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鑽石修整器在化學機械拋光溶液中之腐蝕研究

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Corrosion Investigation of Diamond Disk Conditioner in the Slurry of Chemical Mechanical Polishing

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摘要

鑽石修整器應用於化學機械拋光中拋光墊的修整，已有很長的一段時間。當半導體的線寬逐年下降，相對地，在晶圓表面平整性以及拋光效率的要求更是嚴苛。然而，在化學機械拋光的過程當中，鑽石修整器扮演一個維持拋光墊工作效率的重要角色，在充滿研磨漿的環境下，鑽石修整器必須要有優良的抗腐蝕能力，以確保不因腐蝕而產生表面剝離，進而影響受拋光晶圓的平整性。

由於類鑽薄膜良好的化學鈍性及高硬度特性，因此廣泛用於保護底材的用途。在本文中，我們採用物理氣相沉積法在修整器上沉積一層類鑽薄膜並且與沒有類鑽薄膜的修整器，進行動態極化測試、交流阻抗分析以及掃描式電子顯微鏡觀察腐蝕後的表面型態。結果指出，經過動態極化測試，鍍上類鑽薄膜的鑽石修整器可得到較優良的抗蝕能力；交流阻抗分析中，可得到較大的阻抗值，腐蝕後鍍層表面型態也較完整並無明顯遭受孔蝕與鍍層剝落的跡象。

關鍵詞：腐蝕；化學機械拋光；鑽石修整器。

ABSTRACT

Diamond disk conditioners have long served the semiconductor chemical mechanical polishing (CMP) process for polish pad dressing. While the diameter of wafers has steadily increased and the lower line gap distance is developing in order to improve its efficiency, a better polish performance is our pursuing target. However, the slurry in polishing processes, which can lead not only to uniform corrosion but also to crevice attack and pitting for pad conditioners. To further improve the performance and quality of diamond disk conditioners, the corrosion

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resistance is the first consideration of dressing in the CMP corrosive slurry.

Diamond like carbon (DLC) for protecting applications were of great interest to researchers in recent years because of their excellent properties such as dielectric insulation, low friction, high wear resistance, high hardness and corrosion resistance. Improving the corrosion resistance and keeping the diamond powder working well become very challengeing when pad conditioners are immersed in a corrosive environment. In this study, DLC were deposited on the mixed surface layer of diamond powder and Ni/Cr alloy for a protective layer by physical vapor deposition. This study investigated the corrosion behavior of DLC protective layers in the slurry by electrochemical techniques, including the potentio-dynamic polarization test and electrochemical impedance spectroscopy (EIS). SEM was used to analyze the surface morphology of the conditioner after corrosion.

Keywords: Corrosion; CMP; Diamond disk conditioner.

1. Introduction

Chemical mechanical polishing (CMP) is one of the most important processes in the fabrication of integrated circuits (IC). The process contains a large number of variables and interactions, and planarisation of the wafer surface depends on variables such as the polishing pad, polishing slurry and shape of wafer (slurry, pad, conditioner, carrier film, equipment, and end-point detector)[1]. However, the polishing pad has a finite lifetime, which is dictated by falling removal rates and out of uniformity removal[2]. Maintaining the optimum polishing ability of the pad is the job of the conditioning process, which is used to regenerate the pad surface by breaking up the glazed areas. Therefore, the pad conditioning during CMP process is a necessary process for constant removal rate and good non-uniformity. Published experimental work also found that in situ conditioning was better in terms of transporting and mixing the polishing slurry[3].

CMP pad conditioners are typically made by bonding diamond grit to a flat substrate (e.g. stainless steel). During the CMP operation, diamond pullouts must be prevented as the dislodged diamond may cause severe scratches on expensive wafers. Diamond grit is bonded to the substrate by electroplating with nickel, sintering with nichrome powder, or brazing with nickel chromium alloy[4]. The CMP process is a corrosive environment, and in order to withstand the corrosive reactions, the bonding metal of the CMP pad conditioners must be anticorrosion resistant, or, it will be dissolved in the slurry that may result in contamination of the delicate circuitry. Diamond like carbon (DLC) for protecting applications were of great interest to researchers in recent years because of their excellent properties such as dielectric insulation, low friction, high wear resistance, high hardness and corrosion resistance[5~7], for example, it is used in the case of hard magnetic recording heads and disk systems as a protective layers[8]. This study is focused on the electrochemical performance of DLC coating on diamond disk by physical vapor deposition when compared with uncoated.

2. Experimental

2.1 Material preparation

CMP pad conditioners are made by bonding diamond grits to a flat stainless substrate. Diamond grits are bonded to the substrate by sintering with nichrome powder. The sintering of nichrome powder also holds diamond by mechanical entrapment. In order to prevent

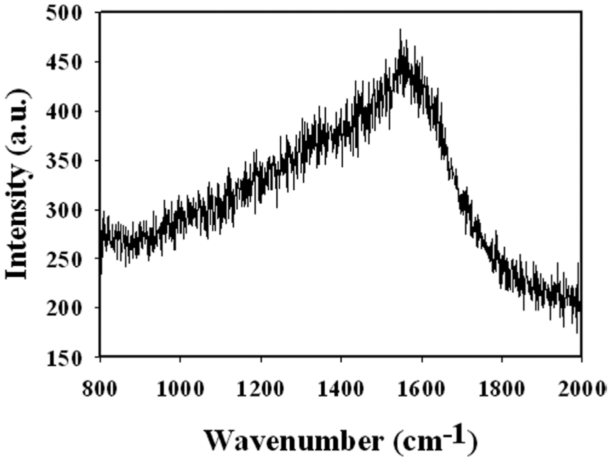

Figure 1 Raman spectra of sample A, coated DLC.

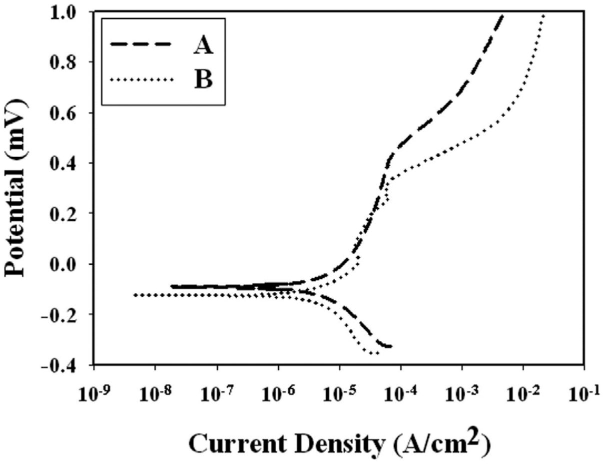

Figure 2 Potentiodynamic polarization curves of sample A (coated DLC) and B (uncoated).

diamond from falling off, a molten nickel chromium alloy is used to infiltrate the sintered matrix and to braze diamond in place. The DLC film was deposited onto the CMP pad conditioner by physical vapor deposition, and was also characterized by Raman measurement. Fig.1 shows a typical Raman spectrum of a DLC film. The Raman spectrum is characterized a clear band at approximately 1540 cm^{-1} and a broad band at approximately 1340 cm^{-1} by two Gaussian distribution functions[9]. The conditioners were coated and uncoated for sample A and B in this experiment, respectively.

2.2 Corrosion testing

Potentio-dynamic polarization test was determined with an EG&G Princeton Applied Research Model 273A potentiostat and carried out in a slurry of pH 7.7. The exposed area was 1 cm^2. Reference and counter electrodes were used for a saturated calomel electrode (SCE) and platinum, respectively. The potential of the electrode was swept at a rate of 0.166 mV/s from the initial potential of -250 mV versus E_{corr} to the final potential of 1000 mV.

Electrochemical impedance spectroscopy (EIS) has been frequently used as a non-destructive testing method for assessing the protective performance of coating. EIS has been recognized as a powerful instrument to examine the surface of the specimens. EIS data were obtained by a M5210 system for AC measurement. Impedance measurements were performed by applying a sinusoidal wave of 10 mV in amplitude to the working electrode at a frequency range from 10 kHz and 10 mHz. The conditioners were immersed in the slurry and measured once at 1, 5, 15, 30, and 50 hours of immersion, respectively.

2.3 Surface analysis

The SEM investigations were used to examine the surface morphology of the specimens after the corrosion test. The SEM investigations took place with a voltage of 20 keV.

3. Results and discussion

3.1 Potentio-dynamic measurements

In order to investigate the stability against localized corrosion of conditioners, potentio-dynamic polarization measurements were performed. Potentio-dynamic polarization curves for sample A and B are shown in Fig.2 and electrochemical parameters are presented in Table 1. It can be seen that the passive film was formed on the conditioners. Especially, sample A was well passivated, with low passive current density and wider passive potential range than sample B. The

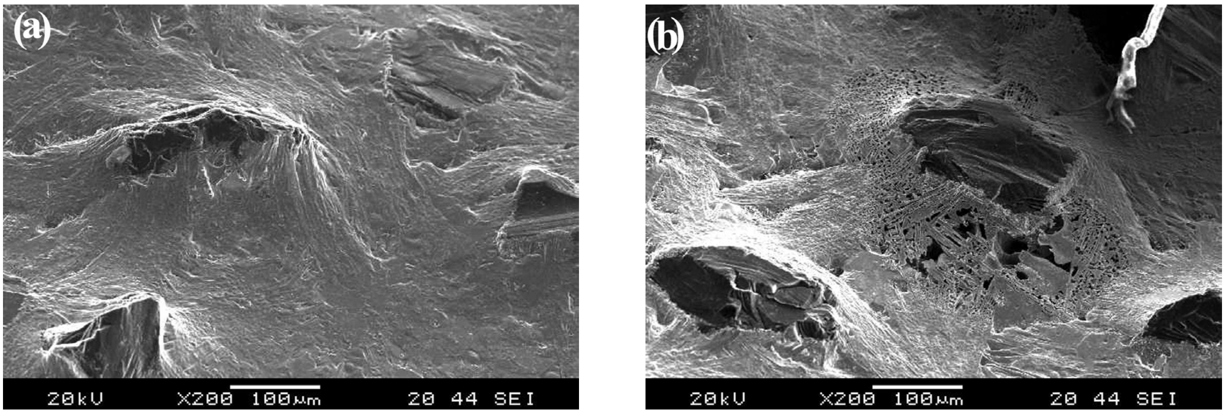

Figure 3　SEM images of (a) sample A (coated DLC) and (b) sample B (uncoated) after potentio-dynamic polarization test.

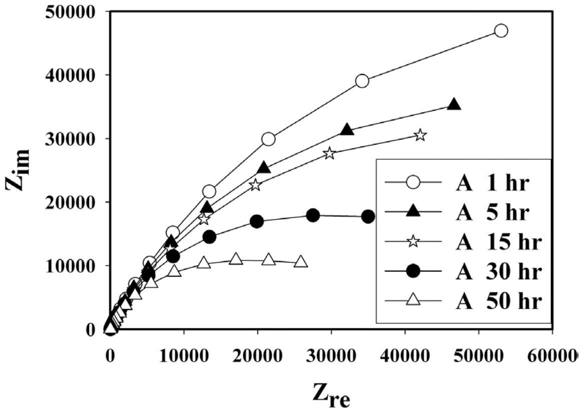

Figure 4　Nyquist plot of sample A (coated DLC) on different immersed time.

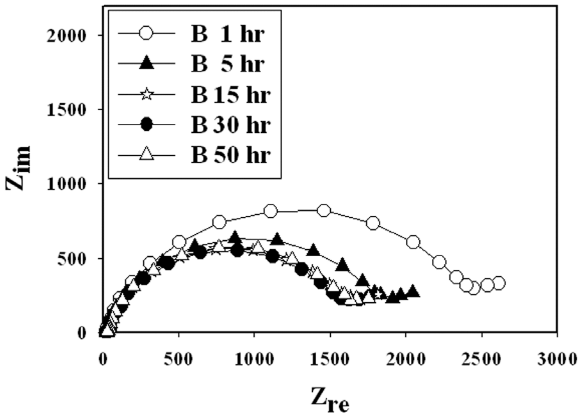

Figure 5　Nyquist plot of sample B (uncoated) on different immersed time.

corrosion current density in sample A is also lower than sample B. Although, the addition of Cr to alloys can improve the corrosion resistance of alloys in a corrosive environment due to the formation of a Cr-rich layer[10], pitting corrosion can still be seen in Fig.3b. The higher potential of corrosion (E_{corr}) in corrosion environment indicated that the material is noble, the more difficult corrosion occurs[11], the higher corrosion current density (I_{corr}) also presents higher corrosion rates[8]. Electrochemical parameters of Sample A show higher E_{corr} and lower I_{corr} than sample B, this result illustrated the good protective ability of DLC coating in the slurry environment.

Table 1　A (coated DLC) and B (uncoated) results of potentiodynamic polarization test.

	Rp (ohm)	I_{CORR}(μA)	E_{CORR}(mV)
A	7677	2.83	-90.6
B	6873	3.16	124.1

3.2 EIS measurements

EIS data from conditioners at different immersion times are shown in Fig.4, 5. These are so-call Nyquist plots which present the real and imaginary parts of the conditioner impedance as function of the applied frequency perturbation. To interpret such EIS data, an

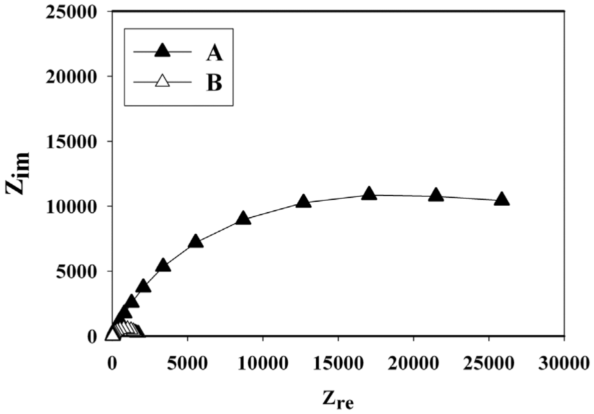

Figure 6 Nyquist plot of sample A (coated DLC) and B (uncoated) immersed 50 hour.

equivalent circuit consisting of a different type of element (e.g., resistor, capacitor, inductor, etc.) can be proposed by applying physical models descriptive of the corrosion occurring at the electrochemical interface. However, a useful way to quickly evaluate the corrosion property of conditioners is to compare the diameters of the circles which can be obtained by extrapolation of the existing part of the semicircle[12]. These circle diameters are known as the charge transfer resistance of test system[13]; thus, the bigger diameter of semicircle, the higher charge transfer resistance, and the better corrosion resistance. It is therefore clear that the sample A exhibits much better corrosion resistance than sample B. A. Zeng et al.[14] reported that the decrease in the value of resistance with immersion time, indicates the water molecules and ions would have migrated to the substrate surface. It can been seen that the decrease in diameter of semicircle of sample A depends on immersion times, but the charge transfer resistance of sample A still great higher than sample B during an immersed time of 50 hours, as shown in Fig.6. The DLC coating shows the good anti-corrosion resistance on pad conditioner which consistent with previous test.

3.3 Surface analysis

After the potentio-dynamic test, the surface morphology and corrosion features of sample A and B were inspected by SEM, the resulting micrographs are shown in Fig. 3a and b. The surface morphology of sample A almost indicated no evidence of penetration of water and ions, as shown in Fig.3a. The Fig. 3b showed the serious attack by pitting corrosion in the bonding place of diamond grid and substrate. The corroded surface morphology confirms the results from the potentio-dynamic polarization test. This clearly indicated that sample A has excellent corrosion resistance and no significant damage has been observed.

4. Conclusions

We coated the DLC film on the conditioner by PVD and compared with uncoated one using potentio-dynamic polarization test and EIS analysis. The conditioner with DLC coating showed lower corrosion current density and higher corrosion resistance, indicating better anti-corrosion ability than uncoated one. From SEM images, the pitting corrosion was found in the conditioner without DLC protected.

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