Anisotropy of dissolution and defect revealing on SiC surfaces

1999 J. Phys.: Condens. Matter 11 10041

(http://iopscience.iop.org/0953-8984/11/49/322)

J. Phys.: Condens. Matter **11** (1999) 10041–10046. Printed in the UK PII: S0953-8984(99)04285-X

Anisotropy of dissolution and defect revealing on SiC surfaces

M Syväjärvi†§, R Yakimova†‡, A-L Hylén† and E Janzén†

† Department of Physics and Measurement Technology, Linköping University,
S-581 83 Linköping, Sweden
‡ Okmetic AB, Box 255, S-178 24 Ekerö, Sweden

E-mail: `msy@ifm.liu.se`

Received 13 May 1999

Abstract. Micropipes and dislocations in silicon carbide single crystals are revealed by chemical etching. Micropipes are shown to be interconnected with other structural defects and the reason for this is discussed. The Si and C faces are attacked by molten KOH preferentially and isotropically, respectively. The mechanism is discussed in relation to the different surface free energies on the Si and C faces. The revealing of micropipes is more pronounced on the Si face. The hexagonal pattern of micropipes are revealed by rapid etching provided by a large undersaturation at the surface. It is shown that etching from a melt gives a disintegration of the SiC crystal at the micropipe via spiral dissolution which is due to etching near equilibrium conditions. The temperature dependence of the etch rate follows an Arrhenius dependence with an apparent activation energy of about 12–15 kcal mol^{-1} derived from measuring etch rate and weight loss.

1. Introduction

Silicon carbide (SiC) is a very attractive material for semiconductor devices in high-power and high-frequency applications. Typically structural defects like micropipes and domain (grain) boundaries in the substrate are inherited by the epitaxial layer. Micropipes are small channels which penetrate the crystal along the growth direction (c-axis in hexagonal unit cell). They are believed to originate mainly from open dislocation cores but also from local stress in the crystal. The presence of micropipes and screw dislocations in the grown crystals may cause a premature failure in devices manufactured on SiC wafers. However, micropipes, domains boundaries and dislocations are difficult or impossible to observe on as-polished substrate surfaces. Therefore a method for revealing them is needed. One way to do this is to use a wet etching (dissolution) process. High interatomic bonding energy makes SiC temperature stable and chemically inert. Molten KOH ($T > 450\,^{\circ}$C) is most frequently applied to achieve preferential etching of SiC crystals. A limited number of studies have, however, been reported on the effect of etching conditions on the patterns produced and on the process using preferential chemical etching of SiC. In this work we investigate the etch pit appearance and etch rate on SiC surfaces treated by molten KOH at different temperatures. In addition, SiC surfaces dissolved in molten Si were examined as well.

---

§ Corresponding author. Telephone: +46 13 285708. Fax: +46 13 142337.

0953-8984/99/4910041+06$30.00

2. Experiment

The SiC wafers studied were cut from 6H- and 4H-SiC crystals grown with the seeded sublimation technique [1]. The wafer surfaces were (0001) or slightly off-axis oriented toward $[11\bar{2}0]$. Both the Si and C terminated faces of 6H and 4H polytype wafers were examined. The etching was carried out in a high-temperature etching set-up with KOH in a temperature range of 480–570 °C for 1–20 minutes. Dissolution with molten Si was obtained by placing the wafer in contact with Si at 1750 °C. The etched surfaces were studied using an optical microscope with Nomarski interference contrast.

3. Results and discussion

3.1. Surface appearance

Due to the crystal symmetry of 6H- and 4H-SiC most of the etch pits exhibit a hexagonal shape.

On the Si face we observed three types of hexagonal etch pattern due to (I) threading micropipes, (II) deep and shallow voids, and (III) screw dislocations. Defects of type I and type II have similar etch pit appearance depending on size but the type II defects have a flat bottom. For this reason they are believed to be related to micropipes starting and probably stopping at a certain stage of the boule growth. Type III defects have pointed bottoms and they are due to screw dislocations.

The two large hexagonal features in figure 1(*a*) are micropipes which together with very deep pits appear black in the micrographs since they do not reflect light. Very often the dislocations are gathered around micropipes, figure 1(*b*). In this figure dislocation rows of closely spaced etch pits are connected with the micropipe forming a three-fold node. Three dislocation rows are propagating from the micropipe. This type of dislocation row is an often observed pattern for etched low-angle grain boundaries. This suggests that micropipes may be generated at locations with large structural defects like domain boundaries. On the other hand, since micropipes are relatively large defects (from several to tens of micrometres), they may deform the crystal and cause dislocations.

The sides of the defects with hexagonal symmetry correspond to the six $\{1\bar{1}00\}$ planes of the SiC lattice. The small hexagonal (sometimes rounded) and shell-like pits, figure 2, are believed to be screw dislocations running parallel to the c-axis and slip dislocations in the basal plane intersecting the (0001) SiC surface, respectively [2]. Molten KOH attacks the Si face and the C face in different ways, the first one being etched preferentially, whereas the second one is etched nearly isotropically. This different behaviour can be related to the difference in the surface free energies of the two faces. One can still resolve the micropipe outcrop on the C face but the openings are at least a factor of 10 smaller in size and the shape is round. This finding illustrates the interconnection between the surface free energy, anisotropy of dissolution and dissolution (etching) rate.

The etch pits occur when an undersaturation in the vicinity of the surface is present. The driving force for the formation of an etch pit is an energetic relaxation (release of the core energy) at the dislocation. Similar to the nucleation in crystal growth, the crystal disintegration in etching is affected by the surface free energy of the solid surface. A higher surface free energy gives an anisotropic etching at defects and a low surface free energy results in a smoother etched surface.

In order to achieve preferential etching at screw dislocations (micropipes) the process must be rapid [3]. This is provided by a large undersaturation. Etching near equilibrium conditions

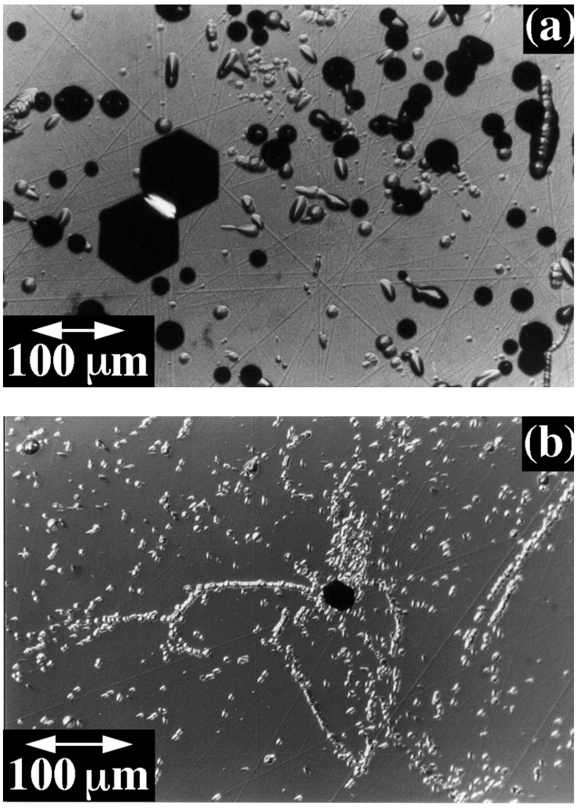

Figure 1. Defect appearance on Si face of SiC after etching in molten KOH: (a) a general view, (b) a micropipe surrounded by dislocations.

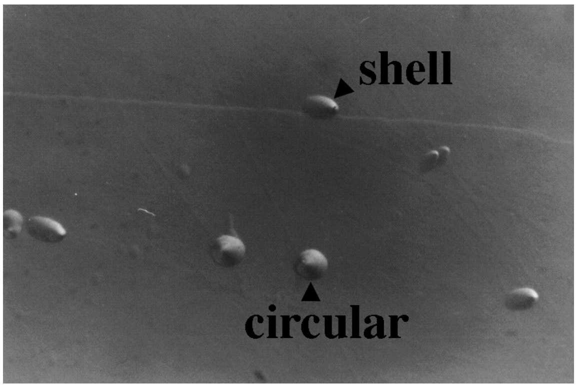

Figure 2. Circular and shell-like etch pits.

causes a macroscopic disintegration of the crystal. For SiC this is illustrated in figure 3 where a dissolution spiral at a micropipe is observed after treating with molten Si. The micropipe is located in the centre of the spiral. Dissolution occurs at near equilibrium conditions similarly to the process in liquid phase growth. Thus the dissolution spiral appears if the etching process is not rapid. The crystal disintegrates by spiral dissolution. Since the etching rate is low

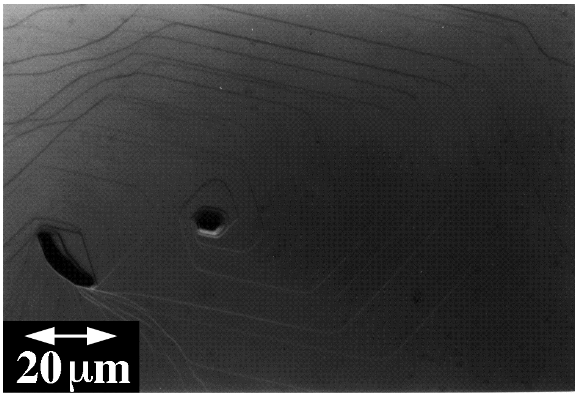

Figure 3. Anisotropic dissolution spiral on the Si face of a 4H-SiC wafer.

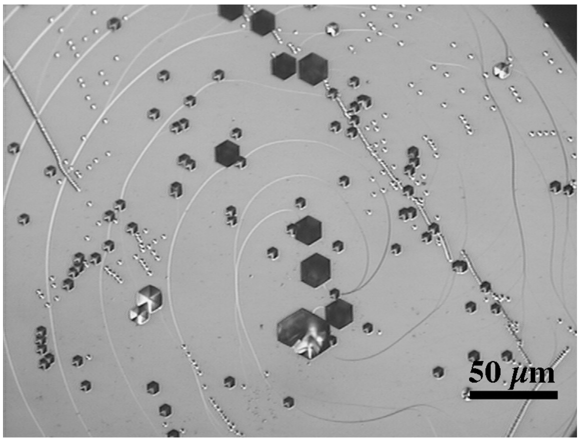

Figure 4. A 6H-SiC as-grown surface after etching with molten KOH.

and SiC is a semiconductor with anisotropic properties, the dissolution spiral is polygonized following hexagonal symmetry.

Rapid etching on SiC, however, does not result in a dissolution spiral but etch pits appear in the centre of the spiral. After a short period of rapid etching, spirals on the as-grown surface were obliterated and in the centre of the spiral a small pit appeared [3]. Successive etching enlarged and deepened the etch pit. At high undersaturation (providing a rapid etching process) and at prolonged etching, hollow channels occur which penetrate the crystal. In case of SiC the hollow channels are typically due to micropipes. In figure 4 a KOH etched as-grown surface of a 6H-SiC crystal is shown. There are several spirals which have united into one major spiral by which the crystal was grown. At each point from which a spiral step emerges, a micropipe is located. From the results it seems that spiral etching occurs below a certain critical undersaturation. If this critical value is exceeded, the etching mechanism changes. The presence of a micropipe in the centre of the spiral is in agreement with theoretical calculations [4] where it was reported that above some undersaturation limit, the core of the spiral is unable to remain closed and a pit appears in the centre of the screw dislocation. The above results show that a selective etch process with sufficiently low undersaturation and rapid etching can be used to locate spirals and micropipes in SiC, respectively.

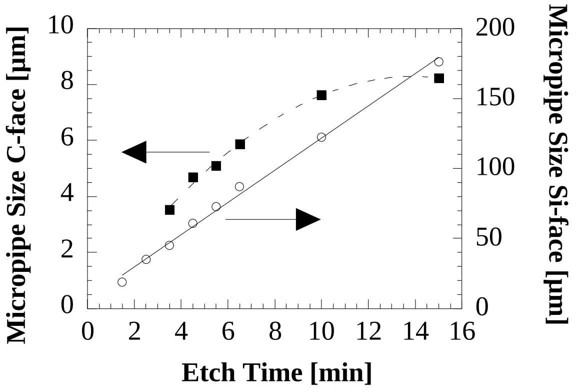

Figure 5. Micropipe related pit diameter against etching time for Si and C faces.

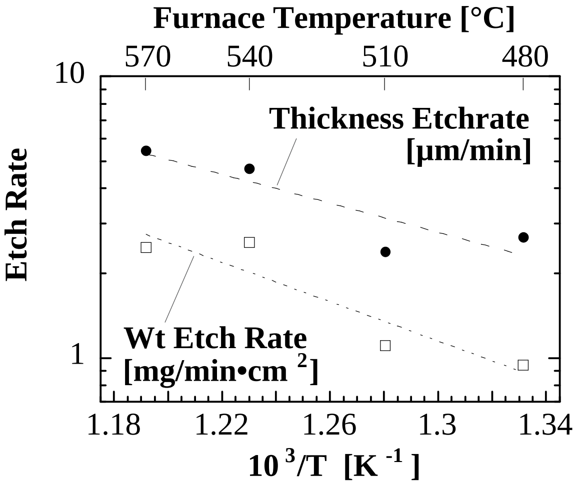

Figure 6. Temperature dependence of the etch rate and weight losses.

3.2. Micropipe size and etch rate

The dependence of micropipe related pit-diameter on etching time by molten KOH is shown in figure 5. It is linear for the Si face and sublinear for the C face. The difference in micropipe size with etching time is due to different etching behaviour on the two faces as a consequence of the different surface energies. When the etching is isotropic, long-term etching does not result in any new information when investigating the C face. On the other hand, on the Si face etch pits and micropipe outcrops become larger but there exists an optimum etching time above which the etch pits merge and it becomes difficult to obtain information from the rough surfaces. It appears that the optimal etching time for defect revealing is between 2 and 6 min, depending on the crystal perfection. An overetching can cause a merge of neighbouring defects.

The total etch rate by molten KOH (both faces etched) was determined to be $\approx 2.6\ \mu$m min at 480 °C and it is exponentially dependent on the temperature. The weight loss and its temperature dependence was determined as well, figure 6. It is worth noting that the apparent activation energies of the etching process derived from the Arrhenius plots of these dependencies are quite close, being 12 kcal mol^{-1} and 15 kcal mol^{-1}, respectively. These values are much above the energy reported for a diffusion limited etching of compound semiconductors [5], which suggests that in case of SiC etching surface reaction limitations are probably implied. Other studies on etching of SiC by molten KOH reported that the etching rate is about four times higher on the C face than on the Si face [6]. This difference is attributed to the surface free energy diversity of the two faces which affects the etching mechanism. This provides a higher undersaturation on the C face compared with the Si face and consequently a larger etching rate. Other studies have reported that the etching rate is enhanced as the hexagonality of the SiC crystal increases [6]. In our study no difference was observed when comparing the etch rate or the etching behaviour of 6H- and 4H-SiC. This may be explained with the small difference in bonding energy and enthalpy of formation between the polytypes

4. Summary

We have shown that in SiC single crystals typical defects like micropipes, domain boundaries and dislocations are well revealed by chemical etching of Si-terminated (0001) surfaces. Due to the relationship between anisotropy of dissolution, surface free energy and dissolution (etch) rate different etch pattern are observed reflecting different dissolution mechanisms.

Acknowledgments

The authors acknowledge the SSF Program SiCEP, as well as Okmetic Ltd for support.

References

[1] Tuominen M, Yakimova R, Prieur E, Ellison A, Tuomi T, Vehanen A and Janzen E 1997 *Diamond Relat. Mater.* **6** 1272

[2] Takahashi J, Kanaya M and Fujiwara Y 1994 *J. Cryst. Growth* **135** 61

[3] Horn F H 1952 *Phil. Mag.* **43** 1210

[4] Cabrera N and Levine M M 1956 *Phil. Mag.* **1** 450

[5] Sangwal K 1987 *Etching of Crystals: Theory, Experiment and Application* (Amsterdam: North-Holland) p 260

[6] Katsuno M, Ohtani N, Takahshi J, Yashiro H, Kanaya M and Shinoyama S 1998 *Mater. Sci. Forum* **264–268** 837