Electrochemical investigations on the corrosion and inhibition during W post-CMP cleaning

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INTRODUCTION

Tungsten (W) is a widely used transition metal as contact via/plug for intermetallic lines in microelectronic devices [1]. The chemical mechanical planarization (CMP) of W leaves various contaminants on the surface of wafers which includes slurry particles, organic residues, metal contaminants, *etc.* [2]. These contaminants are cleaned from the surface during the post-CMP process and it is usually performed with the help of a PVA brush in advanced technology nodes to improve the cleaning efficiency. Alkaline cleaning solutions have natural cleaning properties for removing slurry particles and adsorbed particulates during the post-CMP cleaning process. In conventional technology devices, ammonia cleaning and DHF cleaning are used for W post-CMP cleaning process. However, W plugs undergo accelerated corrosion in alkaline media, and this restricts the commonly used ammonia-based cleaning solutions for advanced node devices with less than 10 nm technology [3]. The W post-CMP cleaning solution for the advanced devices requires superior cleaning efficiency in the removal of metal contaminants, slurry particles, and organic residues with negligible corrosion of metallic parts. Active and galvanic corrosion during post-CMP cleaning is one of the critical problems that reduce the yield in semiconductor device fabrication. In this work, the galvanic corrosion between W and TiN under various conditions is evaluated and reduced with the addition of a combination of corrosion inhibitor and chelating agent.

BACKGROUND

Galvanic corrosion occurs when two dissimilar materials are in contact with each other in a corrosive environment [4]. Ti/TiN materials are usually used as the barrier material for W plug to improve the adhesion of W and reduce the diffusion of W, into the dielectric material. Hence, the bi-metallic junction is exposed to the corrosive environment during CMP and post-CMP processes and it is susceptible to galvanic corrosion [3, 5]. Depending on the potential of W and Ti/TiN in the solution, galvanic corrosion can occur to W or TiN, and it can lead to either W recess formation or fang formation. The material with lower potential acts as the anode and undergoes galvanic corrosion and the material with higher potential acts as the cathode and is protected galvanically from corrosion. Electrochemical experiments such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are primarily used to evaluate the corrosion and inhibition phenomena under conditions similar to post-CMP cleaning.

EXPERIMENTAL

To estimate the galvanic corrosion current (i_{gc}), electrochemical experiments were performed with CVD-coated W and PVD-coated TiN coupons of sizes 2×2 cm (~3000 Å thickness: supplied by BASF, Republic of Korea). W and TiN coupons were pretreated with 2 wt% NH_4OH and DHF respectively for 1 min before experimenting. A conventional 3-electrode arrangement with W/TiN was used as the working electrode, Ag/AgCl in saturated KCl as the reference electrode, and Pt mesh as the counter electrode was used to perform the electrochemical experiments. The schematic representation of the conventional electrochemical cell is shown in Fig. 1a. The PP experiments were performed for both W and TiN at different pH conditions to evaluate the galvanic corrosion between them. To acquire the polarization data, the potential was scanned over a range of ±250 mV above and below the open circuit potential (OCP) with a scan rate of 1 mV s^{-1}. Before each polarization experiment, the OCP was allowed to stabilize for 300 seconds. The direct measurement of i_{gc} with time was obtained with the help of a 2-electrode cell arrangement as shown in Fig. 1b. In all electrochemical experiments, 0.1 M $NaClO_4$ was used as the supporting electrolyte to reduce the solution resistance.
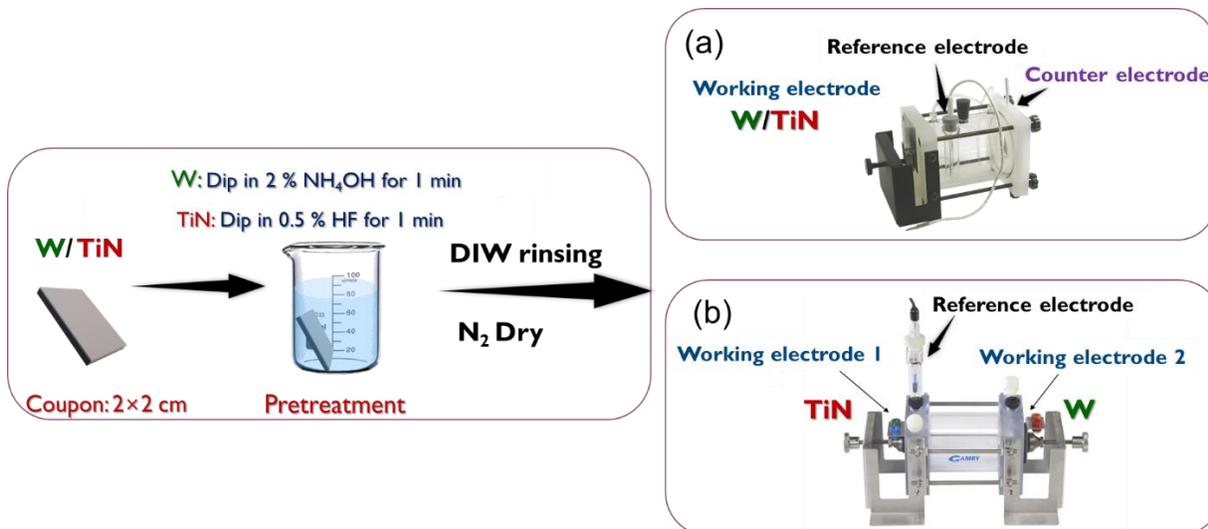
Fig. 1 Experimental setup used to perform electrochemical experiments. (a) conventional 3-electrode cell and (b) 2-electrode cell

DISCUSSION

The PP curves of both W and TiN obtained at different pH conditions are shown in Fig. 2. The polarization current of W increases with the increase in pH of the solution due to the active OH$^-$ assisted active dissolution of W. However, the polarization current of TiN changes very little with pH and remains low due to the passivation of the surface with the protective oxide layer. In Fig. 2, the i_{gc} was estimated from the intersection of the anodic and cathodic branches of both the materials as shown in Fig. 2.
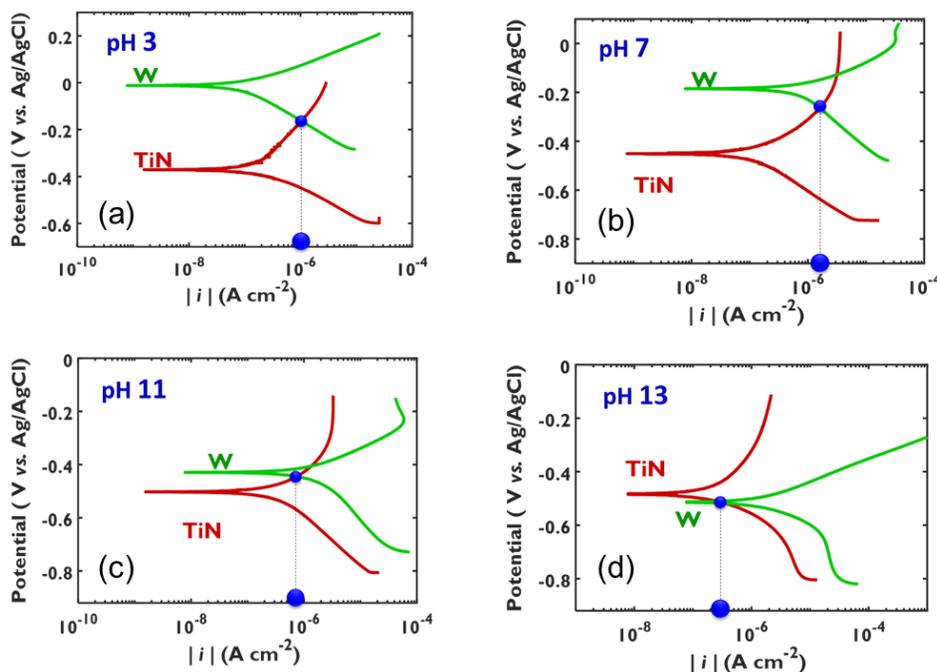
Fig. 2 Potentiodynamic polarization curves of W and TiN at various pH. (a) pH 3, (b) pH 7, (c) pH 11, and (d) pH 13. Markers represent the i_{gc}

In general, the i_{gc} increases as the potential difference (ΔE) between W and TiN increases. However, i_{gc} also strongly depends on the polarization currents of both materials. The maximum i_{gc} occurs when the ΔE is maximum with high polarization currents for both W and TiN. This implies that the i_{gc} can be low even if the ΔE is high where the polarization currents are low. Inversely, the i_{gc} can be high even if the ΔE is low

where the polarization currents are high.

The ΔE and i_{gc} estimated from the polarization curves at different pH values are shown in Fig. 3a and 3b respectively. The positive value of the ΔE indicates that W acts as the cathode and TiN acts as the anode and Fig. 3a shows that the ΔE decreases with the increase in pH from 3 to 11, whereas at pH 13, ΔE is negative indicating W as the anode. Nevertheless, the magnitude of the ΔE is the least at pH 13. The i_{gc} estimated from the polarization data, as shown in Fig. 3b, indicates that the maximum galvanic corrosion occurs at pH 7 and the minimum occurs at pH 11. Although the ΔE is maximum at pH 3, the low polarization current of both W and TiN resulted in a moderate i_{gc} value of 1.04 $\mu A/cm^{-2}$. On the other hand, the low ΔE at pH 11 resulted in a low i_{gc} value, even though the polarization current of W is maximum at pH 11. At pH 7, the moderate value of ΔE and polarization current of W together resulted in the maximum i_{gc}. At pH 13, a very low value of i_{gc} was obtained due to the small ΔE value. Although the i_{gc} estimated from the polarization plots gives an average estimation of the galvanic current, this method has limitations especially when the galvanic corrosion changes significantly with time and the entire process time is very short. The post-CMP cleaning process is usually performed over a short period (~1 to 2 min), hence the measurement of the variation of i_{gc} with time is critical in the post-CMP cleaning process.
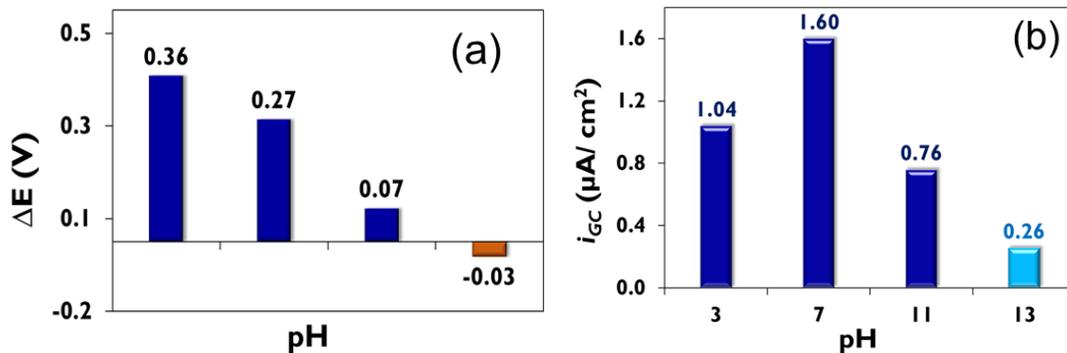
Fig. 3 (a) ΔE and (b) i_{gc} at different pH, estimated from polarization data as shown in Fig. 2

The variation of i_{gc} with time (300 seconds) at different pH of the solution is shown in Fig. 4. The large markers shown in Fig. 4 represent the i_{gc} estimated based on the polarization data of both W and TiN as shown in Fig. 3b. In Fig. 4, a positive current value indicates the galvanic corrosion of TiN and a negative current indicates the galvanic corrosion of W. From pH 3 to 11, the galvanic corrosion of TiN occurs throughout the measurement time. At pH 3, the i_{gc} is low and remains more or less the same with time, whereas at pH 11, the i_{gc} is significantly high at the beginning of the process and decreases fast, and finally saturates at a lower value. However, the i_{gc} at pH 7 starts at a moderate value, decreases slowly, and saturates. In the case of pH 13, up to 60 to 70 seconds, galvanic corrosion of TiN occurs followed by the galvanic corrosion of W. However, the i_{gc} remains low throughout the measurement time at pH 13.
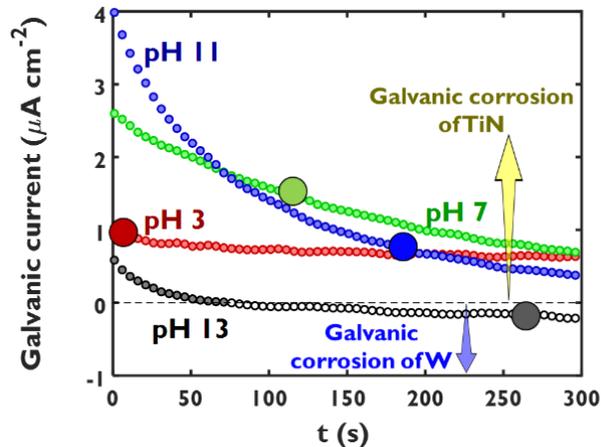
Fig. 4 Variation of i_{gc} as a function of time at different pH. Markers represent the i_{gc} from Fig. 1b.

Significant i_{gc} was observed at pH 7 and 11, and the effect of additives on the reduction of i_{gc} at pH 7 is shown in Fig. 5. The additives used to reduce the i_{gc} comprise corrosion inhibitors and chelating agents. Figure 5a shows that the ΔE reduces from 270 to ~0 mV and the polarization current of W decreases due to corrosion inhibition of the W surface. Hence, a very low value of i_{gc} is expected, but it can not be determined accurately from the polarization plots. However, the 2-electrode measurement with the additives, as shown in Fig. 5b clearly shows a very low value of i_{gc} throughout the measurement time. This indicates that the galvanic corrosion between W and TiN can be controlled by the proper combination of additives in the cleaning solution.
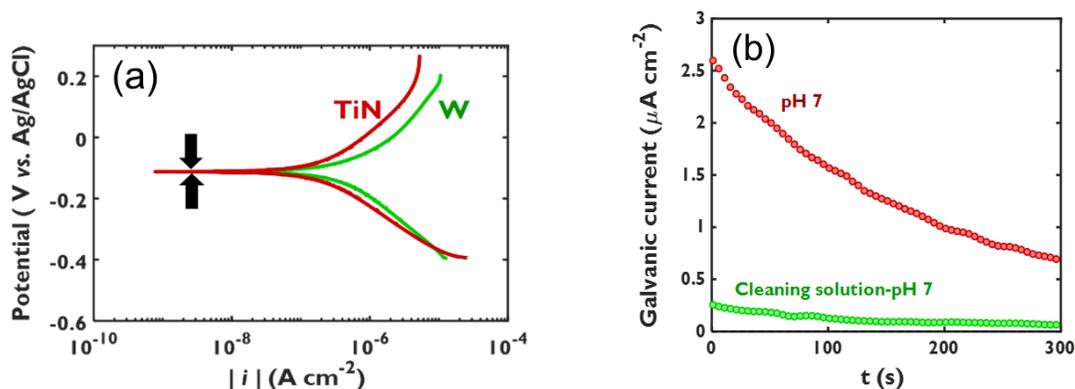
Fig. 5 Reduction of i_{gc} with the additive at pH 7. (a) polarization measurement from conventional 3-electrode cell and (b) direct measurement of i_{gc} from 2-electrode cell

CONCLUSIONS

The galvanic corrosion between W and TiN at different pH conditions was studied by using electrochemical measurements. The conventional polarization measurements showed that TiN undergoes galvanic corrosion from pH 3 to 11 and the maximum i_{gc} was observed at pH 7. It also showed that W undergoes galvanic corrosion at pH 13. The continuous variation of i_{gc} with time was measured with the help of a 2-electrode cell arrangement and significant i_{gc} was observed at pH 7 and 11. In the case of pH 13, galvanic corrosion of TiN occurs at the beginning of the process and later W becomes the anode and undergoes galvanic corrosion. The addition of corrosion inhibitor and chelating agent reduces the galvanic corrosion and it was verified with both conventional polarization and 2-electrode cell measurements.

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