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Nanoscratching of copper surface by CeO_2

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ABSTRACT

CeO_2 nanoparticles based slurries are widely used for chemical mechanical polishing in integrated circuit manufacturing. However, the fundamental processes of material removal and planarization remain elusive. By combining a nanoindenter system with a homemade CeO_2 tip, we investigated the nano-scratching behavior of copper film quantitatively under both constant load and ramp load modes. Based on the evolution of the coefficient of friction, the nanoscratching behavior can be divided into three regimes. For regime I, the coefficient of friction decreases sharply along with the increasing normal load and the copper undergoes mainly elastic deformation. The friction wear begins to enter regime II once the normal load reaches a critical value from where both the coefficient of friction and scratch damage begin to exhibit a changing elastic-plastic characteristic with the increasing of normal load. In regime III, the coefficient of friction reaches a steady value and becomes independent of the normal load and the deformation of copper film enters a steady elastic-plastic state. The coefficient of friction in regime I and II can be well modeled by Hertz contact theory and the classical friction models, respectively. Detailed analysis demonstrates the transition between the two models occurs when the stress concentration approaches the yield strength of copper and the material removal rate can be predicted by adjusting the parameter of the normal force and the abrasive particle size.

1. Introduction

Chemical-mechanical polishing (CMP) is a standard and ubiquitous method to get local or global planarization on wafers and thin films in IC manufacturing [1–5], such as in the fabrication of the ultra large scale integrated (ULSI) involving shallow trench isolation (STI), inter-level dielectrics (ILD), Cu interconnects, and so on. During CMP, high material removal rates (MRR) and high quality planarization are required in order to achieve a stress-free, defect-free and atomically smooth surface on the wafer. The continuous development of ULSI requires unprecedented surface quality and planarity as the feature size of electronic devices reach the level of nanometers. In order to realize the high MRR and high quality surface planarization, nanoscale particles, such as SiO_2 [6] and CeO_2 [7] are introduced as slurry abrasives. To figure out the mechanism of material removal in CMP several studies have been carried out to investigate the influence of the intrinsic properties of abrasive particles on the polishing effectiveness [8–10]. By employing the fluorescence technology, Luo et al. [11] investigated the real-time particle movement during the CMP. They found that the fixed particles with steady velocity play a leading role for the two body abrasion in CMP material removal. To some extent these results help us understand better the material removal mechanism in CMP. However, because of the wide range of control factors influencing CMP, such as the type of abrasive particles, properties of pad and wafer, chemical environment, down force and rotation speed etc. [11–14], the fundamental mechanisms of the effects of these control factors on polishing performance remains elusive, even though CMP has been extensively adopted in the industry [5,15]. The interaction between abrasive particles and the materials being polished are considered to be one of the key factors controlling the effectiveness of CMP [11–13]. In order to figure out the key parameters that control the effectiveness of CMP while at the same time without being puzzled by the many affecting factors, pure tribology studies had been carried to mimic real CMP process. In addition, the friction and wear introduced by a single particle at

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the micro- and nano-scale is interesting in its own right for fundamental research of tribology [16,17].

The atomic force microscope (AFM) is the most widely used tool for studying tribology at a fundamental level due to the single-asperity contact between the nanoscale tip and sample [18–20]. It has been employed to study the mechanism of planarization and removal of materials of the single abrasive particle in CMP through nanoscratching [21–25]. In these studies, a nanoscale tip made of silica was used to mimic the friction behavior of single silica particle on various surfaces. Due to high MRR and high selectivity (lager difference of the MRR between two kinds of materials), the CeO_2 nanoparticle based slurries are widely regarded as a typical abrasive [7] for the shallow trench isolation (STI). Methods with the aid of AFM had been also developed to study the planarization and removal of materials by CeO_2 particles. Abiade et al. [26] used a silica AFM tip to scratch the CeO_2 film in order to study the interaction between CeO_2 and silicon. Sokolov et al. [27] studied the interaction behavior of CeO_2 with silica by attaching some CeO_2 nanoparticles to AFM tips. These works advanced the understanding of the mechanism of material removal on silica surface by nanoscale CeO_2 abrasive. However, because that the CeO_2 film cannot represent the properties of the CeO_2 particle [26] and the attached nanoparticles have a great randomness of the morphology and size in polishing process [27], there is a pressing need to develop improved method to reveal the mechanism of the friction and wear by a single scratching particle in a quantitative manner.

In this work, by combining a homemade CeO_2 tip and a TriboIndenter with a 2D transducer, we are able to mimic the mechanical interaction of a single CeO_2 particle with Cu and TEOS (SiO_2) film, respectively. We found that based on the evolution of the coefficient of friction force, the nanoscratching behaviors during the two systems (CeO_2/Cu, CeO_2/SiO_2) both can be divided into three regimes. Because copper is a model material with well-established properties, in this work, we use the nanoscratching of copper film to the homemade CeO_2 tip to demonstrate our findings. The μ in regime I and regime II can be well modeled by Hertz contact theory and the classical friction models, respectively. Detailed analysis demonstrates the transition between the two models occurs when the interior stress concentration approaches the yield strength of copper. Our work is expected to improve the understanding of the mechanism of planarization and removal of material at nanoscale. In addition, the newly developed method in this study can also be employed in exploring other material systems.

2. Materials and experiment set-up

2.1. Preparation of the homemade CeO_2 tip

Preparation process of the homemade CeO_2 tip is shown in the flow diagram of Fig. 1. In order to prepare the bulk sample, the nanoscale CeO_2 particles were synthesized by hydrothermal method at 180 °C for 12 h with $Ce(NO_3)_3$ and KOH as raw materials. From the TEM image (Fig. 1b), it can be seen that the CeO_2 particles with the mean size of 20 nm have polyhedron morphology. Then the CeO_2 nanoparticles were dried and mixed with Polyvinyl Alcohol (PVA, 3%), pulverized and sieved with a 150 μm mesh. Next the green compacts of CeO_2 bulk sample with size of 10 mm in diameter and 2 mm in thickness were formed through compacting under 30 MPa for 10 min, and then the green compacts were sintered at 1200 °C for 2 h in a stainless steel mold. X-ray diffraction was used to confirm the CeO_2 phase in the sintered sample. The microstructure of sintered CeO_2 ceramic was examined by a field emission scanning electron microscope (FESEM, Model: S6600, Hitachi, Japan). As shown in Fig. 1c, micrometer-sized grains are formed in the bulk CeO_2 ceramic. Then the TriboIndenter (TI950, Hysitron, USA) was used to measure the Young's modulus, hardness and roughness of the bulk CeO_2 ceramic and copper film. The hardness of CeO_2 tip is about 7.4 GPa, which is much higher than that of the copper film (1.2 GPa). The ratio of hardness between CeO_2 and copper, i.e., H_{CeO2}/H_{cu} is about 6.2 which is much higher than the critical value (0.7–1.3) [28–30] for generating scratch damage on copper. Therefore, for limited scratching force and distance, CeO_2 tip can be regarded as a rigid particle during the nanoscratching tests.

From Fig. 1a, the sintered sample was then cut into small slices with size of 1 mm × 2 mm × 1 mm and then ground into rods with ~200 μm in diameter and ~1000 μm in length. After careful examinations, one rod was selected and further ground into needle shape with front curvature of ~30 μm. Following this first step, the larger end of the CeO_2 needle was inserted into a metal tip base and glued with organic metal glue manually. To ensure the CeO_2 rod be positioned in the central axis of the tip base, the entire manipulation process was carried out under a stereo microscope. After the glue was fully cured, the tip of the needle CeO_2 was milled into a rectangular pyramid by focused ion beam (FIB, 30 KeV, FEI, USA). By using fine ion beam, the front curvature of the CeO_2 tip can be fabricated as small as ~100 nm. In our study, three different tip radii (120, 180, 270 nm) have been used which are comparable to the particle size used for real CMP process. And one typical example with the tip radius of 180 nm is shown in Fig. 1d and e. Even though the rod used are polycrystalline materials, the top end of the tip is usually a single crystal because of its small size, comparing with the larger average grain size of ~3 μm (Fig. 1c).

2.2. The nanoscratch experiment

The nanoscratch experiment setup is shown schematically in Fig. 2a. The scratch tests were carried out in both ambient and dry atmosphere (humidity less than 5%, dry by silica gel desiccant for 12 h) by using TI 950 TriboIndenter with a 2D transducer, which can yield high precision displacement and force data in both normal and lateral directions. The copper film used in this work was deposited on a commercial blank silicon wafer with the stack of Cu/Ta/TaN/SiO_2/Si and the Cu thickness is 1.5 μm. For each data point, five repeated experiments were performed to reduce the test errors. A SEM was used to observe the scratch morphologies of copper and the CeO_2 tip after the scratch tests. Both ramp (the normal force increases from 0 at a constant rate during the whole scratch process) and constant (the normal force maintain constant during the scratch process) load modes were used. The scratch length was set to be 8 μm and the normal force ranged from 0 μN to 300 μN. As shown in Fig. 2b and c, each scratch experiment procedure of CeO_2 tip on copper film surface is composed of 3 steps. Firstly, a prescan with a constant normal force of 2 μN was performed to get the initial surface information (height and roughness) of the tested sample which will be used to correct the final scratch depth and residual depth (named tilt correction). Then, the tip turned back and scratched the copper film with 0.5 μm/s. The normal load increased from 0 to 300 μN uniformly for ramp mode and maintained a constant for constant mode. Finally, a postscan of the tip with a normal force of 2 μN was carried out to get residual depth information of the scratch.

3. Results

3.1. Variation of the scratch depth during the scratch experiment under ramp force mode

Five scratch tests were carried out in total under ramp load