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Hydrogen etching of 4H–SiC(0001) facet and step formation

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ABSTRACT

SiC has attracted much interest due to its vast applications in high power, high frequency and radiation-hardened electronics at high temperatures. Although the growth and processing technology for SiC wafers has matured, scratches created during surface preparation will unavoidably deteriorate both device performances and the quality of materials which are fabricated on it. Hydrogen etching has been proposed as an effective approach to obtain ideal SiC surfaces with large atomically flat steps. Here, we reported a systematical investigation on the effects of processing parameters to the hydrogen etching of 4H–SiC (0001). Accordingly, a new two-step etching method was developed with a specifically designed crucible to take advantage of the found correlation between those parameters and the terrace features. The method demonstrates high efficiency to realize atomically uniform SiC surface morphology with more than 70% coverage of the sample surface. It offers a possible route for large scale industrial SiC wafer planarization.

1. Introduction

Owing to its wide bandgap, very large breakdown voltage and thermal conductivity, SiC has great potential for fabricating high power devices with high running frequency under high temperature [1]. It is also an ideal substrate for group III-nitrides and graphene growth due to their close lattice constants [2,3]. But, the procedure of cutting and polishing create large amount of surface scratches on SiC wafers, which will unavoidably deteriorate device performance and the quality of materials grown on it. Thus substrate preparation prior to device fabrication and materials growth is essential [4–6]. Hydrogen etching has been proposed as an effective approach to obtain ideal surfaces with large atomically flat steps, which anneals the sample at a high temperature with hydrogen flow at 1 atm [7–9]. The obtained step heights are equal to the unit c-lattice parameter (c = 1.512 nm for 6H–SiC and 1.008 nm for 4H–SiC) [10].

Several plantation mechanisms and the relations between etching parameters and the terrace features have been proposed. Early on, a flow model was conceived to explain the step motion [11,12], later a step bunching model was proposed to interpret the formation of steps during SiC growth for 4H–SiC and 6H–SiC [13], which can be pictorially viewed as in Fig. S1. Based on these models, Nakajima et al. classified the step bunching on 6H–SiC (0001) etched surface into three different types and suggested a mechanism for their formation [14]. In 2009, the KMC (Kinetic Monte Carlo) method was successfully applied to describe the growth-induced and etching-induced step bunching of 6H–SiC (0001) [15].

Etching temperature and time are considered as two key controlling parameters which determine the terrace features. Systematic studies of hydrogen etching on the surface morphology of on-axis 4H–SiC (0001) wafers reveals that the best temperature for surface planarization is 1400 °C [16]. Anzalone et al. found that the etching time highly depends on defects and step bunching density [17]. Recently, a new approach was proposed to lower the step bunching rate on SiC (0001) by applying extremely slow heating and cooling rate, which can keep the step height less than 2.75 nm [18].

Even though there have quite a few experimental explorations and several proposed theoretical models on hydrogen etching [7,19], the precise control of the terrace width and step height of etched surfaces is still challenging [20,21]. The key of industrializing SiC wafers

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Table 1
N type 4H Silicon Carbide Specifications.

Specification	Fabrication Method	Micropipe Density	Resistivity	Wafer Orientation	Doping concentration
4H–SiC	Physical vapor transport	≤15 cm^{-2}	0.015–0.025 Ω cm	<0001>±0.5°	~10^{18} cm^{-3}

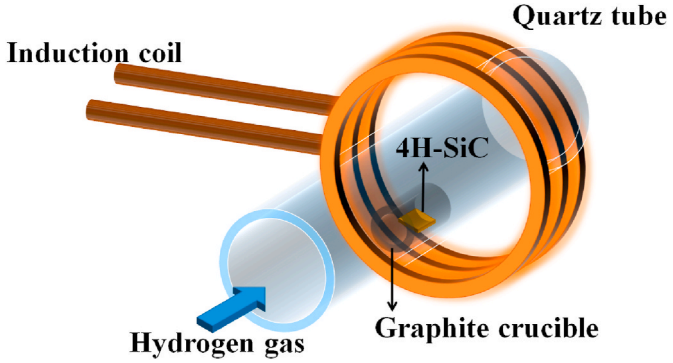

Fig. 1. Schematic diagram of the experimental setup.

planarization through hydrogen etching processes is to maximize the coverage of the effective etching area [22]. Here, we systematically studied the correlation between etching parameters and the terrace features on the 4H–SiC (0001). Furthermore, according to the results, a new two-step etching recipe was developed with a specifically designed crucible, which realized the evenly distributed terrace features and up to 70% effective etching area.

2. Experiment

The samples (4.5 × 3.5 mm^2, with thickness of 0.35 mm) were diced out from off-axis ±0.5° (0001), N-doped 4H–SiC crystals rod with diameter of 25 mm. Additional information of the 4H–SiC samples is shown in Table 1. After mechanical polishing, an AFM inspection was conducted that shows the existence of 2.5-7 nm deep scratches on the surface. Prior to hydrogen (H_2) etching, the samples were sequentially cleaned in an ultrasonic bath using acetone, ethanol and deionized water for 30 min in each step.

A homemade horizontal induction furnace was used for hydrogen etching as shown in Fig. 1. A graphite crucible with 14.8 mm length and 5.5 mm diameter was employed as heating body and sample container. It was placed in a quartz tube with a 25 mm diameter and surrounded by an induction coil. The detailed design of the crucible can be seen in the Supplementary Fig. S2.

The etching starts by heating wafers to a temperature from 1500 °C to 1630 °C, which is measured by a colorimetric thermometer DIT-6H2. The etching time ranges from 10 to 60 min. Before the hydrogen (99.999%) was feed into the furnace, it has to be further purified by passing through liquid nitrogen cooled oxygen-free copper tubing with a flow rate of 200 sccm to 300 sccm. The temperature is raised at a rate of 100 °C/min until it reaches the set etching temperature, followed by simmering for a set holding time, and then it is cooled down to the room temperature at a rate of -50 °C/min. During the whole process, the pressure inside the etching chamber is kept at 1atm. Hydrogen flow is started before heating up the crucible and stopped after the sample cools down to room temperature. The etched samples are characterized by optical microscopy (OM) and atomic force microscopy (AFM) in the non-contact mode (NCM).

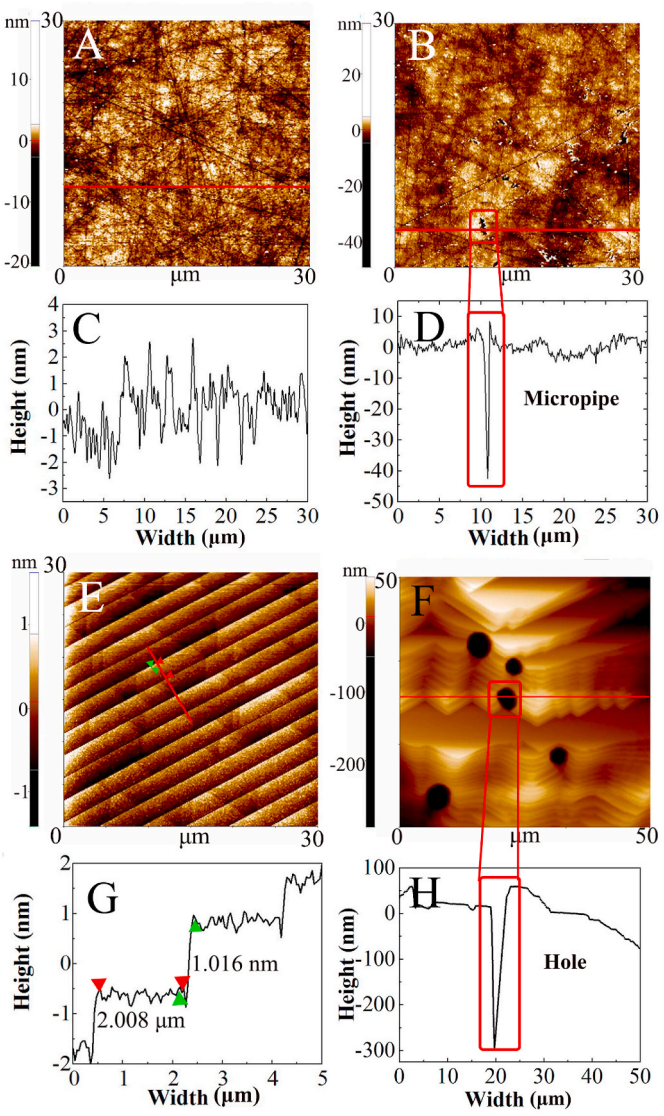

Fig. 2. AFM images of mechanically polished 4H–SiC wafer which have (A) large number of scratches and (B) several micropipes. (C) and (D) are the surface profiles along the red lines in (A) and (B). The rectangle in (D) is the profile corresponding to the small square in (B). AFM images of hydrogen etched 4H–SiC wafer with (E) atomically flat steps etched at 1600 °C for 30 min. (F) shows several holes and step bunching which was etched at 1600 °C for 40 min. (G) and (H) are the surface profiles along the red lines in (E) and (F). The rectangle in (H) is the profile corresponding to the small square in (F) which indicates a deep hole.

3. Results and discussion

As shown in Fig. 2A and B, AFM images of polished 4H–SiC (0001) show large amount of scratches with depths and width up to 7 nm and 270 nm, respectively, whose average surface roughness (Ra) ranges from

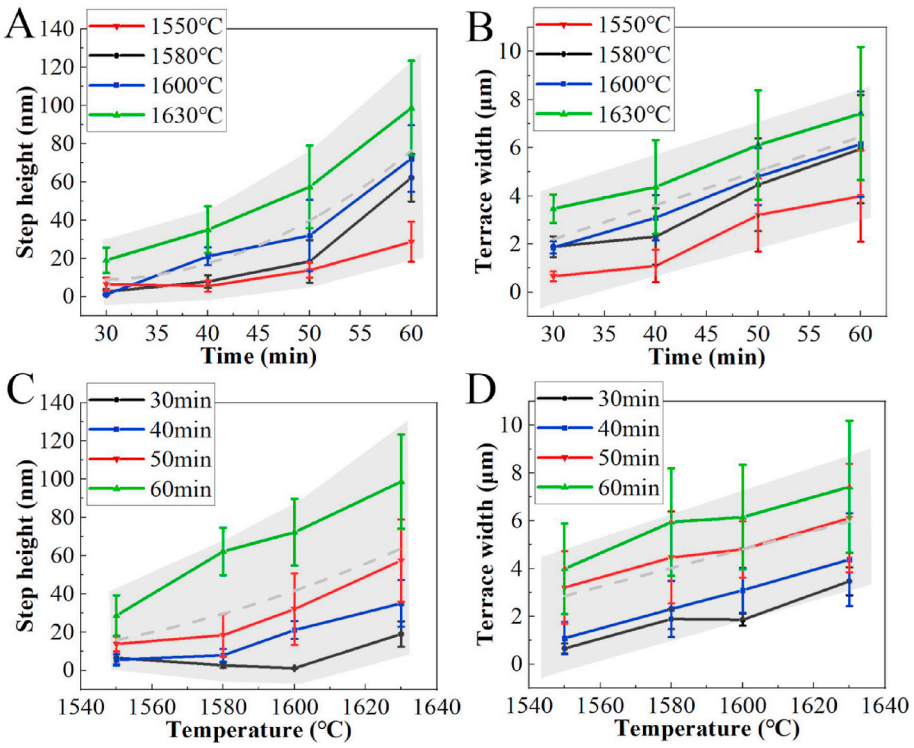

Fig. 3. Correlation between etching parameters with the average height and width of etched terraces, error bar represents the variation scope of measured values. (A) step height and (B) terrace width as a function of hydrogen etching time at 1550°C, 1580°C, 1600°C and 1630°C; (C) step height and (D) terrace width as a function of hydrogen etching temperature for 30 min, 40 min, 50 min and 60 min. The dash lines in the graphs indicate the general trends of all curves, for A and C are parabolic and B and D are linear.

0.6 to 1.8 nm. Besides, there are a small number of micropipes that can significantly influence the formation of terraces [10,16]. After etching at 1600 °C for 30 min, the scratches vanished completely, as shown in Fig. 2E, and the surface were fully covered with atomically flat steps, which had width of 1.5~2.1 μm and a 10 Å height. It worth noting that the steps bunched together to form large terraces after keeping the SiC at 1600 °C for 40 min, which have width of 2~5 μm and 7–15 nm of height (see Fig. 2F). This is the so called step bunching, defined as the formation of multiple-height steps. It leads to the formation of the cliffs and large roughness [13,23,24]. Moreover, some deep holes (150–350 nm) formed on the etched surface, they evolved from micropipes. Again, it demonstrates the effect of the conditions and sample defects to the etching results [25]. The morphology of etching surfaces at 1600 °C for 10 min , 20 min , 50 min and 60 min are shown in supporting information Fig. S3.

3.1. *Effects of processing parameters on one-step hydrogen etching*

Etching temperature and time are considered as the two most critical parameters to determine the average width and step height of etched terraces [17,26]. Fig. 3A and (B) show the correlation between the etching time and the average height and width of terraces at 1550 °C, 1580 °C, 1600 °C and 1630 °C. The steps start to appear at about 30 min, and disappear eventually due to over-etching (Shown in Fig. S4 in the supporting information). Simultaneously, the terrace width distribution became less uniform that can be reflected by the error bars which stands the variation scope of measured values in Fig. 3. Fig. 3C and (D) show the change of terrace height and width with the etching temperature at heating temperature of 30 min, 40 min, 50 min and 60 min. It indicates that higher temperature needs less time for step growth, as expected and higher temperature also leads to fast terrace growth speed. Furthermore, the results also shows that the terrace width increases roughly linearly with time, while the increase of step height close to be parabolic, which is much faster than the width growth rate. This could be qualitatively interpreted as following: Since the edge has less average coordination number then that of surface which means higher surface energy, in such a case when the terraces grow the energy minimization is realized by elimination of edges which is shown as the terrace height growth or step bunching. Besides, as the energy of surface atom is greater than the energy difference between the atom on the edge and the surface, therefore in order to keep the energy of system going down the step bunching speed has to be faster than the terrace growing speed. In conclusion, the higher etching temperature results in a better elimination of scratches and faster steps formation. The longer etching time not only can lead to larger terrace width but also could increase the growth speed of the steps. The step bunching shows rather high sensitivity to the etching time.

3.2. *Two-step etching with a specifically designed crucible for large area and uniformly covered terraces*

As discussed above, directly increasing etching temperature and time will enhance the step bunching, which also will further result in the large variation of step height and terrace width of the etched surface. Consequently, the effective etching area is limited at only about 30% of the surface as indicated in Fig. 5 (The procedure for evaluating the effective etching area can be found in supporting information). Therefore, we proposed a new two-step method based on the correlation between etching parameters and terrace features. The main idea of this two-step method is to take the advantage of the both high temperature and long annealing time but applied at the different stage of surface etching for achieving large terrace width and extremely smooth terrace surface. The first step is to etch the surface at high temperature for a certain amount of time (T_1: Step-1) aiming for eliminating scratches and producing an unstable terrace morphology, succeeded by the second step of keeping the sample at a lower temperature for a set time (T_2:

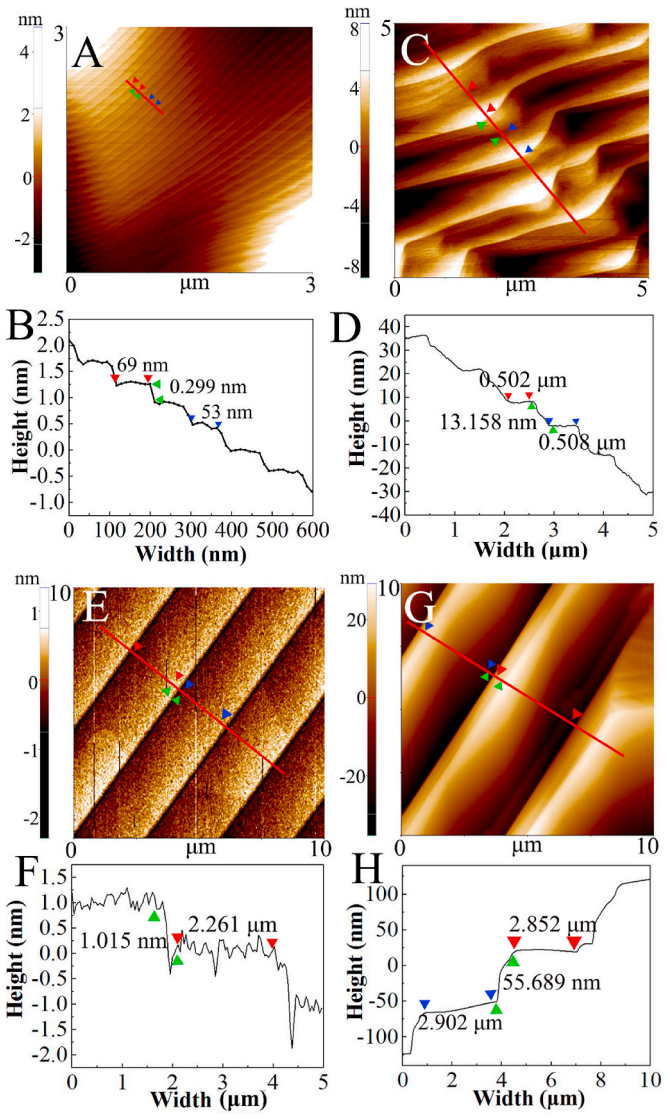

Fig. 4. AFM images of the two-step etched SiC surfaces, the two stages are: T_1 (Step-1) and T_2 (Step-2): (A) T_1 at 1600 °C for 20 min, T_2 at 1450 °C for 40 min; (C) T_1 at 1600 °C for 20 min, T_2 at 1500 °C for 40 min; (E) T_1 at 1600 °C for 25 min, T_2 at 1450 °C for 40 min; (G) T_1 at 1600 °C for 25 min, T_2 at 1500 °C for 40 min. (B), (D), (F) and (H) are the height profiles along the red lines in (A), (C), (E) and (G), respectively.

Step-2) to realize the uniform growth of terraces.

Fig. 4 shows the results obtained using this two-step method with different but correlated set parameters, the AFM image of samples and the grown condition with their set parameters share the same names as A, C, G, and E. Notably, terraces have much smooth surfaces and are evenly distributed. ***Condition A:*** Fig. 4 (A) shows the sample obtained under the condition of T_1 at 1600 °C for 20 min, and T_2 at 1450 °C for 40 min, the resulting terraces have width of 0.05~0.07 μm and height of 0.2~0.4 nm; ***Condition C:*** When we applied the exact same condition in Step-1, but raised the temperature T_2 from 1450 °C to1500 °C and still kept same duration of 40 min for Step-2, the terraces reach 0.5~0.7 μm wide and 12–14 nm high as shown in Fig. 4 (C). ***Condition E:*** Fig. 4 (E) is the AFM image of a sample grown under the conditions of T_1 = 1600 °C for 25 min, and T_2 = 1450 °C for 40 min, where the terraces are 2~2.5 μm wide and 1~1.4 nm high; ***Condition G:*** When the growth condition was set to T_1 = 1600 °C for 25 min, and T_2 = 1500 °C for 40 min, the AFM image shown as Fig. 4 (G), which yield the terraces with a width of 2.7~3 μm and height of 53~56 nm. Comparisons between the results from ***Condition E*** and ***condition G***, also the ones from ***Condition E*** and ***Condition A***, indicate the key function of Step-1 to determine the terrace width and the decisive role of Step-2 to control the terrace height. In summary, the obtained etched surface with the two-step method can form very uniform terraces [19–21].

With a specifically designed crucible, the two-step method can further improve the effectively etched area up to 70% of the sample surface. This crucible was made of a graphite rod with a diameter of 9.5 mm and a length of 14.5 mm. The long axis coincides with the direction of gas flow, it has a 5.5 mm diameter hole at one end with a depth of 10.85 mm and a clear hole of 3.5 mm diameter at the other end for gas leakage as shown in Fig. S2. Fig. 5 shows optical and atomic force microscopy images of the sample surfaces etched in both a conventional and the specifically designed crucible for comparison. They are all etched at T_1 of 1600°C for 25 min, and T_2 of 1450°C for 40 min. The etched sample surface, using the conventional crucible (Fig. 5A), has significant morphological variation along the direction of the gas flow, the effective etched area is a narrow region in middle of the sample and the coverage rate is about 30% of the surface. In contrast, the effective etching area is largely improved both on uniformity and coverage rate by using the new crucible (Fig. 5B), where the coverage rate is more than 70% of the surface. To gain more insight, finite element analysis (COMSOL Multiphysics) software was applied to simulate both the hydrogen flow and temperature distribution inside the original and the specifically designed crucibles. The results indicate that inside the specifically designed crucible, both the gas flow and temperature are much more uniformly distributed than that in the original one (see Fig. S2 in supporting information).

4. Conclusion

The relation between growth conditions and final surface quality of hydrogen-etched 4H–SiC (0001, N-type) wafers have been systematically studied with detailed characterization through both optical and atomic force microscopy. The results reveal that increased etching temperature can effectively improve the elimination of scratches and the formation of steps, while increasing the etching time also will accelerate the growth rate of the steps and led to step bunching. Accordingly, a new two-step etching method has been proposed and a new SiC etching crucible has been designed. Combined applications of those two demonstrated much better uniformity of terrace morphology, and increased the effective etching area from 30% to 70% of the sample surface than the conventional ones. It potentially can benefit to developing both silicon carbide based and epigraphene based two dimensional electronics.

CRediT authorship contribution statement

Rui Li: Investigation, Methodology, Writing – original draft, Data curation. **Kaimin Zhang:** Data curation. **Yi Zhang:** Formal analysis, Methodology. **Zhenzhen Zhang:** Data curation. **Peixuan Ji:** Data curation. **Chengqian Shi:** Data curation. **Danni Hao:** Writing – original draft. **Yipeng Zhang:** Data curation. **Ramiro Moro:** Writing – review & editing. **Yanqing Ma:** Writing – review & editing. **Lei Ma:** Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Writing – review & editing.

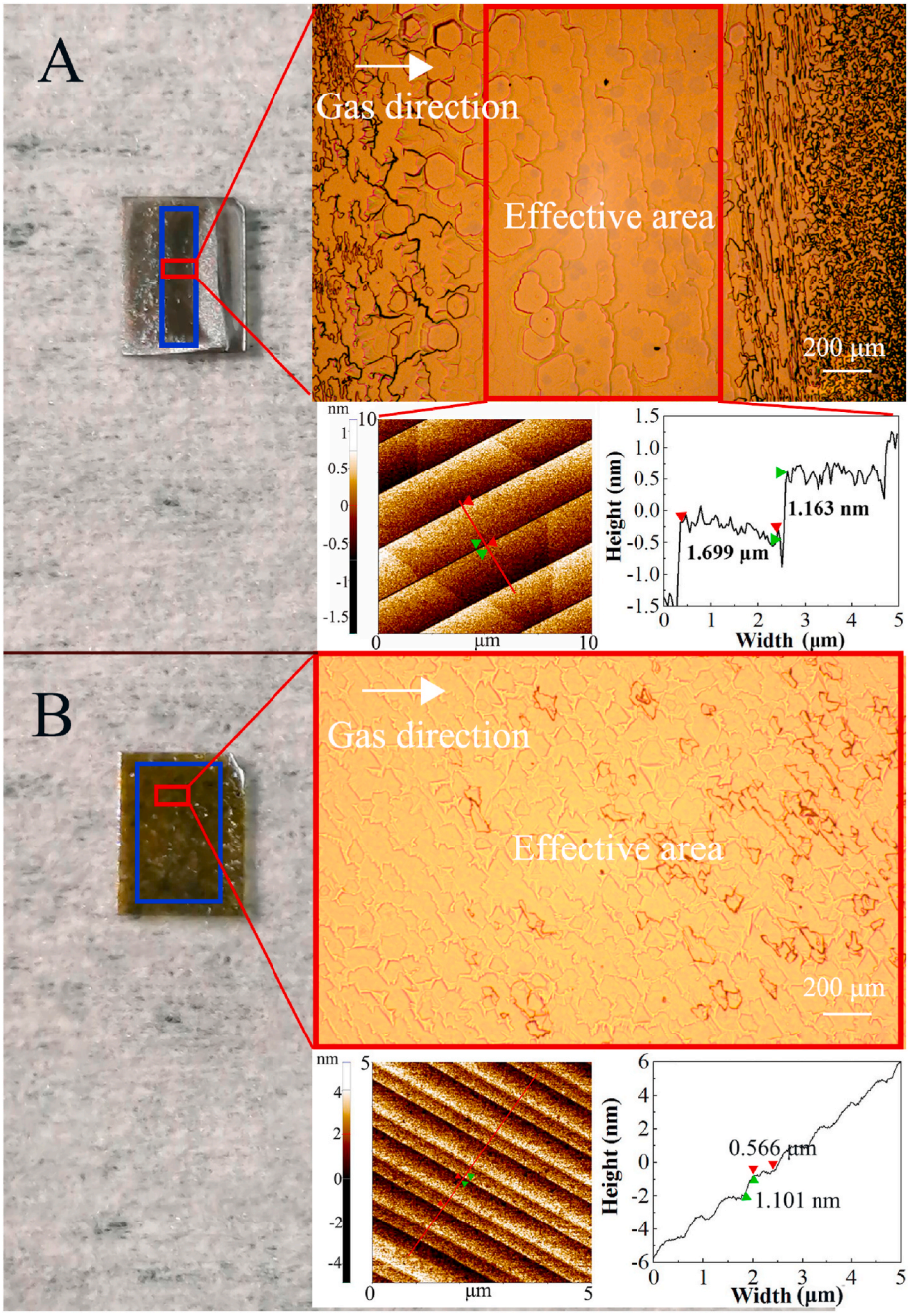

Fig. 5. Optical (OM) and Atomic Force Microscopy (AFM) images of the etched surface obtained by (A) original crucible and (B) specifically designed crucible under the same two-step etching process. The samples are etched at T_1 of 1600 °C for 25 min, and T_2 of 1450 °C for 40 min. The left panels show the etched samples, and the blue rectangle in the left represents the effective etching area. The rectangle on the right is the OM (upper) and AFM (bottom) images corresponding to the small red rectangle. The arrow in the upper left corner indicates the direction of the hydrogen flow.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mssp.2022.106896.

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