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High-aspect ratio microstructures in p-type GaAs and InP created by proton beam writing

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ABSTRACT

With proton beam writing (PBW) and subsequent electrochemical etching in HF-solution the creation of high-aspect ratio microstructures in p-type InP was performed for the first time. Microstructures with high surface quality as well as high-aspect ratio possessing lateral dimensions down to 1 μm were produced. Furthermore, free-standing microstructures were created in this material by a combined irradiation with 2.25 MeV protons and 1.125 MeV H_2^+ molecules, were the smallest structure dimension of 0.6 μm was achieved for a horizontal needle. The creation of nearly perfect circular microstructures indicates that the crystal structure has little effect on the structuring process by PBW in this material. Moreover, the effect of reduced etching inside of closed irradiation patterns, already known from Si and GaAs, was observed also in InP. In further PBW experiments and subsequent electrochemical etching with KOH-solution p-type GaAs microstructures were produced. By using a 4-fold higher etch current density of 45 mA/cm^2 compared to former PBW experiments on this material the quality of the microstructures could be improved significantly leading to high aspect-ratio structures with minimum lateral sizes of ~1 μm, nearly vertical side walls as well as circular microstructures. This shows the reduced influence of the crystal structure on the shape of the microstructures compared to experiments with lower etch current density where only flat microstructures with inclined side walls determined by the crystal structure could be created.

1. Introduction

Since the III-V semiconductors InP and GaAs are well suited materials for high frequency and optoelectronic devices, simple and fast methods for their structuring also for prototypes and small batch series are required. It was already shown that microstructures could be created in these materials by proton beam writing (PBW) and subsequent electrochemical etching [1,2]. However, the high and partly free-standing microstructures in p-type GaAs produced by PBW exhibit relatively large lateral dimensions of some micrometers while the shape of microstructures with smaller lateral dimensions are strongly influenced by the crystal structure resulting in flat structures with inclined side walls [3]. For the creation of smaller microstructures with more vertical side walls, experiments with larger etch current density and thereby reduced etching time were carried out in order to minimize the possible pure chemical etching influenced by the crystal structure. Furthermore, for InP only PBW experiments with n-type and semi-insulating material were carried out up to now resulting either in hardly etched microstructures embedded in porous material or in microstructures with small height differences due to a very small etch rate of the irradiated material, respectively [2]. The different electrochemical reaction processes of the p-type InP could possibly lead to the creation of high-aspect ratio microstructures in this material by PBW, similar to p-type Si [4] and GaAs. Therefore, the microstructure creation in p-type InP by PBW is also investigated in this study.

2. Experimental details

For the PBW experiments Zn-doped p-type GaAs and InP with (100)-orientation were used, both supplied by CrysTec GmbH. The charge carrier concentrations were 1×10^{18} cm^{-3} for GaAs and 3–6 $\times 10^{18}$ cm^{-3} for InP, respectively.

The irradiations were carried out at the LIPSION ion nanoprobe with 2.25 MeV protons as well as with 1.125 MeV H_2^+ molecules using pieces of 1×1–2×2 cm^2 cut from the semiconductor wafers. The ion beam was focused down to ~1 μm in diameter. The used irradiation fluences were 4.6–230.3 $\times 10^{15}$ H^+/cm^2 for GaAs and 6.9–237.2 $\times 10^{15}$ H^+/cm^2 and 1.2–62.4 $\times 10^{15}$ H_2^+/cm^2 for InP, respectively, with ion beam currents of 287–1200 pA for protons and 30–350 pA for molecules. It has to be considered that by using the H_2^+ beam, the molecules will split into two protons,

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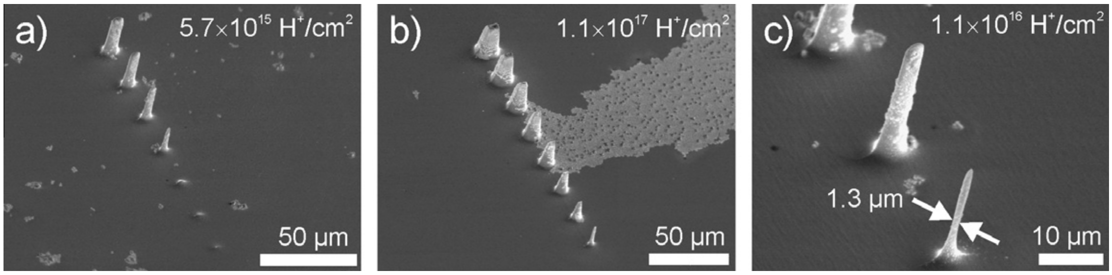

Fig. 1. SEM images of GaAs micropillars of different size, created by irradiation of square patterns with 2.25 MeV protons and the mentioned fluences and subsequent electrochemical etching. Pillar formation for irradiation pattern sizes of (a) 5 μm and (b) 1 μm and larger as well as (c) the smallest created GaAs pillar with diameter of 1.3 μm and aspect ratio of 15.

each with half the kinetic energy of the molecule, immediately at the surface of the irradiated sample. This results in a much shorter penetration depth as well as in a twice as high fluence in H^+/cm^2 compared to the same number of incident particles of 2.25 MeV protons.

For the subsequent electrochemical etching procedure the irradiated samples were pressed against an O-ring of a Teflon etching cell by a stainless steel plate. The electrical backside contact was established by an In/Ga eutectic alloy. The GaAs samples were etched for 20–22 min with 39–46 mA/cm^2 at 1.6–1.9 V in 10% KOH. KOH exhibits a higher etch rate than Tiron used by Mistry et al. for PBW experiments of GaAs [5], and results in smoother etched surfaces compared to other etchants [6]. For the InP samples a diluted HF solution, consisting of HF:H_2O:ethanol (1:17:2), was used, which leads also to a very smooth etched surface [7]. Here, the etch process took 17–80 min depending on the etch current density of 13–43 mA/cm^2 at 3.0–6.8 V. After the electrochemical treatment the samples were washed in deionised water and dried.

3. Results

3.1. GaAs

The ion bombardment of the GaAs samples leads to the creation of defects and thereby to a different electrochemical etch behavior of the irradiated areas compared to the unirradiated regions. SRIM2006 simulations [8] of 2.25 MeV protons using displacement energies of E_d = 10 eV for Ga as well as for As atoms [9] result in a defect production of 2.1×10^{-4} vacancies/ion/nm at the sample surface and of 2.0×10^{-2} vacancies/ion/nm at the Bragg peak shortly before the end of ion range of 39 μm. For an irradiation fluence of 1×10^{16} H^+/cm^2 this leads to a defect density of 2.1×10^{19} defects/cm^3 and 2.0×10^{21} defects/cm^3, respectively, which is up to three orders of magnitude larger than the charge carrier concentration of the GaAs samples.

Former experiments concerning the structuring of p-type GaAs by PBW at the LIPSION nanoprobe showed that the crystal structure has a strong influence on the etch process [3]. In this case, current densities of 2.5–9 mA/cm^2 were used for electrochemical etching resulting in flat structures with inclined side walls and different inclination angles.

In order to avoid a possible pure chemical etch process, that is influenced by the crystal structure, proceeding simultaneously with the electrochemical material dissolution, about 5 times higher etch current densities of 39–46 mA/cm^2 were used in the latest experiments.

In fact, these changes of the etch parameters result in high microstructures with almost vertical side walls, as can be seen in Fig. 1. For squares irradiated with the lowest fluence of 5.7×10^{15} H^+/cm^2 the formation of pillars for irradiation pattern sizes of 5 μm and upwards can be observed (Fig. 1(a)), while for the highest fluence of 1.1×10^{17} H^+/cm^2 pillar formation occurs also for the smallest irradiation pattern sizes of 1 μm (Fig. 1(b)). The cross-section size of the pillars depends on the irradiation pattern size and the fluence. However, the cross-section shape is still slightly influenced by an anisotropic material dissolution, resulting in rectangular or elliptic cross-sections despite of quadratic irradiation patterns. In Fig. 1(c) the smallest pillar with a diameter of 1.3 μm has a height of 20 μm resulting in an aspect ratio of 15.

Sometimes, residues are left on the sample surface after the electrochemical etching as shown e.g. in Fig. 1(b). It has to be tested in future experiments whether they can be removed by an increase of the etch current density to 100–300 mA/cm^2 for a few seconds at the end of the etching process or not.

Inside of closed irradiation patterns a fluence dependent reduction of the etch rate of the unirradiated material was observed (Fig. 2(a)). This effect was already seen for p-type Si [10] and explained by the deflection of the *E*-field lines, which are responsible for the hole transport and thereby for the electrochemical dissolution, outside of the irradiated areas as well as of the regions nearby due to the accumulation of positive charges at the irradiation induced defects [11]. For the highest fluence of 9.1×10^{16} H^+/cm^2

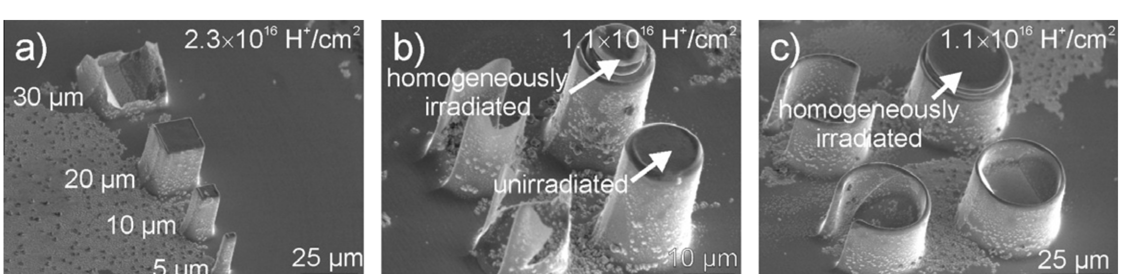

Fig. 2. (a) Rectangular and (b,c) open and closed circular GaAs microstructures showing the reduced etch rate of unirradiated material that is surrounded by closed irradiation patterns. As can be seen in (a) the amount of reduction depends on the structure size.