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Investigation of the TiN/photoresist interface degradation during a wet etch ☆

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ABSTRACT

In the context of titanium nitride (TiN) patterning in presence of photoresist, the formation of stains in large resist patterns during Standard Clean 1 (SC1) wet etches was investigated. These stains were found to be caused by surface modifications of the TiN layer below the photoresist, with the appearance of large bumps at its surface. XPS and ToF-SIMS characterization techniques were applied to study the TiN surface modification during the SC1 treatment. The TiN film was found to be globally etched by the SC1, with chemical modifications inside the bump area. It is hypothesized that the TiN was attacked after the penetration of wet etchants through the photoresist, but that the confined environment did not enable reaction products to be evacuated, resulting in bumps at the TiN surface.

1. Introduction

Integrated circuits manufacturing requires several wet etching operations in presence of photoresist (PR). Indeed wet etching is often preferred to plasma etching that can damage the integrity of materials like metal gates or gate oxides [1]. The photoresist provides local protection to the underlying materials from the chemical etchant. Hence this protection provided by the resist must be kept intact during the entire wet etch process, which becomes more and more challenging with the continuous shrinking of critical dimensions. Lift-off of photoresist patterns is often observed during prolonged wet etches, or on materials with poor adhesion properties [2,3]. This phenomenon occurs first on small dimensions patterns, due to a direct penetration of the etchants at the resist/material interface. The detachment of large dimension patterns (several micrometers in length and width) occurs much later during the etching, because of a much weaker role of edges in the adhesion. Optical microscopy observations sometimes reveal the appearance of numerous stains in these large resist areas during long wet etches, even though there is no lift-off. Similar stains have already been described on a SiO_2 surface with HF etchant [2–4]. They correspond in this case to a localized detachment at the photoresist/underlying material interface, with the formation of "blisters".

The present paper focuses on the study of stains formation in a TiN/photoresist stack, with SC1 etchant. In a first part, using optical microscopy and AFM, we identify that stains are formed due to modifications on the TiN surface because of etchants penetration down to the photoresist layer. In the second part, we focus on the chemical modifications of the TiN surface by the SC1 treatment, through XPS and ToF-SIMS analyses. We finally conclude by proposing a mechanism for this bumps formation.

2. Experimental

300 mm Si wafers (100) were used for this study. A first layer of HfSiON was deposited by Metalorganic Chemical Vapor Deposition (MOCVD). These substrates were then covered with 35 Å TiN using Radiofrequency Physical Vapor Deposition (RF-PVD) at ambient temperature. Finally, a blanket lithographic stack – made of a 248 nm deep UV photoresist on a developable Bottom Anti-Reflective Coating (dBARC) – was coated on the TiN film.

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A Hexamethyldisilazane (HMDS) vapor treatment was applied pre-coating to TiN to improve the photoresist adhesion.

The wet etch was performed using a Standard Clean 1 solution (SC1: $NH_4OH/H_2O_2/H_2O$ with a 1/4/27 ratio) at ambient temperature on a Dainippon Screen SU3100 single wafer cleaning platform at various dispense durations (between 120 and 270 s).

A photoresist and dBARC stripping was performed using a dimethyl sulfoxide (DMSO) based alkaline organic solvent. After this treatment, about 2 nm organic residue stayed adhered on the TiN surface. This stripping enables the TiN/dBARC interface analysis by XPS or ToF-SIMS without damaging the TiN surface. The photoresist/dBARC system has also been stripped using a N_2/H_2 plasma. In this case, no residual carbon layer is left on the TiN surface.

Optical microscopy was performed using a Carl Zeiss Axiospect 300 instrument, and the images were treated with the ImageJ software.

A Bruker Dimension FastScan instrument was used for the AFM analyses. The profiles were recorded using a Si tip on a silicon nitride cantilever in tapping mode, with a resonant frequency $f_0 = 70$ kHz and a spring constant $k = 0.4$ N/M. The scanned area was $93 \times 93\ \mu m^2$.

The XPS measurements were carried out with a Revera Veraflex II photoelectron spectrometer, with a monochromatic Al Kα radiation (1486.6 eV). The analyzed area was $150 \times 150\ \mu m^2$, and the samples surfaces were probed on a depth of about 8 nm. All XPS data were treated using the CasaXPS software. Spectrum backgrounds were subtracted using the Shirley method and the fittings processed using 70% Gaussian/30% Lorentzian peaks. All peak positions were calibrated relatively to the C1s peak, whose C–C component's energy was fixed at 284.8 eV.

ToF-SIMS analyses were performed with an Ion-TOF TOF.SIMS^5 instrument, on negative ions, with a dual beam acquisition. A Bi^+ (25 kV) beam was used for analysis, with a $100 \times 100\ \mu m^2$ raster, 50 μs cycle time and a 512 pixels resolution. The sputtering was performed using a Cs (500 eV) beam, with a $500 \times 500\ \mu m^2$ raster. An electron flood gun with –20 V bias was also used, to overcome charging problems. Each acquisition was carried out over 300 scans. On the sample presenting bumps, ion profiles were extracted for each zone – inside and outside the bumps. These extractions were made based on the O^- ion 3D visualization (cf. Appendix 1): the amount of collected ions being much larger inside the bumps than outside, it was possible to perform threshold based on the maximum ion intensity. For intensities between 0% and 20% of the O^- maximum value, the area's pixels were considered "outside bumps", whereas the "inside bumps" zone was determined for pixels with intensity values between 50% and 100% of the maximum value. To be able to compare the extracted profiles between each area, it was then necessary to normalize the respective intensities. Each intensity series was then normalized with respect to the amount of pixels extracted from the image, and related to the pixels resolution (512×512).

Due to possible ToF-SIMS etching rate variations between each material, the depth parameter in *x*-coordinate were left in number of scans (i.e. of etchings) instead of nanometers.

3. Results and discussion

3.1. Stains position and morphology analysis

Optical microscopy revealed the appearance of large circular stains after prolonged SC1 treatment (Fig. 1a), with diameters between 5 and 10 μm depending on the SC1 duration – the longer the SC1 time, the larger the stains.

To detect if these stains originate at the TiN/dBARC interface, the SC1 treated sample was stripped with a solvent that removes the polymers (dBARC and resist), but leaves a 2 nm thick organic layer on TiN. The thickness of this residue is constant on the whole wafer. AFM analyses performed post solvent stripping showed that the sample surface presents a high surface topology, with 10 nm thick bumps (Fig. 1b). These bumps exhibit the same size and shape as the optically observed stains, confirming that this phenomenon comes from morphological modifications of TiN/dBARC interface.

However, because of the remaining organic layer on the TiN surface, an uncertainty remained on the origin of the stains formation. Either it was caused by the formation of voids between the TiN surface and the remaining organic layer as observed in previous studies [2–4] or it was attributed to TiN surface modification. To verify the latter hypothesis, a full plasma stripping was applied on an SC1-treated sample before AFM analysis, to analyze the TiN surface only. The obtained image (Appendix 2) is similar to the one obtained after partial solvent stripping in Fig. 1b: large bumps on the TiN surface with 5 μm diameter and approx. 10 nm maximum height.

These results prove that the stains observed by optical microscopy result from morphology variations of the TiN surface caused by the penetration of etchants through the photoresist during the SC1 treatment.

The penetration mechanism of etchants into the photoresist bilayer has been studied and results are presented in another study [5].

3.2. TiN surface analysis

In this second part, we focused on the chemical modifications of the TiN surface induced by the SC1 treatment, through XPS and ToF-SIMS analyses. For this study, blanket samples of the resist bilayer on TiN were exposed to SC1 treatment with durations comprised between 120 and 270 s, then stripped with a solvent, leaving about 2 nm of organic residue.

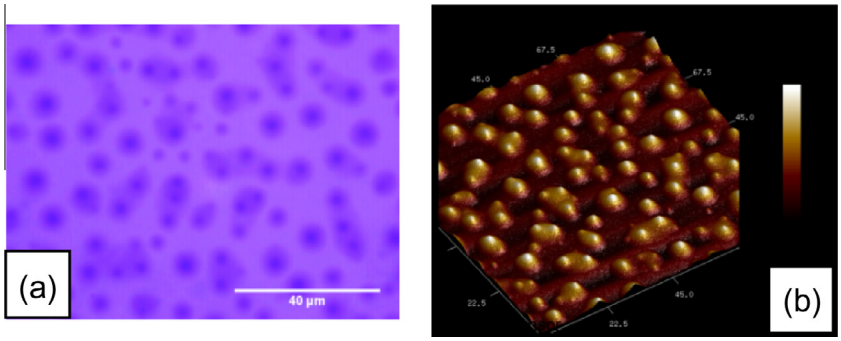

Fig. 1. Optical image of a TiN/dBARC/photoresist blanket wafer after 270 s SC1 (a), and AFM profile of a similar sample after 270 s SC1 and solvent stripping (b).