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Journal of Colloid and Interface Science 299 (2006) 233–237
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

# Effects of cleaning procedures of silica wafers on their friction characteristics

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Received 14 December 2005; accepted 21 January 2006

Available online 13 February 2006

**Abstract**

Silicon wafers with thermal silicon oxide layers were cleaned and hydrophilized by three different methods: (1) the remote chemical analysis (RCA) wet cleaning by use of ammonia and hydrogen peroxide mixture solutions, (2) water-vapor plasma cleaning, and (3) UV/ozone combined cleaning. All procedures were found to remove effectively organic contaminations on wafers and gave identical characteristics of the contact angle, the surface roughness and the normal force interactions, measured by atomic force microscopy (AFM). However, it is found that wafers cleaned by the RCA method have several times larger friction coefficients than those cleaned by the plasma and UV/ozone methods. The difference was explained by the atomic-scale topological difference induced during the RCA cleaning. This study reveals the lateral force microscopy as a very sensitive method to detect the microstructure of surfaces.


*Keywords:* Friction; AFM; Silica; Surface cleaning; Hydrophilic surface

## 1. Introduction

The fast development of devices with high performance in the microelectronic industries requires a very good control of physico-chemical properties of $Si/SiO_2$ surfaces. Since the presence of organic contaminants and mechanical impurities reduces the quality of silicon oxides, such as the uniformity and reproducibility of functionalized surfaces, the cleaning of silica surfaces is of crucial importance [1]. The quality of cleaned surfaces has been characterized using various methods, such as the measuring methods using the contact angle, the atomic force microscope (AFM), the Fourier transform infrared reflectance (FTIR), the X-ray photoelectron spectroscopy (XPS), and the spectroscopic ellipsometry (SE) [2–5].

Recently we have conducted a series of lateral force measurements by AFM, using micron-size silica particles and silica wafers in solutions, such as measurements between silica surfaces in surfactant solutions [6] and in electrolyte solutions [7]. Most recently, the effects of pH-induced silica surfaces on the friction force were investigated [8]. Other researchers also conducted measurements of the lateral force between silica surfaces [9,10]. In these experiments we noticed that, even though wafers are of identical chemical composition and of identical surface hydrophilicity and roughness, there exits a significant difference among their frictional coefficients if wafers were supplied from different companies, the elapsed time from the production is different, and most importantly the cleaning procedure is different.

Here we pay attention to the effect of cleaning procedures on the surface property. We conducted a systematic investigation to know how the cleaning procedure affects the surface properties of silica. Three types of cleaning procedures commonly used in the industry and in research investigations are examined: the RCA cleaning, the plasma cleaning, and the UV/ozone cleaning. As the results, we demonstrate that the lateral force microscopy may be used as a simple but powerful method to detect the slight difference of the property of cleaned surfaces.

## 2. Experimental

Silicon wafers of $(1, 0, 0)$ crystal orientation with the thermal-oxide surface layer of 10-μm thickness were obtained

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0021-9797/$ – see front matter 
doi:10.1016/j.jcis.2006.01.044

from Silicon Quest Int. Pure nonporous colloidal silica particles of mean 20-μm diameter were kindly provided by Fuso Chemical Co., Japan. The root mean square (RMS) roughness of surface of as-received silica particles and wafers was measured to be ca. 0.15 nm over 1 $\mu m^2$ area, using the AFM. The details of the three cleaning procedures of wafers employed here are explained below. Before these cleanings, the wafers were washed by acetone, ethanol and DI water, as the preliminary cleaning.

### 2.1. RCA cleaning

This peroxide-based and wet-chemical process was developed by Kern and Puotinen at Remote Chemical Analysis (RCA) Laboratories in 1970 [1,11], and it has been adopted as the standard cleaning method in the silicon semiconductor technology. Here the SC-1 process (Standard Clean Solution #1) was used, which is referred as "RCA" in this study. The cleaning solution was a mixture of ammonium hydroxide ($NH_4OH$), hydrogen peroxide ($H_2O_2$), and deionized water ($H_2O$). This solution is prepared as follows. A 5:1 mixture of DI water and 28 wt% ammonia aqueous solution of 60 ml was heated up to 70 °C and then a 30 wt% hydrogen peroxide aqueous solution of 10 ml was added. Samples were immersed for 15 min in the solution, and then washed thoroughly with copious amount of DI water.

### 2.2. $H_2O$-vapor plasma cleaning

In this treatment, which is referred to as "Plasma" in the present study, wafers were exposed to the plasma for 1 min in argon–water moisture atmosphere of 80 Pa, using a plasma kit (Kit-BP1, Samco Co.) combined with a 1.0 W plasma generator of 13.6 MHz radio frequency (RF) (ENI ACG 98).

### 2.3. UV/ozone cleaning

Wafers were exposed to the field of 3 quartz–mercury vapor lamps of 4.5 W and wavelengths of light, 185 and 254 nm, in a chamber filled with pure oxygen to generate ozone for 1 h (NL-UV253, Nippon Laser & Electronics Lab.).

Both the imaging of surfaces and force measurement between surfaces in solutions were carried out with an AFM (Digital Instruments Nanoscope III) equipped with a liquid cell. Triangular cantilevers (Olympus) of spring constant $K_N = 0.15 \pm 0.02$ N/m were used to take AFM images and to measure the normal interaction force, and rectangular tipless cantilevers (MikroMasch) of spring constant $K_N = 14 \pm 0.5$ N/m were used to measure the lateral force. The colloidal probes were prepared by attaching a silica particle of ca. 20-μm diameter on the cantilever end, using a small amount of thermoplastic epoxy adhesive (Shell Epikote 1004). Prior to each measurement, the colloidal probe was treated by plasma for 1 min under the same experimental condition as in the case of wafer cleaning. The normal force measurements were carried out by the same method introduced by Ducker et al. [12] and the lateral force measurements procedure details are given elsewhere [6,7]. The water used for all the experiments was produced by a Millipore filtration system, with an internal specific resistance no less than 17.6 MΩ/cm. The pure water used in the AFM experiments was within a natural pH of $5.6 \pm 0.5$.

## 3. Results and discussion

### 3.1. Contact angle measurements and surface roughness measurements

The degree of hydrophilicity of surfaces was evaluated by the contact angle of water droplets on the surfaces, as a measure of the degree of surface contamination. The angle was determined averaging the angles given by the horizontal images of droplets, after several droplets of a given volume were placed on the wafer. In the case of as-received wafers, the contact angle was approximately 60°, which implies that the wafers are significantly contaminated, probably because of organic compounds from the storage box and laboratory atmosphere. The consecutive washing of the wafers with acetone, ethanol and deionized water reduced the contact angle down to 30°–20°. When the same washing was carried out in a sonicated vessel, the contact angle was able to be reduced to about 10°. Then, the wafers were further cleaned by one of the procedures of RCA, plasma, and UV/ozone. It was found that the wafers were completely wetted by water, whichever procedure is used. This high hydrophilicity of wafers implies that the organic contaminations are removed completely and there is a layer of high density of silanol groups on the surface.

The roughness of wafers was evaluated by using the AFM images of wafer surfaces. The silicon nitrate tip of the nominal spring constant 0.15 N/m was cleaned by plasma treatment to obtain a better sensitivity. The root mean square roughness of surfaces (RMS) defined as the standard deviation of the height values within a given area was evaluated by using the off-line software of the Nanoscope III. The RMS data listed in Table 1 were determined by averaging the values measured over a 1 $\mu m^2$ area on the surface at five different locations. It is clear

Table 1
Summarized properties of surfaces treated by different cleaning procedures

| Cleaning procedures | Contact angle (°) | RMS (nm) | Surface potential (mV) | Adhesion in water[a] (mN/m) | Friction coefficient (–) |
|---|---|---|---|---|---|
| Acetone/ethanol/water | $30 \pm 5$ | $0.10 \pm 0.09$ | – | – | – |
| RCA | <5 | $0.08 \pm 0.01$ | 65 | Undetectable | $0.100 \pm 0.010$ |
| Plasma | <5 | $0.07 \pm 0.02$ | 75 | Undetectable | $0.022 \pm 0.005$ |
| UV/ozone | <5 | $0.09 \pm 0.01$ | 70 | Undetectable | $0.025 \pm 0.004$ |

[a] Adhesion in pure water at the high loading force, $F/R = 50$ mN/m, and the long contact time, 50 s.