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Galvanic Corrosion of TiN-W Electro-couple During Tungsten Chemical Mechanical Polishing

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Abstract: Chemical-mechanical polishing (CMP) is a process whereby mechanical and chemical forces are combined to remove material from a wafer and polish it to a flat surface. Tungsten CMP is an important process to gain the global planarity of silicon wafers with tungsten (W) plugs. Tungsten is actually deposited on a thin adhesive layer of titanium nitride (TiN) on silicon. When close to the final stage of polishing, TiN and W will be simultaneously exposed to the polishing chemistry, forming a galvanic couple. The corrosion of TiN and W couple will result in different polish rate.

This work studied the potential difference and galvanic currents on particulate contamination of the abrasive on the patterned surface and on corrosion behaviors of TiN and W. The polarization curves of TiN and W were, respectively, obtained in 0.01 mol/L KNO_3 solutions in the absence and presence of three typical oxidants (H_2O_2, KIO_3, $Fe(NO_3)_3$) by DC polarization technique. The corrosion potentials and galvanic currents were measured when TiN and W were placed in a specially designed electrochemical cell to form electro-couple. The preliminary results revealed that the corrosion rate of TiN-W electro-couple significantly increased in the presence of 4.5 % H_2O_2 at pH 4.0, while reduced to the minimal in the presence of $Fe(NO_3)_3$ at pH 1.5. Agitation significantly enhanced the corrosion rate of TiN-W couple.

Key words: Chemical mechanical polishing, Galvanic corrosion, Global planarity

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Introduction

Chemical-mechanical polishing (CMP) has become the planarization technology of choice for sub-0.5 μm devices. It can reduce interlayer alignment problems with sub-0.5 μm geometry. It can also minimize the troublesome metal thinning over steep topography that is common with old planarization techniques[1]. CMP requires the use of an applied force on the wafer, and the use of chemicals as well as abrasives in the slurry. In a typical polishing process, the wafer is mounted on a rotating carrier which is held down on a rotating polishing pad in the presence of a polishing slurry. The slurry reduces friction between the wafer and polishing pad, and promotes chemically induced erosion of the film. The slurry used to polish metal films is generally acidic in nature, and is based on alumina or silica particles dispersed in an aqueous solution. An oxidant is added to the slurry in order to provide the chemical action.

Tungsten CMP is an important process to gain the global planarity of silicon wafers with tungsten plugs[2]. Polishing of tungsten films has become a viable, low cost alternative to the formation of tungsten plugs/studs by etch back techniques. When polishing, an oxidant is added to passive the low-lying areas, while the mechanical-chemical polish removes material from the high spots. "Dishing" can be observed over tungsten plugs caused by polishing very hard to remove the TiN underlayer between the tungsten and the silicon dioxide. Particle contamination can be minimized in the tungsten plug polishing by keeping the pH high.

The goal of this work is to study the effect of the potential difference of TiN-W on particulate contamination of the abrasive on the patterned surface and on corrosion behavior of TiN and W so that a particle-free surface with no dishing of tungsten can be produced.

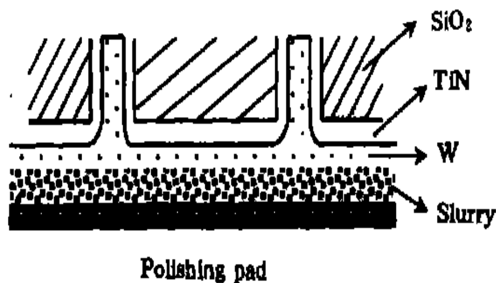

Fig. 1 A schematic representation of the tungsten chemical-mechanical polishing (CMP) process

Experimental

The testing samples, obtained from Texas Instruments Inc., were patterned silicon wafers on which the thicknesses of TiN and W coatings were a few nanometers. The DC polarization measurements were carried out in a conventional 3-electrode cell. The exposed area was fixed at 1 cm^2. The counter and reference electrodes were platinum foil and double junction Ag/AgCl electrode. The chemicals used were of semiconductor grade. An EG&G Model 273A Potentiostat, operated by a PC computer, was used for the polarization tests. All measurements were performed at 25 ±0.05 ℃ with a room light being turned on.

Results and Discussion

The tungsten CMP process is schematically shown in Fig. 1. Tungsten is actually deposited

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on a thin adhesive layer of TiN on silicon. A wafer is placed face-down on a polishing pad containing a slurry of abrasive particles in a liquid medium. The objective of the CMP is to polish the wafer until it is flat and a particular insulator thickness or metal-insulator junction has been reached. However, when close to the final stage of polishing, TiN and W will be simultaneously exposed to the polishing chemistry, forming a galvanic couple, causes different polishing rate, as clearly illustrated in Fig. 2.

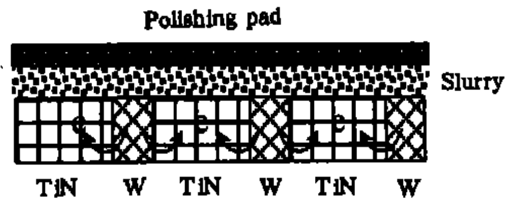

Fig. 2　Electro-coupling formed between TiN and W during the final stage of tungsten CMP process

The electrochemical measurements were then conducted to obtain polarization curves in the absence and presence of various oxidants in 0.01 mol/L KNO_3 solutions, the results are provided in Fig. 3. It is apparent that the open-circuit potentials of TiN were more positive than those of

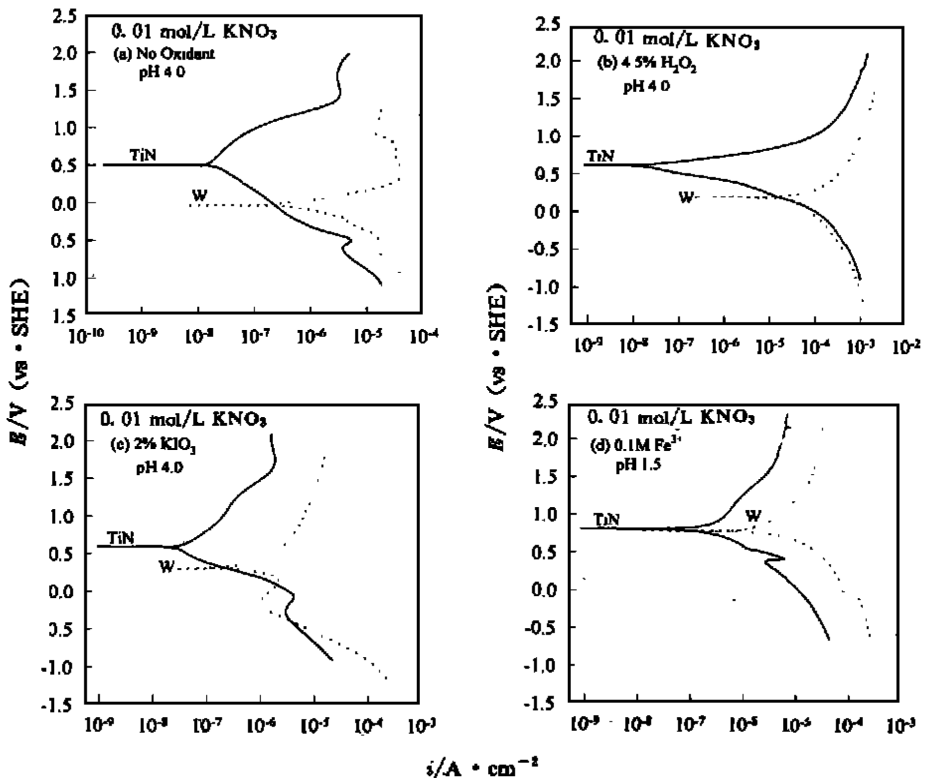

Fig. 3　Typical polarization curves of TiN and W in the absence and presence of various oxidants in 0.01 mol/L KNO_3 solutions

(a) No oxidant　(b) 4.5 % H_2O_2　(c) 2 % KIO_3　(d) 0.1 mol/L $Fe(NO_3)_3$ (pH 1.5)

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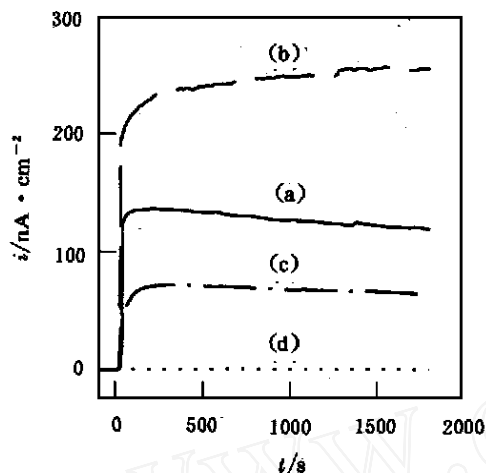
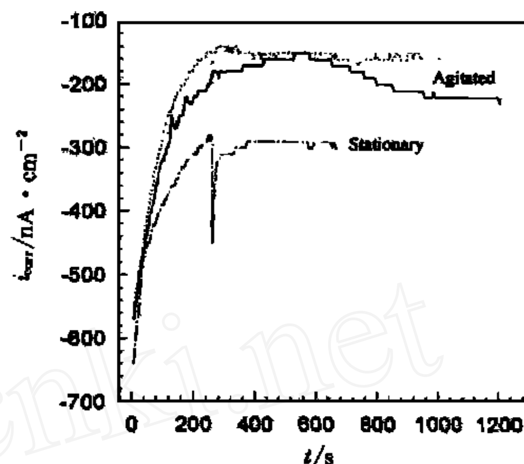


Fig. 4 Galvanic currents between TiN and W measured in 0.01 mol/L KNO_3 solutions at pH 4.0

(a) No oxidant (b) 4.5 % H_2O_2 (c) 2 % KIO_3 (d) 0.1 mol/L $Fe(NO_3)_3$ (pH 1.5)



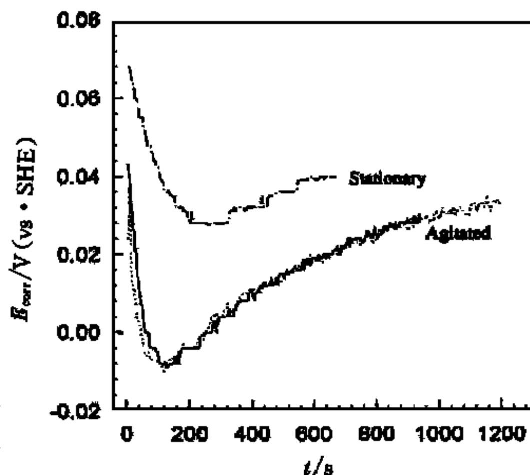


Fig. 5 Galvanic currents and corrosion potentials measured between TiN and W in 0.01 mol/L KNO_3 solution at pH 4.0 under stationary and agitated conditions

(a) galvanic currents (b) corrosion potentials

tungsten and the corrosion rates of tungsten were faster as well. In the absence of oxidants, the anodic curves of TiN and W appeared activation-passivation behavior similar to iron corrosion, as evident in Fig. 3(a). In the presence of H_2O_2 (Fig. 3(b)), the polarization curves of both TiN and W exhibited similar anodic and cathodic behaviors, implying that the reactions occurred at the surfaces of TiN and W were corresponding to redox reactions of H_2O_2. In the presence of 2 % KIO_3, similar cathodic behaviors were observed for TiN and W, while their anodic behaviors were different as can be seen in Fig. 3(c). In Fig. 3(d), the open-circuit potentials of TiN and W were very close, and their polarization behaviors also appeared to be similar.

The current and potential at the intersections of anodic curve of W and cathodic curve of TiN indicate the corrosion tendency when TiN and W are in touch with each other. The galvanic currents were then measured with the cell by replacing the platinum counter electrode with another working electrode, so that both working and counter electrodes were TiN and W, respectively, but the reference electrode remained unchanged. The results are present in Fig. 4.

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It is evident from Fig. 4 that the galvanic currents measured in the presence of 4.5 % H_2O_2 were quite large and increased with an increase of time, while those in the presence of 0.1 mol/L $Fe(NO_3)_3$ were very small (near zero). These results agreed well with those obtained by polarization measurements, as discussed previously.

As shown in Fig. 2, at the final stage of W CMP polishing, TiN and W will be simultaneously exposed to the polishing chemistry, forming a galvanic couple. Electrochemical cells can be set up between TiN and W, where TiN behaves as a cathode, while W as an anode. In this case the area of TiN is much larger than that of W, forming harmful "small anode larger cathode" situation, resulting in severe corrosion behavior and causing an increase in the polishing rate of W and a decrease in the polishing rate of TiN. Therefore, the microroughness of the patterned wafer will be increased.

Fig. 5 shows galvanic currents and corrosion potentials measured between TiN and W obtained under stationary and agitated conditions in 0.01 mol/L KNO_3 solutions at pH 4.0. The galvanic currents became more anodic when TiN and W formed electro-couple. The potentials, however, dropped rapidly at the beginning then increased after 100～200 seconds of galvanic contacts. It is apparent that the values of i_{corr} and E_{corr} were larger under agitation. This suggests that the galvanic interaction between TiN and W is greatly enhanced under agitation when they form electro-couple. In W CMP process, the mechanical force is applied, the polishing pad is under rotating condition. Therefore, the corrosion tendency of TiN and W electro-couple in a real CMP process is much larger than what can be observed in laboratory tests.

Summary and Conclusion

In this work, the polarization curves of TiN and W were, respectively, obtained in 0.01 mol/L KNO_3 solutions in the absence and presence of various oxidants. The preliminary results revealed that the corrosion rate of TiN-W electro-couple significantly increased in the presence of 4.5 % H_2O_2 at pH 4.0, while reduced to the minimal in the presence of $Fe(NO_3)_3$ at pH 1.5. It is confirmed that the polishing chemistry plays an important role in W CMP process, accordingly, the global planarity of silicon wafers will be detrimentally influenced. The corrosion tendency of TiN and W electro-couple in a real CMP process is expected to be much larger than what can be observed in laboratory tests.

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钨的化学机械抛光过程中 TiN-W 电偶的腐蚀行为

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摘要: 化学机械抛光(CMP)技术是同时利用化学和机械作用来获得固体表面亚微米尺度上平整性非常有效的方法 ,从 90 年代初期起已成为制备高质量镜头和镜面及集成电路制造过程中硅片表面预处理工艺中最常用的技术之一. 钨的化学机械抛光是用钨坯获得硅片球面平整度的重要工艺. 其过程实际上是先将钨沉积到硅上已有的薄粘附层 - 氮化钛上 ,然后进行化学机械抛光. 当抛光阶段接近终了时 ,氮化钛和钨表面将同时暴露在化学抛光液中形成电偶对 ,并在界面上发生腐蚀行为 ,从而影响硅片的球面平整度 ,降低半导体器件的性能与可靠性.

本文通过采用电化学直流极化技术 ,分别获得钨与氮化钛在 0.01 mol/L KNO_3 溶液中或含有三种典型的研磨剂(H_2O_2 , KIO_3 , $Fe(NO_3)_3$)溶液中的极化曲线 ,同时设计了一种特殊的电解槽以测量钨和氮化钛之间相互作用的电流 ,初步研究了 patterned 硅片上钨和氮化钛界面形成电偶对时的腐蚀行为. 根据所测的钨和氮化钛电位可知 ,当钨和氮化钛表面同时暴露在抛光液中时将形成电偶对 ,氮化钛成为阴极 ,钨为阳极 ,并于界面发生电化学反应 ,表面的不均匀腐蚀将造成硅片平整度的降低. 结果表明 ,当溶液中含有 H_2O_2 时钨和氮化钛界面的腐蚀速度最大 ,而当溶液中含有 $Fe(NO_3)_3$ 时的钨和氮化钛界面则几乎不发生腐蚀. 搅拌条件下测得的钨和氮化钛之间相互作用的腐蚀电流要比静止条件下测得的大.

关键词: 化学机械抛光 ,电化腐蚀 ,球面平整度

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