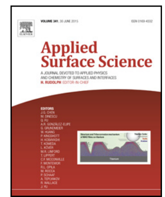
Applied Surface Science 341 (2015) 37–42

Contents lists available at ScienceDirect

Applied Surface Science

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



Time-varying wetting behavior on copper wafer treated by wet-etching

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ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form 7 January 2015
Accepted 7 January 2015
Available online 9 March 2015

Keywords:
Contact angle
Wetting
Cuprous oxide

ABSTRACT

The wet cleaning process in semiconductor fabrication often involves the immersion of the copper wafer into etching solutions and thereby its surface properties are significantly altered. The wetting behavior of a copper film deposited on silicon wafer is investigated after a short dip in various etching solutions. The etchants include glacial acetic acid and dilute solutions of nitric acid, hydrofluoric acid, and tetramethylammonium hydroxide. It was found that in most cases a thin oxide layer still remains on the surface of as-received Cu wafers when they are subject to etching treatments. However, a pure Cu wafer can be obtained by the glacial acetic acid treatment and its water contact angle (CA) is about 45°. As the pure Cu wafer is placed in the ambient condition, the oxide thickness grows rapidly to the range of 10–20 Å within 3 h and the CA on the hydrophilic surface also rises. In the vacuum, it is surprising to find that the CA and surface roughness of the pure Cu wafer can grow significantly. These interesting results may be attributed to the rearrangement of surface Cu atoms to reduce the surface free energy.

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1. Introduction

Copper (Cu) has replaced aluminum as the interconnection for the manufacture of nanoscale integrated circuits because of its higher electrical conductivity and better resistance to electromigration. The fabrication of copper-based chips often involves chemical mechanical planarization (CMP) [1–3]. As a result, large amounts of contaminations including abrasives, metal oxide residues, and organic residues are left on the wafer surface. To avoid the reduction of the yield performance, aqueous cleaning processes like post Cu CMP cleaning is thus used to remove unwanted residues. The wet cleaning process includes the immersion of the whole wafer surface into a liquid medium. Owing to the exposure to oxidants like oxygen during the cleaning step, the Cu surfaces may be oxidized and the relevant properties are affected [4,5]. In fact, the presence of copper oxide results in high electrical resistance and may alter the reliability and the performance of the device.

The removal of unwanted residues on a surface by a cleaning solution is often through the mechanism of either wettability or etching. In the former approach, the surface has a higher wettability for the cleaning solution than for the residue and thus the residues prefer being dissolved in the solution. The wettability of a solid surface is generally characterized by the contact angle (CA) measured through the liquid, where a liquid/vapor interface meets the solid substrate [6]. The latter approach is involved with etchants and often used in semiconductor industry. The contaminated solid surface is slowly etched first and the undesired residues are then removed by lift-off. The typical etchant is acid such as dilute nitric acid solution ($HNO_{3(aq)}$) or dilute hydrofluoric acid solution ($HF_{(aq)}$). Recently, base like ammonium hydroxide or tetramethylammonium hydroxide (TMAH) is used as well. Since metal oxide can be easily etched and lifted off in an aqueous solution, the cleaning solution often consists of hydrogen peroxide to promote the formation of a thin oxide layer [7]. Owing to the negatively charged nature associated with both particle and solid surface, electrostatic repulsion prevents the re-deposition of lifted materials.

After a short-time immersion in an etchant solution, the surface layer of a Cu film may suffer oxidation and etching and thereby its surface properties may be altered. In general, the chemical composition of a thin film on the surface can be examined by

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http://dx.doi.org/10.1016/j.apsusc.2015.01.048
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X-ray photoelectron spectroscopy (XPS) [8–10]. Nonetheless, the sampling depth of XPS is greater than 50–100 Å and thereby it is impractical to attempt to conduct chemical analysis on the topmost surface of the film by XPS. Moreover, it is difficult to distinguish the difference between Cu and Cu_2O by XPS spectra because the peaks at Cu $2p_{3/2}$ are overlapped [11]. However, since the wetting behaviors between hydrophilic Cu and hydrophobic Cu_2O are significantly different, the CA is a suitable property to characterize the chemical nature of the Cu surface. For a heterogeneous surface consisting of two types of patches that have different solid–fluid interfacial tensions, an apparent CA can be acquired by regarding such as surface as a smooth one [6]. The apparent CA can be related to the intrinsic CAs of patches based on the Cassie–Baxter model, $\cos\theta_a = f_1\cos\theta_1 + f_2\cos\theta_2$, where f_i and θ_i denote the surface area fraction and the CA of patch i, respectively [12]. Recently, chemically modified copper surfaces or CuO films are found to be able to show superhydrophobic ($\theta > 150^\circ$) or superhydrophilic ($\theta < 10^\circ$) characteristics, which have potential applications in self-cleaning surfaces and microfluidic devices [13–16]. The synthesis of such surfaces generally involves the treatment of cleaning, etching, or oxidation on the Cu substrate. Evidently, the oxidized states or chemical compositions of the surface layer of a Cu film after immersion in a cleaning solution affect the outcome of the subsequent processes. Therefore, investigation of the characteristic properties of the Cu surfaces after various chemical processes is an important issue on Cu cleaning/corrosion/protection. The wetting properties on the Cu substrate can provide insightful information associated with surface characterization.

Since PVD Cu wafer is commonly used in semiconductor industry, the wetting behavior of physical vapor deposited (PVD) Cu film on a silicon wafer after a short dip in various etching solutions will be studied. After the treatment of etching solutions, the top layer of the Cu film may contain Cu, Cu_2O, CuO, and $Cu(OH)_2$ [8,17,18]. The etchants including glacial acetic acid (HAc) and dilute solutions of $HNO_{3(aq)}$, $HF_{(aq)}$, and $TMAH_{(aq)}$ are able to dissolve all copper compounds but the dissolution rates are different. Owing to the selective removal of etchants, the surface properties of the Cu film depend on their relative amounts. The selectivity can be indicated from the dissolution rates of pure powders of Cu compounds in etchants. The Cu wafers stored in nitrogen environment are examined first and an oxide layer is clearly observed on the surface. In order to explore the effects of etchants on pure Cu surfaces, the removal of the oxide layer is necessary. In the ambient condition, the variations of the thickness of the oxide layer and CAs are monitored simultaneously. The wetting property on the thin film is found to be time-dependent and the deoxidation mechanism is therefore proposed [13]. To make comparisons, the change of the CA with time in the vacuum is also studied.

2. Experimental methods

2.1. Materials

Copper (99%, Cu) powder was purchased from Sigma–Aldrich. Cuprous oxide (97%, Cu_2O) powder was obtained from Acros Organics. Cupric oxide (98.5%, CuO) and copper hydroxide (90%, $Cu(OH)_2$) powders were purchased from Showa Corporation. The particle size of Cu powders is in the range of 20–60 μm and other oxides of copper are in the range of 1–3 μm. Glacial acetic acid (CH_3COOH) was the product of Scharlau. Nitric acid (65%, HNO_3) was obtained from MERCK. Hydrofluoric acid (49%, HF) was purchased from Sigma–Aldrich and diluted with deionized water (DIW) by the ratio of 1:100. Tetramethylammonium hydroxide (25%, $(CH_3)_3N(OH)C_6H_5$) was obtained from Sachem. All chemicals in this work are at least reagent grade and used as received without further purification. The PVD Cu wafer was achieved by ion implantation on silicon substrate and the layout of the Cu film from top to bottom are Cu (1 kÅ), Ta (250 Å), and TEOS (5 kÅ).

2.2. Characterizations

The Optima^{TM} 8300 inductively coupled plasma-optical emission spectrometer (ICP-OES) equipped with segmented-array charge-coupled device detector was used to analyze the copper ion concentration. The M-2000 spectroscopic ellipsometer (JA Woollam) was used for measuring the thickness of copper oxide (Cu_2O, CuO, and $Cu(OH)_2$) in clean room of class 100. CA was measured by Ramé-Hart M500 digital goniometer carried out in an air environment at room temperature. The chemical composition of the substrate surface was analyzed by XPS with the tool of Thermo VG Scientific K-Alpha. Atomic force microscopy (AFM) was conducted in air with Auto-probe LS (Park Scientific Instruments) operating in the constant-force mode. The roughness average, 10-points mean roughness, and peak-to-valley roughness were determined using the Spiwin software.

2.3. Powders dissolution tests

Cu powders of 0.3 g weight were immersed in the etching solution with the volume of 15 ml for 30 min. The remaining solids were then filtered out. The filtrates were collected for ICP-OES analysis of dissolved copper ion concentration. Since the powders dispersed in solution were not used up, the data of ICP-OES can be employed to obtain dissolution rate. The solutions were diluted 100–10000 fold to ensure that all measured values would fall within the range of the calibration curve. The same process was repeated for powders of Cu_2O, CuO and $Cu(OH)_2$, respectively. The final copper ion concentration determined from ICP-OES is in the unit of ppb.

2.4. Etching tests of PVD Cu wafer

The etching treatment of PVD Cu wafer by $HF_{(aq)}$, $HNO_{3(aq)}$, and $TMAH_{(aq)}$ involved a short dip of 5 s at room temperature. After a quick-dipping in etching solutions, Cu wafers were shortly rinsed by DIW for 2 s to remove residues and then dried by nitrogen gas. Note that the presence of residues affects the measurements of the thickness of the oxide layer and CA. For HAc, however, Cu wafer was immersed for 5 min at 35 °C with the stirring rate of 500 rpm, then directly dried with nitrogen gas. The etched Cu wafers were subsequently subjected to the measurements of the oxide thickness and the CA. For the study of the effect of DIW rinse on the surface oxidation, the wafer after etching treatment was rinsed with DIW for 30 s and then dried by nitrogen gas.

2.5. Vacuum treatment

Some of pure Cu wafers after HAc treatment were placed in a vacuum oven for a period of time. The "vacuum treatment" was conducted at a pressure of 1–5 Torr, using a vacuum dry oven (DOV-30, Deng Yng Corp., Taipei, Taiwan) connected with ULVAC GLD-N051 rotary pump (ULVAC Inc., Tokyo, Japan). During this process, the sample was simply laid in the vacuum oven without inert gas purge and then the air was pumped out from the oven by the rotary pump at room temperature. The vacuum level can reach medium vacuum (25 to 1×10^{-3} Torr) after pumping for less than 5 min. The sample was taken out after the vacuum treatment and analyzed by CA measurement and AFM in ambient condition. No load-lock systems were used in our vacuum treatment.

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