出國報告（出國類別：參加學術會議）

The 6th International Conference on Technological Advances of Thin Films & Surface Coatings

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摘要

薄膜表面塗層技術進展國際會議是一個知識的交流和互動的平台，從工業，研究實驗室和學術界的研究人員和工程師的一年兩次的事件。薄膜 2012 年是本系列的第六屆。會議的主要目的是進一步推動薄膜和表面塗層中的應用以及其相關领域的技術發展，加强該领域海内外專家學者的交流與合作。本人很榮興得到學校之機票補助，能參與此活動，並將本人的研究成果發表給學術界的研究人員分享，並與一些研究學者作一些交流。

目錄

一. 目的

參加薄膜表面塗層技術進展國際會議(The 6th International Conference on Technological Advances of Thin Films & Surface Coatings) 主要目的為將本人的研究成果發表於此會議上,並與研究實驗室和學術界的研究人員和工程師作一交流，同時吸取新知，冀能對自己未來之研究有所助益。

二. 參加會議過程

大會議程從 7 月 14 日到 7 月 17 日共有 4 天，第一天為註冊日 (Registration)，並無安排任何議程。第二天早上為開幕典禮(Welcome Reception)與請一些學者作專題演講，第二天下午至第四天為論文發表議程，每個時段皆有 6 個部門(sections)同時進行。筆者於 7 月 14 日早上約 7:30 搭乘長榮飛機到新加坡，約 12:00 到達新加坡機場，並搭車至飯店後便到會場辦理註冊，隔天並參加了開幕典禮與聽了幾場學者專家的專題演講。下午便是各部門的論文發表，筆者也參加了幾場有興趣的主題去聆聽。傍晚 5:30 是海報展示時間，筆者有一篇論文在此海報時段發表，題目為" Impact of Plasma treatment on Structure and Electrical Properties of Porous Low Dielectric Constant SiCOH Material"，期間有些外國學者與筆者討論我的研究論文，同時也遇到幾位台灣的教授，互相交流並且互換名片，並期許有機會可一起在研究上合作。第三天也再至會場聆聽一些口頭報告並參與傍晚的海報發表，當天晚上是會晚宴時間，在席間與本校陳素霞老師同桌，其餘皆是大陸的教授，除了在研究上互相交流外，同時對於大陸與台灣高等教育的發展也作了一些了解。由於經費及時間的緣故，第四天的議程就沒再參加，就搭機回台了。

在會議期間，本人也抽空至新加坡管理學院及理工大學一遊，並至新加坡一些景點作參觀，於 7 月 17 日結束此次之行程。

三. 與會心得與建議

此次研討會其收集了膜和表面塗層中的應用以及其相關领域近 200 篇的各式論文，也見識到國際上各國學生的研究水準，深感自己的研究內容應該要再多充實與創意，回國後對研究生之研究與國際化，期許能答到相同之程度，有朝一日自己指導的學生也能親自參加這種國際會議必上台報告。

本次會議的研究主題，TiO_2 以及 ZnO_2 的材料主題最多，代表其具有研究發展之潛力，這也給了我一些想法，可朝向這些的研究主題在作深入的研究。同時本人目前的研究主題高介電材料 HfO_2，仍有一些人在研究，這也代表不管研究題目如何，只要有好的想法與創意，仍可創造出不錯的成果。

綜觀此次研討會，台灣參加的人數及發表的數量頗多，但對岸大陸參加人數以及發表的數量也不惶多讓，雖然內容或研究深度參差不齊，但少數研究也具有不錯之水準，這股力量與代表之意義，值得我們學習與警惕。

能夠有幸與會著實獲益良多，對本人未來研究更能夠有進一步的啟發。

四. 附錄

附錄 1 發表論文之全文

Impact of Plasma treatment on Structure and Electrical Properties of Porous Low Dielectric Constant SiCOH Material

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Abstract

Porous low dielectric (low-*k*) films are needed for advanced technologies to improve signal propagation. The integration of porous low-*k* films faces more severe challenges due to the presence of porosity. Plasma treatments have been considered to be critical steps to impact the low-*k* films' properties. In this study, the effect of various H_2/He plasma treatments on the porous low-*k* dielectrics deposited by plasma enhanced chemical vapor deposition was investigated. All the plasma treatments resulted in the formation of a thin and dense layer on the surface of the porous low-*k* films. Additionally, the properties of this top dense layer are modified and changed for the standard H_2/He plasma treatment, leading to a degraded electrical and reliability performance. However, H_2/He plasma-treated low-*k* dielectric by the remote plasma method shows a better electrical and reliability performance. As a result, the remote plasma treatment on the porous low-*k* dielectrics appears to be a promising method in the future interlayer dielectrics application.

Keywords: Low-*k* dielectric, H_2/He, Plasma, Remote plasma, Reliability, Breakdown.

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Introduction

As feature sizes of integrated circuits continuously shrink to sub-micro, interconnect resistance-capacitance (RC) delay begins to dominate overall device speed in copper (Cu)/ low dielectric (low-*k*) metallization. To decrease RC delay time, interconnection resistance has been reduced using Cu instead of aluminum while interlayer capacitance has been lowered by replacing conventional silicon dioxide (k~4.0) with low-*k* materials ($k < 4.0$) [1-3].

For low-*k* materials, they should introduce the porosity within the film in order to reduce the permittivity below 2.5 [4,5]. However, the porous low-*k* materials would suffer multiple challenges to their integration in the damascene interconnects either due to their mechanical weakness or the degradation during integration [6]. Additionally, in the integration process, the plasma treatments are indispensible step, and are thought to be one of the most critical step in regarding to the modification of the porous material [7,8].

Before Cu barrier layer was deposited, H_2/He plasma treatment was commonly used to reduce CuO_x layer [9,10]. At the same time, this plasma treatment was also performed on the neighboring low-*k* materials. Understanding of the plasma damage mechanism on the low-*k* materials is therefore one of the key factors for interconnects integration. This work investigates the impact of the various H_2/He plasma treatments on the physical, electrical properties, and reliability of the porous low-*k* film. The dielectric reliabilities and the integrated interline electromigration (EM) are also examined.

Experimental details

The as-deposited porous low-*k* material is a SiCOH film, deposited on a p-type (100) silicon substrates by plasma enhanced chemical vapor deposition (PECVD). The porous low-*k* films were deposited from diethoxymethylsilane and alpha-terpiene as a matrix and porogen precursor, respectively. A small amount of oxygen was also introduced as an oxidant. The deposition temperature, pressure, and power were 300 ^{o}C, 1.0 x 10^{4} Pa, and 600 W, respectively. After deposition, UV curing with 200~450 nm wavelength was performed to remove the organic porogen. The average pore size and porosity of the resulting porous low-*k* films are around 1.4 nm and 12 %, respectively, which were determined from the isotherm of ethanol adsorption and desorption using ellipsometric porosimetry. The dielectric constant is ~2.54. Then, the porous low-*k* film (blanket wafer) was tested by various H_2/He plasma treatments, whose conditions are listed in Table I.

The thickness and refractive index (at a 633 nm wavelength) of as-deposited films were analyzed on an optical-probe system with an ellipsometer. The water contact angle (WCA) was determined as the average of five measurements (Reme Hardt, Mode 100-00-230). The chemical composition of low-*k* films was identified using atomic compositional depth profile analysis (AES) with 5 keV Ar ion sputtering (VG Scientific Microlab 350). The electrical characteristics of low-*k* films were examined by capacitance-voltage measurements at 1 MHz using a semiconductor parameter analyzer (HP4280A). Leakage and breakdown measurements were done at room temperature (25^{o}C) on metal-insulator-silicon (MIS) and 0.126 μm-pitched line-to-line comb structures. The breakdown voltage is defined as the voltage at a sudden rise of at least three decades of the leakage current. The MIS capacitors with *p*-type silicon as the substrates and aluminum as the metal electrodes were fabricated. The thickness of low-*k* dielectric is 0.3 μm. The capacitors had an area of 30 x 30 μm^2. The line-to-line comb structure of 0.126 μm pitch and 0.062 μm Cu line width was fabricated using Cu single damascene process. EM test structure of 250 μm length and 0.062 μm width was fabricated using Cu double-layered dual damascene interconnect. After etching the low-*k* dielectric layer, various H_2/He plasma treatments were performed before Cu interconnects deposition. A 30 nm dielectric barrier of SiCN was deposited on the top of Cu lines using PECVD after completing Cu chemical mechanical polishing process. The stress temperature was 275^{o}C at a fixed current density of 2.0 MA/cm^2 for EM test. A sample size of 30 samples was used for each experiment. Resistance increase with time was monitored until failure. A failure criterion of 10 % resistance increase was employed. More details on test structure fabrication and EM characterization can be found elsewhere [11].

Results and Discussion

Figure 1 shows the thickness variations of porous low-*k* films after the various H_2/He plasma treatments. We used a bi-layer model of ellipsometry measurement to measure the thickness and refractive index of the top modification layer and the bottom bulk low-*k* film. As shown, a thin modification layer was formed on the top of the porous low-*k* films after the plasma treatment. Additionally, the thickness of the top modification layer is dependent on the plasma treatment time and method. The thickness of the modified top layer increased with increasing the plasma treatment time. Moreover, in comparison to the standard plasma treatment, the remote plasma treatment can lead to a thinner thickness of the modified top layer. Furthermore, the thickness shrinkage in the bulk low-*k* film after the plasma treatment was also observed. The thickness shrinkage is obvious for the standard plasma treatment and becomes larger with increasing the treatment time. The results of refractive index also follow this trend. For the remote plasma treated sample, the refractive indexes of the modified top layer and the refractive index of the bulk low-*k* film remained unchanged with a value of 1.451. As for the standard H_2/He plasma treated samples, the refractive indexes of the modified top layer and bulk low-*k* film increased to 1.497 and 1.467, respectively. The results indicate that in addition to ion bombardment effect, the deep UV light emitted by the H_2/He plasma in the standard plasma condition reduces the bulk low-*k* film thickness and modifies the top thin layer. On the other hand, there are only radicals without deep UV light and ion bombardment in the remote H_2/He plasma condition. The radicals only modify the top thin layer and this effect is relatively weak.

To further investigate the properties of the modified top layer and the bulk low-*k* film, we used the diluted HF solution (1 % volume) to etch the plasma-treated low-*k* materials with different times. The results of the etching rates for the modified top layer and the bulk low-*k* film are shown in Figure 2. For plasma-treated low-*k* films using the remote H_2/He plasma, the etching rates of the modified top layer and the bulk low-*k* film are comparable, which have a similar value to that of non-treated samples. This indicates that the top modification layer induced by the remote H_2/He plasma treatment has a similar film property as the bulk low-*k* film. In the case of the standard H_2/He plasma-treated low-*k* films, the etching rates of the modified top layer are increased to ~50 and ~67 nm/min. for 25 s and 100 s treated samples, respectively. Moreover, the etching rates of the bulk low-*k* film are also increased to ~17 nm/min. The results indicate that the properties of the top layer and the bulk low-*k* film treated by the standard H_2/He plasma are modified, which are different from those induced by the remote plasma treatment or the pristine low-*k* film. It can be further deduced that the top modification layer induced by deep UV light, ion bombardment, and radicals in the standard plasma condition is totally changed and have distinct film properties. However, this layer induced only by radicals in the remote plasma condition remains the similar characteristics as the pristine low-*k* film.

Further investigation the top modification layer was performed using AES analysis. Figure 3 shows the depth profile of the carbon content in the plasma treated film, indicating that the carbon content decreases in the top modification layers induced by the standard H_2/He plasma treatment. Moreover, the depth of the damage layer (carbon loss) is lager for the standard H_2/He plasma treatment and becomes larger with increasing the treatment time. In the case of the remote H_2/He plasma-treated sample, the carbon profile remained unchanged, which is consistent with the result of Fourier transform infrared spectroscopy (Nicolet 460).

WCA measurements were performed to check the low-*k* films' hydrophilization after the various H_2/He treatments. The averaged results from 5 sites are shown in Figure 4. A larger WCA (~90^{o}) was observed for the porous low-*k* film without plasma treatment,, indicating this porous low-*k* film seems to be hydrophobic. As expected, the WCA value of the remote H_2/He plasma-treated low-*k* films is not degraded, instead of slightly increase possibly due to moisture desorption, indicating that the porous low-*k* film after the remote plasma treatment becomes more hydrophobic. On the other hand, the WCA value is decreased for the standard plasma-treated low-*k* films, and the magnitude is amplified with enlarging the treatment time. This result indicates that the porous low-*k* films treated by the standard H_2/He plasma attack have lost their hydrophobic property and become hydrophilic, leading to a water-uptake.

Dielectric constants of the porous low-*k* films after the various H_2/He plasma treatments are shown in Figure 5. The dielectric constant of as deposited porous low-*k* films after UV curing process is 2.54. After performing the remote plasma treatment, the dielectric constant of the porous low-*k* films decrease to 2.48. On the other hand, the dielectric constants increase and become larger with increasing the treatment time for the standard plasma treatment. This implies that the dielectric property of the porous low-*k* film layer treated by the standard H_2/He plasma was deteriorated.

The leakage currents of the porous low-*k* films after various H_2/He treatments were evaluated. Two tested structures: MIS and line-to-line comb structures (pitch/line= 0.126 μm/0.062 μm), were used to measure the dielectric property of the low-*k* films under various H_2/He treatments. Figure 6 compares the leakage currents at 2 MV/cm for the porous low-*k* films after various H_2/He plasma treatments in two different structures. As shown, the leakage currents remain unchanged for both H_2/He plasma treatment methods in the MIS structure. For the standard H_2/He treatment with 100 s treatment time, the leakage current slightly increases by only ~2 %. However, in the case of the line-to-line comb structures, the leakage current is related to the plasma treatment method and plasma treatment time. The remote plasma treated sample shows the comparable line-to-line leakage current as that without plasma treatment, but shows a better line-to-line leakage current than that of the standard plasma treated sample. Moreover, for the standard plasma treated sample, line-to-line leakage current becomes worse with increasing the plasma treatment time. This also demonstrates that the standard plasma treatment deteriorate the dielectric property of the porous low-*k* films. Moreover, a different behavior in the leakage current for these two structures was observed, indicating that the top modification layer induced by H_2/He plasma treatment has different effects on the leakage current of the porous low-*k* films. For MIS structures, this top modification layer has no significant impact on the leakage current due to a relatively thinner thickness in comparison to the bulk low-*k* film. On the contrary, in the line-to-line comb structures, this modified top layer between two conductors plays an important role in the leakage current. The modified top layer induced by the deep UV light and ion bombardment in the standard H_2/He plasma treatment becomes an activating diffusion path, increasing the leakage current. Based on the results, we can also infer that the leakage conduction mechanism between the conductors is dominated by the surface migration, rather than by the bulk film diffusion for the line-to-line comb structures.

To further understand the dielectric reliability, voltage ramping-up to dielectric breakdown of the porous low-*k* under various plasma treatment conditions was measured. Figure 7 shows the distributions of voltage ramping-up to dielectric breakdown of the porous low-*k* under various plasma treatments using line-to-line comb structures. As shown, the remote plasma treated sample has better voltage ramping-up to dielectric breakdown performance, while the standard plasma treated sample shows a lower breakdown voltage as compared to the non-treated sample. Moreover, the dielectric breakdown voltage becomes lower as the plasma treatment time increases. This also demonstrates that the standard plasma treatment with deep UV light radiation and ion bombardment degrades the low-*k* film reliability.

Figure 8 presents the cumulative failure distribution of EM lifetime for typical Cu interconnect lines. The cumulative failure distribution is plotted by measurement of 30 sample's failure times using lognormal distribution. Although the difference of the measured failure times of Cu interconnect lines is not significantly large, it also can be observed that the failure times of Cu interconnect lines with the standard H_2/He treatment slightly decrease and become worse with increasing the treatment time. More obviously, the failure times of early failure samples degrade significantly for the standard H_2/He treatment condition with a longer treatment time. It is well known that the EM performance is controlled by the Cu interface and the bulk Cu film [12]. Therefore, the worse integrity between the plasma-treated low-*k* film and the Cu line at the side walls leads to a decreasing EM failure time for the standard plasma treatment condition.

Conclusions

In this study, the effect of various plasma treatments on the porous low-*k* dielectrics deposited by PECVD was investigated. All the plasma treatments resulted in the formation of a thin and dense layer on the surface of the porous low-*k* films. Additionally, the properties of this top dense layer are modified and changed for the standard H_2/He plasma treatment, causing the degraded electrical and reliability performance. However, H_2/He plasma-treated low-*k* dielectric by the remote plasma method shows a better electrical and reliability performance. As a result, the remote plasma treatment on the porous low-*k* dielectrics without deep UV light and ion bombardment appears to be a promising method in the future interlayer dielectrics application.

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附錄 2 張貼發表海報簡影