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Etching nano-holes in silicon carbide using catalytic platinum nano-particles

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ABSTRACT The catalytic reaction of platinum during a hydrogen etching process has been used to perform controlled vertical nanopatterning of silicon carbide substrates. A first set of experiments was performed with platinum powder randomly distributed on the SiC surface. Subsequent hydrogen etching in a hot wall reactor caused local atomic hydrogen production at the catalyst resulting in local SiC etching and hole formation. Secondly, a highly regular and monosized distribution of Pt was obtained by sputter deposition of Pt through an Au membrane serving as a contact mask. After the lift-off of the mask, the hydrogen etching revealed the onset of well-controlled vertical patterned holes on the SiC surface.

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1 Introduction

Various experimental methods for the synthesis of nanoporous materials are reported in the literature. Mainly based on electrochemistry, porous semiconducting nanostructures can be obtained in silicon [1], silicon carbide [2–4], gallium nitride [5] and gallium arsenate [6–9] in a nearly routinely manner. Most of these porous materials exhibit irregular structures. Regular pore structures have been reported for silicon [10–12], alumina [13, 14] and recently for silicon carbide [15, 16]. These porous materials exhibit interesting new photonic, electronic and mechanical properties. Especially silicon carbide has many favourable properties compared to silicon and the achievement of vertical nanopores and regularly distributed holes in SiC is a research field of increasing interest. A few experimental approaches for SiC have been reported so far. In all these cases, pre-structured holes in the substrate are etched with hydrogen at elevated temperatures in the final process step. Pre-structured holes can be obtained either by focused ion beam etching [15], reactive ion etching through a physical mask [17] or via the revealing of defects in an electrochemical process [18]. As a pre-treatment of the semiconducting surface, hydrogen erosion of SiC is used for the preparation of clean, flat SiC surfaces [19, 20]. In the present paper, we report on the catalytic reaction of platinum nanoparticles during a hydrogen etching process of silicon carbide. The reduction of molecular hydrogen to atomic hydrogen, occurring in the platinum metal, gives rise to a locally enhanced etching process of SiC. Similar studies have been reported for the silver-silicon system [21]. The catalytic reaction of deposited silver particles on a Si(100) surface gave rise to nanoholes when etched in a solution containing HF and H_2O_2. An irregular network of pipes several micrometers deep was obtained.

2 Experimental results

SiC samples were cut from an on-axis, nitrogen-doped, n-type (resistivity 0.03–0.12 $\Omega\,m^{-1}$) silicon terminated 6H-SiC(0001) wafer from SiCrystal [22]. Before the patterning process, the wafer has been etched in a hot wall reactor at 1700 °C for 20 min [23]. This procedure leads to a SiC surface with a well-defined smooth morphology [19, 20, 24]. In a first set of experiments, platinum powder with a grain size between 100 and 450 nm, dissolved in ultra-pure alcohol, was placed on the SiC surface. After drying of the solvent, the obtained Pt clusters revealed an irregular shape and were randomly distributed as investigated with scanning electron microscopy (SEM) (see inset in Fig. 1). The SiC surfaces covered with Pt particles were subsequently etched in hydrogen in a horizontal graphite hot wall reactor [23]. Hydrogen etching was performed at a hydrogen pressure of 13 mbar. The samples were etched in a temperature range between 700 °C and 1000 °C. This temperature is too low to allow significant etching without the presence of the catalyst.

The etching time intervals were varied between 30 and 120 min each. The hydrogen flow was kept at 6 l/min during the whole experiment. Figure 1 shows a typical image of a former irregular Pt particle, obtained with powder, after hydrogen erosion at 800 °C for

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30 min. During the etching at elevated temperature, the particle recristallized and eventually fragmented into one bigger and several smaller islands. A hole has been etched around the Pt islands on the surface. Indeed the Pt island acts as a catalyst to produce hydrogen atoms, which are the etching agent for SiC removal. Without Pt, no significant etching can be observed. The hole exhibits a hexagonal cross-section, characteristic for the preferential etching of the low surface energy directions in SiC [24]. The side-walls are inclined around parts of the Pt particle, still remaining in the hole. The depth of the etched hole was estimated to a few hundred nm. Regular, straight streaks visible on the SiC surface around the hole represent steps, 0.75 nm and 1.5 nm high, characteristic for clean SiC surfaces etched at elevated temperatures as done for the used SiC wafer before Pt deposition [19, 20, 24].

In a second set of experiments, a regular Pt particle array was obtained by sputter deposition in vacuum of Pt through the hexagonal ordered hole array of a shadow mask. Au-nanotube membranes were employed as a shadow masks in this work. The mask preparation was done by replication of a master pattern structure from a nanoporous anodic aluminium oxide (AAO), according to our method reported previously [25]. In brief, a thin metallic gold film was first sputtered onto the surface of the AAO. This process resulted in a thin conducting metal layer on the top part of the inner nano-channel surface as well as on the top surface of the AAO membrane. Subsequent electrochemical deposition of Au homogeneously thickens the metal layer, resulting in a tubular metallic nano-structure inside the alumina nano-channels. After removal of the alumina template in 30 wt. % H_3PO_4 (60 °C), the resulting gold membrane floated on the surface of the etching solution. After a cleaning procedure the Au nano-tube membrane was transferred onto SiC substrates from the solution (see Fig. 2a). As a next step, Pt was sputter deposited through the holes of the Au nano-tubes and the Au membrane was removed (see Fig. 2b). For the analysis the Pt covered SiC samples were investigated with atomic force microscopy (AFM).

A typical AFM image obtained on the as-prepared sample before hydrogen

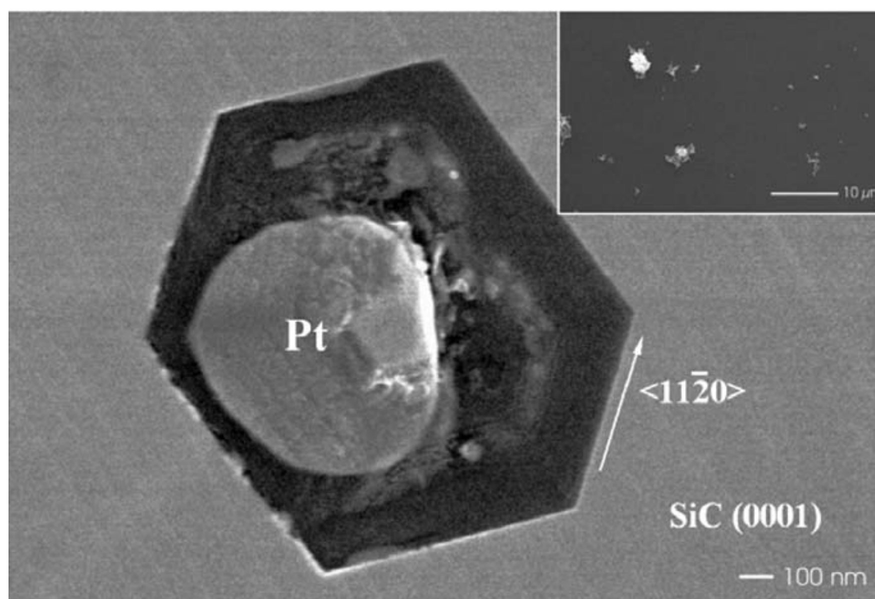

FIGURE 1 A typical SEM micrograph of a faceted hole on 6H-SiC (0001) wafer generated by reacting with H_2 in the presence of catalytic Pt particle (see text). The *inset* shows randomly distributed Pt nanoparticles on SiC substrate

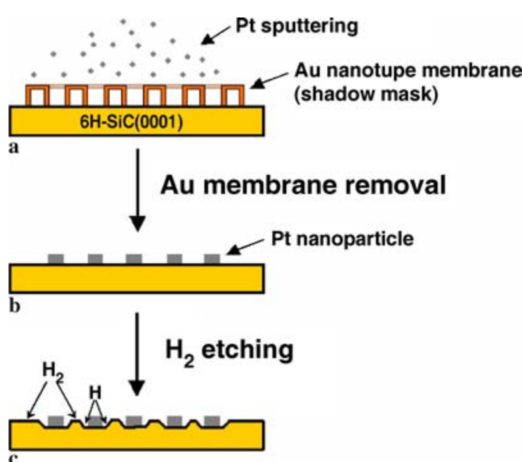

FIGURE 2 Schematic illustrating the experimental procedure for the fabrication of long-range ordered SiC nanohole arrays

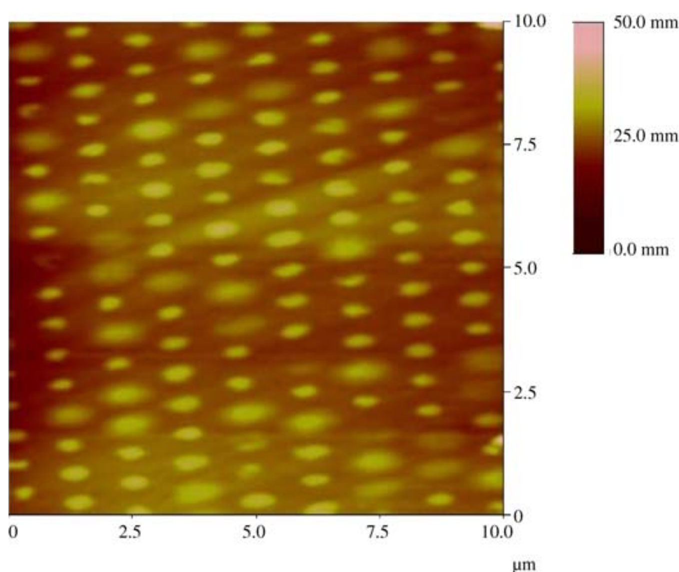

FIGURE 3 A representative AFM image of arrays of Pt nanodots on 6H-SiC(0001) obtained by sputter deposition of Pt through Au nanotube membrane

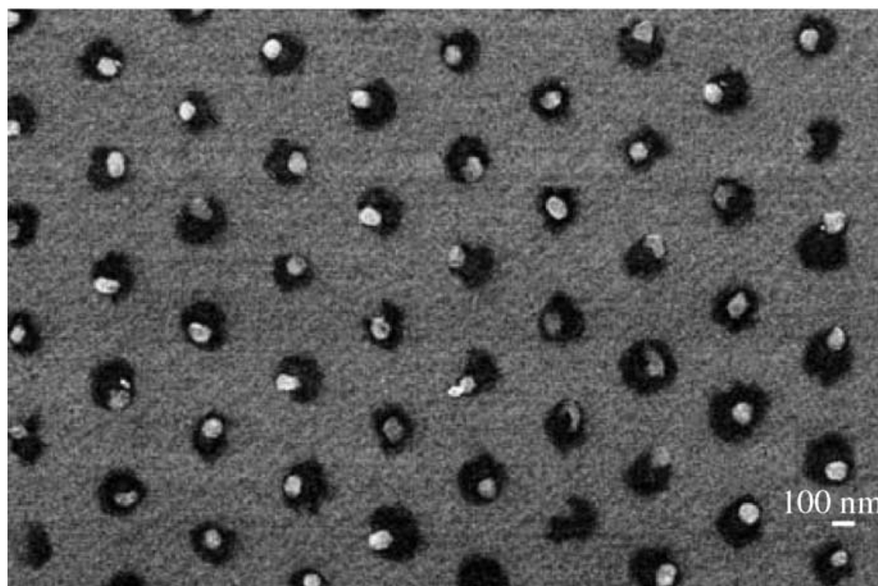

FIGURE 4 SEM image of arrays of SiC nanoholes

etching is shown in Fig. 3. On the flat SiC surface, 20 nm high Pt patches are visible that are arranged in a regular, hexagonal pattern reflecting the pattern of the Au contact mask. The distance between the patches is 500 nm and the extension of each patch is between 100 and 300 nm. The sharpness of the patch edge varies considerably most likely due to variations of pore diameter of the short Au nanotubes and the spacing of the Au membrane during deposition. The deviation in position of the patches from the ideally regular lattice is much less and at most 50 nm.

After hydrogen etching for 30 min at 800 °C the beginning of a hole formation around the deposited Pt particles can be observed analogous to that of sub-micrometer Pt particles. Figure 4 shows an SEM image of the same sample previously observed by AFM after the etching process. The Pt particles are seen as bright islands. Each particle is surrounded by a darker grey circle corresponding to the hole. Obviously, the local etching due to the catalytic properties of Pt also works for the sputtered Pt patches. Due to the well-ordered nano-particle arrays, the etched holes are ordered, as well. The contraction of the Pt patches to the islands has not lead to a significant disordering. This implies that a pattern of Pt catalyst structure can be transferred well to an etched SiC surface with 50 nm-resolution. The characteristic SiC surface reorganisation into steps and terraces can also be seen on the mesa structure between the hole pattern due to the pre-etching of the wafer.

3 Conclusion

The catalytic reaction of platinum during a hydrogen etching process has been used to perform the controlled vertical nano-patterning of silicon carbide substrates on a large scale. First experiments clearly show the beginning of a hole formation, due to the local reduction of molecular hydrogen into atomic hydrogen at the catalyst. A highly regular, mono-sized Pt particles network was obtained by sputter deposition through so-called Au nanotube membrane used as evaporation mask in this work. During a hydrogen etching process at elevated temperatures an arrays of well-organised holes was formed. The erosion temperatures during the hydrogen reduction experiments could be lowered by a factor of two compared to our previous experiments [24]. This novel patterning process for the fabrication of large scale nano-hole arrays, will have potential applications in fields like electronic devices, photonic crystals and biology.

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