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深次微米半導體化學機械研磨技術之研究—子計畫四

低介電常數高分子介電膜之化學機械研磨特性研究（2/2）

Studies on the chemical-mechanical polishing characterization of low dielectric constant polymers

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中文摘要

本研究探討兩種低介電常數高分子材料(PAE-2 及 Flare2.0)之薄膜性質及其化學機械研磨特性。由實驗結果顯示薄膜機械性質，粉末硬度，研磨液 pH 值及界面活性劑對薄膜化學機械研磨特性有重要影響。Flare 2.0 因較 PAE-2 之擁有較剛硬結構因此研磨速率較低小。所使用 Al_2O_3 粉末硬度較 SiO_2 大而增加研磨速率。研磨液 pH 值及界面活性劑則影響粉末與高分子之接觸面及電荷吸斥力進而影響研磨速率。

關鍵詞：化學機械研磨、低介電常數高分子、研磨粉體、界面活性劑。

Abstract

In this article, the film properties and the chemical-mechanical polishing (CMP) characteristics of two different low dielectric constant poly (arylene ethers): PAE-2 and Flare 2.0 were studied. The experimental results show that the mechanical properties of polymer films, the abrasive hardness and surfactant affected significantly the CMP characteristics. The mechanical property of the PAE-2 film was inferior to the Flare 2.0 film and thus a higher polishing rate was found for the PAE-2 film than the Flare2.0 film. The order of the removal rates for both polished films was 8105 > 8104 > SS-25, which was the same trend as the hardness of the abrasive. The addition of surfactants into the slurries significantly modified the surface contact area and the electrostatic force between the abrasive and the polymer film. Therefore, the polishing rate was affected by *surfactants.*

Introduction

Low dielectric constant polymers have been studied extensively because they can minimize the propagation delay, power consumption, and cross talk. CMP is an important to integrate the low k polymers into the IC device[1-6]. Different abrasive-based slurries have been used to study the CMP characteristics of low k polymer films. However, the effects of the structure and properties of abrasives on the CMP characteristics are rarely studied. Furthermore, most of the CMP study concern about the slurry chemistry, the effect of the molecular structure of the low k polymers on the CMP characteristics requires further exploration.

Poly(arylene ethers), PAE-2 and Flare 2.0 are two potential low k materials with a similar molecular structure as shown in Figure 1. Fundamental understanding on the film properties and their CMP characteristics of these two materials is very important for integrating them into IC devices. In this study, the polymer structures and film properties of PAE-2 and Flare 2.0 were investigated first and then their CMP characteristics were studied.

Experimental

Film Processing

PAE-2 and Flare2.0 coated by the

CEE Model#100CB coater with 2000rpm 20sec and 3000rpm 20sec respectively. PAE-2 were cured at 60℃ /1min, 270℃/1min, and finally at 425℃ for 30min in 80%N_2 20%O_2 ambient. Flare2.0 were cured at 150℃/1min, 200 ℃ /1min, and 250 ℃ /1min with hot plates, and then were cured at 400℃ for 1hr with ASM/LB45 furnace both. The thickness (t) of the prepared films were measured by the Nanospec 210XP (Nanospec Inc.). FTIR spectra were measured by Bio-Rad QS300 FTIR spectrophotometer (Bio-Rad Inc). The atomic force microscope (Digital Instrument Inc.Model DI5000 AFM) was used to probe the surface morphology of the coated films.

CMP Process

The CMP experiment was carried out on a Westech Model 372M CMP Proocessor. The downforce pressure was fixed at 5 psi for studying the effects of the slurry formulations on the polishing properties. Both the carrier and table were rotated independently, the table at 20 rpm, and the carrier at 25 rpm, respectively. Three kinds of polishing slurries were used in this study: SS-25 (Cabot, Co., PH =10.9~11.20, 25.0 wt %, medium and mean particle size are 62 nm and 71 nm , respectively), 8104/H_2O (85-90% of α phase content, PH =6.74, 6 wt %, medium and mean particle size are 112 nm and 210 nm, respectively), and 8105/H_2O (90-95% of α phase content, PH =6.60, 6 wt %, medium and mean particle size are 126 nm and 181 nm, respectively).[19] The slurry SS-25 was diluted to become 6 wt % before the CMP experiment. The 8105 slurry was adjusted to be 1 wt % for the PAE-2 film and 6 wt % for the Flare 2.0 film from the consideration of film removal rate. The slurry flowing rate was 150 ml/min in this study. Two different kinds of surfactants were added to slurry to modify the contact angle between the abrasive and polymer film and also the surface charge on the abrasive. They were Triton X-100 (Aldrich, $C(CH_3)_3CH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_{10}OH$), and dodecylsulfate sodium salt(DSSS, Aldrich, 99%, $CH_3(CH_2)_{11}OSO_3Na$).

Results and discussion

The chemical structures and properties of PAE-2 and Flare2.0 films

Figure 2 illustrates the FTIR absorption spectra of the PAE-2 and Flare 2.0 films after the baking process. For both polymers, the absorption bands due to different chemical bonds can be assigned as below. The absorption bands at 1170 cm^{-1} and 1240 cm^{-1} are assigned to the C-O-C stretching vibration bands. The absorption bands at 1450 cm^{-1}, 1490 cm^{-1} and 1600 cm^{-1} are attributed from the C=C stretching vibration bands of the aromatic rings. The C-H stretching vibration bands on the aromatic rings can be observed from the absorption bands at 3020 cm^{-1} and 3040 cm^{-1} The FTIR spectrum of PAE-2 suggests that the molecular structure is aromatic rings connected by an ether linkage. However, two extra absorption bands at 1660 cm^{-1} and 1742 cm^{-1} are observed in the FTIR spectrum of Flare 2.0. These two bands are probably due to the ester or ketone linkage in the molecular structure of Flare 2.0, as shown in Figure 1. It will find out that the molecular structure difference causes a significant difference both on the film properties and CMP characteristics.

The dielectric constant measured by a MIM structure at 1 MHz was 2.51 and 2.76 for the PAE-2 and Flare2.0 films, respectively. These values are in a satisfactory agreement with data reported in the literature. Since the k values are less than 3.0 for both polymers, they can be regarded as low dielectric constant materials.

Effect of Slurry Chemistry

Figures 3 and 4 illustrate the variation of the slurry formulations on the removal rates of the polished PAE-2 and Flare 2.0 films, respectively. A few interesting features can be obtained from these two figures. The order of the removal rate for different abrasives are 8105 > 8104 > SS-25 for both polished films. Since the polymer film is inert to chemical reaction during CMP, the abrasive hardness plays a major role on removing the polymer film. Hence, the polishing result can be probably explained from the abrasive hardness. The hardness of Al_2O_3 abrasive with α phase is 9 on Mho's scale, which is higher than that of $SiO_2$with 6-7 on

Mho's sacle.[5] The 8105 abrasive has a larger portion (90-95%) of the high crystal density α phase than 8104 abrasive (85-90%). Hence, the hardness of 8105 is higher than that of 8104. Therefore, the hardness of the three studied abrasive is in the order of 8105 > 8104 > SS-25, which matches with the polishing results. Furthermore, the 8105 abrasive with the largest hardness makes it easier to polish the polymer film. Hence, the non-uniformity of the polishing films using the 8105 abrasive is only 6.6% but more than 10% by suing the other two abrasives.

The effect of the molecular structure on the CMP characteristics can be also observed from Figures 3 and 4. The removal rates of the polished PAE-2 films are higher than those of the polished Flare 2.0 films for all three slurries. The thermal stress analysis shows that the mechanical property of the PAE-2 film is inferior to that of the Flare 2.0 film and thus is easily removed by mechanical grinding. This explains the higher removal rates of the polished PAE-2 films. Since the mechanical grinding is the primary driving force for polishing the polymer film, the removal rate increases with the abrasive content. The removal rate of the polished Flare 2.0 film increased from 1985 A/min using 1 wt % of 8105 slurry to 4281 A/min using 6 wt% of 8105 abrasive. On the other hand, the polished PAE-2 film has a very high removal rate of 3850 A/min using 1 wt% of 8105 slurry. Hence, it is not surprising that the PAE-2 film was peeled off using 6 wt % of the 8105 abrasive. Figure 7 shows the AFM diagrams of the polished PAE-2 and Flare 2.0 films by using 8104 and 8105 slurries, respectively. Since polymer film is usually too soft compared with the studied abrasive, scratches were found in both polished film. The addition of lubricating chemicals,[11] abrasive with medium hardness, or using a soft pad instead of using the IC 1400 pad was a possible approach for reduced the scratches in the polished film.

Surfactants can improve the contact area between the abrasive and the hydrophobic polymer surface. From the polishing results shown in Figures 3 and 4, it is found out the removal rates is significantly improved by using Triton X-100 for all three abrasives. However, the addition of the DSSS surfactant only shows a slightly increase on the removal rates using the SS-25 abrasive and a surprising decrease for the Al_2O_3 abrasive. Hence, both surfactants improved the contact surface area between the abrasive and polymer surface, especially Triton X-100. Hence, it explains the significant increase of the removal rate by adding Triton X-100 into slurries. The decreasing removal rates of both polished films by adding DSSS into the 8104 and 8105 Al_2O_3-based slurry can be probably explained by the electrostatic interaction between the abrasive charge and the surfactant. The PH value of the 8104 and 8105 slurry by adding the DSSS surfactant was 6.34, which is smaller than the IEP value of 9.0 for Al_2O_3.[5] Hence, the Al_2O_3 is charged positive in the slurry system of Al_2O_3 /DSSS.[22] The anion ($CH_3(CH_2)_{11}OSO_3^-$) from DSSS was probably neutralized with the positive charged Al_2O_3 in the slurry and resulted in the sedimentation of Al_2O_3 abrasives. Hence, it was observed that the 8104 and 8105 abrasives were condensed from the slurry with the addition of DSSS during the experiment. Hence, the Al_2O_3 abrasive available for the mechanical polishing was reduced by adding DSSS into the 8104 and 8105 slurries and resulted in decreasing the removal rates. This result suggests that the addition of the ionic surfactant into the polishing slurry must be carefully controlled to maintain the stability of the slurry. The experimental results from the effect of the surfactant on the slurry suggest that the removal rates of the polished film can be controlled by the amount of the added surfactant and their charge status.

Conclusions

In the study, the film properties and chemical-mechanical polishing (CMP) characteristics of two different low dielectric constant poly (arylene ethers): PAE-2 and Flare 2.0 are presented. The removal rates and surface properties of the polished films were significantly affected by the following parameters: structural rigidity, different abrasives, and surfactant. The mechanical property

of the PAE-2 film was inferior to the Flare 2.0 film from their molecular structure analysis. Hence, a higher polishing rate was found for the PAE-2 film than that of the Flare 2.0 film. The order of the removal rates for both polished film was 8105 > 8104 > SS-25, which was the same trend as the hardness of the abrasive. The addition of the nonionic surfactant Triton X-100 into the slurries largely decreased the contact angle between the abrasive and the polymer film and thus the removal rate was enhanced. The experimental results suggest that the removal rates of the polished film can be controlled by the amount of the added surfactant and their charge status.

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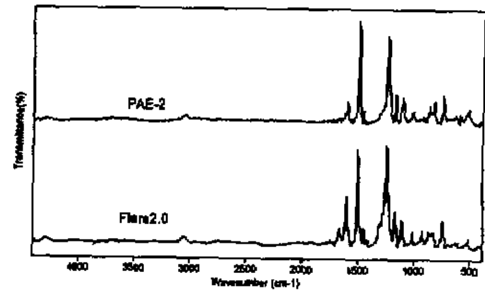

Fig.2 The FTIR spectra of PAE-2 and Flare2.0

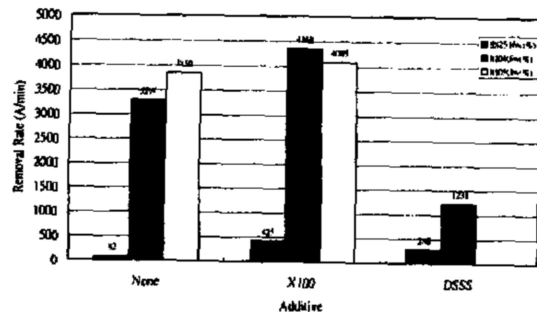

Fig.3 Variation of removal rate on the polished PAE-2 film using SS-25, 8104, and 8105 slurries with different additives

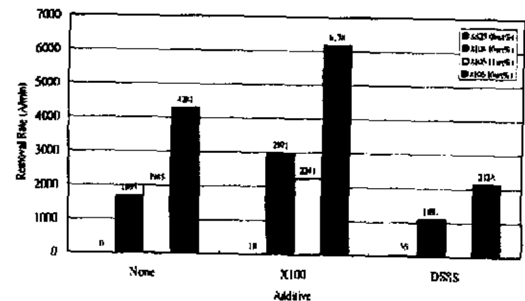

Fig.4 Variation of removal rate on the polished Flare2.0 film using SS-25, A8104, and 8105 slurries with different additives

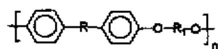

Fig.1 The chemical structures of PAE-2 and Flare2.0