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Study of Eutectic Etching Process for Defects Analysis in n-type 4H-SiC

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ABSTRACT

Silicon Carbide (SiC) is a wide bandgap material with unique properties attractive for high power, high temperature applications. The presence of defects in the crystal is a major issue prior device fabrication. These defects affect the performance of the device. To delineate and identify the defects an easy and quick method is desirable. In this study defects delineation in n-type 4H-SiC has been carried out by KOH, KOH+NaOH and KOH+Na_2O_2 melts. Variation in etch pits size was found at various concentrations of the NaOH in KOH and for different total etching times in the KOH+Na_2O_2 melt. The eutectic solution etching technique is found to be more efficient to delineate defects and provides control on etching and surface roughness. The etching rates have been estimated under different experimental conditions. Detailed morphological investigations have been performed by wide field high resolution optical microscopy and scanning electron microscopy.

Keywords: 4H-SiC, Dislocation; KOH+NaOH etching; KOH+Na_2O_2 etching; Etching parameters

1. INTRODUCTION

Silicon Carbide (SiC) is a wide bandgap semiconductor, which exhibits unique physical and chemical properties such as high critical electric field of dielectric breakdown, high thermal conductivity and extreme chemical inertness. These properties make SiC a suitable material for high power and high temperature electronic devices[1-3]. Defects-free crystals of SiC are required for the development of SiC-based devices, a lot of which relies on the bulk and epitaxial growth technology. Development of SiC based devices is highly concerned with the presence of high density of defects in the as grown SiC crystals. Among these are the micropipes, threading screw dislocations, threading edge dislocations and basal plane dislocations. These defects cause increase in leakage current and degrade the breakdown voltage resulting in fatal damage of high power and high current devices[4,5].

Lattice distortions during the growth of bulk single crystals arise due to variations in the temperature, composition ratio and pressure resulting into the creation of dislocations. The distorted regions within the crystal have higher strain energy as compared to the perfect crystalline regions. Moreover, the strained regions are more prone to the chemical attack than normal regions due to the higher chemical potential of the prior. Under optimal conditions during defects-selective etching, the strained areas get etchedout much quickly and much easily to develop etched pits. Sizes and shapes of these pits are as per the strain fields of the dislocations and determined by the size of Burgers vectors[6]. In fact, the etch pits are categorised depending on their sizes and hence the Burgers vectors of the dislocations present. The large hexagonal etch pits without bottoms are known as micropipes (MPs), while, large hexagonal etch pits with bottoms are treading screw dislocations (TSDs) and small hexagonal etch pits with bottoms are treading edge dislocations (TEDs)[6,7]. Furthermore, sea-shell pits are known as basal plane dislocations (BPDs). Besides the above types of dislocations, there are round pits without core on the wafer surface which are known as TED-BPD complexes in the literature. A shallow dislocation without core, i.e., half loop type dislocation, is often observed on the SiC wafer surface[8]. The shape of the etched pits depends on the magnitude correlation between the depth of the half loop and etched thickness. Whereas, the size of the etched pits varies depending on the etching time and wafer temperature. It is extremely difficult task to understand the dislocations completely from the analysis of their sizes and numbers only. The dislocations' geometry, morphology along with the sectional view is also crucial factor for better understanding of their presence and dynamics.

To study the above mentioned defects in SiC crystals, chemical etching is the most frequently applied method. Chemical etching of SiC crystal has been carried out using various molten salts such as KOH, NaOH and Na_2O_2, and their mixtures in appropriate proportion in a temperature range. The KOH etching method is commonly applied method for defect delineation in SiC crystals[9-13]. Dong[14], *et al.,* reported molten KOH etching method for defect revelation and obtained good etching patterns by adding Na_2O_2 in highly doped and semi-insulating 4H-SiC substrates. Wu[15] studied the etching process for defects in 4H- SiC with KOH+NaOH+Na_2O_2 melt under various experimental conditions. Yao[16], *et al.,* reported that KN (KOH+Na_2O_2) etching is more reliable than KOH etching for identifying dislocation type in SiC.

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In this paper, we have studied the KOH salt, KOH+NaOH and KOH+Na_2O_2 salt mixtures based etching method for dislocation revelation in n-type 4H-SiC crystal and optimised the etching parameters.This work was done for understanding the effects of NaOH and Na2O2 in the etching process of SiC for defects delineation with respect of time and temperature. The etched pits morphology was analysed in detail by wide-field high-resolution optical microscopy and scanning electron microscopy. After analyzing the pits morphology, we found comparatively difference in pits size, etching rate and surface roughness obtained from etching by pure KOH and eutectic mixture salts. The eutectic solution etching method found to be more effective method in comparison of pure KOH method for defects delineation in n type 4H-SiC wafer.

2. EXPERIMENTAL

Commercially available 4 inch (0001) single crystal n-type 4H-SiC wafer having thickness of ~350 µm and resistivity ≤ 0.03Ω cm was used for our experiments in the current study. The wafer was cut into 10mm×10mm sample pieces. The samples were ultrasonically cleaned in trichloroethylene, acetone, isopropanol and DI water, each for 5mins. A nickel crucible was used to heat the KOH and mixture of KOH+NaOH, KOH+Na_2O_2 granules. Ni is chemically inert and shows no reaction with KOH, NaOH and Na_2O_2. Quartz beaker was used to protect heating coils from hot chemical solutions. The 10 mm × 10 mm sample was placed in Ni crucible having holes in it and crucible was dipped in the melt for particular times. After etching process, each sample was dipped in acidified water to neutralize the KOH followed by ultrasonic cleaning in deionised (DI) water. A number of experiments were carried out with variations in the compositions of NaOH and Na_2O_2 in their mixtures with KOH. Etching rate was estimated from the difference in the thickness of the wafer due to the etching process. The etched pits were analysed by morphological investigations using an Olympus optical microscope (Microscopy model MX61) and a scanning electron microscope (SEM model Zeiss supra 55).

3. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) represent the optical microscope images of n-type 4H-SiC wafer etched by KOH at 500°C for 30min and 45min, respectively. From these results, it can be seen that the etch pits size varies from 15 µm to 54 µm with the increasing etching time from 30 min to 45 min. The etch pits can be distinguished by comparing the size of the etch pits[7,17]. The etch pits on the sample etched for 45min are more delineated and BPDs are more visible. Larger hexagonal etch pits with bottoms are the threading screw dislocations. From a close inspection of the morphology in Fig. 1(b), it can be concluded that mixed type dislocations are the combination of threading screw and threading edge dislocations. An etch rate of ~0.33 µm/min was estimated from these results.

Figures 2(a)-2(b) are the optical micrographs of n-type 4H-SiC surfaces etched by the mixture of KOH+NaOH having 10 wt% of NaOH in KOH (Fig. 2a) and 50wt% of NaOH in KOH (Fig. 2(b) at 500 °C for 30 min duration. From Fig.

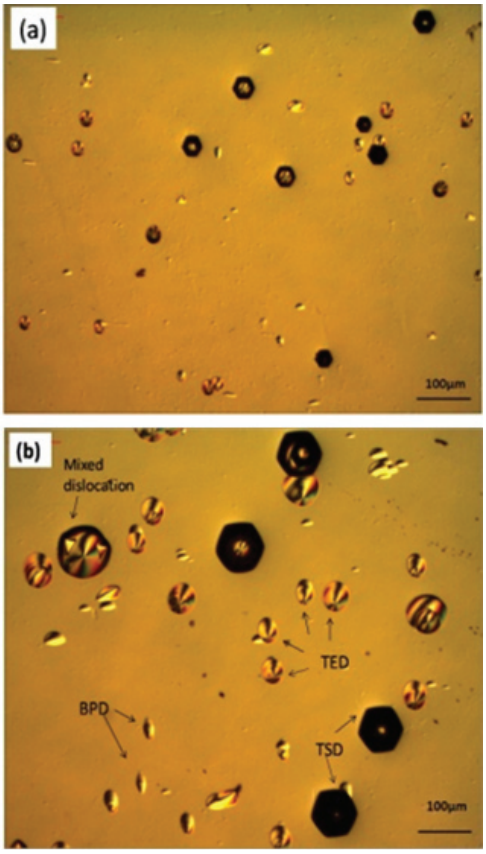

Figure 1. Optical microscope images of etched n-type 4H-SiC wafers after KOH etching at 500 °C for (a) 30 min (b) 45 min.

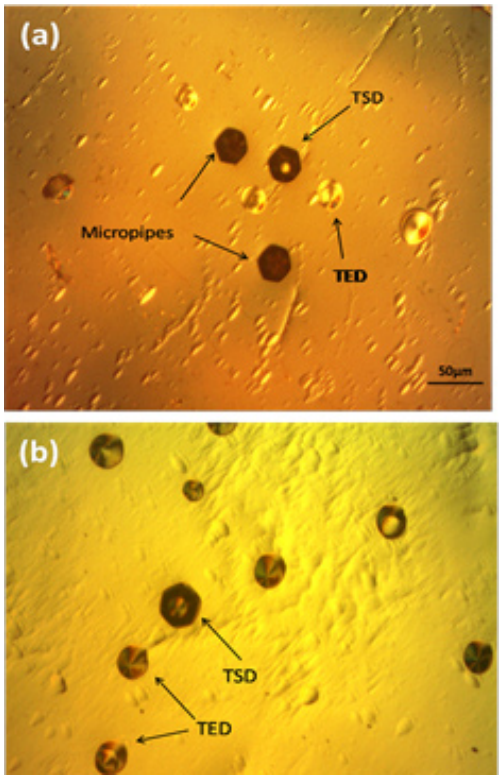

Figure 2. Optical microscope images of etched n-type 4H-SiC wafers after eutectic solution of KOH+NaOH etching at 500 °C for 30 min with (a) 10 wt% of NaOH in KOH, and (b) 50 wt% of NaOH in KOH.

2(a) and 2(b), it can be seen that by increasing the NaOH concentration from 10wt% to 50wt%, the etch pits overlap with each other and become oval, i.e., isotropic etching seems dominant. A decrease in the etching rate from 0.33µm/min for pure KOH etching to 0.16µm/min for eutectic mixture of KOH+NaOH is the result from this set of experiments. The etch pits size observed in eutectic solution of KOH+NaOHis ~30-40 µm whereas in pure KOH solution, the size is ~15 µm. The possible reason of this result may be, as NaOH is strong base than KOH. When we added NaOH in KOH then concentration of KOH becomes less and solution becomes more basic in nature, which slows the reaction rate. Therefore solution gets enough time to break the Si-C bond in defects prone regions. Therefore, by comparing the pure KOH etching with eutectic solution of KOH+NaOH etching under the same etching conditions, the eutectic solution of KOH+NaOH etching technique with lower etching rate is found to be more efficient to delineate etch pits, providing a much better control of etching and maintaining the uniform roughness of the surface.

The images shown in Fig. 3(a)-3(c) are the optical micrographs of the n- type 4H SiC wafer etched at 500 °C by the mixture of KOH+Na_2O_2 with wt% ratio of KOH:Na_2O_2= 90:10. The etching time varies from 20 min (Fig. 3(a)), to 25 min (Fig. 3(b)), and 30 min (Fig. 3(c)). The etch pits for 20 min etching time are difficult to differentiate as the pits seemoval in shape and are not completely delineated. By increasing the etching time, the pits become more hexagonal and hence more distinguishable. The etch pits size for 30 min etching time (Fig. 3(c)) is about 44 µm - 49 µm. This is much larger than the size (15 µm) that was obtained using pure KOH for an etching time of 30 min (Fig. 1(a)).

By comparing the results obtained using eutectic solution of KOH+Na_2O_2 with pure KOH, it is found that the etching rate gets enhanced when Na_2O_2 is added in the molten KOH. One of the possible reasons to this fact is due to the dissolved oxygen in the later which enhances the Si-C bond breaking rate and oxidation rate in defect prone regions[18]. A comparison of the results due to varying etching times is presented in Table 1.

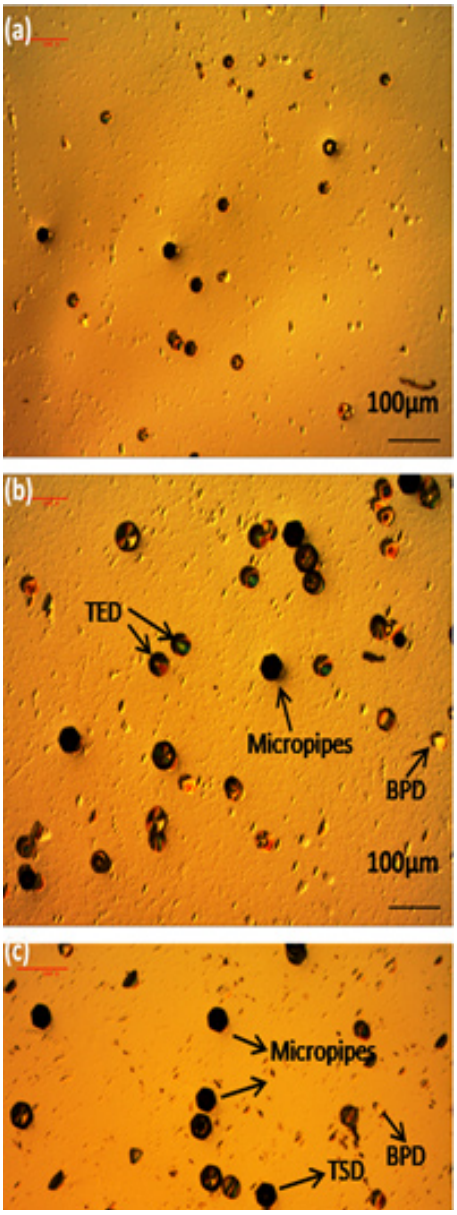

Figure 3. Optical microscope images of etched n-type 4H-SiC wafers after eutectic solution of KOH+Na_2O_2 (KOH: Na_2O_2=90%:10%) at 500 °C : (a) 20 min, (b) 25 min, (c) 30 min.

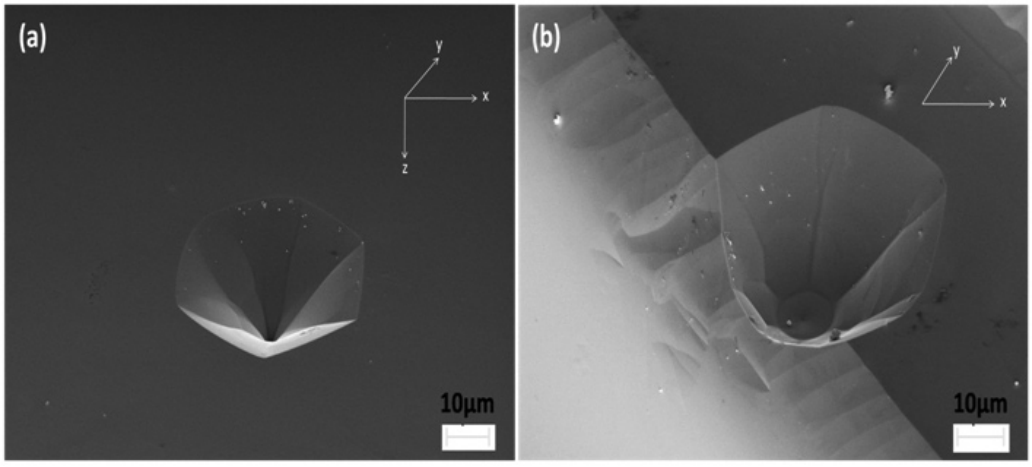

Figure 4. SEM images of TSD and TED after tilting the stage at 50° angle.

Table 1. Etching rate at various time for KOH+Na_2O_2.

Na_2O_2 + KOH etching time (min)	Etching rate (µm/min)
20	0.75
25	0.68
30	0.66

Clearly, with the increasing time, the etching rate starts to decrease. The possible reason of decrement in etching rate may be due to oxidation rate starts to decrease with time as the number of reactants becomes less available for reaction.

Figure 4 shows the SEM image of the etched sample after tilting the stage by 50 degrees. From these, one can easily differentiate between the threading screw dislocation and threading edge dislocation. The dislocations have higher strain energy and corresponding chemical potential and hence lead to higher chemical erosion. Threading screw dislocation has Burger vector n<0001> (n=1,2) along <0001> direction while threading edge dislocation has Burger vector $\frac{a}{3}<11\bar{2}0>$, along <0001>direction[1]. This means threading screw dislocation has strain energy along all the x,y,z directions while threading edge dislocation has strain energy along x and y directions only. Therefore chemical erosion occurs along all three directions in the case of threading screw dislocation while it occurs along only x and y directions in the case of the threading edge dislocation. Careful inspection of the SEM images reveals that the result in Fig. 4(a) is due to chemical erosion along x, y and z directions and hence should be associated to the threading screw dislocation. On the other hand, from the result in Fig. 4(b), chemical erosion seems to have occurred along x and y directions only, hence, it is attributed to the threading edge dislocation.

4. CONCLUSIONS

The defect selective etching with eutectic mixture of KOH+NaOH and KOH+Na_2O_2 etching technique has been performed for defects delineation in n-type 4H-SiC. The eutectic mixture technique has been found more reliable as with KOH+NaOH solution defects were delineated more efficiently at lower etching rate and less destructive for the sample surface. With eutectic solution of KOH+Na_2O_2, defects were delineated more effectively with substantial increase in etching rate. Threading screw dislocation and threading edge dislocation have been distinguished from SEM image analysis.

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In the current study, She has performed all the experiments and analyse the data.

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In the current study, he has corrected the manuscript and given many valuable inputs.

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In the current study, he has given the idea, continuously provided the guidance during experiments.