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Characterization of critically cleaned sapphire single-crystal substrates by atomic force microscopy, XPS and contact angle measurements

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ABSTRACT

A contaminant-free surface of single-crystal α-Al_2O_3 (or sapphire) substrates is key to the experimental studies of its surface and interfacial properties at ambient conditions. Here we critically evaluated methods reported in the literature using comprehensive surface analysis techniques including atomic force microscopy, XPS and contact angle measurements. We found that reported methods did not perform well in terms of removing both organic and particulate contaminants from the (0 0 0 1) basal surface. After thoroughly examining the cleaning effect of various chemical solutions and UV light and plasma irradiation, and based on modified RCA cleaning protocols, we proposed a new wet-cleaning method showing outstanding cleaning performance. This new reliable method will be very useful for the next-step surface chemistry study of single-crystal α-Al_2O_3. It was also demonstrated that AFM, due to its high spatial resolution and sensitivity as a local probe technique, was an indispensable tool for surface contamination control studies.

1. Introduction

Alpha alumina (α-Al_2O_3) – one of most important inorganic oxide materials, has been traditionally used in both powder form [1] for structural and fine ceramic applications and in single-crystal form as sapphire substrates [2,3] for GaN film deposition and LED application and for aqueous geochemistry and catalysts study as model systems [4–6]. The processes of adsorption, reaction, and deposition occur on the surface and interface of α-Al_2O_3 with or without presence of water. The surface and aqueous interfacial structure and chemistry of α-Al_2O_3 powders and single-crystals have been studied intensively to enable gaining deep insight into various key properties like interfacial charging, relaxation and reconstruction, defects evolution, etc. [7–9]. The basal plane or (0 0 0 1) *c*-plane of single-crystal α-Al_2O_3 is frequently chosen as a model system, which is quite stable in routine ambient and aqueous conditions with well-studied surface structure [10–13].

Contaminants may be bulky or in trace amount in the forms of particles, islands or thin films. A sample, a sapphire singe-crystal for example, may be contaminated in every step of polishing, storage, and measurements. In ambient and liquid conditions, surface contamination is inevitable as long as a sample needs to be handled [14–19]. Researchers have tried many cleaning methods such as wet, UV or plasma irradiation, annealing, or combination of above, aiming to remove surface inorganic and/or organic contaminants [20–24]. If a sample is carefully cleaned and handled cautiously, its surface contamination can be well controlled and reduced to a low level [25–31]. The surface and interfacial properties such as point of zero charge (PZC) of solids can be very sensitive to foreign inorganic and organic contaminants [32–35].

Table 1 summarized recent cleaning methods used on sapphire single-crystal substrates. It is surprising that, except in one case, comprehensive characterization was seldom applied. Surface morphology characterization by atomic force microscopy (AFM) was reported only in a few cases [36,37]. Ducker et al. [37] studied the surface morphology of untreated samples; unfortunately, others provided only surface roughness information without showing AFM images [38–40]. Regarding XPS tests, most efforts were directed to rule out silica contamination, whereas organic contaminants were rarely checked [41–44]. Contact angle measurements, which have been routinely used to study contamination removal, were used only scarcely in the past to justify the cleaning method for sapphire [43–46].

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Table 1
Various literature cleaning methods: Evaluation of their cleaning performance for single-crystal α-Al_2O_3 in terms of water contact angle measurements and XPS results.

Cleaning methods	Surface characterization[a]	Contact angle (°)[a]	XPS (C 1s %)[a]	PZC[a]	Contact angle (±2°)[b]	XPS (C 1s ±1%)[b]	Ref.
10^{-3} M HNO_3; 300 °C N_2-purged tube furnace; DI water	Roughness	×	Greatly reduced	4.1	40	16	[38]
Chloroform; MeOH; 10^{-2} M NaOH	×	×	×	<6	40	14	[41]
I Sonication detergent solution (detergent + EtOH + DI water 1:20:79)–EtOH–DI water; UV light	Roughness	×	7.02	4.8–5.2	8	9	[39]
II Sonication acetone–EtOH–0.1 M KOH–0.1 M HNO_3					38	12	
III Detergent solution; EtOH; UV light					8	8	
Sonication acetone–MeOH–DI water–10^{-2} M HNO_3	×	×	Minor (amorphous Al_2O_3 film)	6.3	38	13	[44]
1% detergent; EtOH; 30% HNO_3; UV light	×	×	×	5–5.9	8	8	[43]
Sonication concentrated HNO_3–EtOH + 1% detergent (1:1)	Roughness	×	Cannot rule out	4.2	35	10	[40]
$H_2SO_4 + H_2O_2$ (4:1)	×	×	Reduced	5.9	10	10	[45]
EtOH refluxing	×	×	×	<6.7	45	14	[42]
Fuming HNO_3; EtOH; UV light	Untreated	0	×	3	8	12	[37]
Sonication EtOH; plasma treatment	Annealed	Reduced	3.1–4.2 (annealed); 7.5 (untreated)	4–4.5	8	11	[36]
Acetone; EtOH; DI water	×	25–30	Reduced	4.5–7	40	13	[46]

[a] Results reported in the corresponding reference.
[b] Results tested for the same batches of as-received samples used in this study.

Therefore, it is far from satisfactory, at this stage, to claim that the cleaning of sapphire substrates is thoroughly studied because trace inorganic and organic contaminants on the surface can very likely alter the intrinsic properties of sapphire surface, which has been shown to be very active towards foreign adsorbates. We thus believe that large scattering in reported PZC values, from as low as pH 3 to 9 [47] is largely related with these diversified cleaning methods.

Here we are going to systematically evaluate, for the first time, various cleaning methods reported in the literature using several surface analysis techniques – AFM, XPS and contact angle measurements. Then the performance of various chemicals, UV light irradiation and plasma treatments are evaluated by assessing the surface cleanliness of sapphire substrates. Finally a new method, based on the traditional RCA method – the standard multi-step method for cleaning silicon wafers, is developed as a reliable cleaning method for removing surface contaminants. It was also demonstrated that AFM, due to its high spatial resolution and sensitivity as a local probe technique, was an indispensable tool for surface contamination control studies.

2. Experimental

2.1. Materials

EPI polished single-crystal c-plane (basal (0 0 0 1) plane) α-Al_2O_3 substrates were purchased from two crystal suppliers – Epistone (Shenzhen, China) and MTI (California, USA) for comparison purposes. All substrates ordered were sealed in original plastic bags until experiments. The specification for Epistone substrates:size of 10 mm × 10 mm × 0.43 mm, off-cut angle of 0.2°. The specification for MTI substrates:size of 10 mm × 10 mm × 0.50 mm, off-cut angle of 0.5 ± 0.2°. Epistone substrates were stored in the original plastic bag for more than 12 months and MTI substrates were used less than ten days upon received. Most samples used in this study are Epistone substrates if otherwise specified.

Analytical grade chemical reagents were used. Ultrapure water of resistivity of 18.2 MΩ/cm was used throughout. Cleaning detergent used was Liqui-Nox (White Plains, NY, USA) which is supplied in plastic bottles as concentrated anionic liquid as ordered from SPI Company (West Chester, PA, USA). For cleaning purpose, it was diluted with water to a mild alkaline 1:100 solution.

2.2. The standard multi-step method for cleaning silicon wafers (RCA method)

The standard wet method for cleaning silicon wafers, i.e., RCA method, consists of three major steps – SPM ($H_2SO_4 + H_2O_2$ 3:1), SC1 ($NH_3 + H_2O_2 + H_2O$ 1:1:5) and SC2 ($HCl + H_2O_2 + H_2O$ 1:1:5) [48]. The details were as follows:soaked in the SPM ($H_2SO_4 + H_2O_2$ 3:1) solution for 20 min at 80 °C, rinsed in DI water and blown dried under nitrogen gas, then soaked in the SC1 ($NH_3 + H_2O_2 + H_2O$ 1:1:5) solution for 20 min at 80 °C, and rinsed in DI water and blown dried under nitrogen gas, then soaked in the SC2 ($HCl + H_2O_2 + H_2O$ 1:1:5) solution for 20 min at 80 °C, and rinsed in DI water and blown dried under nitrogen gas.

2.3. Substrate cleaning and surface characterization

In the same lab room, both wet cleaning and plasma treatment and contact angle measurements were carried out. The UV cleaner was portable–it was placed in either the wet cleaning room or AFM room.

To avoid silica contamination, polyfluortetraethylene (PTFE) plastic wares were used for each wet cleaning step. Following each wet cleaning step, the substrate was fully rinsed with water and blown-dried with a stream of high speed nitrogen (≥99.99%) using a nitrogen gun (KITZ, Japan). Cleaned substrates were stored in a sealed PTFE container prior to XPS and AFM analysis. Contact angle measurements were carried out immediately after cleaning.

A commercial low-pressure plasma cleaner (PDC-32G-2, Harrick Plasma Inc., USA) was used. The plasma chamber, which is made

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