

Tribocorrosion of Tungsten: Effect of Potential on Wear

Chemical-mechanical polishing (CMP) is an industrial established method for planarizing different metal layers constituting integrated circuit. Material removal in CMP can be described as a tribocorrosion phenomenon involving mechanical and chemical interactions among the wafer, pad and slurry. These interactions are complex and at present little understood. There is a need to identify the critical mechanisms by which the interplay of concurrent mechanical (wear) and chemical (corrosion) loading determines materials deterioration.

The aim of this work is to investigate tribocorrosion mechanisms of W as a typical microelectronics metal. Of particular interest is the effect of the electrochemical potential imposed by the oxidizing power of the slurry.

Sulphuric acid with the same pH as commercial CMP slurries was chosen as a model solution. Electrochemical and tribocorrosion techniques were used to investigate the influence of electrochemically applied potential on the corrosion and tribocorrosion behavior of tungsten.

The obtained results show that the tribocorrosion rate is critically affected by the electrochemical conditions. The mechanisms are discussed in the terms of passive film removal, repassivation and wear particles behavior.

Keywords: tribocorrosion, tungsten, CMP

1. INTRODUCTION

CMP process is a tribocorrosion process in which material interacts with chemicals, slurry components and the material removal rate results from the interaction of mechanical wear and corrosion. The term tribocorrosion designates the process of irreversible transformation of a material, which results from simultaneous physicochemical and mechanical surface interactions and takes place in a tribological contact [1].

Due to the complex chemical and electrochemical interactions the material behavior cannot be predicted on the basis of separate mechanical and chemical criteria.

The tribocorrosion behaviour of metals is generally studied [2] by using sliding wear test rigs coupled with an electrochemical control of the samples.

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The coupling of mechanical and electrochemical methods offers the possibility to carry out friction tests under well defined corrosion conditions by imposing suitable electrode potentials simulating practical oxidising powers of the solution. In addition, by measuring the current, it is possible to quantify using Faraday's law the metal loss due to corrosion process occurring during rubbing. The principle of these techniques is schematically described in Figure 1.

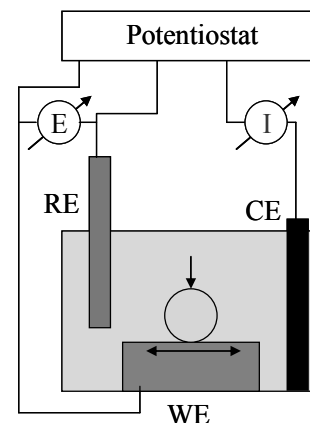


Figure 1 Schema of potentiostatic set-up for tribocorrosion experiments.

The potentiostat maintains the selected potential between working (WE) and reference (RE) electrodes by passing an appropriate current between working (WE) and counter electrodes (CE).

Bielmann [3] et al. already showed that wear of tungsten under an electrochemically imposed potential was equivalent to wear under the same potential but established by adjusting the oxidizing power of the solution.

The goal of the present work was to evaluate the effect of applied potential on the tribocorrosion behavior of tungsten as a typical microelectronics metal.

2. EXPERIMENTS

Potentiodynamic polarization curves of tungsten were measured in a 0.01M H₂SO₄ solution using an Autolab potentiostat. Electrochemical cell consisted of a stationary tungsten electrode connected to the potentiostat as a working electrode (WE). For this purpose tungsten samples of 5.3 mm diameter were embedded in an epoxy resin and polished with grit paper 600. Graphite electrodes were used as counter electrodes (CE) and the reference electrode (RE) was a mercury sulphate electrode (MSE, +658 mV vs. SHE). The potentiodynamic scan began at a cathodic potential -2 V MSE and was increased to an anodic potential of 2 V at a scan rate of 2 mV/s.

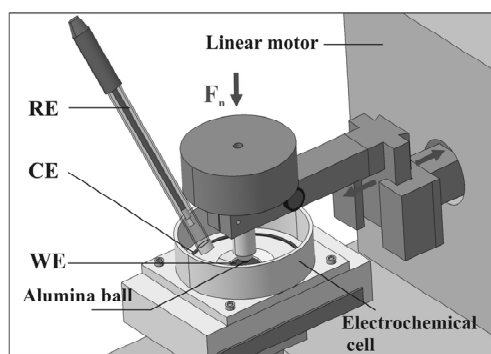


Figure 2 Schema of the tribometer for tribocorrosion experiments (tungsten working electrode (WE), reference electrode (RE), and counter electrode (CE)).

Tribocorrosion tests were performed on the tribometer, configuration ball on disk with reciprocating sliding motion, schematically shown in Figure 2.

Tungsten samples were fabricated by machining bars supplied by Good Fellow (purity 99.95 %) in form of 20 mm diameter discs, 6 mm in thickness.

A platinum wire served as the counter electrode and a mercury sulphate electrode as reference electrode.

The tungsten disc and the contacting alumina ball (6 mm diameter) were immersed in the 0.01M H₂SO₄ model. The metal sample disk to be investigated, platinum and mercury sulphate electrodes were connected to a Wenking LB 95 L Auto range Laboratory Potentiostat.

Tungsten disks were mirror polished and exposed to cathodic cleaning in the 0.01M H₂SO₄ solution during 5 min at -1.7 V MSE. Afterwards, the surface was stabilised at open circuit potential during 5 min, and passivated by applying the imposed potential during 5 min before starting rubbing at the same potential during 50 min. The rubbing was followed with static exposure of the sample surface at the imposed potential during 5 min. The tribocorrosion experiments were performed at imposed potentials of -1V, -0.46V, -0.2V, -0.1V, 0.2V, 0.5V and 1V vs. MSE selected on the polarisation curve (Figure 3).

The applied normal force was 6 N for all potentials. Frequency of rubbing cycle was 1Hz.

Each measurement was repeated two times with new alumina ball to check for reproducibility.

The width of the wear track, extracted from cross section UBM profiles, was used to determine the wear volume by assuming a circular segment shape wear profile. Secondary electron microscopy SEM (JEOL 6300) was used to characterise wear patterns.

3. RESULTS

Figure 3 shows the polarization curve of tungsten in 0.01M H₂SO₄. Except for the lowest value, all selected tribocorrosion potentials lie within the passive domain, where a passive WO₃ film forms.

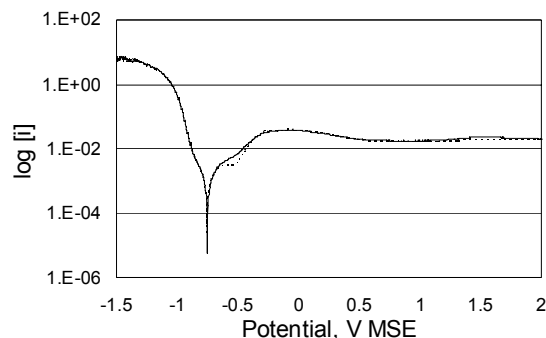


Figure 3 Tungsten polarization curve in a 0,01M H₂SO₄ solution.

Fig. 4 represents the coefficient of friction and current during rubbing at a potential of 0.2 V. At the onset of rubbing the current increased sharply due to the abrasion of the passive WO_3 film covering the tungsten surface. The repassivation of the bare metal surface requires a certain time during which corrosion (and thus anodic current) is enhanced. When rubbing ceased, the current decreased again to the value observed before rubbing. The metal volume V_{chem} removed by oxidation was calculated from the measured current using Faraday's law assuming a valence of oxidation of 6.

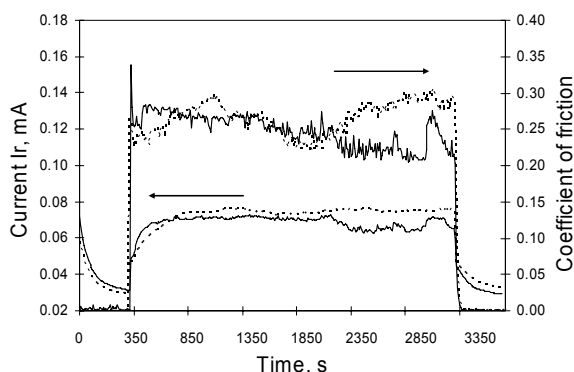


Figure 4 Evolution with time of the coefficient of friction and current during sliding of a smooth alumina ball against tungsten at passive potential 0.2 V MSE

Figure 5 illustrates the variation of the wear track volume (V_{tot}) and of V_{chem} as a function of applied potential. The comparison of V and V_{chem} indicates that most of tungsten is removed as oxidised metal (V_{chem}) and that only a part is removed as metallic debris. No significant wear of the alumina ball was observed.

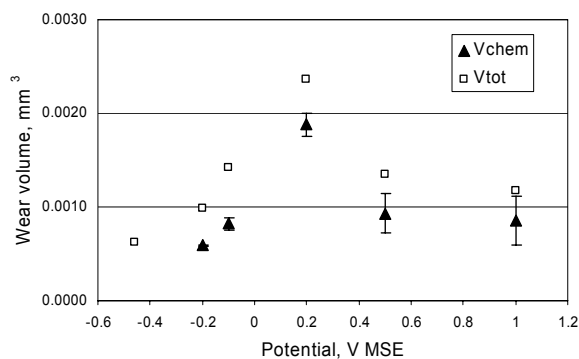


Figure 5 Effect of the applied potential on the wear volume

SEM images of the wear tracks obtained during rubbing (Fig. 6) at different imposed potentials indicate the presence of compacted wear debris.

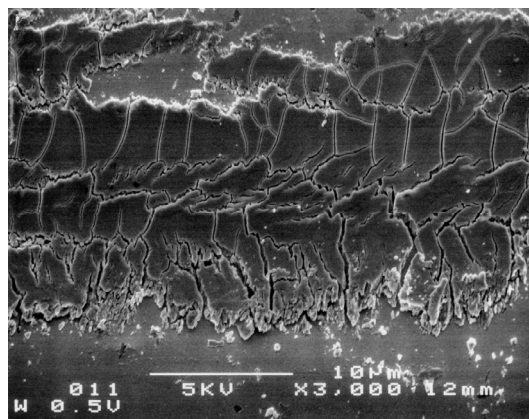


Figure 6 SEM micrograph of the wear track formed on tungsten after rubbing at applied potential of 0.5 V. Cracking of a compacted debris layer is visible.

4. DISCUSSION

Kaufman model [4] is a well accepted mechanistic view of CMP and describes the CMP process as the removal of the WO_3 passive film by mechanical action of abrasive slurry which is followed by a rapid reformation of the protective film. Cyclic removal and reformation of the passive film leads to continuous material removal.

The present results indicate that chemical wear (V_{chem}) accounts for most of the overall material removal (V_{tot}). This is in agreement with Kaufman's model, which assumes that only oxidized tungsten is removed by abrasion.

The WO_3 passive film thickness is known to increase with potential [5]. According to Kaufman's model wear is expected thus to increase steadily with increasing potential. This behavior is observed here (Figure 5) only up to a potential of 0.2 V while at higher potential lower wear values are found. The reason for this transition lies probably in different mechanical properties of the WO_3 passive film according to the prevailing potential.

5. CONCLUSIONS

The present tribocorrosion results show that the total wear rate of tungsten sliding against alumina in sulphuric acid varies with the prevailing electrode potential and goes through a maximum for a potential of 0.2 V MSE. This effect was attributed to a change in mechanical behaviour of the surface passive WO_3 film covering tungsten.

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