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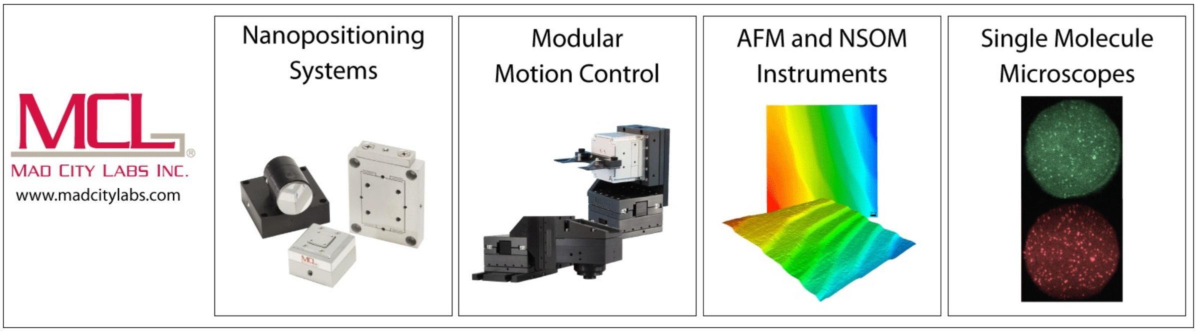

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ABSTRACT

An abrasive-free polishing method using water and a Pt catalyst, called catalyst-referred etching (CARE), has been developed for the finishing of optical and semiconductor surfaces. This method realizes well-ordered surfaces with a smoothness of several tens of picometers without crystallographic disturbance. In this study, we propose a new CARE method using a Ni catalyst with *in situ* electrochemical plating and dissolution, which enable enhancing the catalytic capability of Ni. This method has advantages to realize more than ten times higher removal rate and better stability compared with the conventional CARE method.

I. INTRODUCTION

Recently, the short wavelength light regime comprising, for example, extreme ultraviolet (EUV) and x rays has attracted attention[1,2] because of its excellent potential to realize microscopy and/or lithography with an extremely high spatial resolution. Light sources for this short wavelength regime have also experienced rapid development toward advancing their applications. In the short wavelength regime, an optical surface requires unprecedentedly high precision and smoothness with root mean square values of several tens of picometers. In Bragg optics, crystallographic ordering is also required in addition to surface smoothness. Highly ordered surfaces, both geometrically and crystallographically, are also in demand in the field of semiconductor materials. Atomically controlled and damage-free surfaces are critical for the fabrication of high-performance electronic devices.

In the past, chemical mechanical polishing (CMP) has been utilized as a final surfacing method.[3,4] The CMP method employs a slurry containing chemicals and abrasives, wherein the workpiece surface is chemically modified and removed with the abrasives.[5,6] Due to the usage of abrasives, physical damage to the surface is unavoidable.[7,8] This damaged layer significantly reduces the optical reflectance, especially in the short wavelength regime.[9–11] In addition, abrasives remaining on the surface after CMP processing are difficult to remove and cause yield reductions in the products.

We previously developed an abrasive-free polishing method called the catalyst-referred etching (CARE) method.[12,13] This method employs chemical etching with the assistance of a catalyst. The CARE instrument is nearly the same as that used for the CMP method; the only difference is a pad on which a metal thin-film catalyst layer with a thickness of less than 50 nm is deposited. Etching proceeds preferentially at the topmost sites of the workpiece surface because these sites make more frequent contact with the catalyst surface. Accordingly, the workpiece surface is flattened with reference to the catalyst surface. The catalyst is deposited on the pad, and although the pad surface is not entirely flat, it is copied onto the workpiece surface with an averaging effect. The process takes place under the condition that the workpiece and pad rotate independently and randomly. This mechanism to obtain a smooth surface with a pad that has a relatively rough surface is the same as that employed in the CMP method.

In the past, Pt and pure water have been utilized in the CARE method as a catalyst and etchant, respectively. On crystalline quartz, sapphire, SiC, and GaN, crystallographically and geometrically highly ordered surfaces have been obtained with straight step-and-terrace structures in which the step height is one bilayer.[14–17] This method is also applicable to amorphous materials including optical and low thermal expansion glasses.[16] The removal mechanism has been clarified as a hydrolysis reaction using first-principles calculations.[14,17,18] The catalyst surface assists the dissociation of water molecules, and OH^- with a high nucleophilicity is generated and adsorbs to the step-edge atom on the workpiece surface to form a hypervalent state. This state weakens the back bond to breaking, leading to etching. The hypervalent state is unstable without the catalyst but is stabilized by the interfacial chemical interaction between the workpiece surface and the catalyst. The roles of the catalyst were elucidated as assistance of water molecule dissociation and stabilization of the hypervalent state. In addition, catalysts other than Pt have also been investigated,[19] and Ni was found to be an excellent and cost-effective candidate; the removal rate was 10 times higher than that of the Pt catalyst. The Ni catalyst is advantageous in that Ni metal contamination after CARE processing is more easily removed by rinsing in an acidic solution compared with the case of Pt. However, the removal rate of the Ni catalyst decreases by more than 60% within 30 min. In this study, we found that the oxidation of the Ni catalyst is the cause of degradation. *In situ* refreshment of the Ni surface is effective in overcoming the problem. We proposed a cyclic electroplating and dissolution of the Ni catalyst during CARE processing, which is a suitable method for the CARE being a kind of wet process. Electroplating can produce an active Ni catalyst film, and dissolution can remove Ni before the film becomes too thick to appropriately maintain the elasticity of the pad surface. Therefore, the removal rate using the Ni catalyst was stabilized more than 8 h, and the atomically well-ordered surface on SiO_2 and SiC was obtained.

II. EXPERIMENTAL

The CARE experimental setup is shown in Fig. 1. The workpiece was placed inside the holder and pushed onto the catalytic pad with a controlled pressure. The workpiece and the pad were then dipped in a solution. In this configuration, they rotate independently, similar to a conventional polishing machine. The size of the workpiece employed was 20 × 20 mm^2, and the diameter of the pad was 140 mm. A three-electrode potentiostat was equipped to precisely control the potential of the catalyst surface during electrochemical treatment, e.g., electroplating, oxidation, and dissolution of the Ni film. The working electrode (WE) was the Ni catalyst on the pad, a Pt sheet also dipped in the solution was used as a counter electrode (CE), and an Ag/AgCl electrode was employed as a reference electrode (RE). As a base electrode for Ni electroplating, an Au thin film with a thickness of ~100 nm, which is electrochemically stable and does not catalyze the CARE reaction,[17] was deposited on a polyurethane pad by magnetron sputtering. For electroplating, a 0.01 M $NiSO_4$ solution with a pH of 5.5 was employed without any additives, e.g., pH buffer or brightener. The WE potentials for oxidation, electroplating, and dissolution of the Ni film were selected, as discussed for each experiment. The WE potential was expressed by the difference from the standard hydrogen potential through this paper. The workpiece was quartz glass, and the pressure and relative speed between the surfaces of the workpiece and the catalyst were set to 40 kPa and 125 mm/s, respectively.

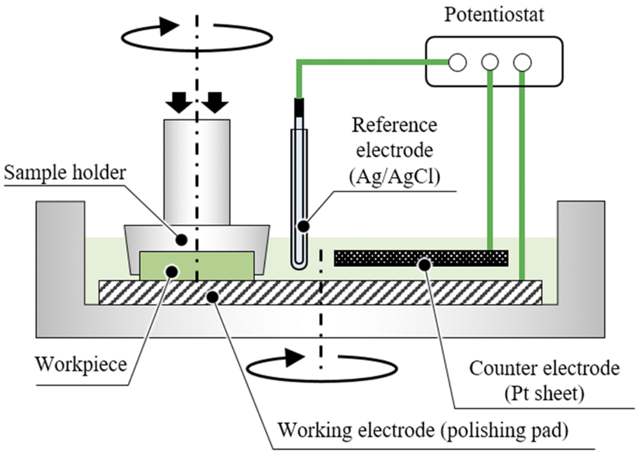

FIG. 1. Schematic of the CARE experimental setup. The size of the workpiece is 20 × 20 mm^2, and the diameter of the polishing pad is 140 mm; the workpiece and pad rotate at their axes. A potentiostat consisting of three electrodes is equipped with a Ni catalyst working electrode (WE) and Pt sheet counter electrode (CE) dipped in the solution. The reference electrode (RE) is Ag/AgCl.

We conducted the following three experiments. First, we investigated the reason for the decrease in the removal rate with processing time. For this issue, we investigated the removal rate under various WE potentials from the viewpoint of oxidation of the Ni surface. Next, to optimally control and maintain the Ni surface, we proposed a cyclic treatment of electroplating and dissolution in which the Ni surface condition is adjusted for the CARE reaction. To realize the proposed treatment, we investigated and optimized WE potentials for electroplating and dissolution of the Ni film. Finally, the performance of the CARE method under the optimal conditions was evaluated regarding removal rate stability and characteristics of the processed surface. The removal rate was evaluated by the difference in workpiece weight before and after processing.

III. RESULTS AND DISCUSSION

A. Catalytic characteristics of Ni

A potential/pH diagram of Ni is shown in Fig. 2,[20] where the vertical and horizontal axes are the Ni potential and solution pH, respectively. Each line indicates an equilibrium state between neighboring Ni compounds. The diagram reveals that various oxidation states of Ni appear on changing the WE potential in both acidic and alkaline solutions. We investigated the relationship between the removal rate and Ni oxidation states under the conditions indicated by black circles in Fig. 2. In all cases, the Ni film was prepared at a

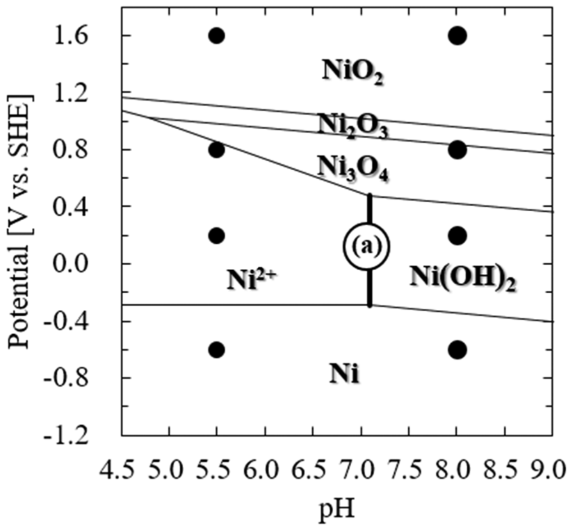

FIG. 2. Potential/pH diagram of Ni at a Ni^{2+} concentration of 0.01 M. Line (a) indicates the equilibrium conditions of $Ni^{2+} + 2OH^{-} \leftrightarrows Ni(OH)_2 + 2e^{-}$. Black spots indicate employed experimental conditions.

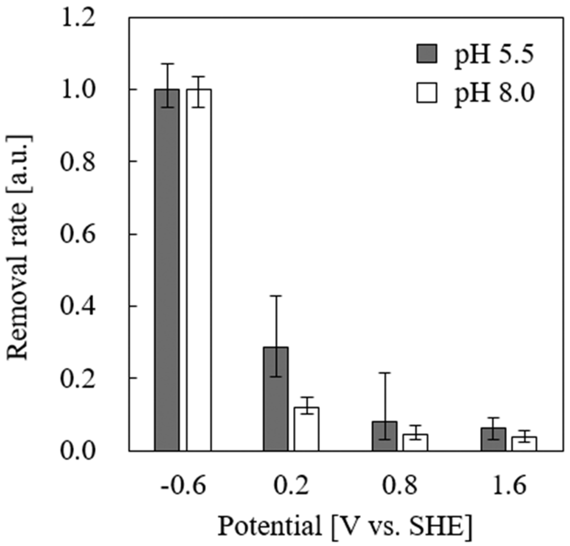

FIG. 3. Dependence of the removal rate on the WE potential. Black and white bars show removal rates at pH 5.5 and 8.0, respectively. Removal rates are normalized by those at a WE potential of −0.6 V.

WE potential and pH of −1.0 V and 5.5, respectively. Then, the WE potential and pH were quickly changed to objective values, and the removal rates were obtained for 60 s of processing. In the experiments at a pH of 5.5, the WE potential was changed soon after Ni plating. In the experiments at a pH of 8.0, the pH was adjusted by adding the KOH solution, and then the WE potential was changed to meet the selected conditions. For all the experiments, the Ni film was prepared by electroplating using the same conditions to fix the initial conditions.

The results of these experiments are summarized in Fig. 3. The removal rate decreased rapidly with an increase in the WE potential at both pH values. At a pH of 8.0, Fig. 2 shows that the Ni surface gradually becomes oxidized with an increase in the WE potential. This implies that oxidation or hydroxidation could degrade the capability of the Ni catalyst during CARE processing. At a pH of 5.5, Ni is also oxidized with an increase in potential, but Fig. 2 shows that the stable product is not the oxide or hydroxide but instead Ni^{2+} at a WE potential of 0.2 V. This suggests that the Ni surface at a pH of 5.5 and WE potential of 0.2 V is not oxidized or hydroxidized under ideal conditions without dissolved oxygen. However, in practical CARE processing, oxygen is dissolved in the solution at the saturation concentration. Thus, boundary (a) shifted to a lower pH, and the Ni surface was partially oxidized or hydroxidized even at a pH and WE potential of 5.5 V and 0.2 V, respectively. This agrees with the experimentally observed low removal rate at a WE potential of 0.2 V compared with that under reduction conditions at a WE potential of −0.6 V. From these results, we concluded that surface oxidation of the Ni catalyst reduces its catalytic capability and causes the observed decrease in the removal rate with processing time. These findings led to the proposal of *in situ* electroplating and dissolution for the Ni catalyst as a refreshment method at sufficiently short intervals.

B. Electroplating

Taking the above results into account, we proposed an *in situ* treatment for the Ni catalyst to maintain its catalytic nature via cyclic electroplating and dissolution. As discussed above, a higher removal rate is expected at a lower WE potential; in other words, reduction conditions are better for the CARE method. Accordingly, CARE can proceed during electroplating in the cyclic treatment, and the optimal electroplating conditions should be determined to maximize the removal rate. We investigated, in detail, the removal rates in the

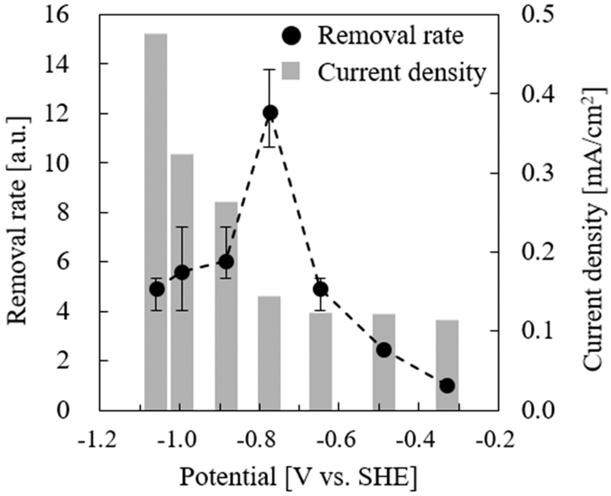

FIG. 4. Dependency of the removal rate and current density on the WE potential in the range of electroplating conditions.

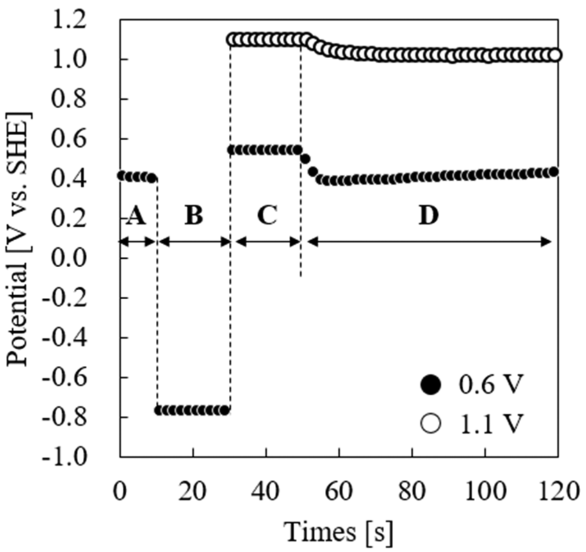

FIG. 5. Plot of experimental WE potentials. In interval A, the WE potential of Au was measured for 10 s under open-circuit conditions. The Ni film was plated in interval B at a WE potential of −0.8 V. In interval C, we selected WE potentials of 1.1 V and 0.6 V for Ni dissolution for comparison. In interval D, the WE potential was measured again under open-circuit conditions to determine if the Ni film had been removed.

potential range lower than the equilibrium potential of the reaction Ni $\rightleftarrows$ $Ni^{2+} + 2e^-$. The employed solution was 0.01 M $NiSO_4$, and the pH and equilibrium potential were 5.5 and −0.28 V, respectively, as shown in Fig. 2.

The results are shown in Fig. 4 with the current densities on the Ni film. As the potential decreased, the removal rate increased, reached a maximum at −0.8 V, and decreased at potentials lower than −0.8 V. In contrast, the current density gradually increased with a decrease in potential and quickly increased below −0.8 V. In accordance with Faraday's law, the electroplating rate increased proportionally to the current density in the potential range from −0.2 V to −0.8 V, indicating that a fresh Ni surface was continuously prepared. In contrast, in the potential range below −0.8 V, the current density was much higher than that used for Ni plating; the current was instead used for H_2 gas generation. From these results, the CARE removal rate increases under reduction conditions but also decreases due to H_2 gas generation, which can disturb the chemical interaction between the surfaces of the workpiece and catalyst. The maximum removal rate was observed at −0.8 V, which is thus the optimal potential for electroplating in the cyclic treatment with regards to removal rate.

C. Electric dissolution

For the cyclic treatment of the Ni catalyst, optimization of the dissolution conditions is also required. Dissolution proceeds under oxidation conditions, wherein the removal rate of CARE becomes low, and thus, the dissolution time should be shortened. We investigated the relationship between the WE potential and the dissolution property of Ni. The experimental procedure was as follows. The Au electrode, as a base electrode for Ni electroplating, was dipped into the solution, and the open-circuit potential of the Au electrode was measured for 10 s as indicated by interval A in Fig. 6. Then, the WE potential was set to −0.8 V for 20 s for Ni electroplating (interval B) and then switched from plating to dissolution conditions and maintained for 20 s (interval C). Finally, we measured the open-circuit potential again in interval D to determine whether the Ni film had been removed; Ni was identified as having been removed if the WE potential returned to that of the Au electrode. In interval C, Fig. 5 shows 1.1 V and 0.6 V WE potentials as typical results. In the case of 0.6 V, the potential returned to that of the Au electrode (0.4 V); however, this did not occur for 1.1 V. The excessively higher WE potential induces Ni oxidation and reduces the dissolution rate. Therefore, we employed 0.6 V as the optimal WE potential for Ni dissolution.

D. Characteristics of CARE under cyclic electrochemical treatment

We evaluated the processing characteristics of the CARE method with the proposed cyclic electrochemical treatment. The WE potentials for electroplating and dissolution of the Ni catalyst were set to −0.8 V and 0.6 V, respectively, and the potential was switched every 20 s during CARE processing. The workpiece was quartz glass, and the surfaces before and after processing were observed by phase-shift interference microscopy (ZYGO NewView 200CHR) and atomic force microscopy (AFM; SHIMADZU 9700HT) with view areas of 190 × 140 μm^2 and 1.0 × 1.0 μm^2, respectively. The removal rate was measured every 120 min. Figures 6(a) and 6(b) show the surface profiles before and after CARE processing, respectively, which show that the peak-to-valley (PV) roughness and rms were greatly improved. Figures 7(a) and 7(b) show the

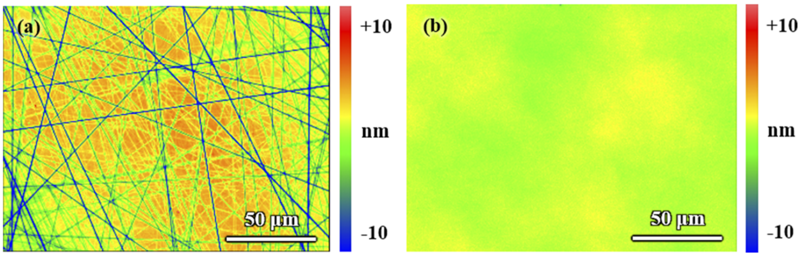

FIG. 6. Optical profiler images of (a) pre-processed surface (PV: 40.278 nm, rms: 3.406 nm, and R_a: 2.343 nm) and (b) CARE-processed surface (PV: 2.348 nm, rms: 0.350 nm, and R_a: 0.284 nm) of silica glass.

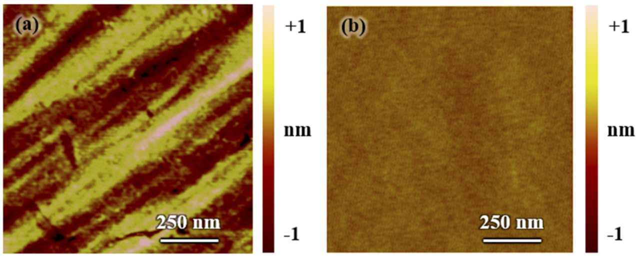

FIG. 7. AFM images of (a) pre-processed surface (PV: 4.061 nm and rms: 0.400 nm) and (b) CARE-processed surface (PV: 1.026 nm and rms: 0.053 nm) of silica glass.

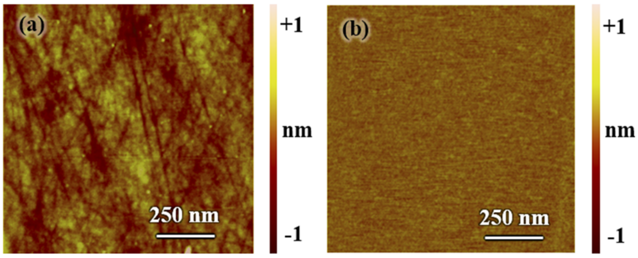

FIG. 9. AFM images of (a) pre-processed surface (PV: 3.521 nm and rms: 0.172 nm) and (b) CARE-processed surface (PV: 0.838 nm and rms: 0.069 nm) of a 4H–SiC(0001) 4°-off-axis wafer.

AFM images before and after processing, respectively. The roughness was reduced significantly from 0.400 nm to 0.053 nm rms, indicating that the surface was atomically smoothened. Under the same experimental conditions, the removal rate using the Pt catalyst was 33 nm/h. In contrast, the removal rate using the Ni catalyst with the *in situ* cyclic treatment was 321 nm/h, which is ~10 times higher. Figure 8 shows the stability improvement provided by the treatment, where filled circles indicate results from after application of the treatment. The post-treatment removal rate was stabilized over 8 h, whereas the removal rate without the treatment decreased to 20% after 2 h of usage. The proposed treatment method is a type of *in situ* refreshment of the Ni surface and has been confirmed as a promising technique to appropriately utilize Ni as a superior catalyst to Pt with respect to the removal rate, stability, cost-effectiveness, and ease of post-cleaning. Finally, Figs. 9 and 10 show the surface images of a 4H–SiC (0001) 4°-off axis and on-axis wafer surfaces as an additional confirmation. Both surfaces are highly smoothened. The on-axis wafer surface shows to have a step-terrace structure, indicating a crystallographically well-ordered surface, which is the same as that obtained for the Pt catalyst.[14]

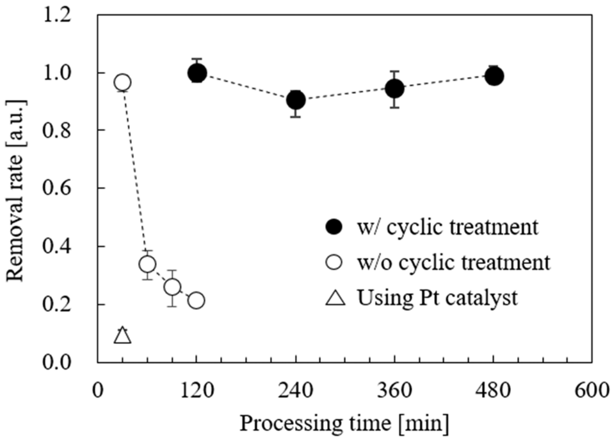

FIG. 8. Dependence of the removal rate on processing time. Filled and open circles indicate removal rates of the Ni catalyst with and without cyclic treatment, respectively. Triangle indicates the removal rate of the Pt catalyst.

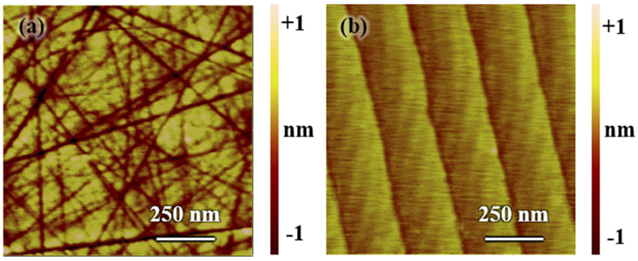

FIG. 10. AFM images of (a) pre-processed surface (PV: 3.100 nm and rms: 0.346) and (b) CARE-processed surface (PV: 1.280 nm and rms: 0.134 nm) of a 4H–SiC(0001) on-axis wafer.

IV. CONCLUSION

In CARE processing, the removal rate using a Ni catalyst is much higher than that using a Pt catalyst. However, the removal rate drastically decreases within 30 min due to the oxidation of the Ni surface. In this research, we proposed a new CARE method with *in situ* cyclic electroplating and dissolution of the Ni catalyst to maintain its catalytic capability. We applied the modified CARE method to quartz glass and 4H–SiC wafers to obtain geometrically and crystallographically highly ordered surfaces. The removal rate was ~10 times higher than that of CARE using the Pt catalyst. The catalytic capability of the Ni catalyst was completely stabilized for more than 8 h, owing to the *in situ* cyclic electrochemical treatment.

This method is applicable to optical glass materials and also to semiconductor materials to realize the demonstrated highly ordered surfaces. Chemically prepared, undamaged surfaces are in particular demand for high-precision optical elements and functional crystalline substrates. In addition, utilization of this abrasive-free planarization method offers cost-effectiveness, environmental friendliness, ease of post-cleaning, and high compatibility with clean room usage.

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