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Metal Oxide Nano Film Characterization for CMP Optimization

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This paper focuses on the planarization of metallic films in microelectronics manufacturing by CMP through investigation of metal oxide thin films forming as a result of the chemical component of the process. Tungsten planarization is discussed as a model to establish the role of metal oxide nano-films in achieving material removal through their formation characteristics during polishing. The findings indicate a protective oxide film formation on tungsten, which tends to nucleate at high concentrations of oxidizers and enables material removal through the interaction of nano-particles in the slurry with the surface oxide hillocks.

Introduction

New generation materials introduced to the microelectronics manufacturing bring in new demands on chemical mechanical planarization (CMP) process (1). Metal CMP applications necessitate formation of a protective oxide film in the presence of surface active agents, corrosives, pH regulators etc.' to achieve global planarization (2). Chemical additives in CMP slurries result in significant changes in the mechanical properties of the surface to be polished and consequently their formation and material properties must be taken into account in the development of predictive methodologies for CMP applications. Formation and mechanical properties of the chemically modified metal oxide thin films can help predict the material removal rates as well as the probability of defect generation (3). The balance between the stresses built in the film structure versus the mechanical actions provided during CMP can be used to optimize the process variables and furthermore help define new planarization techniques for the next generation microelectronic device manufacturing (4).

The preliminary studies were conducted on the very well established tungsten films with the basic knowledge on the properties of chemically modified tungsten oxide nano films. Kaufman explained the material removal in tungsten polishing based on the formation of a protective oxide layer on the wafer surface (2), which is removed by the abrasive particles at the elevated topography of the wafers. In agreement with this proposed mechanism, Bielman showed that no material removal was obtained in the absence of an oxidizer in the polishing slurry in tungsten CMP (5). It was also demonstrated by wear experiments that, as the particles abraded this chemically modified top passivated layer, the fresh metal surface is exposed to the slurry environment and passivated immediately in a fraction of a second (6). These findings indicate the continuous formation and removal of the passivated oxide layer as an enabler of the material removal in tungsten CMP. The physical nature of the oxidized tungsten film as discussed in an earlier study (7) and its affect in material removal mechanism in tungsten CMP is discussed here to demonstrate the atomic scale removal mechanisms on the surface.

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Experimental

Tungsten test wafers with ~10000Å tungsten film deposited on a TiN/Ti adhesion layer were donated by Texas Instruments after a standard CMP was applied. For the contact angle and surface roughness analyses, 8" size wafers were cut into smallar pieces and dipped into H_2O_2 solutions as an oxidizer for 5 minutes at pH 4.0. Before dipping the samples into the oxidizer solution, all the wafer pieces were treated by dipping into a 1M KOH solution to remove the accessive surface oxide and then rinsed with DI water and dried through nitrogen gas and kept in clean petri dishes in a dessicator. All samples were characterized for contact angle responses through sessile drop method measurements using DI water droplet with a KSV ATTENSION Theta Lite Optic Contact Angle Goniometer. Five drops were measured on each sample and the results were averaged. Surface roughnesses were evaluated by Nanomagnetics Instruments Atomic Force Microscope (AFM) on 5-µm by 5-µm scans using tapping mode to protect the naturally formed oxide films from deformation during scanning. X-Ray Reflectivity (XRR) analyses were also conducted on the oxidized W wafers as a function of H_2O_2 concentration. Mass density and thickness of the oxidized layers were obtained from simulations of the (XRR) curves acquired with an Analytical XPert MRD instrument operated at a voltage and current of 45 kV and 40 mA, respectively. FTIR/ATR analyses were conducted on the polished W wafers as a function of oxidizer concentration to determine the intensity of the tungsten oxide peaks to obtain how the oxide concentration is changing by the oxidizer concentration. Polished wafer pieces were placed on the ATR crystal after they were dipped into the H_2O_2 solutions and the intensity of the tungsten oxide peaks were compared to determine the thickness relative to the XRR analyses.

Results and Discussions

Tungsten forms a protective oxide film in the CMP applications as it was shown in literature earlier (2,5,6). Electrochemical analysis indicated that the passivation takes place in sub seconds and the formed protective oxide film of tungsten is approximately 5-7 nm in thickness (8). Figure 1 illustrates the changes in XRR profiles of the tungsten surface pre and post treatment with 1M H_2O_2. It is clear that without the oxidizer, the nature of the surface cleaned in a high pH KOH solution was different as compared to the profiles obtained after dipping the cleaned surface into a 1 M oxidizer solution for five minutes. Detailed analyses by resolving the XRR data into the thickness values have shown that the surface tungsten oxide film formed gradually as a composite of W and WO_x mixture and reached a depth of approximately 10nm in total (7). Among the formed layers, only the very top 7-8 Å of pure WO_x tends to be unstable during CMP. This observation clearly underlines the need for mechanical abrasion for the removal of the remaining thickness of the oxide layer, which is accomplished by the abrasive particles of the CMP slurries. Furthermore, as it is shown in Figure 2, the surface roughness and contact angle analyses conducted on the tungsten surface as a function of dipped oxidizer concentration (0, 0.05, 0.075, 0.1, 0.5 and 1M) have shown a critical change taking place in surface topography starting at 0.075 M concentration. Above this concentration, surface oxidation occurs through formation of hillocks and a transition through a granular surface topography is observed. This is believed to be due to Ostwald ripening of the tungsten oxide crystals at the elevated oxidizer concentrations (9). This affect results in increasing surface roughness and a change in the contact angle response of the roughened surface (7).

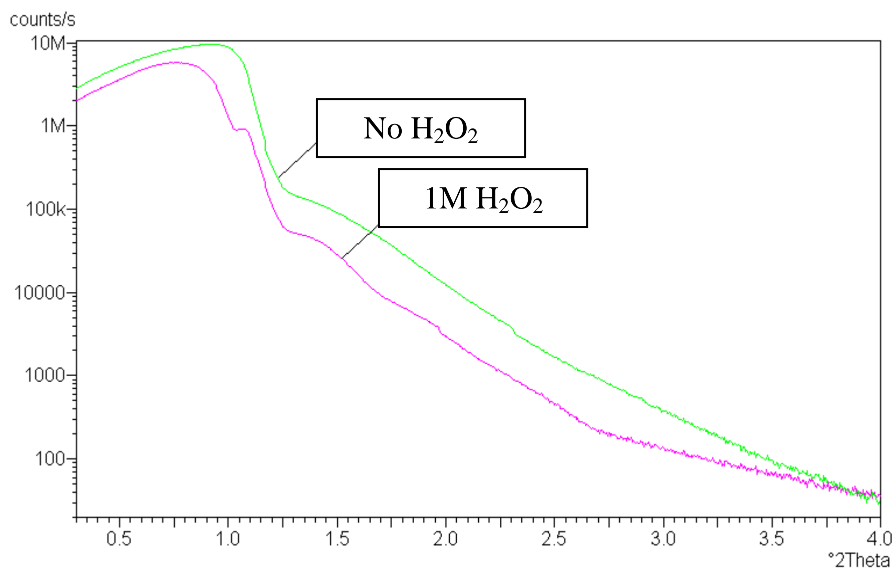

Figure 1. Changes in XRR profiles of the oxidized thin films on the tungsten surfaces between the pure KOH (1M) treated surface versus the surface treated with 1M H_2O_2 after the KOH treatment.

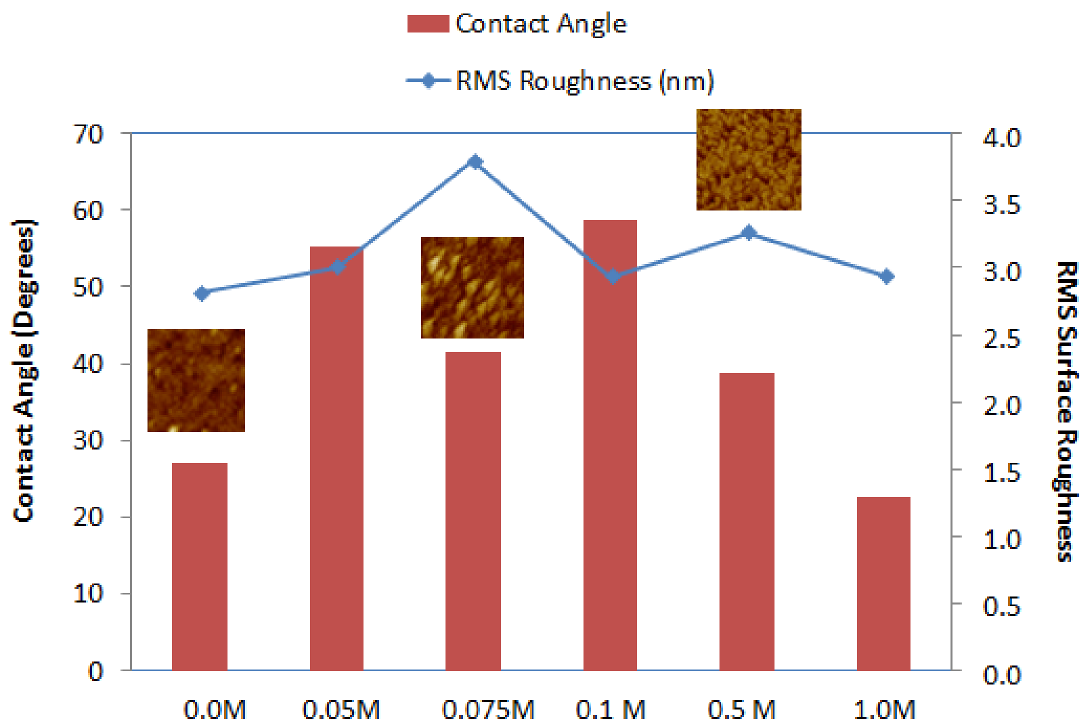

Figure 2.Contact angle versus RMS surface roughness values on the tungsten wafers dipped into the various concentrations of H_2O_2 solutions for 5 minutes. AFM micrographs illustrate the change in surface topography.

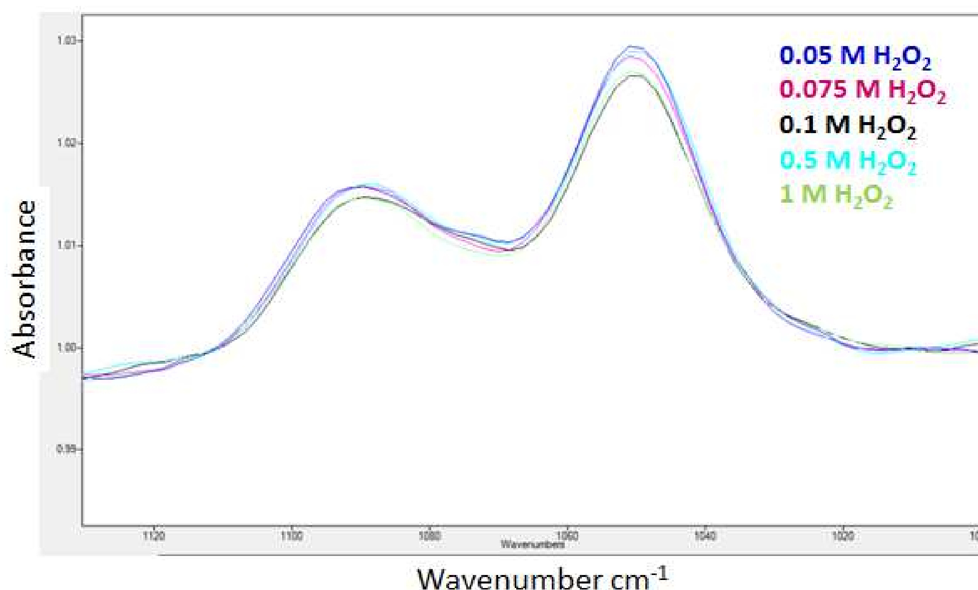

Figure 3. Intensity of the Wox peaks after the tungsten is dipped in solutions at different H_2O_2 concentrations. Peak intensities are statistically the same indicating the formation of a similar tungsten oxide film in all the conditions.

The FTIR/ATR peaks were also analyzed on the oxidized tungsten surfaces as a function of the oxidizer concentration through evaluating the peak intensity corresponding to the W-O-W bond wave number at around 900- 870 cm^{-1} and 1116-1010 cm^{-1} which are in the same range with the values reported in the literature (10). The intensities of the FTIR/ATR peaks were calculated based on the area under the absorbance versus wave number curves were found to be similar as can be seen in Figure 3. This observation was in parallel to the results of the XRR analysis indicating the oxidized layer thickness remained almost the same between 0.05 M versus 0.5 M H_2O_2 concentrations (total ~10 nm in both cases). Based on these results it can be concluded that regardless of the oxidizer concentration, a protective oxide layer forms on the tungsten surface limiting the thickness growth. However, the nature of the surface oxide film may be different which may be depending on the crystallization of the surface oxide film.

The impact of the chemical nature of the oxide film on the material removal mechanisms can be discussed based on the earlier data in the literature. It has been shown by using 0.29μm size alumina abrasive based slurry at pH 4, the material removal rate of tungsten reached a plateau at ~750 nm/min (12.5nm/sec) after 10%wt solids loading up to 15%wt solids loading(6). Therefore, the particles can be assumed to be in a hexagonal closed packed formation within the pad-wafer interface as shown earlier on the silica-silica CMP system (11). Based on the closed packing the frequency of the particle abrasion on a given spot on the wafer surface has to be equivalent to the particle diameter divided by the rotational velocity. By taking into account that only 0.33% of the pad surface is in contact with the wafer surface (11), it is predicted that an abrasion takes place every 0.65x 10^{-4} seconds. At this frequency of abrasion, if it is assumed that every single particle results in material removal, the approximate removal thickness per particle

is calculated to be 0.5 x 10^{-3} to 0.5 x 10^{-4} Å. Since this is a very small value and even a single tungsten lattice is about 7-10 Å thick, it can be concluded that only 1 in a 1000 to 10000 of the slurry particles contacting the surface can results in material removal. Hence it can be suggested that only the protruded oxide hillocks are removed by the abrasive particles during the CMP process. Since the increased oxidizer concentration results in formation of oxide columns on the surface (as shown in Figure 2), the removal rates tend to get elevated with the increased oxidizer concentrations as it is seen in the literature.

Summary

It is important to understand the chemical and mechanical nature of the CMP process to better control the process variables. This study summarizes findings on the chemically formed metal oxide thin films on tungsten wafer surfaces as a function of the oxidizer concentration. Changes in the surface roughness and topography with the oxidizer concentration and their effects on the material removal mechanisms are outlined.

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