Precision Engineering xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Precision Engineering

journal homepage: www.elsevier.com/locate/precision

The influence of concentration of hydroxyl radical on the chemical mechanical polishing of SiC wafer based on the Fenton reaction

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ARTICLE INFO

Keywords:
Hydroxyl radical
Fenton reaction
Silicon carbide
Chemical mechanical polishing

ABSTRACT

Aiming at the chemical mechanical polishing (CMP) of single crystal silicon carbide (SiC) based on the Fenton reaction, the concentration of hydroxyl radical (·OH) produced in the Fenton reaction and its influence on the chemical reaction rate of SiC were detected by using visible spectrophotometry. The formation rule of ·OH using Fenton's reagents with different components, and the influence of Fenton's reagents on CMP of SiC wafer, were studied. The experimental results show that ·OH can chemically react with the SiC surface to produce an SiO_2 oxide layer with low hardness. The larger the concentration of ·OH, the quicker the chemical reaction rate on the SiC surface and the better the polishing quality of SiC wafer. The Fe^{2+} and H_2O_2 concentrations, and pH in the Fenton's reagent influence the concentration of ·OH produced in the Fenton reaction, therefore influencing the polishing quality of SiC surface. Excessive Fe^{2+} concentration ($FeSO_4 \geq 0.03$ wt.%) and pH value (pH ≥ 5) can lead to the production of flocculent complexes or precipitates during the reaction while an excessive amount of H_2O_2 ($H_2O_2 \geq 10$ wt.%) can capture ·OH produced in the Fenton reaction, thus resulting in a poor polishing quality of SiC surface. Under the condition where the pH value, Fe^{2+} and H_2O_2 concentrations are 3, 0.02 wt.% and 5 wt.%, respectively, high-concentration ·OH can be produced in the Fenton reaction. Based on this, a smooth surface of SiC wafer with a roughness of 0.1869 nm *Ra* can be obtained after polishing for 1 h.

1. Introduction

As a third-generation semiconductor material, single crystal silicon carbide (SiC) is characterised by wide energy band gap, high saturated electron drift velocity, high breakdown voltage and high thermal conductivity. With these properties, single crystal SiC can be used in extreme conditions and is one of the most promising semiconductor materials [1]. While being applied in the growth of epitaxial film, single crystal SiC is required to have a smooth, damage-free surface without defects. However, as single crystal SiC has good chemical stability and high hardness (Moh's hardness 9.2), it is extremely difficult to planarize SiC wafer with ultra-precision and high efficiency [2,3]. Chemical mechanical polishing (CMP) is a global planarization method widely used in the polishing of brittle and hard materials [4]. During the CMP process, the alternation of chemical reaction and mechanical removal of material can polish efficiently the workpiece's surface. Critical to realising CMP process, oxidising agent in the polishing slurry directly influences the proportion of chemical and mechanical removal effects and further affects the polishing quality of workpiece [5].

As one of the strongest oxidation reactions [6,7], the Fenton reaction can produce hydroxyl radical (·OH) with strong oxidising property in the reaction between hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}). CMP process of SiC can be conducted based on the principle of the Fenton reaction. Kubota et al. [8] used an iron bar to rub the SiC surface for 6 h in H_2O_2 solution. They observed that a scratch of 20 nm in depth and 3.4 nm in diameter appeared on the SiC surface in contact with the iron bar. This verified the feasibility of processing SiC through the Fenton reaction. Dai et al. [9] polished an SiC optical material on a cast iron plate by carrying out a Fenton-like reaction, and obtained an SiC surface with a roughness of 1.93 nm *RMS* after polishing for 15 min. Xu et al. [10] compared the catalytic effects of different catalysts in the Fenton reaction and their influence on the CMP of SiC, and obtained a smooth surface of SiC wafer with a roughness of 0.47 nm *Ra* using the Fe_3O_4 catalyst.

Aiming at research into the chemical reaction mechanism during the CMP process of SiC, Yagi et al. [11] polished SiC via a Fenton-like reaction using zero-valent iron as the catalyst. After analysing the elements on the SiC surface by X-ray photoelectron spectroscopy (XPS), it can be seen that ·OH produced in the Fenton-like reaction can produce SiO_2 oxides by breaking the Si-C bonds. Pan et al. [12,13] studied the removal mechanism of SiC in CMP by applying silicon dioxide polishing slurry that contains H_2O_2, and found that only the polishing slurry that

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https://doi.org/10.1016/j.precisioneng.2017.12.011
Received 15 March 2017; Received in revised form 22 November 2017; Accepted 20 December 2017
0141-6359/ © 2017 Published by Elsevier Inc.

contains H_2O_2 and silicon dioxide can produce ·OH to corrode the SiC surface. Moreover, KOH can promote the production of ·OH so as to improve the material removal rate. However, the characteristic and formation rule of the oxidizing agent ·OH, as well as its effect on the CMP of SiC, are not clarified.

In this paper, polishing experiments on single crystal SiC were conducted to explore the effect of ·OH produced in the Fenton reaction on the polishing of single crystal SiC. Moreover, the influences of various parameters (such as Fe^{2+} and H_2O_2 concentrations, and pH value) on the production of ·OH and on the polishing quality of SiC were studied.

2. Experimental investigation

2.1. Chemical principle in the CMP of SiC

Fenton reaction is a reaction system with strong oxidising property produced by the reaction between H_2O_2 and Fe^{2+} [14]. Fe^{2+} reacts with H_2O_2 to produce the oxidising agent ·OH, which undergoes a chemical reaction with SiC to produce a soft, easily-removed silicon dioxide layer [8]. Subsequently, the soft layer is removed by abrasive particles due to the mechanical removal effect during the CMP so as to expose the fresh SiC surface. The high-efficiency polishing of SiC surface can be realised by constantly repeating the process. The chemical process is described below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1)$$

$$Si\,C + 4\cdot OH + O_2 \rightarrow SiO_2 + 2H_2O + CO_2 \uparrow \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \cdot OOH \quad (3)$$

Eqs. (1)–(3) show that ·OH plays a crucial role in the chemical reaction on the SiC surface while Fe^{2+} just serves as the catalyst during the Fenton reaction. Fe^{2+} and H_2O_2 concentrations, as well as the pH value of the solution, are primary factors influencing the reaction rate [15,16].

Theoretically, it can be seen from Eq. (2) that the higher the concentration of ·OH produced in the reaction of Eq. (1), the quicker the chemical reaction rate on the SiC surface. In this way, more high-hardness SiC is transformed to soft oxide layer of SiO_2, leading to an easier mechanical removal process. Thus, the concentration of ·OH produced in the Fenton reaction directly influences the removal efficiency and polishing effect of single crystal SiC.

2.2. Detection of the ·OH concentration

Although ·OH produced in the Fenton reaction cannot be directly detected, its concentration can be indirectly measured by using visible spectrophotometry [15]. The detection is conducted on the basis of the reaction between 1.8 mol/L salicylic acid solution and ·OH, which produces purple 2, 3-dihydroxy benzoic acid radicals and 2, 5-dihydroxy benzoic acid radicals (equation shown in Fig. 1). The reaction product shows the largest absorption peak at a wave length of 510 nm, at which the concentration of the absorption can be detected by using a UV-2501PC ultraviolet-visible absorption spectrograph. The detected concentration is that of ·OH produced in the Fenton reaction.

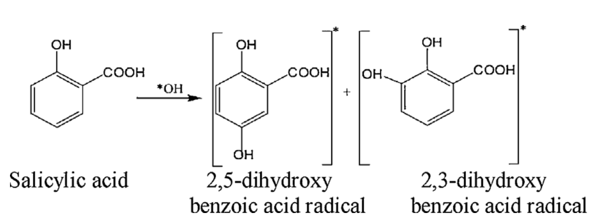

Fig. 1. Dihydroxy benzoic acid radical produced in the reaction between salicylic acid and ·OH.

Measurement of the ·OH concentration by using visible spectrophotometry requires a stable chemical reaction. During the chemical reaction between SiC and ·OH, the chemical reactions in Eqs. (1)–(3) occur synchronously and constantly, which causes a constant change in the ·OH concentration. If the reaction solution is extracted in this context to detect the ·OH concentration, the result is random and uncertain. Therefore, in the experiment for detecting the ·OH concentration, the Fenton's reagents of corresponding concentration are mixed, that is, only those Fenton reactions in Eqs. (1) and (3) occur.

2.3. Chemical reaction on the SiC surface

The rate and extent of the chemical reaction between the SiC surface and ·OH to produce SiO_2 soft layer directly influence the material removal efficiency and the polishing quality of SiC [10]. To study the influence of the ·OH concentration on the chemical reaction rate on the SiC surface, an SiC chemical reaction experiment was conducted under varying reaction times by using Fenton's reagents of different concentrations. Moreover, the chemical reaction rate can be judged according to the thickness of the chemical reaction layer on the SiC surface.

Four Fenton's reagents were prepared by using H_2O_2 at a concentration of 5 wt.% to react with ferrous sulphates ($FeSO_4$) with the concentration of 0, 0.01, 0.02 and 0.03 wt.%, respectively. The ·OH concentrations in the four Fenton's reagents for different reaction times (10, 40, and 70 min) were measured by applying visible spectrophotometry. Additionally, single crystal SiC was immersed into the four Fenton's reagents to undergo chemical reaction. SiC was removed after 3 h so that the SiO_2 layer on the SiC surface can be thick enough. Moreover, the C-face reaction layer of SiC wafer was observed under a scanning electron microscope (SEM) after cleaning and drying, while the chemical composition of the reaction layer was analysed by applying XPS. To avoid consumption of the Fenton's reagents in the chemical reaction with SiC, the reagents were replaced every 1 h.

2.4. Polishing experiment on the SiC surface

To study the influences of ·OH with different concentrations on CMP of SiC, the polishing experiments of SiC wafer were conducted after three important factors were selected as research objectives: H_2O_2 and Fe^{2+} concentrations, and pH value.

The compositions of the CMP polishing slurry are shown in Table 1. Among them, the colloidal silica abrasives with an average particle size of 50 nm were chosen, and the deionised water was used as a base solution. The pH value of the solution was adjusted by using dilute sulphuric acid and sodium hydroxide while it was measured by use of an ST3100/F pH meter. The C-face of 6H-SiC (0001) measuring approximately 2 inches in diameter was adopted for polishing whose original surface roughness was about 1 nm *Ra*. The polishing experiments were conducted on the LGP-15S CMP machine and every CMP process was performed for 1 h with a polyurethane polishing pad. The polishing pressure was 0.02 MPa, the slurry supplying rate was 60 ml/min, and the rotation speeds of the workpiece plate and the polishing plate were both 60 rpm. Polished SiC wafer was subjected to ultrasonic cleaning with acetone, ethyl alcohol, and deionised water, successively.

Table 1
Compositions of chemical mechanical polishing slurry.

Compositions	Parameters
$FeSO_4$ concentration (wt.%)	0, 0.01, 0.02, 0.03
H_2O_2 concentration (wt.%)	2.5, 5, 7.5, 10
pH value	1, 3, 5, 7
Abrasives	20 wt.% colloidal silica
Base solution	Deionised water

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