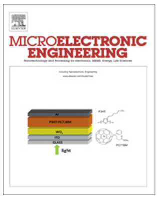
Microelectronic Engineering 128 (2014) 79–84

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee



# Wetting behavior of plasma treated low-k films in dHF cleans solutions

T.S. Smith [a], K.M. Lynch [a], C.M. Cooper [a], O. Okobiah [a], E. Osei-Yiadom [a], M. Bischof [a], A. Kouloumpis [b], M. Baikousi [b], K. Dimos [b], R.F. Reidy [a,*]

[a] Department of Materials Science and Engineering, University of North Texas, Denton, TX, USA
[b] Department of Materials Science and Engineering, Ioannina University, Ioannina, Greece

## ARTICLE INFO

*Article history:*
Received 18 June 2013
Received in revised form 2 May 2014
Accepted 6 May 2014
Available online 15 May 2014

*Keywords:*
Low-k
Wetting
Evaporation loss
Contact angle

## ABSTRACT

Post-ash and post-etch cleaning of low-k structures require significant wetting of their surfaces. This work focuses on the interactions between dilute HF cleaning chemistries (dHF—1:50 to 1:1000) on porous low-k surfaces ($k = 2.3$) as a function of time. Wetting of these solutions was measured by a contact angle goniometer within a high humidity environment. Because ashing low-k films can change their surface chemistry and structure, the contact angles of dHF on $N_2/H_2$ and $O_2$ ashed porous low-k films were measured as well. Ellipsometry has shown that 1:50 HF removes an ash-damaged layer from the low-k. Based on thickness loss measurements (ellipsometry and profilometry), the composition of the dilute HF droplet changes minimally as it etches the dielectric surface. Under more concentrated dHF solutions, changes in contact angle, droplet radius, and volume indicate that the droplet spreads for an initial period and then reaches a steady state, perhaps due to the creation of an etch inclusion on the surface. The steady state volume changes show volume loss rates similar to those expected from evaporation; however, the total volume losses are less than expected from only evaporative processes.

## 1. Introduction

As the integrated circuit device fabrication industry strives for smaller and more advanced technologies, the efficiency and precision of their fabrication processes become progressively more relevant. One of the key processes in microfabrication is the etching and cleaning of features. As feature sizes scale, wetting of cleans chemistries is crucial to the removal of etch debris in sub-45 nm structures. How these chemistries and their wetting behavior change as a function of time will relate to how effective the cleaning process can become [1]. Porous low-k films are of particular interest as they are more affected by plasma processes than more chemically robust films and have greater surface roughnesses than dense dielectric layers (in addition to roughness due to porosity). In this study, the wetting behavior of dilute HF (dHF) solutions on plasma-etched low-k substrates is analyzed as a function of time and HF concentration.

To achieve a successful wetting behavior, three factors must be understood: the surface chemistries (and surface energies) of substrates, the chemical interactions between the HF solution and the substrate, and the effective evaporation of the HF solution. The surface chemistries of the substrate are influenced by the plasma ashing that was previously applied. These ashes can degrade a substrate's resistance to the wet etch process by removing hydrophobic groups, thus, rendering the hydrophilic surface more vulnerable to HF attack [2]. In HF dissolution of silica, $HF_2^-$ and $F^-$ react with the $SiO_2$ to form $SiF_4$ and then $H_2SiF_6$ [3].

When dealing with the wetting behavior of a droplet, the competing surface energies between solid, liquid, and gas must be taken into account as described by Young's equation [4].

$$\gamma_{sl} + \gamma_{lg}\cos\theta_c = \gamma_{sg}$$

For a clean chemistry to wet a low-k surface, the surface energy of the low-k-gas interface must exceed the sum of the clean-gas and low-k-liquid interfaces, and must also be greater than the surface energy of the low-k-liquid interface. Thus, the adhesive forces are stronger than the cohesive forces, and wetting of the surface occurs.

Evaporation of the HF solution can also affect the wetting behavior of a substrate. A prolonged wetting time can result in evaporation of the HF solution. With this loss of liquid volume, the contact angle can be affected. To quantify this behavior, contact angles that are formed at the solid–liquid interface are measured and examined with respect to surface chemistry, roughness, and profile.

---

* Corresponding author. Tel.: +1 940 369 7115; fax: +1 940 565 4824.
*E-mail address:* reidy@unt.edu (R.F. Reidy).

http://dx.doi.org/10.1016/j.mee.2014.05.006
0167-9317/

## 2. Experimental

Samples were chemically vapor deposited SiOCH low-k films (~2700 Å on a silicon wafer) with porosities of about 25–30%, pore diameters of approximately 2 nm, and *k* values of 2.3. The films were plasma-ashed under the following conditions: $N_2/H_2$ (30 s, 900 sccm, 2000 W, 2 Torr, 260 °C), $N_2/H_2$ (60 s, 900 sccm, 2000 W, 2 Torr, 260 °C), and $O_2$ (20 s, 25 °C). These films were individually mounted onto a Rame Hart contact angle goniometer in a humidity-controlled environment. A relative humidity of ~63% was achieved by placing a hot water beaker on a stage inside the goniometer set-up. The water was heated to create a humid environment, but did not exceed the dew point as to avoid condensation on the camera lens. Each film was exposed to 6 µl droplets of 1:50, 1:100, 1:200, and 1:1000 solutions of HF. Contact angles of each sample were measured as a function of time at 30 s intervals using the FOControl image processing software. The wetting angle, height, and width of each droplet were calculated using the collected images from Image J software (NIST). Surface roughness was measured using a Veeco Multimode Nanoscope III atomic force microscope (AFM) in tapping mode. Changes in film thicknesses were measured using a JA Woollam Variable Angle Spectroscopic Ellipsometer (VASE) for 3 angles (65, 70, and 75 degrees) and 300–1000 nm wavelengths. Different functionally-graded Cauchy models were developed to determine the film thickness for each unetched low-k sample. These respective models were then used on each etched (30 s exposure 1–50 dHF) sample. The width, and depth of substrate removed during this process was measured using a Veeco Dektak 150 Profilometer. Chemistries of the film surfaces were characterized by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 Versaprobe. Although Young's equation is a good model for describing the wetting behavior of a solid substrate, it assumes a perfectly smooth surface, and does not take into account the roughness found in low-k films. In this work, the plasma-ashed and as-cured (unashed) substrates not only involve the interactions between their respective chemistries, but also the adhesive and cohesive interactions between the liquid and the roughness of the film surface [5]. To study these features, AFM was used to analyze the topographies of the low-k dielectrics and revealed their respective roughness values, root mean squared roughness, $R_q$ [6]. In addition, XPS was used to characterize the carbon concentration of the respective surfaces. A loss of surface carbonaceous groups suggests a concomitant loss of hydrophobicity. Table 1 shows previous results relating the $R_q$ values, the percentage of carbon on the surface, and the resulting water contact angles [7].

## 3. Results and discussion

As expected, the as-cured sample has lower $R_q$ compared to the plasma-ashed samples. The roughnesses of the ashed samples are very similar; therefore, the wetting behavior may be more affected by the surface chemistry. Previous work has also shown that because of the formation of bridged siloxanes, the oxygen ashing densifies the topmost layer of a low-k preventing liquid intrusion into the film [2,8]. As expected, the as-cured sample contained the highest carbon percentage on the surface, and exhibited the highest contact angle of $H_2O$. The lower percentage of carbon in the plasma-ashed substrates corresponds to lower contact angles due to their greater hydrophilicity. It should be noted that these carbon losses during the ashing process occur only to a depth of about 30–40 nm [9].

Ellipsometry data were used to determine film thickness losses after a 30 s 1:50 HF exposure (followed by a DI water rinse). From this data, an etch rate was calculated to provide some insight into the etching behavior of these substrates. In Table 1, we see that the etch rate for this dHF concentration relates well to the measured contact angles after 30 s. When comparing data from Table 1 to Fig. 1a, it is seen that the most pronounced changes in contact angle ($N_2/H_2$ at 30 and 60 s) correspond to the highest initial etch rates. Alternatively, the as-cured sample has the most gradual change in contact angle (CA) and the slowest etch rate. Using these etch rates and the 1:50 HF exposure time for each sample to calculate total film thickness loss, the dHF likely etched through the film to the $SiO_2$. Visual inspection, as well as FTIR analysis suggests this occurred as well. Additionally, profilometry data indicated that the surface film losses were greater than or equal to the ~2700 Å of low-k material for 1:50 and 1:100 HF.

In this work, the factors that affect the wetting behavior of the as-cured and plasma-ashed low-k films were studied by measuring the contact angles of dHF as a function of concentration and time. The results are presented in Fig. 1a. In Fig. 1b, the initial water contact angles for each of the respective moieties are shown with the dHF contact angles as a function of time. This large change in contact angle is in some part due to the chemical reaction between dHF and the low-k. The CA of the as-received substrate at an HF concentration of 1:50 decreases at a steady rate. The shaded region in Fig. 1a indicates the initial period where significant etching likely occurs, specifically, in the plasma-ashed substrates. Within this region, $N_2/H_2$ ashes appear to be more affected than the $O_2$-ashed and as-cured films.

There is not a large change in the wetting behavior of the as-cured sample when the cleaning solution of dHF is changed from 1:50 to 1:100, as shown in Figs. 1a and 2. The oxygen-ashed sample appears to be more affected by this concentration than the 1:50 while the changes in the 30 s $N_2/H_2$ contact angles show a more gradual change than observed in the more concentrated dHF. Significant changes in the CA of $N_2/H_2$ at 60 s behavior are still evident at 1:100 dHF. For lower HF concentrations such as 1:200 and 1:1000, a gradual decrease in CA is observed for all substrates as shown in Figs. 3 and 4. Surface discoloration of the films at the spot of dHF exposure suggests that the substrates chemically react at these concentrations although no large drops in CA are observed in these figures. When one examines the "time lapse" contact angle images for all samples exposed to 1:200 and 1:1000 dHF, it is clear that the droplet radii are effectively unchanged as a function of time—the droplet edges appear "pinned" on the substrate surface.

**Table 1**
Roughness measurements given in RMS values by AFM, surface chemistry in terms of percent carbon on the surface given by XPS, the contact angle of water measured in degrees, and the etch rate calculated from ellipsometry data in units of nanometers per minute for all substrates.

| Sample | RMS roughness | %C on surface (XPS) | $H_2O$ contact angle (deg) | Etch rate calculated from ellipsometry (nm/min) |
|---|---|---|---|---|
| As cured | 0.39 ± 0.005 nm | 28.1 | 92 | 24 |
| $O_2$ 20 s | 0.45 ± 0.012 nm | 3.3 | 43 | 36 |
| $N_2/H_2$ 30 s | 0.48 ± 0.012 nm | 6.1 | 48 | 52 |
| $N_2/H_2$ 60 s | 0.49 ± 0.021 nm | 6.1 | 50 | 64 |