Investigation of micropipe and defects in molten KOH etching of 6H n-silicon carbide (SiC) single crystal


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A R T I C L E   I N F O

Article history:
Received 9 January 2013
Accepted 14 March 2013
Available online 23 March 2013

Keywords:
Semiconductors
Defects

A B S T R A C T

Silicon carbide (SiC) is an attractive wide band gap IV–IV semiconductor material suitable for high temperature, voltage and frequency applications. However, the presence of defects and its identification is the major issue prior to using for electronic devices application. To identify the defects, an easy and quick method is highly desirable. The present study has investigated molten KOH etching of 6H n-SiC for revealing of defects as a function of temperature (400–600 °C) and time. The etch pits were observed using Nomarski microscope and categorized with respect to their morphology. Result revealed that 500 °C was the optimum temperature for identification of micropipes (μP), screw dislocation (SD), threading edge dislocation (TD) and basal plane dislocation (BD). The etch pit and micropipe density were found in the range of ∼1 × 104 cm−2 and (8–10) cm−2 respectively. Also, the etching rate was found to obey an Arrhenius law with activation energy of (19–21) kcal/mol.

1. Introduction

SiC, an indirect wide bandgap semiconductor, has very fascinating and extraordinary electronic properties [1–3]. It is expected to be a promising substrate for GaN-based optoelectronic devices such as blue light emitting diodes and laser diodes due to similarities in their lattice constant and thermal expansion coefficient [4]. Also other material advantages for all forms of SiC include a high radiation and chemical tolerance, high hardness and thermal conductivity make it a useful material for a wide range of sensors and particularly in applications featuring high temperature [5–7].

During the last decade, much work has been directed toward the development of defect free large area SiC single crystal wafer and their commercial availability. However, though the crystal size is improving, commercialization of SiC devices is still limited due to presence of high concentration of structural defects such as—open core dislocations (called micropipes), low-angle boundaries, polytype instabilities, voids, inclusion and other conventional dislocations found in the bulk and epitaxial materials [4,8]. Among these defects, micropipes are the most serious ones since they cause fatal damage to SiC devices. It is basically a hollow tube defect extending along the c axis and shown to be killer defect for high power devices, especially at high voltage [9].

Recently, a significant reduction in micropipe density is achieved and SiC substrate with a few micropipe density have been successfully grown [10–14].

To study defects in single crystal SiC, selective chemical etching has been extensively investigated with numerous molten salts, among them KOH and its mixtures with other salts are currently preferred for revealing the defect and dislocation in single crystal [4,15–18]. The etch pattern depends on the type and concentration of impurities, surface finish, material properties like polytypes, orientation etc. and experimental conditions such as time duration and temperature of the etchant, also on polarity of SiC wafer [19–22]. The aim of the present study is to optimize KOH etching for off-axis 6H-n-SiC to investigate the micropipe and other defects using laboratory muffle furnace without any extra experimental requirement (e.g. melt stirring, etching ambience and addition of different precursor to KOH which were reported earlier).

2. Experimental

The (0001) single crystal samples of area 1 × 1 cm2 and thickness of 300 μm were diced from 2″ diameter 3.5″ off-axis 6H n-SiC single crystal wafers (M/S Tankeblue, China). A resistive heated muffle furnace was used for heating the KOH pellets (Merk purity > 99%). A Nickel crucible, inert for molten KOH, was used for KOH heating and the temperature was measured by a sensor in the vicinity of the crucible placed in the furnace. Diced SiC was immersed in Ni crucible containing the KOH and heated slowly (3 °C min−1) in a temperature range from 400 to 600 °C in steps of 25 °C for different holding times.
Experimental sequence for etching of SiC is represented by the flowchart given in Fig. 1. After KOH heating, etched samples were quickly washed with acidified water to neutralize the KOH, then repeatedly rinsed with DI water and finally cleaned with acetone. For reproducible etching, weight of KOH pellets was measured using a micro balance (Citizen, Model No-CX165, Northglenn) before heating. To calculate etching rate (g min$^{-1}$ cm$^{-2}$), the weight of the sample was taken before and after etching. Finally, the etch pits were observed using Nomarski microscopy (Olympus Microscopes) and categorized with respect to their morphology.

3. Results and discussion

Fig. 2 (a–d) represents the optical micrograph image of 6H n-SiC at different etching temperatures keeping with constant etch-duration of 45 min. It can be seen from micrograph of Fig. 2 (a–d) that the molten KOH does not have any effect when the etching temperature is ≤450 °C. In this situation, only fine scratches were observed on Si surface which might have occurred during the lapping and polishing steps [18]. An increase in the temperature from 450 °C, etch pits were observed at the etching temperature of 475 °C (Fig. 2 (b)), but it is difficult to differentiate. As further increase in temperature (500 °C), different etch pits (hexagonal, circular etc) were observed and can be differentiated according to their size and shape. It seems that the temperature of 500 °C is enough for revealing the defects in SiC. Here the dislocations produce large hexagonal etch pits without bottom on Si face assigned to micropipes (μP, also called a super screw dislocation), medium-size pits to threading screw dislocations (TSD), and small-size pits to threading edge dislocations (TED) etc. [15,19]. Ping Wu investigated the threading edge dislocation in molten KOH etching for 4H SiC single crystal and lightly doped 4H epilayer and reported a well-defined hexagonal etch pits on lightly doped 4H epilayers, whereas the rounded etch was observed on heavily doped bulk 4H SiC crystals [15]. Bondokov et al. demonstrated a method for defect delineation in SiC using KOH vapor in the temperature range from 700 to 1000 °C and reported the activation energy [18]. After further increase in temperature to 550 °C different etch pits (Fig. 2(d)) were observed but they merged with one another and difficult for identification may be due to over-etching.

A further optimization of holding time was also performed in order to obtain proper holding time duration for etching at 500 °C, but observed results revealed not much difference in the etch pattern. Fig. 3(a–d) represents the optimized microscopic image of SiC at different magnifications. A micropipe density of 8–12 cm$^{-2}$ was found in the present study. Density of the etch pits was also calculated and found in the range of $1 \times 10^4$ cm$^{-2}$ at 10$x$ magnifications.

The formation of etch pits using defect selective etching is due to difference in the chemical potential of perfect single crystal and the area which has structural imperfection. For a single crystal material there are areas with structural imperfections having higher strain energies than perfect single crystal regions and

**Fig. 1.** Flow chart for molten KOH etching of 6H n-SiC.

**Fig. 2.** Optical micrograph image of 6H n-SiC at (a) 450 °C, (b) 475 °C, (c) 500 °C and (d) 550 °C with constant etching time of 45 min.
because of a higher chemical potential, strained areas of single crystals are more liable to chemical attack than non-strained areas and as a result under optimum etching condition the strained areas due to defect, produce etching pits [23]. Also the formation of micropipes is based on the Frank's model of hollow core screw dislocation [24]. It is basically a pure screw dislocation creating a micropipe in equilibrium whose radius \( r_0 = \frac{\mu B^2}{8\pi^2\gamma} \), where \( \mu \) is the shear modulus and \( \gamma \) is the surface energy. Heindl noted that the strain field around a dislocation that has a Burger vectors extending more than 1 nm, the strain energy around the dislocation line is very high. So it is preferable to remove some material adjacent to the dislocation line and create an additional surface in the form of hollow tube [25].

In order to estimate the activation energy of the process, etching rate was evaluated using weight loss after etching. It is known that etching rate depends on polytypes (4H, 6H & 15R), crystal orientation, carrier concentration, doping etc and reported, an increase in etching rate from 6H to 15R to 4H polytype, which is in the order of hexagonality as 6H (33%) < 15R (40%) < 4H (50%), indicating that the etching rate is enhanced as the hexagonality of SiC increases [4]. Fig. 4 shows an Arrhenius plot for the etching rate of the 6H-n-SiC as a function of temperature in the range from 400 to 600 °C. The activation energy of etching is estimated to be (19–21) kcal/mol which is consistent with previous results [18,26]. It is noted that for the compound semiconductor etching process with activation energy \( (E_a) > 7 \) kcal/mol is known as reaction rate limited process, which results in preferential etching. Observed activation energy values corresponding to those achieved by molten KOH etching are in agreement with reported one.

### 4. Conclusion

A comprehensive defect analysis has been done on 6H n-SiC using etching in molten KOH and optical microscopy. Etching of SiC, although a destructive process, is found to be very efficient method of detecting defects due to its relative simplicity and cost effectiveness. The SiC sample was etched at 500 °C with 45 min of holding time. Defect revealed in the process include micropipes, screw dislocation and threading edge dislocations. The micropipe density found to be in the range of \( (8–10) \) cm\(^{-2}\) and etch pits density estimated to \( \sim 1 \times 10^4 \) cm\(^{-2}\). Etching rate found to follow Arrhenius law with activation energy of (19–21) kcal/mol.

### References
