Rapid Research Note

Electrochemical pore etching in Ge

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Nucleation and growth of electrochemically obtained pores on (111) and (100) oriented n-Ge in different electrolytes was investigated. On rough surfaces pore density increases as the current density increases, whereas on smooth surfaces the situation is inverse, i.e., the pore density increases as the current density decreases. The macropores show strong anisotropic features with a cone-like shape. This can be understood if the passivation of the pore walls in Ge is less pronounced as in the case of Si or III–V compounds, but strongly anisotropic.

Introduction While there is a wealth of old information concerning the electrochemistry of Ge, cf. [1], there are only 5 more recent studies on pore etching [2-5] and no macropores were found so far by pure anodic etching. While Ge today plays only a marginal role in semiconductor technology, pore formation in Ge could be of interest for applications like photonic crystals [6], sensors or filters. In this letter anodically etched Ge macropores and their morphological features are reported for the first time.

Experimental Ge samples from various sources with a thickness of 1 mm, polished and unpolished surfaces with areas of typically 0.2 cm^2 were etched in an electrochemical double cell described elsewhere [7]. Surface orientations were (111) and (100), all samples were n-type, and the doping levels were 10^{18} cm^{-3} and 10^{15} cm^{-3} , respectively.

The electrolytes used were H_2SO_4 (5%, diluted with water), $H_2SO_4 + CrO_3$ (5%, diluted with water), and HCl (5%, diluted with water); all experiments were done in the dark under potentiostatic or galvanostatic conditions. Etching times were typically 15–120 min; the samples were investigated with a scanning electron microscope (SEM) in plane view and in cross-section (after cleaving). Experiments using backside illumination (standard conditions for macropores in Si [8]) were unsuccessful so far; the necessary hole supply therefore must rely on some breakdown mechanism.

Results On {111} samples no good pore structures could be obtained with all three electrolytes. At best, large triangular or hexagonal pits with some tendency to extend some pores into the bulk (along $\langle 100 \rangle$ directions) were obtained. For {100} samples, however, pronounced macropores growing in $\langle 100 \rangle$ were obtained with the HCl electrolyte; and only these results will be presented here.

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Fig. 1 5% HCl, t = 120 min, T = 20 °C. Rough surface, plane view, a) j = 2.5 mA/cm², b) j = 7.5 mA/cm². c) Rough surface, cross section view, j = 7.5 mA/cm². d) Smooth surface, plane view, single porous domain.

The first (unexpected) result is the general presence of some electropolishing, i.e. constant dissolution of the surface, even during stable growth of pronounced macropores. The plane view micrographs thus do not show (approximately) the original surface, but a cut through the structure at a depth that depends on the total etching time. This seems to be a unique feature that has neither been observed in Si nor in III–V semiconductors.

The second general observation is that homogeneous pore nucleation is quite difficult to achieve. While this effect is also observed in III-V compounds [9, 7] and must be expected to some extent when working in avalanche breakdown conditions, its dependence on etching parameters (current density) is quite different from the other semiconductors.

The homogeneity achieved on rough (= unpolished) and polished {100} surfaces is distinctly different. For rough surfaces the pore homogeneity increases with increasing current (Fig. 1a, b), while for a smooth surface the pore homogeneity decreases. The reason for this seems to be the co-existence of pore etching and electropolishing. Since electropolishing does not need nucleation, it will be dominant on polished surfaces where pore nucleation is difficult. Only by reducing the overall current density, electropolishing can be slowed down to a point where pore nuclei can survive for the time needed to induce a stable pore formation.

Figure 1c shows a cross section of the pore structure obtained at a current density of 7.5 mA/cm^2 and demonstrates that distinct macropores with clear features are obtained. This is a remarkable observation because in n-Si under avalanche breakdown conditions mesopores (diameters < 50 nm) are usually obtained. However, comparable structures are found in n-type III–V compounds etched under breakdown conditions [10].

A particular conspicuous issue preferably found on polished surfaces etched at high current densities is the formation of pronounced pore domains, i.e. clearly expressed systems of secondary pores always centered around a central primary pore, as shown in Fig. 1d. Bearing in mind that pore nucleation under those conditions is enhanced for reduced current densities, domain formation can be understood if the potential and thus the current is significantly reduced in an area around a primary macropore. This is precisely what will happen if there are ohmic losses, particularly in the electrolyte.

The pores show a certain tendency to form side pores growing in $\langle 100 \rangle$ directions. However, since the density is low and the side pores are not contained in the cleavage plane, they are not easily seen in cross section; Fig. 2a shows an exception. Since electropolishing is continuously exposing areas formerly hidden in the bulk, side pores become well visible on the sample surface; this is shown in Fig. 2b. The pictures can also serve to illustrate another new feature in semiconductor pore etching: The pore walls are very well expressed {110} planes, only sometimes with small {100} facets left in the corners. Thus, the difference in passivation between {110} and other crystallographic planes must be relatively large. This has never been observed before; Si macropores have a comparatively weak preference for {100} planes, while III–V compounds strongly favour {111} B planes, i.e. the planes exposing the atoms from the Vth group of the periodic table of elements [11].

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Fig. 2 a) Side pores emerging from a central pore visible at the top, but obscured lower down by uneven cleavage; b) side pores (marked by arrow) rendered visible by continuous electropolishing of the surface; c) conical pores; d) pore walls between close pores.

Figure 2b shows pores with quite different diameters. Larger pores nucleate earlier and therefore have more time to grow laterally. The lateral growth is also evident by the conical shape of the pores (Fig. 2c). Only if neighbouring pores come too close, the lateral growth will stop. The thickness of the pore walls remaining in this case seems to correlate with twice the space charge region width; Fig. 2d shows an example.

Conclusions While it is too early to ponder on details of pore formation in Ge, it appears that two major points can be emphasised:

The lateral growth of pores is consistent with the assumption that the degree of passivation of Ge surfaces in the electrolytes used is far smaller than in Si and III–V compounds while the relative differences between different crystal planes may be even more pronounced. Passivation in this context refers to the density of interface states in the band gap found after prolonged exposure to the electrolyte and with no current flowing [12].

The second assumption follows from the observation of continuously proceeding electropolishing, implying that there is a hole source besides avalanche breakdown at pore tips. This might simply be the leakage current of the reverse biased Ge/electrolyte junction which is intrinsically larger than in Si, and contains an additional component due to the postulated unpassivated surface states.

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