Electrochemical and Solid-State Letters, **7** (11) G264-G265 (2004)
1099-0062/2004/7(11)/G264/2/$7.00 © The Electrochemical Society, Inc.

Delineating Structural Defects in Highly Doped n-Type 4H-SiC Substrates Using a Combination of Thermal Diffusion and Molten KOH Etching

Zehong Zhang, Ying Gao,[a] and Tangali Sudarshan[z]

Department of Electrical Engineering, University of South Carolina, Columbia, South Carolina, 29208, USA

Delineation of structural defects by molten KOH etching is not satisfactory for highly doped n-type Si-face SiC substrates. This difficulty was overcome by converting the substrates to p-type via diffusion of boron, followed by molten KOH etching. Three kinds of typical etch pits were clearly distinguished, corresponding to elementary screw, threading edge, and basal plane dislocations. Comparison of molten KOH etching effects on 4H-SiC samples of different types indicates that molten KOH etching is a combination of chemical and electrochemical processes, during which the preferential and isotropic etchings are competitive, depending on the SiC conductivity type and doping concentration.
© 2004 The Electrochemical Society. [DOI: 10.1149/1.1805500] All rights reserved.

Manuscript received April 9, 2004. Available electronically October 6, 2004.

Silicon carbide (SiC) is a promising material for high-power, high-temperature, and high-frequency devices due to its wide band gap, high thermal conductivity, high breakdown electrical field, and excellent physical and chemical stability.[1,2] In recent years, the performance of various SiC-based devices has been dramatically improved. However, the high density of structural defects in the SiC bulk and epi layer is one of the reasons preventing widespread commercialization of SiC devices.[3,4] Currently, reduction of structural defects has become a priority in the development of SiC semiconductors, and clear delineation of the structural defects is essential for achieving improvements in material quality.

Molten KOH etching has been widely used as a simple and effective method for revealing structural defects in SiC wafers. However, this method is better able to identify specific defects in medium and low-doped n-type SiC wafers than in highly doped wafers via chemical preferential etching.[3] Molten KOH etching would be a more effective and useful defect delineation tool if preferential etching could be enhanced compared with isotropic etching in the above situation. In this work, molten KOH etching was conducted to delineate defects in 4H-SiC samples of different conductivity types and doping concentrations. Based on the experimental observations, an explanation for the molten KOH etching mechanism is proposed. Furthermore, an approach to delineate structural defects on the Si face of highly doped n-type 4H-SiC substrates (currently not possible) by a combination of thermal diffusion of boron and molten KOH etching is developed.

Samples 1, 2, 3, and 5 in this study were cut from an n-type 8° off-axis 4H-SiC(0001) wafer with a doping concentration of $6 \times 10^{18}\ \mathrm{cm}^{-3}$, and sample 4 was cut from a p-type 8° off-axis 4H-SiC(0001) wafer with a doping concentration of $1 \times 10^{18}\ \mathrm{cm}^{-3}$. Both wafers were purchased from CREE Inc.. A 10 μm thick epi layer was grown on samples 2 and 3 in a low-pressure hot-wall CVD system, with n-type $1 \times 10^{15}\ \mathrm{cm}^{-3}$ and p-type $7 \times 10^{15}\ \mathrm{cm}^{-3}$, respectively. Sample 5 was overcompensated by thermal diffusion of boron to p-type with a doping concentration of $1 \times 10^{18}\ \mathrm{cm}^{-3}$ measured by capacitance-voltage (C-V) characterization. The diffusion process is described elsewhere.[5] A brief summary of the samples is listed in Table I.

All the above samples were etched by molten KOH in atmospheric air ambient. A Nickel crucible was filled with KOH pellets and heated to 600°C in a temperature controllable furnace. The etching time was varied from 10 to 50 min. A Normaski Differential Interference Contrast (NDIC) microscope was employed to examine the etched surface.

No etch pits were found on sample 1 after 10 min of etching in molten KOH. By increasing the etch time to 50 min, oval pits appeared (Fig. 1a). No hexagonal etch pits were found. The total etch pit density was very low (less than $10^3/\mathrm{cm}^2$), which is lower than the real defect density, indicating that KOH etching is unlikely to reveal all of the structural defects in n^+ SiC substrates. This result agrees with the published literature.[3] On sample 2, etch pits were observed after 10 min of etching. By increasing the etch time to 20 min, the etch pits became much more distinguishable (Fig. 1b). The three kinds of etch pits on the etched surface correspond to elementary screw, threading edge, and basal plane dislocations. Figure 1c shows the etch pits on sample 3 after 10 min of etching. Although the etch time for sample 3 is less than that for sample 2, the etch pits were clearly observed. The size of the large hexagonal pits (corresponding to elementary screw dislocation) is three to four times larger than that of the small hexagonal pits (corresponding to the threading edge dislocations). Sample 4 is a p^+ substrate. Its etching characteristic is almost the same as that of Sample 3. After 10 min of etching, three kinds of etch pits are clearly observed (Fig. 1d).

The above results clearly indicate that both the conductivity type and doping concentration have significant influence on the etch preference at defect sites. On n^+ SiC substrate, the etching is almost isotropic. On n^- SiC epilayer, the etching is preferential at the defect sites. The etching of p-type SiC substrate is more preferential than that of the n^- epilayer. The etch preference on the Si-face of 4H-SiC is found to be $n^+ < n^- < p^- \approx p^+$. These etching behaviors suggest that an electrochemical reaction is involved in the molten KOH etching of SiC although there is no external bias. In other words, two parallel reactions exist: one is a chemical reaction without the participation of free carriers, and the other is an electrochemical reaction with the participation of free carriers. Such parallel reactions also exist in the etching of silicon in aqueous alkali.[6,7]

The electrochemical dissolution of SiC is known to take place

Table I. Summary of the samples.

Sample no.	Specification	Etching parameters	Figure
1	Si face, substrate, n-type, $6 \times 10^{18}\ \mathrm{cm}^{-3}$	600°C, 50 min	1a
2	Si face, epi layer, n-type, $7 \times 10^{15}\ \mathrm{cm}^{-3}$	600°C, 20 min	1b
3	Si face, epi layer, p-type, $5 \times 10^{15}\ \mathrm{cm}^{-3}$	600°C, 10 min	1c
4	Si face, substrate, p-type, $1 \times 10^{18}\ \mathrm{cm}^{-3}$	600°C, 10 min	1d
5	Si face, substrate, converted from $6 \times 10^{18}\ \mathrm{cm}^{-3}$ n-type to $1 \times 10^{18}\ \mathrm{cm}^{-3}$ p-type by diffusion	600°C, 10 min	3

[a] Present address: Bandgap Technologies, Inc., Columbia, SC, 29203, USA.
[z] E-mail: sudarsha@engr.sc.edu

Downloaded 26 Sep 2011 to 159.226.100.225. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

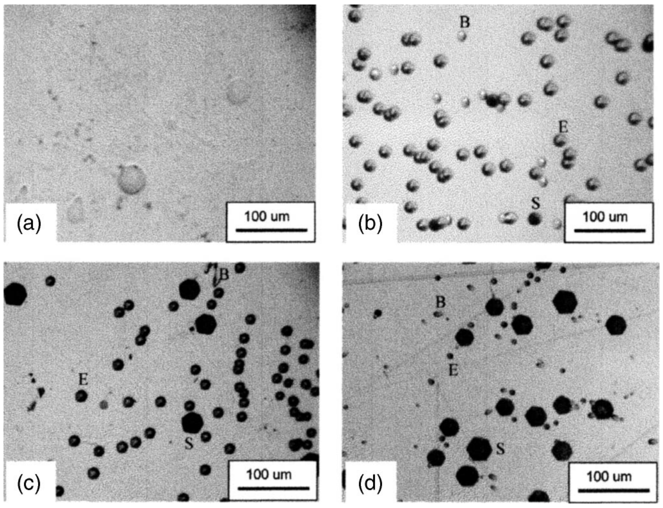

Figure 1. Etched surfaces examined by NDIC microscope; (a) a highly doped n-type Si face substrate, (b) a low doped n-type epi layer, (c) a low doped p-type epi layer, and (d) a highly doped p-type Si face substrate. "S," "E," and "B" denote an etch pit from an elementary screw dislocation, threading edge dislocation, and basal plane dislocation, respectively.

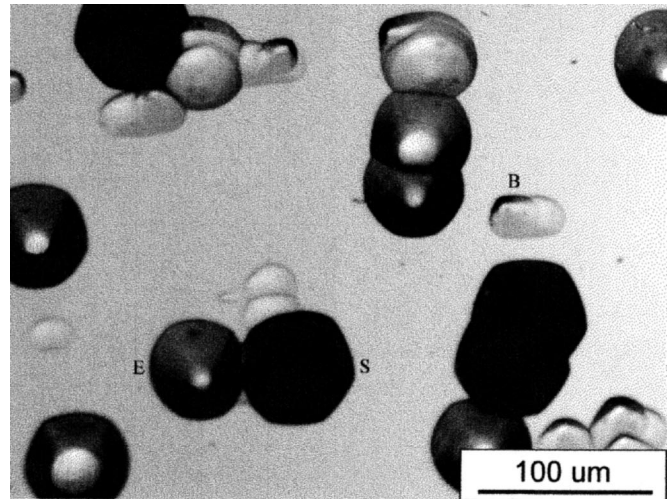

Figure 3. Etched surface of a highly doped n-type Si-face sample after diffusion of boron. "S," "E," and "B" denote an etch pit from an elementary screw dislocation, threading edge dislocation, and basal plane dislocation, respectively.

through anodic oxidation, requiring the presence of holes at the surface for catalyzing reactions to occur.[8] Shor *et al.* have studied the interface between the 3C-SiC and aqueous HF solution.[9] It was shown that under zero bias, the energy band of p-type SiC bends downward at the SiC/solution interface, while that of n-type SiC bends upward. It can be reasonably assumed that 4H-SiC/molten KOH interface has a similar energy band structure as 3C-SiC/aqueous HF, as shown in Fig. 2. At zero bias, a depletion layer is formed in the surface of p-type SiC. Due to the lack of holes in this layer, electrochemical etching is prevented, and, therefore, chemical etching dominates. The chemical etching will preferentially attack the defect sites due to energy relaxation (release of the core energy),[10] and hence the etching on p-type SiC is preferential. For an n-type SiC substrate, if the doping concentration is sufficiently high, an inversion layer will be created in the surface of SiC substrate due to the significant energy band bending.[11] This inversion layer with high density of holes will enhance electrochemical etching. As the electrochemical reaction takes place entirely due to the availability of holes, the above inversion layer surface will be etched uniformly, resulting in layer by layer surface removal. As a result, the molten KOH etching of highly doped n-type 4H-SiC will lead to predominantly isotropic etching.

To confirm the above observations and discussions, sample 5, an original n^+ substrate, was overcompensated to p-type by diffusion of boron. Figure 3 shows the etch pits on this surface after 10 min of molten KOH etching. Three kinds of etch pits can be clearly observed. The large black hexagonal pits are from elementary screw dislocations, while the gray hexagonal pits are from threading edge dislocations, and the shell-like pits are from basal plane dislocations in the substrate. In principle, thermal diffusion is a process which introduces point defects (zero dimensional defects) into the SiC substrate rather than dislocations (one-dimensional defects). Therefore, it can be reasonably affirmed that the etch pits on diffused substrate delineate the structural defect distribution in the original substrate. By using this method, correlation between the etch pits on an epilayer and the n^+ substrate underneath it was successfully made by molten KOH etching (the epi layer was removed by polishing before the substrate was overcompensated by diffusion and etched by molten KOH).

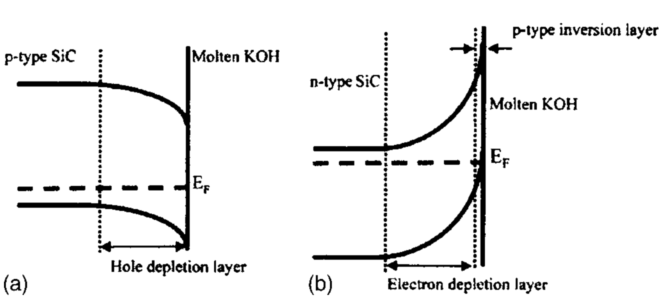

Figure 2. Schematic of the energy band diagram at the 4H-SiC/molten KOH interface; (a) p-type SiC/KOH and (b) n-type SiC/KOH.

In summary, the KOH etching preference *vs.* conductivity type and doping concentration has been studied. The etch preference for Si-face 4H-SiC is $n^+ < n^- < p^- \approx p^+$. It is suggested that two parallel reactions, a chemical and an electrochemical reaction are competitive during the etching of SiC by molten KOH. By doping the n^+ substrate with boron, three kinds of etch pits can be clearly observed after KOH etching.

Acknowledgment

This research was supported by ONR grant no. N00014-03-1-0584. The authors are grateful to Dr. C. Wood for his interest and support of this research. The authors also thank Dr. Robert Bondokov and Stanislav Soloviev for valuable discussions. Z. Z. thanks Julie Morris for her assistance with the technical writing of this paper.

The University of South Carolina assisted in meeting the publication costs of this article.

References

1. M. Bakowski, P. Ericsson, C. Harris, S. Karlsson, S. Savage, and A. Schoner, *Compound Semicond.*, **6**, 75 (2000).
2. Y. Tanaka, N. Kobayashi, H. Okumura, R. Suzuki, T. Ohdaira, M. Hasegawa, M. Ogura, S. Yoshida, and H. Tanoue, *Mater. Sci. Forum*, **338-342**, 909 (2000).
3. S. Ha, W. M. Vetter, M. Dudley, and M. Skowronski, *Mater. Sci. Forum*, **389-393**, 443 (2002).
4. P. G. Neudeck, *Mater. Sci. Forum*, **338-342**, 1161 (2000).
5. S. I. Soloviev, Y. Gao, and T. S. Sudarshan, *Appl. Phys. Lett.*, **77**, 4005 (2000).
6. O. J. Glembocki, R. E. Stahlbush, and M. Tomkiewicz, *J. Electrochem. Soc.*, **132**, 145 (1985).
7. P. Allongue, V. Costa-kieling, and H. Gerischer, *J. Electrochem. Soc.*, **140**, 1018 (1993).
8. J. S. Shor, X. G. Zhang, and R. M. Osgood, *J. Electrochem. Soc.*, **139**, 1213 (1992).
9. J. S. Shor, R. M. Osgood, and A. D. Kurtz, *Appl. Phys. Lett.*, **60**, 1001 (1992).
10. M. Syväjärvi, R. Yakimova, A.-L. Hylén, and E. Jazén, *J. Phys.: Condens. Matter*, **11**, 10041 (1999).
11. H. K. Henisch, *Rectifying Semi-Conductor Contacts*, p. 221, Oxford University Press, Oxford (1957).

Downloaded 26 Sep 2011 to 159.226.100.225. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp