

Comparative analysis on surface property in anodic oxidation polishing of reaction-sintered silicon carbide and single-crystal 4H silicon carbide

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Abstract For effective machining of difficult-to-machine materials, such as reaction-sintered silicon carbide (RS-SiC) and single-crystal 4H silicon carbide (4H-SiC), a novel polishing technique named anodic oxidation polishing was proposed, which combined with the anodic oxidation of substrate and slurry polishing of oxide. By scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDX) observation and atomic force microscopy analysis, both the anodic oxidation behaviors of RS-SiC and 4H-SiC were investigated. Through comparison of the surfaces before and after hydrofluoric acid etching of the oxidized samples by the scanning white light interferometry (SWLI) measurement, the relationships between oxidation depth and oxidation time were obtained, and the calculated oxidation rate for RS-SiC was 5.3 nm/s and that for 4H-SiC was 5.8 nm/s based on the linear Deal–Grove model. Through anodic oxidation polishing of RS-SiC substrate and 4H-SiC substrate, respectively, the surface roughness rms obtained by SWLI was improved to 2.103 nm for RS-SiC and to 0.892 nm for 4H-SiC. Experimental results indicate that anodic oxidation polishing is an effective method for the machining of RS-SiC and 4H-SiC samples, which would improve the process level of SiC substrates and promote the application of SiC

products in the fields of optics, ceramics, semiconductors, electronics, and so on.

1 Introduction

Silicon carbide (SiC) is a promising material for semiconductors, ceramics, and optics [1, 2], since it has remarkable excellent mechanical and chemical properties [3, 4]. In the SiC family, reaction-sintered silicon carbide (RS-SiC) and single-crystal 4H silicon carbide (4H-SiC) have attracted widely interests for their extraordinary capabilities. Besides the common excellences, RS-SiC has the unique advantage of a low manufacturing cost, which makes it an ideal mirror material for space telescope systems [5, 6]. Meanwhile, 4H-SiC is one of the most attractive semiconductor materials for the next-generation power device applications, as it has outstanding electronic properties [7].

However, SiC is a difficult-to-machine (DTM) material because of its high hardness and chemical inertness [8]. Although ultrasmooth 4H-SiC surface can be obtained in chemical mechanical polishing (CMP) [9], plasma-assisted polishing (PAP) [10], and Catalyst-Referred Etching (CARE) [11], the material removal rates (MRR) in these techniques are low. As the composition and structure of RS-SiC are not uniform [12], few of the techniques which have been developed to process RS-SiC substrates can yield smooth surface and obtain high material removal rate simultaneously [13].

Anodic oxidation has been developed for the oxidation of silicon, and we applied it to process SiC [14]. By applying a mixture of hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), and ultrapure water (H₂O) as the electrolyte, both the RS-SiC and 4H-SiC were oxidized.

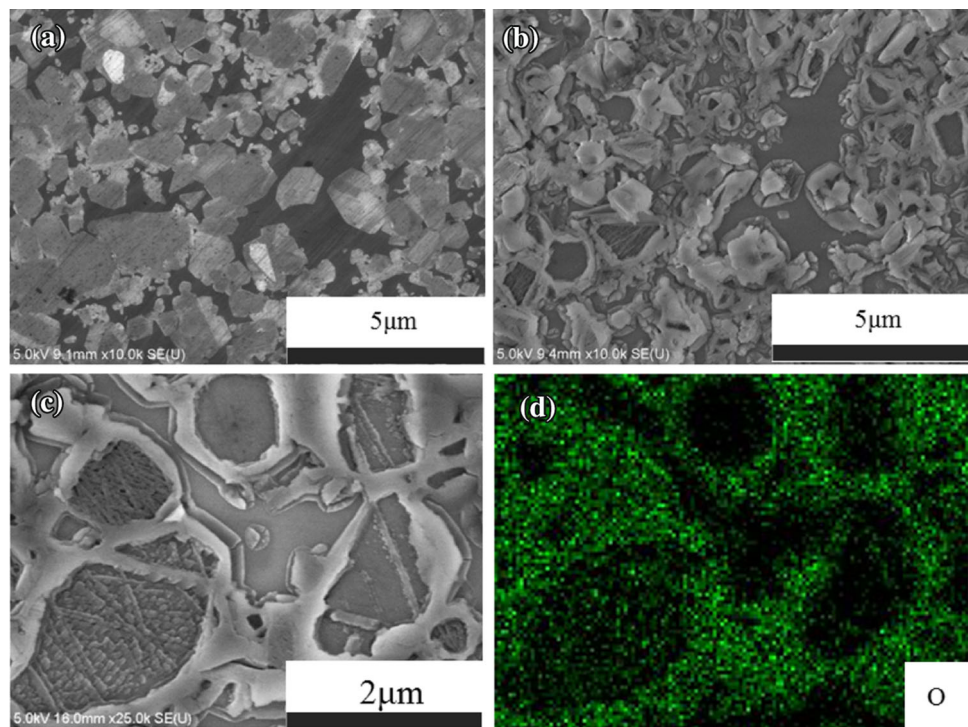
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Table 1 Experimental parameters in anodic oxidation polishing

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Specimen				
Workpiece	RS-SiC		4H-SiC	
Size	Square, 50 mm × 50 mm		1 in.	
Electrolyte (slurry)				
Abrasive size	Ceria, ϕ 190 nm			
Concentration	0.1 wt%			
Oxidation parameters				
Potential	10 V (DC)			
Cathode	Platinum (Pt)			
Abrasive polishing parameters				
Polishing pad	K0017 (FILWEL Co. Ltd.)			
Pad size	Round, ϕ 10 mm			
Load	30 g		150 g	
Pressure	3.75 kPa		18.75 kPa	
Rotation speed	300 rpm			
Scan speed	5 mm/s			
Experimental time	DOAP for 6 h	SOAP for 3 h	DOAP for 2 h	SOAP for 1 h

Fig. 2 Anodic oxidation behaviors of RS-SiC observed by SEM-EDX. **a** Before anodic oxidation. **b** After anodic oxidation. **c** Details of oxide morphology. **d** Oxygen element distribution observed by EDX

all anodic oxidized Si domains, the oxide surface is smooth. We hypothesize that it is because the electric properties and crystal lattices of SiC and Si differ. Furthermore, there were many cracks and projections on the anodic oxidized RS-SiC surface. We hypothesize that it is because the oxidation of Si/SiC to SiO₂ is a volume expansion process, and the swelling pressure is generated

in both the thickness direction and the plane direction. The distribution of this pressure generated by an oxidized grain is determined by the oxidation rate distribution of the grain. Therefore, in the thickness direction, the pressure ejects the oxide, resulting in the formation of projections; in the plane direction, the pressure presses the neighboring grains, introducing cracks in the weak areas.

Fig. 3 Anodic oxidation behaviors of 4H-SiC observed by SEM. **a** Position 1. **b** Position 2

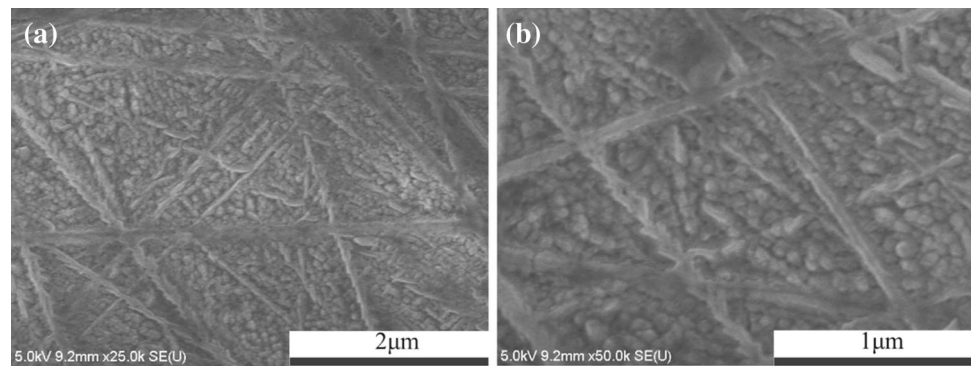
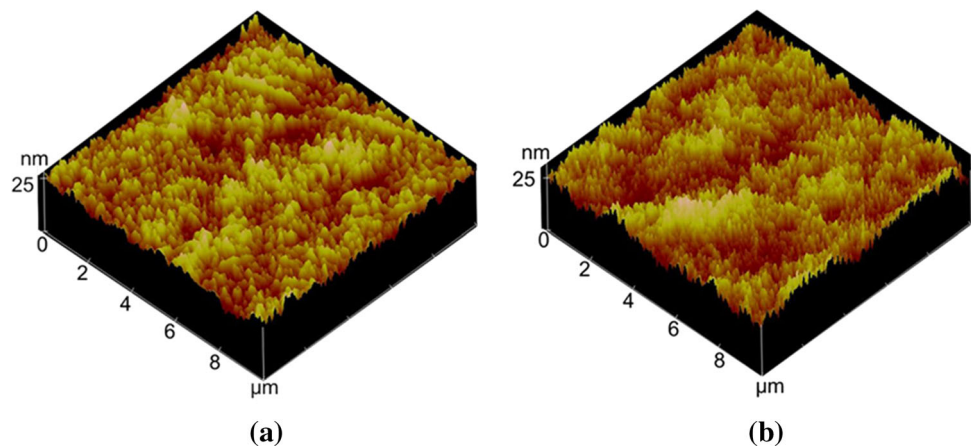


Fig. 4 Anodic oxidation behaviors of 4H-SiC analyzed by AFM. **a** Position 1. **b** Position 2



The oxidation behavior of 4H-SiC obtained by SEM and AFM observation is shown in Figs. 3 and 4. From the SEM and AFM images, it was observed that there were many oxide protuberances on the oxidized surface, and the scratches on the original surface which are introduced by diamond lapping change into linear swellings. That's because the oxidation of SiC is a volume expansion process; thus, the scratches are filled by the bulgy oxides, and the oxidized 4H-SiC surface is covered with bulgy oxides. Comparing with the anodic oxidation behaviors of RS-SiC, there are few cracks or projections on the anodic oxidized 4H-SiC surface. Although the swelling pressure is also generated by the volume expansion in the anodic oxidation of 4H-SiC, it is limited in the thickness direction. Meanwhile, the oxidation behaviors of some SiC grains in the anodic oxidation of RS-SiC are different from that of 4H-SiC, because the crystal directions of each SiC grains in RS-SiC differ.

4 Calculation of oxidation rate

Through the scanning white light interferometry (SWLI) measurements and comparing the surfaces before and after HF etching of the anodic oxidized SiC samples, the oxidation depth corresponding to a certain oxidation time for

RS-SiC and 4H-SiC was obtained, respectively, as shown in Figs. 5a–e and 6a–e, respectively. Moreover, the summarized data for RS-SiC are shown in Fig. 5f and that for 4H-SiC are shown in Fig. 6f, respectively. It can be obviously observed that the oxidation depth is larger with increasing in oxidation time.

From the SWLI measurement results, it can be calculated that the average anodic oxidation depth of RS-SiC corresponding to certain oxidation times of 5, 10, 20, 30, 45, 60, 120, 180, 300, 600, 900, 1200, and 1800 s is 25, 38, 47, 58, 62, 68, 88, 102, 120, 135, 145, 156, and 163 nm, respectively, and the average anodic oxidation depth of 4H-SiC corresponding to certain oxidation times of 30, 60, 180, 300, and 1800 s is 63, 107, 170, 236, and 457 nm, respectively. Through data fitting (isolated singularities were filtered) based on the Deal–Grove model [15], the relationship between oxidation depth x (nm) and oxidation time t (s) for RS-SiC is shown in Eq. 1 and that for 4H-SiC is shown in Eq. 2, respectively.

$$t = 0.01x_{\text{RS-SiC}}^2 + 0.19x_{\text{RS-SiC}} \quad (1)$$

$$t = 0.0047x_{\text{4H-SiC}}^2 + 0.1729x_{\text{4H-SiC}} \quad (2)$$

From the equations, it can be concluded that the oxidation rate can be 5.3 nm/s for RS-SiC and 5.8 nm/s for

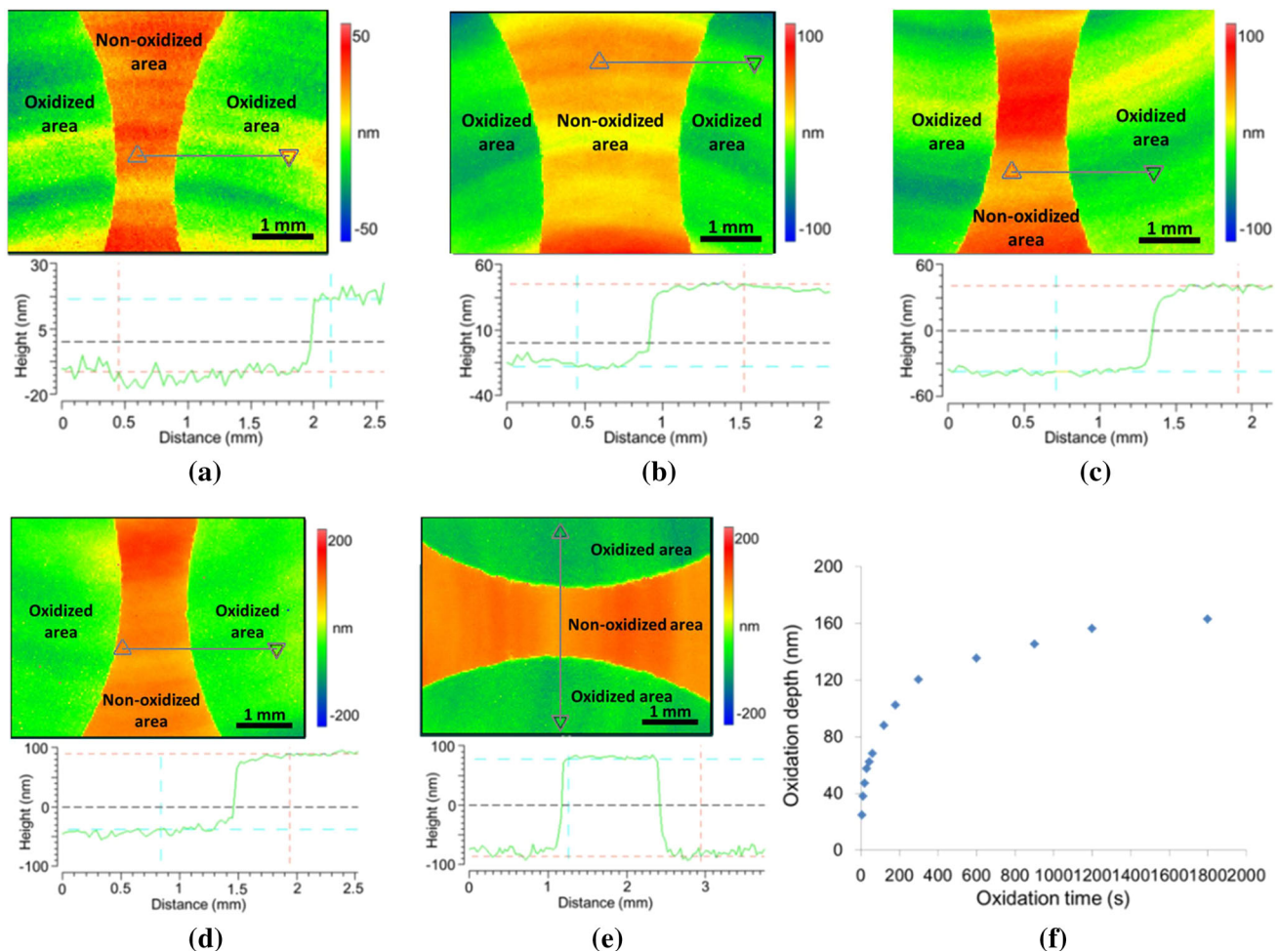


Fig. 5 Measurement of anodic oxidation depth of RS-SiC by SWLI. **a** Oxidation for 5 s. **b** Oxidation for 20 s. **c** Oxidation for 60 s. **d** Oxidation for 600 s. **e** Oxidation for 1800 s. **f** Oxidation depth and oxidation time

4H-SiC in the linear Deal–Grove model [15]. Therefore, if we conduct SOAP of SiC, the MRR would be 318 nm/min for RS-SiC and 348 nm/min for 4H-SiC, which were hundred times of those in CMP (<500 nm/h) [9], PAP (<200 nm/h) [10], and CARE (100–200 nm/h) [11].

5 Comparative analysis of polishing property

We conducted the anodic oxidation polishing of RS-SiC and 4H-SiC by the system shown in Fig. 1b. The surface roughnesses rms of RS-SiC substrate after the conducted four scenarios were measured by SWLI and are summarized in Fig. 7a–d, and those of 4H-SiC are summarized in Fig. 8a–d. The original surfaces which were prepared by diamond lapping had many scratches, as shown in Figs. 7a

and 8a, because the hardness of diamond is larger than that of SiC substrates. After anodic oxidation, the rms roughness of surface was deteriorated, as shown in Figs. 7b and 8b, since there were undulations and fluctuations resulting from the bulgy oxide.

The original SiC samples which were prepared by diamond lapping had many scratches, since the hardness of diamond is larger than that of SiC. After anodic oxidation, both the RS-SiC and 4H-SiC surfaces were deteriorated, because there are undulations and projections on the oxidized surfaces. The rms roughnesses of RS-SiC surface after SOAP were improved to 2.103 nm and that of 4H-SiC were improved to 0.892 nm, as shown in Fig. 7c, d, which were better than those after DOAP, as shown in Figs. 7d and 8d. The experiment results indicated that anodic oxidation polishing of SiC substrates

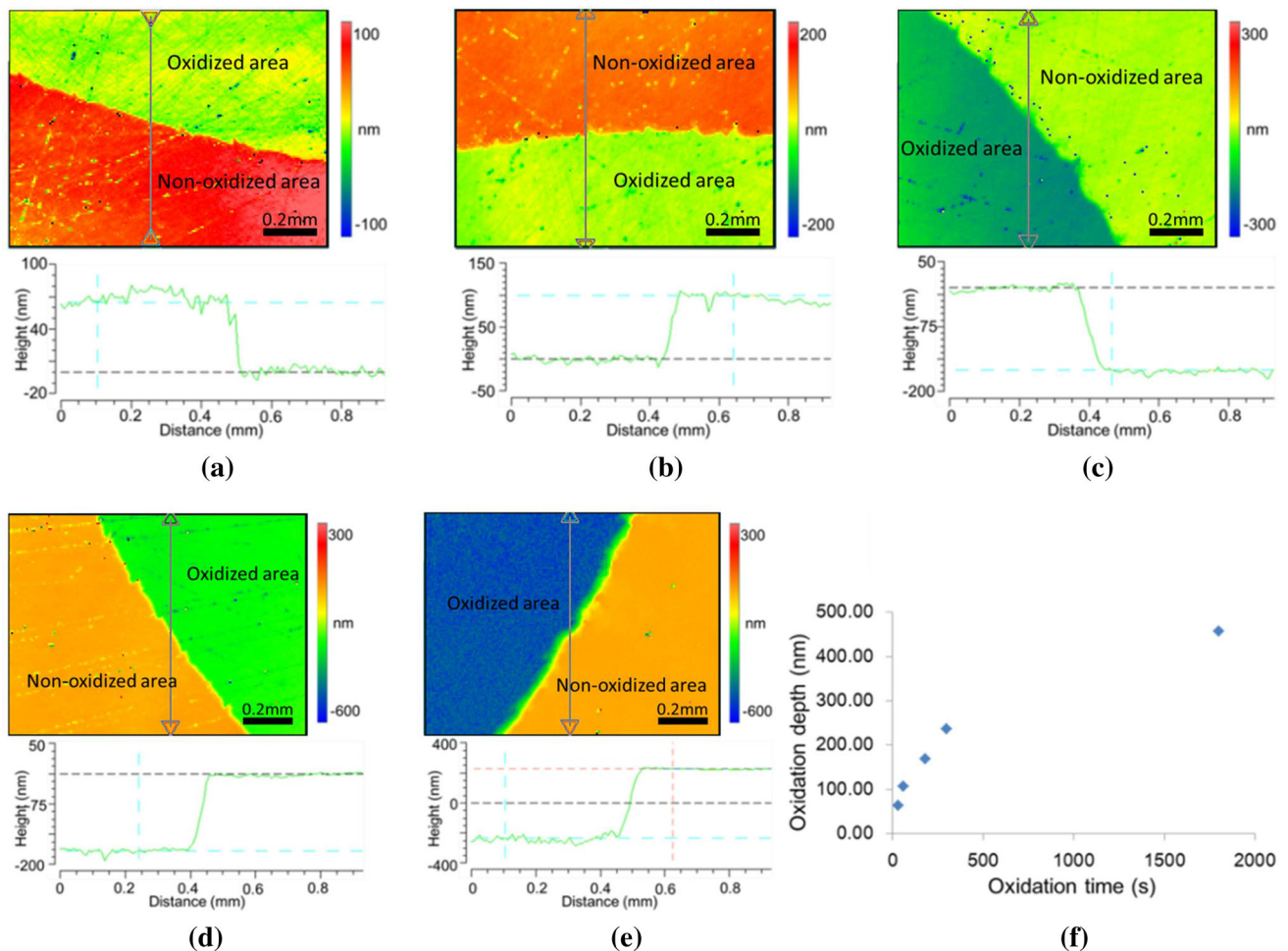


Fig. 6 Measurement of anodic oxidation depth of 4H-SiC by SWLI. **a** Oxidation for 30 s. **b** Oxidation for 60 s. **c** Oxidation for 180 s. **d** Oxidation for 300 s. **e** Oxidation for 1800 s. **f** Oxidation depth and oxidation time

can obtain high MRR and fine roughness simultaneously by SOAP.

6 Summaries

In this study, we conducted a comparative analysis of anodic oxidation polishing of RS-SiC and 4H-SiC. The following conclusions were obtained.

1. For the research on the anodic oxidation of RS-SiC and 4H-SiC substrates, anodic oxidation system and anodic oxidation polishing system were constructed.
2. Anodic oxidation behaviors of SiC substrates were investigated by SEM-EDX observation and AFM

analysis. Characters of the oxide on the oxidized SiC samples were expressed, which would promote the understanding of the anodic oxidation mechanism for RS-SiC and 4H-SiC.

3. By SWLI measurements and comparing the surfaces before and after HF etching of the oxidized SiC samples, the oxidation depths corresponding to a certain oxidation time were obtained. Through data fitting based on the Deal–Grove model, the high MRR in anodic oxidation polishing of SiC substrates was forecasted.
4. Polishing properties of anodic oxidized SiC samples were analyzed by SWLI measurements. The surface roughnesses r_{ms} after SOAP of RS-SiC were improved to 2.103 nm and that of 4H-SiC were to 0.892 nm,

Fig. 7 Comparison of surface roughnesses in anodic oxidation polishing of RS-SiC by SWLI. **a** Original surface obtained by diamond lapping. **b** Anodic oxidized surface. **c** Surface obtained by SOAP for 3 h. **d** Surface obtained by DOAP for 6 h

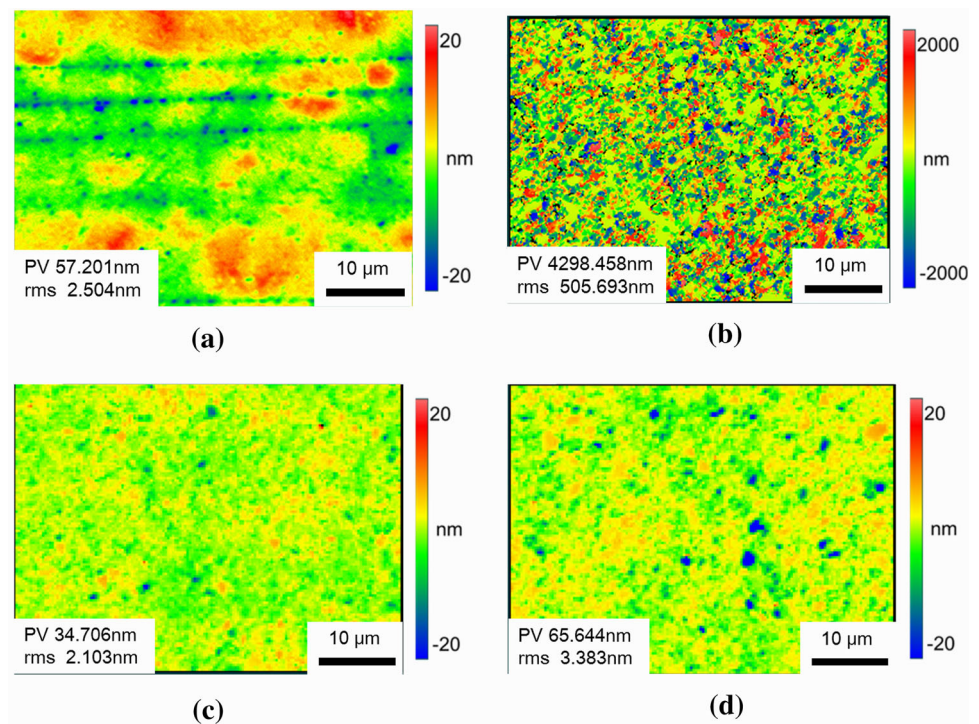
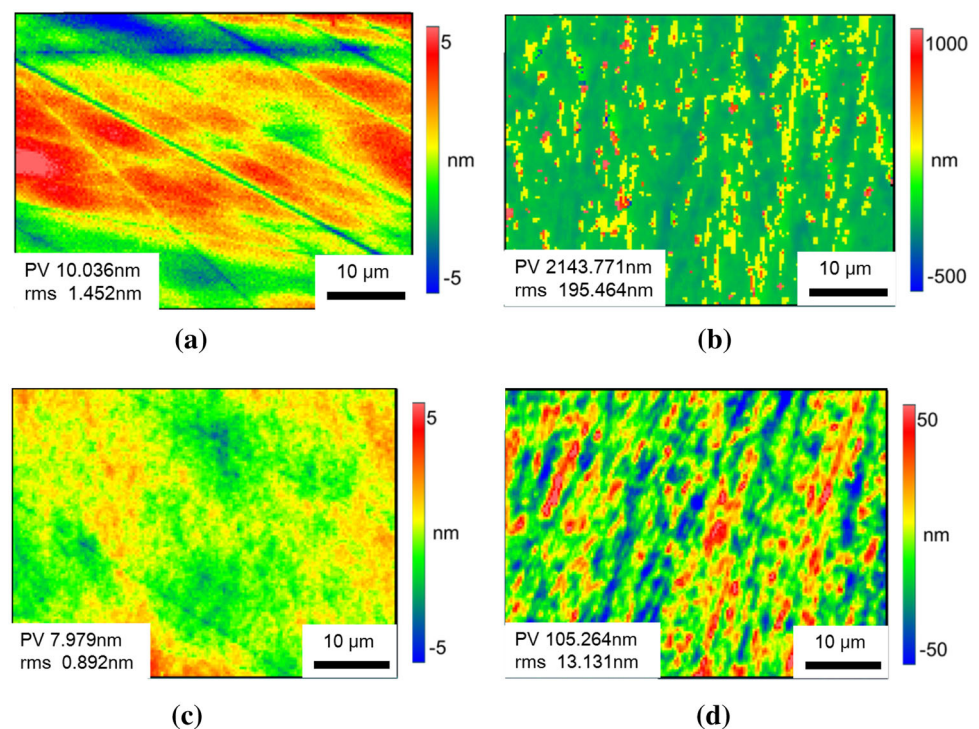


Fig. 8 Comparison of surface roughnesses in anodic oxidation polishing of 4H-SiC by SWLI. **a** Original surface obtained by diamond lapping. **b** Anodic oxidized surface. **c** Surface obtained by SOAP for 1 h. **d** Surface obtained by DOAP for 2 h



which indicated that the anodic oxidation polishing of SiC substrate can obtain high MRR and fine surface roughness simultaneously by SOAP.

Anodic oxidation polishing would improve the machining level of SiC substrates and promote the

application of SiC products in semiconductors, optics, and ceramics fields.

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