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While electrochemical pore etching in semiconductors has become a thriving field for research (and applications) in the past 15 years or so, little work has been done in Ge. Besides Si, Ge is the only semiconductor with a diffusion length large enough to enable the use of backside illumination, which has proved to be the decisive "trick" for the formation of excellent macropores in Si, and experiments in this vein have been conducted. However, Ge proved to behave in rather unexpected ways – the large body of pore etching knowledge obtained with Si and the III–V's was not directly applicable to Ge. While no good pores could be produced in most previous endeavours including our own, we finally succeeded in producing deep pores in n-type but also in p-type Ge of various doping levels and crystal orientations. A host of new and not yet totally understood phenomena was discovered.

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1 Introduction

Ge is the only semiconductor that shares some rather special characteristics with Si that have direct bearing on pore etching: Ge is a (non-polar, indirect) semiconductor available as rather perfect single crystal with large diffusion lengths. This allows macropore etching with backside illumination in principle, the major mode for making rather perfect macropores with large aspect ratios in n-type Si [1] and an in-depth study [2] is that pore etching in Ge is very different in most aspects to what is known from other semiconductors. In this overview a few results will be presented summarily; for more details refer to [2].

2 Experiments

Anodic etching was generally done in an electrochemical double cell described elsewhere [3], under fully controlled parameters including the temperature and pre-programmed current or voltage profiles in time [4]. All kinds of electrolytes have been used, in particular HCl, H_2O and dimethylsulfoxide (DMSO), with the DMSO fraction ranging from 0% ("aqueous" electrolyte) to 100% ("organic" electrolyte). Ge single crystal samples with low, moderate (around a few Ω cm) or high ($\ll 1$ Ω cm) n-type and p-type, having polished, unpolished but etched, or abraded surfaces and areas of typically 0.2 cm^2, and {100}, {110}, {111} orientations were used. A large range of measures for improving the initial nucleation have been tried and used, including surface modifications (e.g. by abrading), initial current or voltage pulses, current or voltage ramps "upwards" or "downwards", and initially higher or lower temperatures as well as combinations thereof. Frontside (fsi) as well as backside (bsi) illumination was tried. However, if not otherwise specified, etching was done in the dark.

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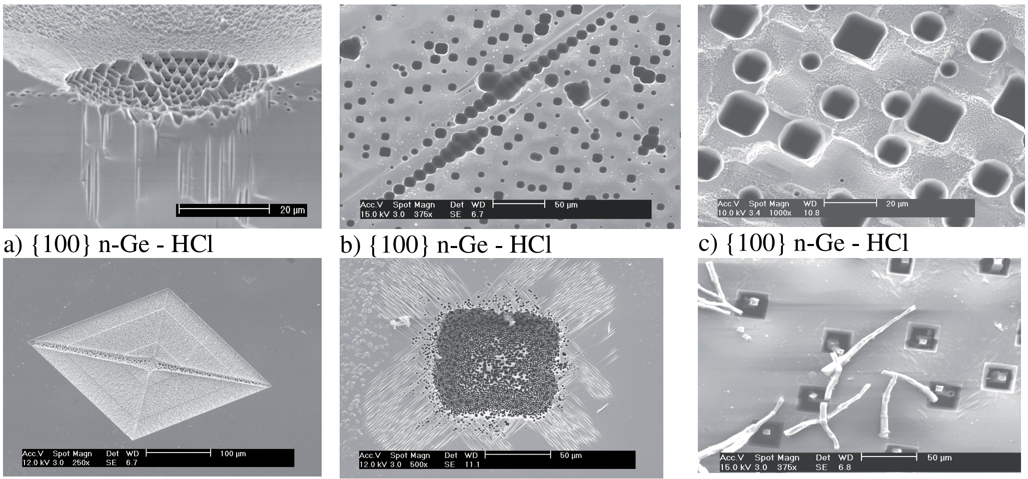


a) {100} n-Ge - HCl b) {100} n-Ge - HCl c) {100} n-Ge - HCl

d) {110} n-Ge - HCl e) {100} n-Ge - HCl f) {100} n-Ge – $AlCl_3$+DMF

Fig. 1 Pores arranged in domains or in non-uniform ways for n-Ge. For details see text.

3 Results

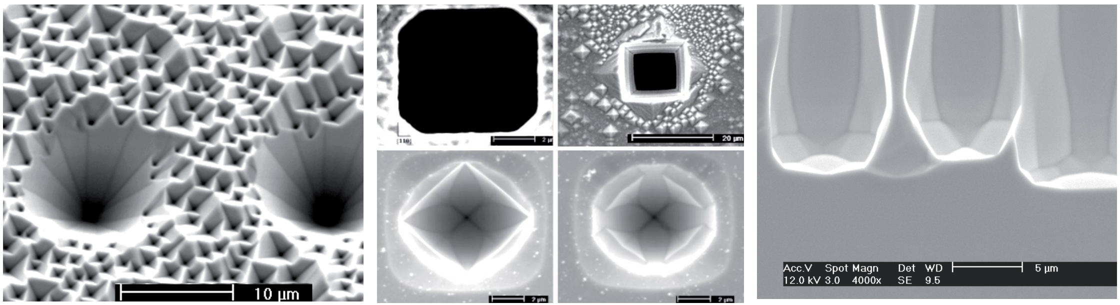
As noticed before [2], there is always a rather large “leakage” current flowing through pore walls and all other surfaces, leading to “electropolishing” on top of the pore etching. This not only tends to make pores conical in shape, but also destroys the original surface, often leaving a rough surface behind that lies considerably below the original one – the specimen gets thinner all the time. However, if a dense array of pores could be achieved (which generally is a difficult task), pore walls were more stable, most likely because they only contain the space charge region (SCR) and thus no free carriers. From classical junction theory this has to be expected, because the ratio of leakage currents I_l in Si or Ge p−n junctions scales with the intrinsic carrier concentration, which is about 2000 times larger in Ge as compared to Si. On the other hand, while almost all leakage current in a Si junction comes from the SCR and not from the bulk, the situation is reversed in Ge, and thin, SCR “filled” pore walls can be expected to efficiently stabilize pores in Ge.

In contrast to most other semiconductors, the doping level does not express itself in an unambiguous way (e.g. by defining a critical length tied to the width of the space charge region). Pronounced doping level effects are only found whenever the nucleation produces dens and uniform pore arrays.

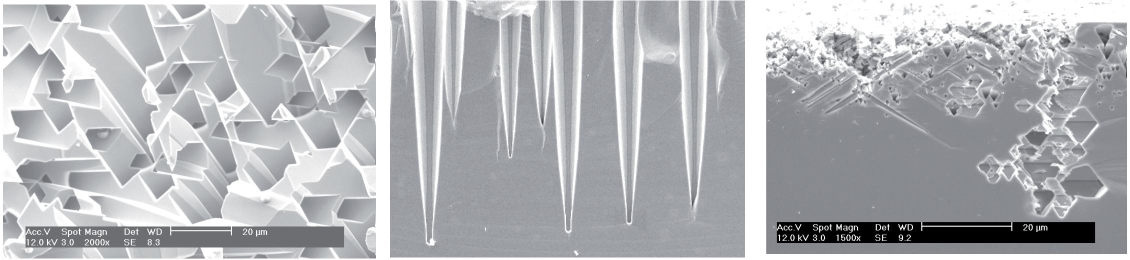
As a rule, uniform pore nucleation in Ge is far more difficult than in most other semiconductors. One attempt at lithographically defined nucleation with the usual techniques was not successful either [2]. Measures that proved successful up to a point have been mentioned above, Fig. 1 gives a few examples illustrating this topic; all kinds of domains were obtained under different etching conditions. The inhomogeneous nucleation can be seen clearly in Fig. 1c. Figure 1f not only shows inhomogeneous nucleation, but rather large pores filled with GeO_2, a new kind of structure not observed before, that tends to occur at low HCl concentrations.

However, much progress has been made. With proper procedures rather homogeneous pore growth can be achieved by now; an example is shown in Fig. 3c.

Pores are often prismatic in shape, i.e. have crystallographic planes as faces. The pore crystallography, however, is not as simple as in most other semiconductors, where usually one dominating “stopping” plane determines the pore shape. Figure 2 gives some examples of the features encountered. Pore tip pyramids can be of either the {111} type or the {110} type (for pores growing in ⟨100⟩), and sidewalls are of the {110} type or {100} type (Fig. 2e), and even {113} (Fig. 2a). In fact, a large pore may have a square cross-section with {110} oriented sidewalls following a {111} tip (Fig. 2c) in the freshly grown part, while the older part, probably due to electropolishing “rotates” to a square cross section with {100}



a) {100} n-Ge - HCl b) {100} n-Ge - HCl c) {100} n-Ge - HCl



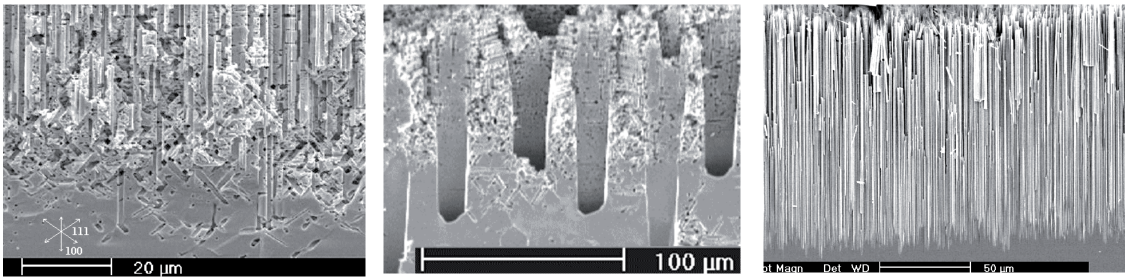
d) {111} n-Ge - HCl e) {100} n-Ge - HCl f) {100} n-Ge - $AlCl_3$ + DMF

Fig. 2 Various nuclei and pores with prismatic shapes, expressing several crystallographic planes. For details see text.

walls. In between the pore is octagonal, as shown in Fig. 2b, e. In transition regions, {113} planes are encountered, too; this is nicely illustrated in the 12-sided etch pit (a precursor of a pore) in Fig. 2a and in the other pore precursors in Fig. 2b.

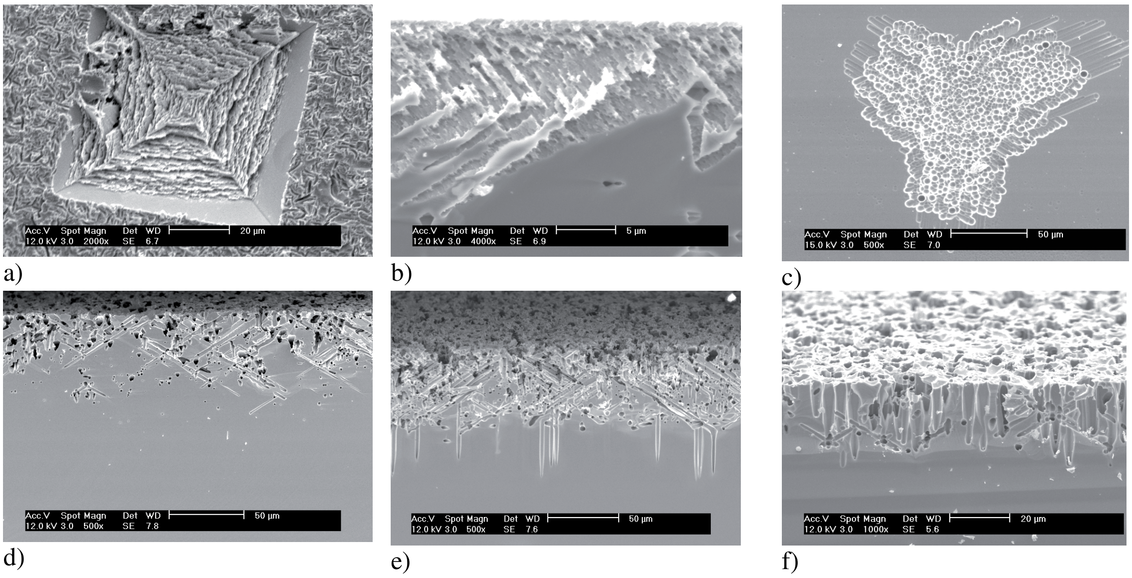
While previously the major growth direction of pores was identified as ⟨100⟩ [5], meanwhile the ⟨111⟩ direction was also found to be a major growth direction. Generally, ⟨100⟩ is preferred for lower HCl concentrations, aqu. electrolytes, and large pores; ⟨111⟩ is observed with org. electrolytes and larger HCl concentrations. Switch-overs as in Fig. 3a are observed or can be induced, or ⟨100⟩ and ⟨111⟩ pores occur simultaneously as in Fig. 3b.

Replacing the H_2O in the standard HCl electrolyte gradually with DMSO to obtain an "organic" electrolyte, produces three major effects: (i) it is possible to etch "good" pores into p-type Ge; something so far only observed with Si and SiC [6–8]. (ii) The major growth direction switches from ⟨100⟩ to ⟨111⟩ via an intermediate state containing "amorphous" pores, showing no pronounced crystallography, as shown in Fig. 2c. (iii) Pronounced domains with complex structures are found more frequently then with aqueous electrolytes. Figure 4 shows some examples with short explanations.



a) b) c)

Fig. 3 Different growth directions and pore sizes (aqu. electrolyte n-type {100} Ge). For details see text.



a) b) c) d) e) f)

Fig. 4 All n-type {100} in HCl-DMSO. a) Domain top view, b) detail, c) intermediate "amorphous" domain, d) ⟨111⟩ macropores in cross-section, e) switch-over from aqu. to org. changes ⟨111⟩ to ⟨100⟩, e) switch-over from org. to aqu. changes ⟨100⟩ to ⟨111⟩.

Pores in p-type Ge are presented in some detail elsewhere in these proceedings; Fig. 5 shows some direct comparisons between n-type and p-type. While changing the electrolyte from aqu. to org. produces significant effects as shown above in n-type Ge, the pores etched into p-type Ge with org. electrolytes resemble the ones found in n-type with aqu. electrolytes.

While no pronounced self-induced current (or voltage) oscillations in the electropolishing regime have been observed with Ge so far (in marked contrast to Si [9]), pronounced voltage oscillations during pore growth in Ge have now been observed for the first time; Fig. 6a gives some examples. Self-induced diameter oscillations can be found, too, as shown in Fig. 6b, c. While some features are reminiscent of similar phenomena found in III–V semiconductors and Si [10], Ge shows new effects, too.

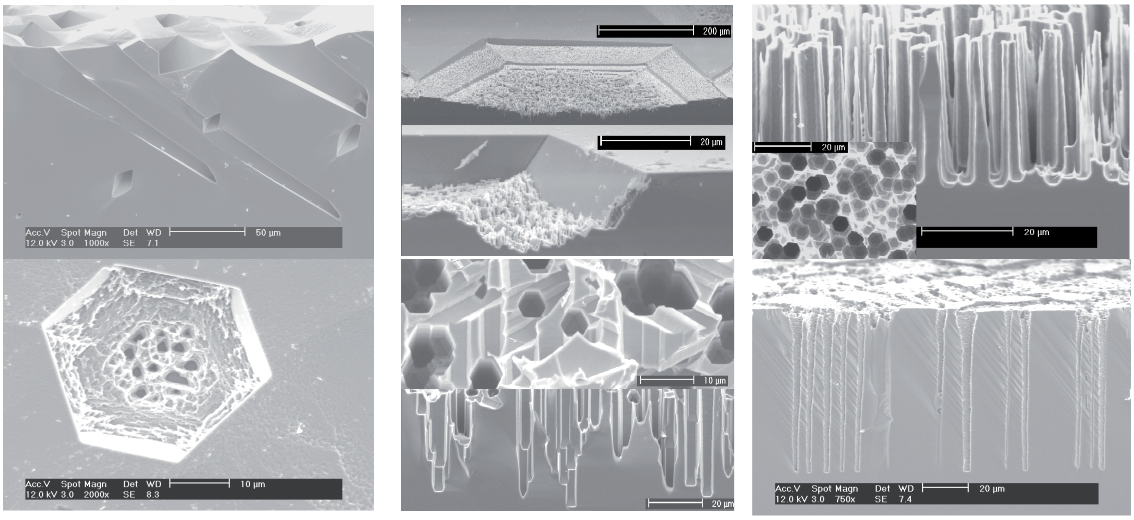


Fig. 5 Some {111} Ge impressions. Upper row: n-type, HCl-aqu.; bottom row: p-type, HCl-DMSO.

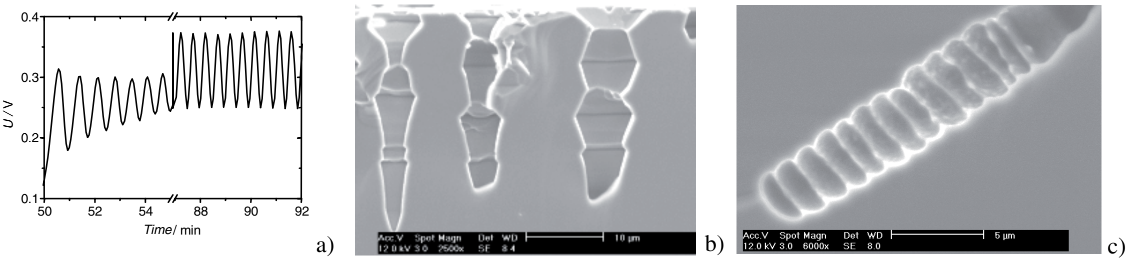


Fig. 6 a) Potential oscillations during pore etching occurring after a current ramp was finished. (n-type, aqu. electrolyte). b), c) Self-induced diameter oscillations (org. electrolytes) for ⟨100⟩ pores (b) and ⟨111⟩ pores (c).

4 Conclusions

Pore etching in Ge produced an unexpected richness of structures that are mostly unique and not easily understood in the contest of what is known form pore etching in other semiconductors. In comparison to other semiconductors, the semiconducting properties of Ge (expressed, e.g. in the hole generation and concentration) are less important for pore etching than its very complex "chemistry". There is now enough experimental data for attempts of modelling; first suggestions have been made, involving in particular the interaction of Ge, GeO_2 and HCl [2].

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