in KOH[3], was experimentally investigated. It was observed that, in the early stages, pores originating from pits in the surface created porous domains of a square based pyramidal structure beneath a thin (~40 nm) dense near surface layer. These then merged into a continuous porous region beneath the dense surface layer. The mechanism proposed for the creation of these structures was based on pore growth solely along the <100> directions at a homogeneous instantaneous growth rate.

This paper presents a numerical simulation of the proposed model. The system to be modeled consists of (100)-oriented S-doped n-type InP, with a carrier concentration of ~4x10^{18} cm^{-3}, anodically etched under potentiostatic conditions in high concentration KOH electrolyte in darkness at room temperature.

The numerical model is based on a three dimensional cubic lattice with solid boundary conditions at the top surface layer, helical[7] boundary conditions for the vertical surface layers and a dynamic boundary at the bottom surface which grows with the porous layer. The lattice lines (<100> directions) represent the paths on which pore growth can occur. Pore growth originates through pits, which form from surface sites (nodes on the top surface layer) with a probability dependant on the applied potential and electrolyte concentration. Once a surface pit has formed the probability of pore growth in a time step, along any of the lattice lines, is determined by the potential at the pore tip and an electrolyte concentration parameter at the pore tip. In both the case of surface pits and the case of pore tips, growth is allowed only if the electrolyte concentration and node potential are greater than set threshold values. Where this is the case, probability of growth at a site is proportional to the site potential. The probability for tip growth is several orders of magnitude greater than the probability of surface pit formation at the same potential.

The electrolyte concentration parameter is modeled by a simple diffusion of electrolyte through the pore channels. A Finite Difference Method using the Forward Time Centered Space approximation of the three dimensional diffusion equation is run for a number of iterations at the end of every pore growth time step to calculate the diffusion of electrolyte through the pore channels.

For pore growth to occur, ionic current must pass through the channels connecting the pore tip to the surface causing a potential drop along the channel. The actual potential across the electrode–electrolyte interface at any pore tip is therefore less than the applied potential by this ohmic drop. The ohmic drop is calculated from the summation of the current flowing through each of the channel nodes connecting the tip to the surface, using the assumption that electrical resistance is constant along the channel length.

The computer algorithm produces similar initial porous domains as are produced experimentally[3] and at extended durations of growth this strong resemblance is maintained. Typical current versus time curves, obtained through simulations, are shown in Fig. 1. These are in good agreement with experimental results. In simulations at a series of constant values of applied potential it is observed that, as the potential is decreased, the current peaks occur at later times, decrease in height and broaden before tailing off. The simulations show that the drop off in current is caused by the decrease in concentration of electrolyte at the pore tip. This may be concluded from the observation that as the diffusion coefficient is increased the peaks become broader.
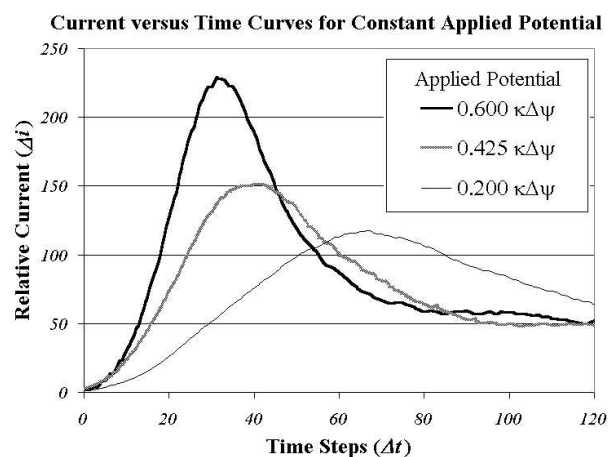
Fig. 1 Simulated current versus time curves for a series of constant values of applied potential. Current is calculated from the number of pore tips growing in a time step. The simulations use a three dimensional dynamic lattice of surface area 70 times 40 nodes.

References

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