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Comparative study on dry etching of α- and β-SiC nano-pillars

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ABSTRACT

Different polytypes (α-SiC and β-SiC) and crystallographic orientations ((0001) and (11–20) of 6H-SiC) have been used in order to elaborate silicon carbide (SiC) nanopillars using the inductively coupled plasma etching method. The cross section of the SiC pillars shows a rhombus, pentagonal or hexagonal morphology depending on polytypes and crystallographic orientations. The favored morphologies of SiC nanopillars originate from a complex interplay between their polytypes and crystal orientations, which reflects the so-called Wulff's rule.

1. Introduction

One-dimensional (1D) SiC materials, in particular nanowires (NWs), have recently attracted much attention due to their unique physical and chemical properties, coupled with the advantages of an 1D structure. Many efforts have been carried out to fabricate the SiC nanostructures by the bottom-up methods, such as the vapor–liquid–solid [1] or the vapor–solid method [2]. However, those as-grown SiC NWs significantly suffer from a high density of structural defects, such as stacking faults, and unintentional high n-type doping level ($\sim 10^{19}$–10^{20} cm^{-3}). These characteristics of as-grown SiC NWs lead to poor electrical performance (such as weak gate effect and low mobility) of the related devices [3]. Therefore, top down approach is considered as a possible solution to achieve highly crystalline SiC nanostructures with less structural defects and controlled doping level. Inductively coupled plasma (ICP) etching is widely used for top-down processing of SiC due to its highly anisotropic profile, high etch rate, and less etch damage compared with other dry etching methods [4,5]. Up to now only few studies on ICP etching on single crystalline SiC substrate have been reported for the fabrication of the SiC nanostructures [6,7]. In our previous etching study using 4H-SiC (0001) substrate [7], the etching profile evolution from a circular to a hexagonal pillar shape has been observed with increasing etching time, which originated from the crystallographic structure of the α-SiC. However, there is still a lack of understanding of the etch behavior, such as dependence of polytypes and crystal orientations.

An interesting property of SiC is that different polytypes (such as, α- and β-SiC) of SiC have different physical properties, that originate from the different stacking sequences of the Si–C layers. If a top-down approach is applied to these different polytypes of SiC layers, the SiC nanostructures may be easily achieved with different physical properties, which can lead to further applications of SiC nanostructures. In this letter, the etching behavior of SiC nanopillars depending on the different polytypes and crystallographic orientations: 4H-SiC (0001), 6H-SiC (0001), 6H-SiC (11–20) and 3C-SiC (001), is presented.

2. Experimental details

Experiments in SF_6/O_2 based plasma are carried out in a commercial high-density plasma etching chamber from Applied Materials Inc. [8]. The α-SiC substrates used in this study were product grade Tankeblue 4H- and 6H-SiC (0001) on-axis substrates [9]. The 6H-SiC (11–20) substrates were grown by the conventional physical vapor transport method, which has been presented elsewhere [10]. For β-SiC (001) substrate, the 3C-SiC layers were heteroepitaxially grown on Si (001) substrates [11]. For the etch masks, circular patterns with 300 ± 10 nm diameter are patterned with the same pitch distance (5 μm) on the Si face of the SiC substrate using electron beam lithography (JSM-7401F, JEOL). After developing the exposed resist, a Ni metal layer with 110 nm thickness was deposited on the Si face of the SiC substrates by e-beam evaporation. Then, the lift-off process is

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performed at 40 °C using the remover AR 300-70. In our previous study, Ni has been evaluated as a better mask material than other materials (Al and Cu) [7].

During the experiment, the parameters total gas flow rate, ICP coil power, substrate bias voltage and chamber pressure remain constant at 50 sccm (SF_6=40 sccm and O_2=10 sccm), 1500 W, 150 V, and 6 mTorr, respectively. The etched profiles of SiC nanostructures were characterized by scanning electron microscopy (SEM).

3. Results and discussions

Fig. 1 shows top-view SEM images of the etched SiC nanopillars with different polytypes and crystallographic orientations after etching for 360 s, 700 s and 840 s. The mask size and thickness considerably decrease during the etching process due to strong physical sputtering of energetic ions, and it is completely removed after the etching for 840 s. Therefore, the SiC nanopillars are no longer protected by the mask after long etching and begin to be etched. Finally, it clearly reveals their transversal cross section, perpendicular to the *z*-axis of the SiC pillar (see top-view images in Fig. 1i–l). Consistent with the results of a previous study [7], continuous etching in SF_6/O_2 plasma on α-SiC (0001) substrates causes the pillar to start to transfrom into a hexagonal symmetry (Fig. 1a, b, e, f, i and j). The 6H –and 4H-SiC (0001) on-axis substrates show exactly the same etching behavior. In both cases, one edge of the hexagon is parallel to the (11–20) direction of the α-SiC.

It is interesting to note that the etched SiC nanopillars on the 3C-SiC (001) substrate gradually transform into a rhombic pyramid structure (Fig. 1c, g and k). To the best of our knowledge, this shape has never been reported in the literature. The two diagonals of the rhombus correspond to the directions of [−110] and [110]. The facet appearing on the top of 3C-SiC (001) nanopillar clearly shows a rhombus shape (Fig. 1k). Generally, most as-grown SiC NWs fabricated by the bottom-up methods are cylinder shaped β-SiC structures oriented towards the [111] direction [1,2]. For heteroepitaxial growth of 3C-SiC on Si substrates, the Si (001) plane is commonly used to minimize the density of planar defects, such as twin boundaries and anti-phase boundaries, with increasing thickness through mutual canceling [12,13]. In addition, it is also possible to achieve thick SiC epitaxial layers on large area substrates using a Si (001) substrate. In the present case, the etched pillars β-SiC exhibits a crystal orientation with [001] direction.

It seems that the etching behavior of SiC nanopillars is quite similar to the growth of SiC structure. The growth of 3C-SiC heteroepitaxial layer on mesa structure with different polytype substrates has gradually expanded into a hexagonal shape on 4H-SiC (0001) and a rhombus shape on Si (001) during reactions [14,15]. These phenomena are well explained by in-plane anisotropy of the growth rate. In the same way, the sufficiently long etching process imposes developing of the planes with the lowest etch rates in all the different polytypes and crystal orientations.

The morphology of etched SiC nanopillars on 6H-SiC (11–20) substrate shows an asymmetric pillar shape at the initial stage of etching (Fig. 1d and h), and further etching makes the pillars appear with a distorted pentagon-based pyramid structure (Fig. 1l). This unique morphology of SiC pillar is related to the unintentional misorientation crystal plane toward the [0001] directions.

For the growth of 6H-SiC (11–20) substrates used in this study, α-plane seeds were prepared by attaching four equivalent rectangular samples (15 mm × 50 mm) of the α-plane in parallel and the additional process (grinding) to obtain a circular shape [10]. The grooves near the connected regions induce the unintentional off-axis of the (11–20) plane. Hence, the α-plane after reactions is slightly misoriented. As a result, the etched SiC pillars on 6H-SiC (11–20) substrate are tilted at an angle of misorientation, just like the leaning tower of Pisa, instead of standing upright. The apex of pillar moves from the center rhombus towards the [0001] direction (Fig. 1h and l).

The misorientation degree (θ) of α-plane can be roughly estimated from the following formula:

$$\theta = \tan^{-1}(d/h), \quad (1)$$

where d is the apex-shift distance and h is the pillar height.

The estimated misorientation degrees (θ) are around 1.6° and 3.0° from Fig. 1h (d_1=160 nm, h_1=5.8 μm) and Fig. 1l (d_2=300 nm, h_2=5.6 μm), respectively. And it ranges between 1.0° and 3.0° over the entire sample area.

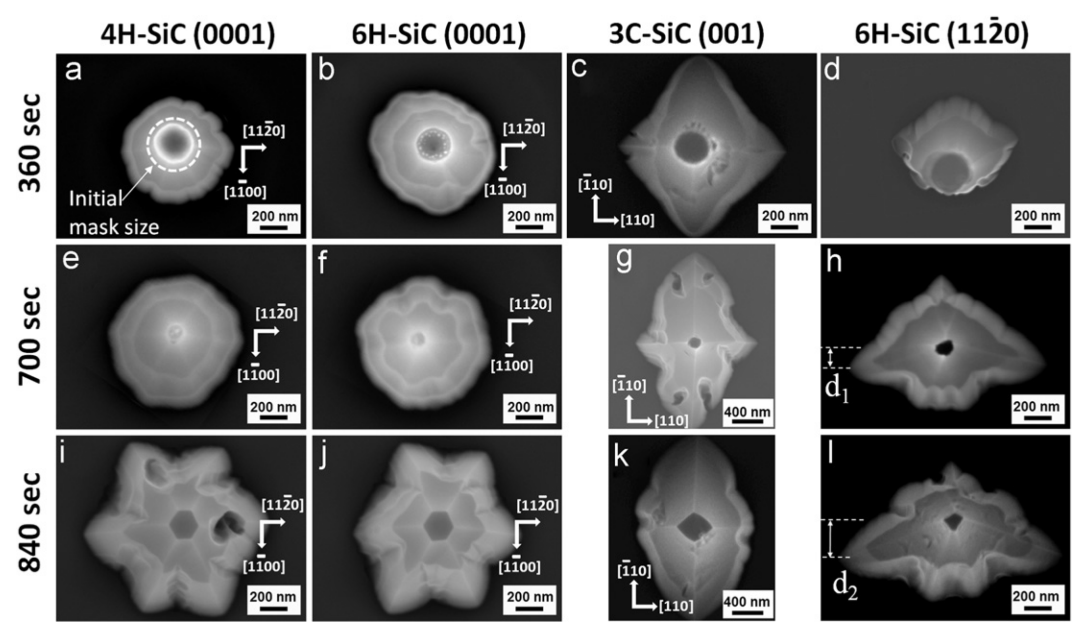

Fig. 1. Top-view SEM images of SiC nanopillar after etching for (a)–(d) 360 s, (e)–(h) 700 s, and (i)–(l) 840 s with different polytypes and crystallographic orientations: (a, e and i) 4H-SiC (0001) on-axis, (b, f and j) 6H-SiC (0001) on-axis, (c, g and k) 3C-SiC (001) and (d, h and l) misoriented 6H-SiC (11–20).