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Effects of plasma treatment on evolution of surface step-terrace structure of critically cleaned c-plane sapphire substrates: An AFM study

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ABSTRACT

Evolution of step-terrace (vicinal or stepped) structure of cleaned c-plane sapphire substrates irradiated with low-pressure air plasma (18 W/12 MHz) was studied with atomic force microscopy (AFM). Depending on plasma irradiation time and post-annealing treatment, original structure with uniform terrace width and sharp steps undergoes distinct morphology changes. With longer plasma irradiation up to 30 min, we observed pairing of neighboring terraces into alternating wider and narrower terraces, steps roughening and terrace etching, and “step-terrace free” morphology with etched pits which are stable against annealing. These phenomena are discussed in terms of surface diffusion and chamber temperature effects. The findings reported here will have important implications for plasma modification and contamination control of sapphire substrates.

1. Introduction

Sapphire single crystals are widely used as LED substrates, optical windows and model systems for metallic oxide/water interface studies [1–5]. The surface structure and chemistry of sapphire substrates determines quality of deposited films, optical transparency and interfacial properties. Pretreatment and post-treatment steps, like wet cleaning, plasma/ion/electron irradiation and annealing may significantly influence the surface state of sapphire crystals. Regarding annealing treatment, there are many reports about effects of annealing temperature and atmosphere on surface relaxation, reconstruction and step-terrace evolution of sapphire substrates with various orientations [6–9]. Plasma treatments have been frequently used for surface modification and contamination control [10–13]. When a gas under sufficiently low pressure is subjected to a high RF oscillating electromagnetic field, the accelerated ions in the gas collide with the gas molecules ionizing them and forming plasma – electrical conducting gas involving electrons and ions. The ionized gas in the plasma interact with solid surfaces placed in the same environment through three major effects: surface sputtering by ion bombardment, chemical reaction of the ionized gas with the surface, cracking of carbon bonds by UV-radiation. Recent studies showed that heavy plasma irradiation causes dramatic surface morphology changes like rippling [14,15]; however, nanoscale characterization of the evolution of step-terrace structure was not carried out.

In our previous report, various cleaning methods, including wet cleaning, plasma and UV-Ozone irradiation were critically evaluated using AFM, XPS and contact angle measurements; a more reliable wet cleaning method (the modified RCA method) was developed for sapphire substrates. Therein, regarding plasma treatments, samples were irradiated with low-pressure air plasma up to 10 min; and time dependence of cleaning effect in terms of organic contaminants removal was revealed. Nevertheless, we have not studied the effect of longer plasma exposure on the evolution of step-terrace structure of cleaned substrates.

Here we report preliminary AFM results about the evolution of step-terrace structure of critically cleaned c-plane sapphire substrates which are subjected to low-pressure air plasma irradiation up to 30 min and post-annealing treatment. Several issues including the irradiation duration effect, cumulative heat effect, and vacuum annealing effect will be addressed.

2. Experimental

2.1. Materials

EPI-ready polished c-plane sapphire substrates were purchased from a commercial supplier (Epistone Inc., Shenzhen, China). The specification of substrates: the purity is 99.995%, the size is

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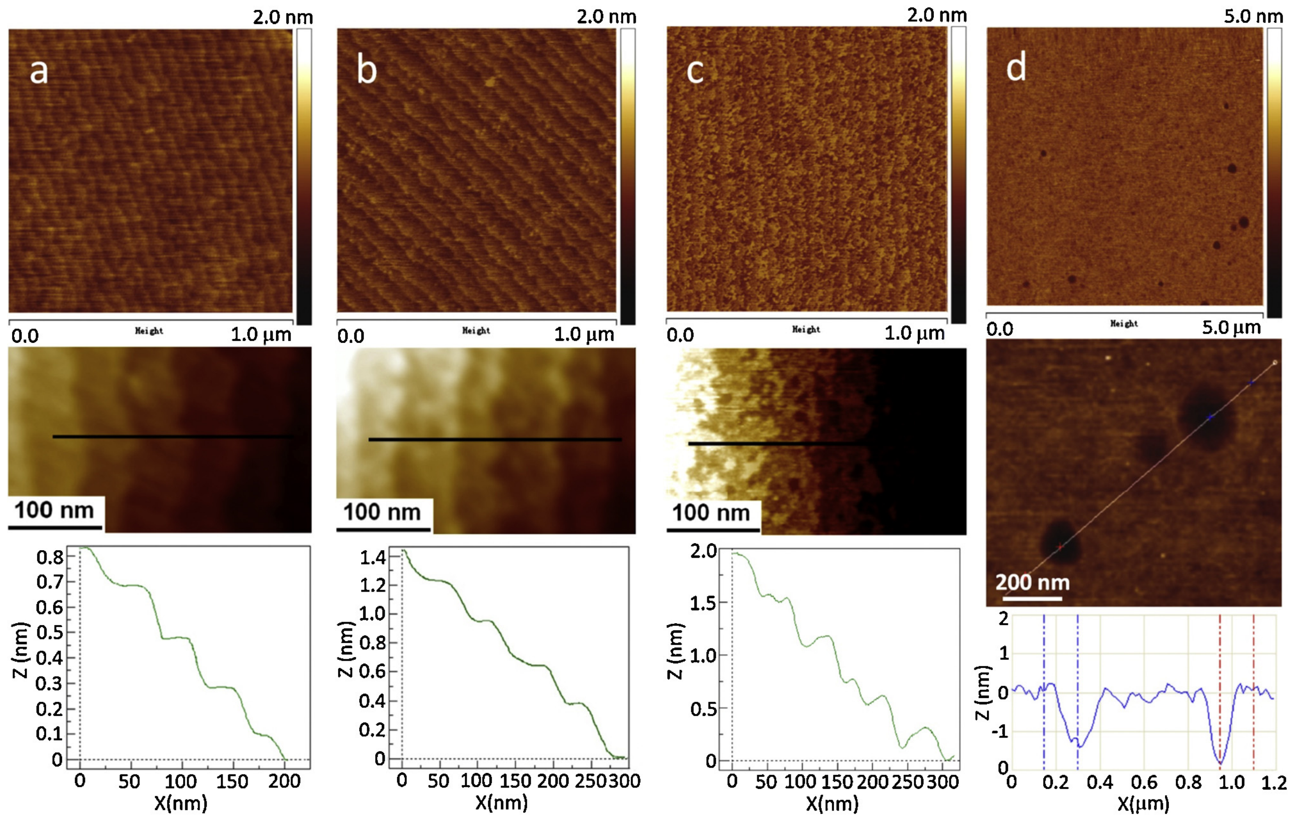

Fig. 1. AFM height images and corresponding profile analysis of c-plane sapphire substrates before and after plasma treatment. (a) Cleaned with the modified RCA method and (b–d) plasma irradiated for 10 min, 20 min and 30 min. Images in (a) and (b) for profile analysis were rotated and low-pass filtered.

10 mm × 10 mm × 0.43 mm, the misorientation angle is 0.2° offset to *M(1-102)/A*(11–20). This batch of substrates showed uniform terrace width. Prior to plasma treatment, substrates were critically cleaned with the new modified RCA method and were used as control samples.

2.2. Methods

A commercial low-pressure plasma generator (PDC-32G-2, Harrick Plasma Inc., USA) was used for plasma treatment. Room air at low pressure was subjected to a high radio frequency (RF) electromagnetic radiation at 12 MHz to create plasma. The RF coil was operated at the conditions of 720 V DC voltage, 25 mA DC and 18 W. The glass plasma chamber (7.62 cm in diameter, 15.24 cm in length) was exposed to lab room air before loading samples, then the chamber was sealed and vacuumed below 0.01 Pa to allow RF plasma to be generated. The chamber and substrates' temperature was not monitored by any instrument.

Vacuum annealing of substrates was conducted with a high purity alumina tube furnace (GSL-1600X-S60, Hefei Kejing Materials Technol., China) at 1000 °C for 1 h under 10^{-6} Pa vacuum conditions. After annealing samples were left in the furnace to cool down to room temperature. Annealed samples were cleaned again with the new modified RCA method [16]. Note that wet cleaning after annealing did not cause morphology change of substrates, as confirmed by AFM observation.

Several experiments were designed to explore effects of plasma irradiation. First, cleaned substrates were subjected to continuous plasma irradiation for different duration of 10 min, 20 min and 30 min. Second, to explore the cumulative effect, substrates were irradiated for 20 min, removed from the chamber for AFM observation, then retreated for the other 10 min. Third, both control and plasma irradiated substrates were annealed to study the temperature dependence of surface structure.

Surface topography was characterized using a commercial Bruker Multimode 8 AFM system working in the intermittent contact (tapping) mode. Silicon probes (PPP-NCHR, Nanosensor) with the nominal spring constant of ~42 N/m and resonant frequency of 330 kHz were used. AFM analysis was carried out in multiple areas of each. Typical AFM images were given here.

3. Results and discussion

AFM images (Fig. 1a) of control substrates, cleaned with the modified RCA method without being subjected to any plasma treatment, showed well-defined step-terrace structure with uniform terrace width of 50 nm and step height of 0.2 nm. The surface roughness is 0.13 nm rms. The experimental terrace width matches well with the calculated values according to the specified misorientation angle (0.2°). The step height is similar to the reported distance between two adjacent closely packed oxygen planes (0.21 nm) [17,18].

Fig. 1b shows that, after 10 min plasma irradiation, step-terrace structure was still distinct. The surface roughness is 0.15 nm rms. Moreover, a quite interesting step-pairing feature was observed. Terrace width and step height are no longer uniform: wider terraces (width of 60 nm) with larger step height (~0.4 nm) alternate with narrow terraces (width of 40 nm) with normal step height (0.2 nm). After 20 min irradiation, Fig. 1c shows that steps and terraces were seriously etched. The step height was around 0.4 nm. The surface roughness is 0.18 nm rms. Roughened step edges became quite irregular, pits (10–20 nm in diameter) were created in terraces, and nanoscale islands formed on terraces.