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Uniform and Nonuniform Nucleation of Pores during the Anodization of Si, Ge, and III-V Semiconductors

S. Langa,[a,b] J. Carstensen,[a] M. Christophersen,[a,*] K. Steen,[a] S. Frey,[a,*]
I. M. Tiginyanu,[b,*] and H. Föll[a,*]

[a]Faculty of Engineering, Christian-Albrechts-University of Kiel, 24143 Kiel, Germany
[b]Laboratory of Low Dimensional Semiconductor Structures, Technical University of Moldova, 2004 Chisinau, Moldova

Morphology is one of the basic characteristics of porous layers. For electrochemically grown pores, morphology is strongly dependent on the starting phase of pore growth, the so-called nucleation phase. This paper addresses uniform and nonuniform nucleation of pores on the surface and consequently the development of pores into the bulk of the following semiconductor substrates: Si, Ge, and III-V compounds (GaAs, InP, and GaP). It was found that nonuniform nucleation can cause formation of domainlike porous structures in all investigated semiconductors. However, depending on the anisotropy of the substrate, these domains show significant differences between them. The particularities of each type of domains are discussed.
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Electrochemistry and photoelectrochemistry[1] of semiconductors have been studied in detail in the past.[2,3] However, the discovery of nano- and macropores in Si at the beginning of the nineties[4,5] started a new phase in understanding semiconductors from the electrochemical point of view. Morphologically, the most astonishing feature of anodically etched macropores in Si is their intrinsic ability to grow without any lithographic mask. This means that, on a flat Si surface, random macropore nucleation leads to (at appropriate anodization conditions, *i.e.*, substrate doping, electrolyte concentration, externally applied voltage/current density, etc.), a rather homogeneous distribution of pores with respect to pore diameters and pore-to-pore distances.[6,7]

Electrochemically etched pores on flat wafer surfaces in other semiconductors, essentially III-Vs, Ge, SiC (and GaN), were achieved as well. However, the results are often quite different from what is already known from Si (see, for example, Ref. 8-13). One main difference between silicon and all other mentioned semiconductors (with the exception of Ge) is the short minority carrier diffusion length. The long minority carrier diffusion length in case of silicon allows the use of back-side illumination (BSI) for pore formation. The high-quality two-dimensional (2D) porous structures[14,15] were mostly (n-type pores) fabricated under back-side illumination. As a result, pores in III-Vs are usually obtained in the dark by means of the so-called avalanche breakdown mechanism.[16] In spite of the fact that breakdown pores show new and interesting features, they also incur many new difficulties, which are rarely observed with back-side illuminated Si.

The most noticeable difference between pores in Si and other semiconductors is generally a rather poor nucleation uniformity in semiconductors different from Si,[16,17] *i.e.*, pores start to grow only at some "special points" on the surface of the sample, leading to a highly inhomogeneous distribution. These special points are usually surface defects,[18,19] where normally more holes (necessary for dissolution) can be generated by a breakdown mechanism. While the nonuniform distribution of surface defects provides a simple explanation for the observed pore nucleation inhomogeneities, it is not the whole explanation. Inhomogeneous nucleation is observed also in cases where homogeneously spaced nuclei, *i.e.*, defects, were provided by lithography,[20] while homogeneous nucleation (following certain procedures[17,21]) can be obtained on indistinct surfaces as well.

A common phenomenon for the semiconductors discussed in this paper is that from one nucleation point often a whole set of pores will develop in time. These pores are normally spatially correlated and are called pore domains. Among the first porous domains were the ones observed in anodically etched GaP and described in detail by Erne et al.[19] The present paper reports other distinct domain types observed in Ge, GaAs, and InP. No domain formation had been observed in Si until the recent discovery of the rather exotic "fractal" pores[22] which form clear surface domains. The aim of this paper is to discuss the etching conditions, the mechanism of domain formation, and the most common and uncommon features by comparing different types of domains. In parallel, some approaches for uniform pore nucleation are discussed as well.

In order to avoid any confusion, note that pores forming the different domains are distinguished to be of two types: (*i*) crystallographically oriented and (*ii*) current line oriented. The following paragraphs summarize briefly the properties of these types of pores.[8]

Crystallographically oriented pores, abbreviated crysto pores, have definite crystallographic directions of growth, *e.g.*, ⟨100⟩ for Si and Ge, and ⟨111⟩*B* for GaAs, InP, and GaP. Along ⟨111⟩ directions the zinc blende lattice of III–V compounds consists of double layers with alternating short (three bonds) and long (one bond) distances, and the layers are occupied by *A* (In, Ga) or *B* (P, As) atoms, respectively. The ⟨111⟩*B* direction then runs from *B* to *A* layers along the shortest distance between *B* and *A* planes (or from *A* to *B* along the longest distance between *A* and *B* planes). It is important to note that *A* planes are generally more stable against dissolution than *B* planes.[23,24] This is consistent with the experimental observations showing the pores growing along {111}*B*,[8] *i.e.*, along the less stable direction.

The current line-oriented pores (curro pores for short) have no preferential crystallographic directions of growth.[25] They exhibit a well-pronounced tendency to grow perpendicular to the equipotential surfaces of the electric field inside the sample (or current flow direction), independent of sample orientation. It also means that, for curro pores, the difference in chemical reactivity between different crystallographic planes is not important anymore.

As a rule of thumb, it can be assumed that crysto pores grow at low, and curro pores at high voltages (U) or current densities (j) applied to the sample. Until now, curro pores have mostly been observed in InP and GaP; however, a particular type of curro pores has been recently found in Si as well.[26] The existence of curro pores in III-Vs is very surprising, taking into account their very strongly expressed anisotropic features during chemical and electrochemical etching.

Experimental

Si, Ge, GaAs, InP, and GaP samples from various sources, with polished or unpolished surfaces, and areas of typically 0.2 (III-Vs and Ge) and 1 cm^2 (Si) were etched in electrochemical cells described elsewhere.[27,28] The surface orientation was (100), all samples were of n-type (with exception of the Si ones), and the

* Electrochemical Society Active Member.