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Chemical polishing of hexagonal p-type 6H-SiC surfaces by HF/Na_2O_2 solutions

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Abstract. In this paper, we present an experimental method on the etching reaction of p-type 6H-SiC, etching that was carried out in HF/Na_2O_2 solutions. The morphology of the etched surface was examined with varying Na_2O_2 concentration, etching time and temperature solution. The surfaces of the etched samples were analyzed using Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and Photoluminescence. The surface morphology of samples etched in HF/Na_2O_2 is shown to depend on the solution composition and bath temperature. The investigation of the HF/Na_2O_2 solutions on 6H-SiC surface shows that as Na_2O_2 concentration increases, the etch rate increases to reach a maximum value at about 0.6 M and then decreases. A similar behaviour has been observed when temperature of the solution is increased. The maximum etch rate is found for 80 °C. Taking account the result a new polishing etching solution of 6H-SiC has been developed. In addition, the result is very interesting when to date no chemical polishing solution has been developed on silicon carbide (SiC). Finally, we have proposed a dissolution mechanism of the silicon carbide in HF/Na_2O_2 solutions.

Key words

Silicon Carbide, chemical etching, SEM, Photoluminescence

1. Introduction

Recently there has been much interest in silicon carbide (SiC) due to its stability in terms of high-temperature treatments, chemical attack and mechanical stresses. The material cannot be etched by acid, neutral, or basic solutions at room temperature and molten KOH is widely used for preferential etching [1, 2]. Chemical etching technology has been widely used in semiconductor fabrication processes. This method process still plays an important role in semiconductor industry. However, there is a need for suitable etching solution for highly resistive SiC. To date no works have been performed on low-doped hot-pressed 6H-SiC and no chemical polishing solution has been developed on the material. There is a need for - suitable etching method for SiC [3-5].
In this paper, a new etching solution of silicon carbide based on HF/Na_2O_2 solutions is developed. Due to the high resistivity of the material, a thin metallic film of aluminium has been deposited onto the SiC substrate prior the etching. The role of Al is to facilitate and entertain the etching in HF and Na_2O_2 by providing hole to the SiC surface [6, 7].

2. Experimental procedure

The wafers used in this work were hot-pressed 6H-SiC, obtained from Goodfellow (U.K). All measurements presented here were performed on squares (5 x 5 mm^2) samples cut from an unpolished wafer of 2 mm thickness with a resistivity of 30 $k_\Omega$cm. Silicon carbide samples were etched in a cylindrical polyethylene reactor, chemicals of electronic grade and deionised water were used to prepare an etching solution of 50 ml. The experimental data were taken in the etching solution of various compositions. For SEM measurements, a Jeol (JSM-6360) are used. The IR spectra were collected by a Thermo Nicolet Nexus Fourier Transform Infrared Spectrometer equipped with a DTGM KBr detector. All FTIR spectra were recorded in absorbance mode in the IR region 400-4000 cm^{-1} at 4 cm^{-1} resolution.

3. Results and discussion

The effect of the etching time on the rate was examined by measuring the etch depth as a function of etching time

(10, 30 and 60 min). The etch depth was calculated by dividing the etched amount of silicon carbide, i.e., a weight difference of SiC before and after the etching process, by surface area exposed to the etching solution and SiC density (2.31 g/cm^3).The etch depth was determined by dividing the etch depth by the reaction time. The etching of silicon carbide in HF (22.5 M) / Na_2O_2 (0.5 M) (2/1 by vol.) solution at 25°C shows that the etch depth increased linearly with time and the etch rate was found about 230 nm/min. In addition, it was found that the etch rate varies with solution temperature, as shown in Figure 1 for a solution of (22.5 M) 2HF / $1Na_2O_2$ (0.5 M). It shows that the etch rate increases with temperature, reaches a maximum at about 80 °C, then decreases slightly. The decrease of the etch rate above the temperature cited is probably due to evaporation of the solution and then a decreases of the solution concentration. The effect of oxidizing agent on the etch rate was examined by varying the Na_2O_2 concentration from 0.05 to 1 M in (22.5 M) HF / Na_2O_2 (2/1 by vol.) at a temperature of 80 °C.

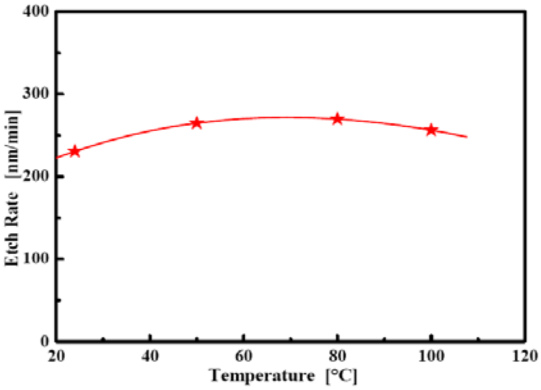

Fig.1. Effect of temperature on the etch rate of 6H-SiC in (22.5M) $2HF/1Na_2O_2$ (0.5M) solution at 80°C - 60 min

The measured etch rates are shown in Figure 2. It is seen that the etch rate increased with increasing the Na_2O_2 concentration to reach a maximum value at about 0.6 M and then decreases. The evolution of the etching is similar to that observed on silicon etched in $HF/K_2Cr_2O_7$ solutions. During chemical etching the silicon carbide is dissolved in a two-step process (oxidation-dissolution). As the concentration of the oxidant (Na_2O_2) increases the process's of the surface oxidation becomes more important than that of the dissolution. The morphology of SiC surface was examined by SEM. It is seen that the etched surface with HF/Na_2O_2 dependents on the solution composition, temperature bath and etching time.

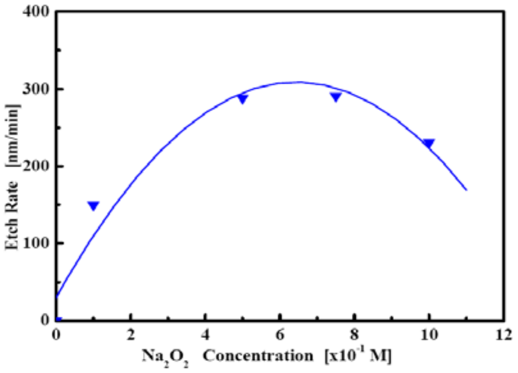

Fig.2. Effect of Na_2O_2 concentration on the etch rate of 6H-SiC in (22.5M) $2HF/1Na_2O_2$ (0.5M) solution at 80°C - 60 min

Figure 3[a] displays a plan view SEM images of bare polished SiC sample. It shows that the surface of the sample is composed by several grains. An examination of a grain by SEM at high magnification (Fig. 3[b] shows that it is of black colour, whereas the adjacent appear grey, probably due to a difference in the grain conductivity.

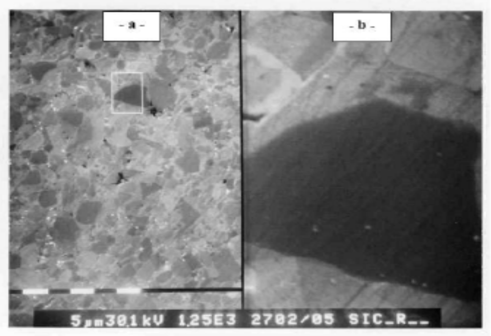

Fig.3. Plan view SEM image of a polished bare 6H-SiC
[a] Magnification (X 1250)
[b] Magnification (X 4200)

Figures 4 and 5 show SEM images of 6H-SiC subjected to (22.5M) HF/ Na_2O_2 (0.1 M) and (22.5 M) HF/ Na_2O_2 (0.5 M) (2/1 by vol.) at 80 °C for 60 min, respectively. It shows that the morphology of the surface varies with oxidant concentration. The observation of the etched surface sample in the solution with (0.5 M) Na_2O_2 shows the appearance of a high density of etch pits. The shapes of the pits are non-uniform and non-regular (**Fig. 4**). Whereas, the increase of the oxidant concentration at 0.5 M leads to the disappearance of the etch pits. The surface appears regular and smooth, indicating that the developed solution is very convenient for the polishing of 6H SiC surface. In addition it shows that the temperature of the etching solution has also an important effect on the surface morphology.

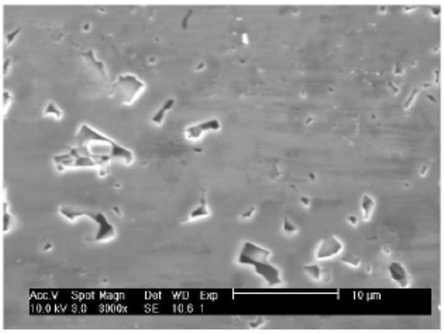

Fig.4. Plan view SEM image of 6H-SiC chemically etched in (22.5M) $2HF/1Na_2O_2$ (0.1M) solution at 80°C - 60 min

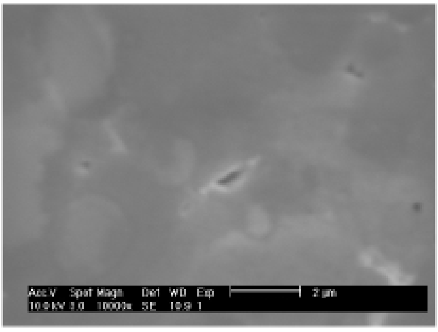

Fig.5. Plan view SEM image of 6H-SiC chemically etched in (22.5M) $2HF/1Na_2O_2$ (0.5M) solution at 80°C - 60 min

Figure 6 shows SEM image of 6H-SiC etched in (22.5 M) HF/ Na_2O_2 (0.5 M) (2/1 by vol.) at 25°C for 60 min, where it shows the presence of etch pits and grains on the surface, indicating that the attack is isotropic. The comparison of **Fig. 5b** and **Fig.6** clearly demonstrates the effect of etching temperature on the surface morphology.

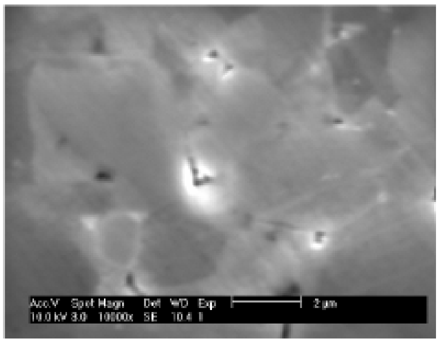

Fig.6. Plan view SEM image of 6H-SiC chemically etched in (22.5M) $2HF/1Na_2O_2$ (0.5M) solution at 25°C - 60 min

In order to evaluate the phenomena occurring at the 6H-SiC surface at chemical etching, FT-IR spectroscopy measurements have been performed. Spectra 1, 2 and 3 of **Figure 7** correspond to bare 6H-SiC unetched sample subjected to (22.5 M) HF/ Na_2O_2 (0.5M) (2/1 by vol.) and (22.5 M) HF/ Na_2O_2 (0.1M) (2/1 by vol.) solution at 80 °C for 60 min respectively, whereas spectrum 3 corresponds to the non-treated 6H-SiC sample. The band situated at 466 cm^{-1} correspond to SiC bonds become narrow, indicating that in the etching process, SiC bonds are fragile and easily broken [8]. We note also the existence of SiH_2 species at 610 cm^{-1}, SiH at 650 cm^{-1} and two peaks at 672 cm^{-1} and 719 cm^{-1} correspond to SiC. These peaks become unchanged after chemical treatments. The large band at 986 cm^{-1} corresponds to SiO_x. The weak band observed at 1636-1646 cm^{-1}, is attributed to CO. The concentration of CO does not increase with the increase of the Na_2O_2 concentration, whereas, the concentration of CO_2, revealed by the band at 2306-2369 cm^{-1}, increases with increasing oxidant concentration (spectra 1 and 2 in **Figure 7**), indicating that is may be the principal reaction product of the SiC dissolution.

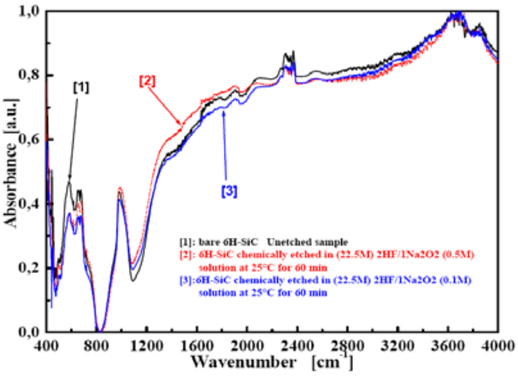

Fig.7. FT-IR Spectra of bare 6H-SiC unetched sample and chemically etched in (22.5M) $2HF/1Na_2O_2$ (0.5M)

Using the electrochemical impedance spectroscopy of 6H-SiC in aqueous hydrofluoric acid Spanier et al. [9] found a same result. By analogy with Si dissolution in aqueous solution where the dissolution mechanism is well admitted [10,11] , the dissolution of SiC in aqueous HF is significantly more complicated, considering that the SiC dissolution can be understood as a local electrochemical process in which the reaction is chemically initiated. Microscopically, anode and cathode sites are formed on the etched surface resulting in a local current flux [12]. The chemical process has to incorporate a source of excess holes and electrons for the charge transfer between the electrodes.

Cathode (Al)

$$Na_2O_2 + 2H^+ \longrightarrow Na_2O + H_2O + 2h^+ \quad (1)$$

Anode (SiC)

$$SiC + 4H_2O + 8h^+ \longrightarrow SiO_2 + 8H^+ + CO\uparrow \quad (2)$$

$$8H^+ \longrightarrow 4H_2\uparrow + 8h^+ \quad (3)$$

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O \quad (4)$$

Global reaction

$$Na_2O_2 + SiC + 6HF + H_2O \longrightarrow SiF_6 + Na_2O + CO_2\uparrow + 3H_2\uparrow \quad (5)$$

Spanier et al. [9] suggested that the SiC dissolution can lead to CO formation according to the following reaction:

$$SiC + 2H_2O + 4h^+ \longrightarrow SiO + CO\uparrow + 4H^+ \quad (6)$$

SiO is presumed to be dissolved in HF. Shor et al. [13] and Rysy et al. [14] have determined by coulometric means the average valency of the chemical reactions and concluded that reaction leading to CO_2 is a slightly higher probable than that of CO.

Luminescence measurements were performed using Perkin-Elmer LS-50B spectrometer with Xenon lamp at excitation wavelength of 325nm. The photoluminescence (PL) of the SiC unetched sample **(Fig. 8a)** presents two bands with a same intensity centred at 430 nm (blue band) and at 560 nm (green band) respectively. The etched samples in $2HF/1Na_2O_2$ solution with 0.5M of Na_2O_2 during 60 minutes in different temperatures of the solution: 80°C, 50°C and room temperature (Figs. 8b, 8c, 8d), induce a decrease in the intensity of the PL peaks compared to the unetched one. In addition, the intensity of the band centred to 430 nm is a less important than the one centred to 560 nm for the temperature 80 °C. However, for temperatures low 80°C, the green band disappears. This type of attack induces a chemical polishing substrate and a surface without defaults.
Finally, this result can be explained by the passivation of the surface when the temperature increases (creation of a protective layer to the SiC surface).

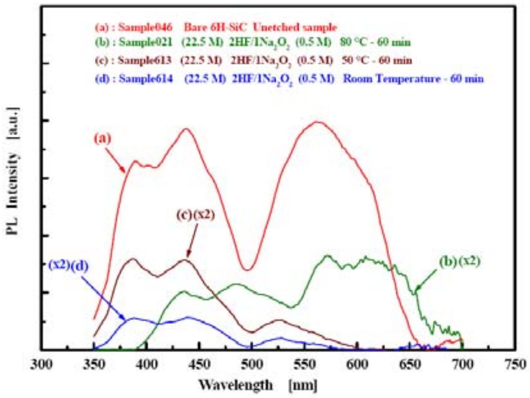

Fig.8. PL spectra of bare 6H-SiC unetched sample and chemically etched in (22.5M) $2HF/1Na_2O_2$ (0.5M)

4. Conclusion

The chemical etching of SiC in $2HF/1Na_2O_2$ solutions has been investigated under various reaction conditions. It was observed that morphology of the etched surface depends on the solution composition, temperature bath and etching time, then an optimum etching condition giving a good surface quality has been determined. Finally, taking into account the results together with FTIR spectra a dissolution mechanism of SiC is presented.

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