NSC93-2216-E-009-023-4 07 31

報告附件: 出席國際會議研究心得報告及發表論文

計畫主持人: 邱碧秀

報告類型: 精簡報告

。<br>在前書 : 本計畫可公開查

行政院國家科學委員會專題研究計畫 成果報告

94 9 2

# **Abstract**

 This study focuses on the processing and reliability of metal-insulator-metal (MIM) capacitors which may be used as embedded capacitors in the integral substrate for system in package (SiP). It was originally proposed as a two-year research project. However, the project was only granted for one year. Hence, some of the research items proposed in the original proposal were not carried out due to time and budget deficiency. In this study, MIM capacitors with PECVD oxide and nitride were treated with  $N_2O$  and  $SiH<sub>4</sub>/NH<sub>3</sub>$ plasma, respectively, after deposition of the dielectric layer. No apparent change in film microstructure is observed after plasma treatment. Plasma post-treatment is effective in eliminating the electrical hysteresis shift of the nitride capacitors. The time dependent dielectric breakdown testing indicates a decrease in both the leakage current and the lifetime of the MIM capacitors treated with plasma. Possible dielectric degradation mechanism is explored. Besides, the dielectric breakdown field is one of the important concerns for device reliability. The breakdown of dielectric is originated at a fatal flaw that grows to cause failure and can be explained by the weakest-link theory. The Weibull distribution function, which is based on the weakest-link theory, is employed to analyze the effect of the electrode area as well as the plasma treatment on the breakdown of the MIM capacitors.

本研究的重點是可作為系統封裝技術中的整合式基板內埋式電容用的金屬-絕緣

-金屬(MIM)架構的電容。本計畫原規劃為兩年期計畫,但只核准一年,所以原計

本研究是針對利用 PECVD 鍍覆氧化矽和氮化矽絕緣層來完成 MIM 架構的電  $N_2O$  SiH<sub>4</sub>/NH<sub>3</sub>

weakest-theory Weibull weakest-theory Weibull weakest-theory weibull 3000 million weibull 300 million weibull 300 million and extensive problem and an extensi

Keywords: Capacitor electrical hysteresis, plasma treatment, reliability, nitride, Weibull distribution, weakest-link theory, dielectric breakdown, PECVD.

#### **Introduction**

Integration of precision metal-insulator-metal (MIM) capacitors into substrate has been a key building block for integral substrate for system-in-package (SiP). Silicon-on-silicon packaging has the advantage of perfect match in thermal expansion. Hence, Si substrate is used in this study, and thin film technology is employ to prepare the embedded capacitor. Plasma enhanced chemical vapor deposition (PECVD) has the advantage of depositing insulators in a clean processing vicinity at very low temperatures. The low temperature processing eliminates the segregation or redistribution of the dopants commonly occurred in conventional high temperature processes.

Metal-insulator-metal (MIM) and metal-nitride-semiconductor (MNS) capacitors with PECVD nitride exhibit trap-induced dispersive behavior and electrical hysteresis, which lead to degradation in capacitor linearity at low frequencies, limiting the accuracy in precision analog circuits [1, 2]. The dominant defect responsible for charge trapping in silicon nitride was suggested to be silicon dangling bonds, which originate from a deficiency in nitrogen. Various methods, such as: use of a PECVD oxide-nitride-oxide (ONO) stacks and/or appropriate  $SiH<sub>4</sub>/NH<sub>3</sub>$  plasma pre-treatment of silicon substrate before the nitride deposition to make the nitrogen to silicon ratio higher at the interfacial region have been employed to eliminate the dispersive behavior and electrical hysteresis [1, 2]. However, very few work reported on the effect of the plasma post-treatment on the electrical behaviors of the dielectric films.

In this study, MIM capacitors with PECVD oxide and nitride were treated with  $N_2O$ and SiH4/NH3 plasma, respectively, after deposition of the dielectric layer. The effects of plasma post-treatment on the microstructure, the electrical behaviors, and the reliability of the dielectric thin films are investigated. The effects of electrode area and plasma treatment on the breakdown strength of the dielectric are investigated using Weibull distribution.

## **Experimental Procedures**

Four inch diameter p-type (100) Si wafers with nominal resistivity of 1 to 10 Ω-cm were used as substrate. After standard RCA cleaning, a  $100$ nm SiO<sub>2</sub> film was grown on the Si substrate. A 100nm Al films were deposited by thermal evaporation coater onto the  $SiO<sub>2</sub>/Si$  substrate to serve as the bottom electrode. Two dielectrics,  $SiO<sub>2</sub>$  and  $SiN<sub>x</sub>$ , were prepared in this study. The amorphous  $SiO<sub>2</sub>$  films, deposited by the decomposition of tetraethyl orthosilicate, with 100nm in thickness were deposited onto the bottom electrode with PECVD. The silicon nitride films, with a thickness of 50nm, were deposited with the same PECVD system using a  $SiH<sub>4</sub>/NH<sub>3</sub>/N<sub>2</sub>$  mixture. The flow rates of  $SiH<sub>4</sub>$ , NH<sub>3</sub> and N<sub>2</sub> were fixed at 20, 80, and 510 sccm, respectively. The  $SiO<sub>2</sub>$  films were treated with N<sub>2</sub>O plasma (with a flow rate of 200 sccm) for 30min, while the  $\text{SiN}_x$  films were treated with SiH4/NH3 plasma (the flow rate are 20 and 700 sccm) for 30min. Aluminum films (150nm) were then deposited as the top electrodes.

 Field emission scanning electron microscope (FESEM) (S-4000 Hitachi, Japan) was employed to observe the surface morphology and microstructure of the films. Atomic force microscope (AFM) was employed to measure the surface morphology and roughness. Auger electron microscope (AES) was employed to analyze elemental depth profiles. A C-V analyzer (model 590, Keithley Instruments Inc., U.S.A.) and a semiconductor parameter analyzer (HP4155B, Hewlett Packard Co., U.S.A.) were employed to measure the capacitance and the leakage current, respectively. The time to dielectric failure was defined when the current density exceeded  $0.5A/cm<sup>2</sup>$ .

The electrode areas of capacitors in this study are:  $0.237$ mm<sup>2</sup> (radius r = 275 µm), 0.159mm<sup>2</sup> (r=225µm), and 0.096mm<sup>2</sup> (r=175µm). The current-voltage (I-V) measurement was carried out with a semiconductor parameter analyzer (HP4155B, Hewlett Packard Co., U.S.A.) at 25°C and 150°C. The breakdown field is defined when the leakage current density exceeds  $4.21 \times 10^{-3}$ A/mm<sup>2</sup>.

### **Results and Discussion**

As summarized in Table 1, the capacitance densities increase from 1.02 to 1.21fF/ $\mu$ m<sup>2</sup> for nitride capacitors and from 0.39 to 0.46fF/ $\mu$ m<sup>2</sup> for oxide capacitors after plasma treatment. The voltage dependence of capacitance (C), as exhibited in Fig. 1, can be approximated by:

 $C=C_0(1+AV+BV^2)$ 

 $(1)$ 

Where  $C_0$  is the capacitance at zero volts, A and B are the linear and quadratic coefficients of the capacitance, respectively. Also listed in Table 1 are the voltage coefficients of capacitance (VCC) from previous works for comparison [1, 3, 4]. The sensitivity of capacitance to bias voltage, i.e., VCC, is one of the important parameters for precision analog design. The specifications demanded by analog designers in the VCC of high precision capacitors are  $A \le 50$ ppm/V and  $B \le 10$ ppm/V [1]. There are many factors which would affect the VCC of the capacitors, including: dielectric composition, processing conditions, dielectric thickness, frequency of measurement, voltage range of measurements and so on.

Plasma treatment eliminates the electrical hysteresis shift of the nitride capacitors. There is a  $0.91V$  shift in the C-V plot for nitride capacitor without plasma treatment (Fig.  $2(a)$ ), while no hysteresis shift is observed for plasma treated ones (Fig.  $2(b)$ ). For oxide capacitors, no hysteresis shift in the C-V curve is observed. The hystersis phenomenon is believed to be induced by the bulk silicon nitride traps such as: silicon dangling bonds near the nitride/electrode interface [2].

The current density (J) versus electrical field (E) curves, shown in Fig. 3, indicates a decrease of the leakage current density after plasma treatment. The leakage current of the oxide capacitors drops from 1.90 $\times$ 10<sup>-7</sup>A/cm<sup>2</sup> of the as-deposited films to 2.91 $\times$ 10<sup>-10</sup>A/cm<sup>2</sup> of the plasma-treated ones at 1.0MV/cm. It is argued that the incorporation of nitrogen into the oxide films after  $N_2O$  plasma treatment reduces strained Si-O bonds and silicon dangling bonds, thus, consequently, reduces interface defects and improves the J-E characteristics of the  $SiO<sub>2</sub>$  films [5]. The leakage current of the nitride capacitors at 1.0MV/cm reduces from  $1.79 \times 10^{-9}$ A/cm<sup>2</sup> (as-deposited) to  $8.99 \times 10^{-10}$ A/cm<sup>2</sup> (plasma-treated). Both the band gap and the barrier heights at the metal-insulator interfaces of the nitride films increase with the increase of the N content [6]. Auger depth profiling results suggest that the nitrogen concentration increases after plasma treatment. Hence, the decrease of the leakage current is attributed to the reduction of the trap densities, the raise of the energy band gap and/or the increase of the barrier height. Fig. 4 exhibits the time (t) dependence of the current density (J) of nitride capacitors at various stress fields. The J-t curves of specimens without plasma treatment show an initial increase of the current density with time followed by a decrease of J with t before the breakdown of the dielectric, while the current density of the plasma-treated samples increases slightly before the breakdown of the dielectric. Besides, although the current density of the plasma-treated capacitors is smaller, the time to dielectric breakdown (TTDB) is shorter.

The breakdown of dielectric is thought to originate at a fatal flaw that grows with time. In the same way that a weak link threatens the integrity of a chain, so too defects of critical size will cause failure in electronic components. The weakest-link theory gives the cumulative probability F(E) that breakdown occurs below electric field E for Weibull distribution as [7] :





 $ln( ln(1 F(E))) = m \times ln(E)$   $m \times ln(E_0)$  (4)

where  $E_0$  is the characteristic breakdown field which is the field when 63.2% of capacitors breaks down, and m is called the slope parameter. Since m is the slope of the  $ln[$  ln(1 F(E))] versus  $ln(E)$  plot.

Figure 5 is the cumulative breakdown fraction at an electric field E versus E plots as a function of electrode area measured at 25°C and 150°C of silicon dioxide MIM capacitors without plasma treatment, while Fig. 6 is that of oxide MIM capacitors with plasma treatment. Figs 7 and 8 are the breakdown fraction versus E of nitride MIM capacitor. The values of m and  $E_0$  are then evaluated from Figs. 5, 6, 7, and 8 and summarized in Tables 2 and 3. Also listed in Tables 2 and 3 are the parameters  $\chi^2$  and  $R^2$ for goodness of fitting. The parameter  $\chi^2$  measures the amount of disagreement between the observed data and the expected data, while the parameter  $R^2$  is the coefficient of determination in the regression [8]. As shown in Tables 2 and 3, the  $\chi^2$  values are smaller than 0.00478 and the  $R^2$  values are close to 1 (larger than 0.952). This suggests that the Weibull distribution function fits the experimental data.

# **Conclusions**

In this study,  $SiH<sub>4</sub>/NH<sub>3</sub>$  and N<sub>2</sub>O plasmas are used to bombard nitride and oxide films

of MIM capacitors, respectively. The SiH4/NH3 plasma treatment eliminates the electrical hysteresis shift of the nitride MIM capacitors. The leakage current density of both the oxide and nitride capacitors decreases after plasma treatment. For oxide capacitors, the incorporation of nitrogen into oxide films reduces interface defects and, hence, the leakage current. For nitride capacitors, there are several possibilities for the decreased leakage current after plasma treatment, such as: the reduction of the trap densities, the raised of the energy bond gap and/or the increase of the barrier height [9].

Weibull distribution function is employed to analyze the electrode area effect on the breakdown strength of the oxide and nitride MIM capacitors. The Weibull distribution function fits the experimental data well with  $\chi^2$  values of smaller than 0.00478 and the R<sup>2</sup> values of larger than 0.952. This suggests that the breakdown of the dielectric can be explained with the weakest-link theory, since Weibull distribution function is based on the weakest-link theory [10].

#### **References**

- [1] S. VAN HUYLENBROECK, S. DECOUTERE, R. VENEGAS, S. JENEI, and G. WINDERICKX, IEEE Electron Device Lett. 23 (2002) 191.
- [2] W.S LAU, Jpn. J. Appl. Phys. 29 (1990) L690.
- [3] A. KAR-ROY, C. HU, M. RACANELLI, C. A. COMPTON, P. KEMPF, G. JOLLY, P. N. SHERMAN, J. ZHENG, Z. ZHANG, and A. YIN, in Proceedings of the 2<sup>nd</sup> IEEE International Interconnect Technology Conference, San Francisco, USA, May 1999 (IEEE, New York, USA, 1999) p. 245.
- [4] J. A. BABCOCK, S. G. BALSTER, A. PINTO, C. DIRNECKER, P. STEINMANN, R. JUMPERTZ, and B. El-KAREH, IEEE Electron Device Lett. 22 (2001) 230.
- [5] S. R. KALURI and D. W. HESS, J. Electromchem. Soc. 145 (1998) 662.
- [6] M. H. W. M. VAN DELDEN and P. J. VAN DER WEL, in Proceedings of the 41<sup>st</sup> International Reliability Physics Symp. Dallas, USA, March 2003 (IEEE, New York, USA, 2003) p. 293.
- [7] M. Ohring, Reliability and failure of electronic materials devices, San Diego California: Academic Press Ltd; 1998, p. 208-11, 310-28.
- [8] LJ. Kitchens, Exploring statistics: a modern introduction to data analysis and inference, 2nd ed. Belmont California: Duxbury Press; 1998, p. 641-5, 737-41.
- [9] C. C. Ho, B. S. Chiou, J. Mater. Sci. Mater. Electron., (submitted)
- [10] C. C. Ho, B. S. Chiou, Micro. Rel., (submitted)



Fig. 1 Capacitance (C) as a function of the dc voltage of (a) oxide and (b) nitride MIM capacitors with ( $\bullet\bullet\bullet\bullet\bullet$ ) and without (-) plasma treatment. The curves exhibit quadratic behavior in the voltage coefficient of capacitance (VCC).  $C_0$  is the capacitance value measured at 0 volt.



Fig. 2 Capacitance (C) as a function of the dc voltage of nitride MIM capacitors without and (b) with plasma treatment.  $C_0$  is the capacitance value measured at 0 volt from  $-10V$ to 10V.



Fig. 3 Current density (J) versus electrical field (E) of as-deposited ( $\square$ ) and plasma-treated ( $O$ ) (a)  $SiO_2$  and (b)  $SiN_x$  MIM capacitors measured at room temperature.



Fig. 4 Time dependence of the current density of nitride capacitors with (O) and without  $(\Box)$  plasma treatment at (a) 6.0MV/cm, (b) 5.5MV/cm, and (c) 5.0MV/cm.



Fig. 5 The cumulative capacitor breakdown fraction F(E) as a function of electric field E of as-deposited  $SiO<sub>2</sub>$  MIM capacitors with various electrode area. Lines are the curves fitted with Weibull distribution function.



Fig. 6 The cumulative capacitor breakdown fraction F(E) as a function of electric field E of plasma-treated  $SiO<sub>2</sub>$  MIM capacitors with various electrode area. Lines are the curves fitted with Weibull distribution function.



**4.0 4.5 5.0 5.5 6.0 6.5 7.0** 1.0 **|** L-25<sup>°</sup>C  **M-25o C S-25o C**  $S-150^{\circ}C$ **Electric Field (MV/cm)**

Fig. 7 The cumulative capacitor breakdown fraction F(E) as a function of electric field E of as-deposited  $\text{SiN}_x$  MIM capacitors with various electrode area. Lines are the curves fitted with Weibull distribution function.

Fig. 8 The cumulative capacitor breakdown fraction F(E) as a function of electric field E of plasma-treated  $\text{SiN}_x$  MIM capacitors with various electrode area. Lines are the curves fitted with Weibull distribution function.



Table 1 Capacitance density and voltage coefficient of capacitance, A and B\*, of several nitride and oxide MIM capacitors at 100kHz.

\*  $C = C_0(1+AV+BV^2)$ .  $C_0$  and C are the capacitances at 0 and V volts, respectively.



Table 2 Weibull slope parameter  $m^*$  and characteristic electric field  $E_0^*$  for the cumulative breakdown of  $SiO<sub>2</sub>$  MIM capacitors with and without plasma treatment.

Table 3 Weibull slope parameter  $m^*$  and characteristic electric field  $E_0^*$  for the cumulative breakdown of  $\sin x$  MIM capacitors with and without plasma treatment.

	Without plasma treatment			
$A^{\zeta}$	0.237	0.159	0.096	0.096
parameter	150	150	150	25
m	11.47	11.58	10.38	9.51
$E_0$	3.55	4.17	4.44	4.52
$\chi^{2\pi}$	0.00484	0.00030	0.00440	0.00366
$R^{\overline{2\#}}$	0.956	0.974	0.967	0.963
	With plasma treatment			
$A^{\varsigma}$	0.237	0.159	0.096	0.096
parameter	25	25	25	150
m	16.26	13.03	17.27	10.31
$E_0$	5.81	5.91	6.02	5.68
$\chi^{2\pi}$	0.00064	0.00368	0.00159	0.00183
$R^{2#}$	0.992	0.952	0.983	0.980

\* Derived from data measured at 25°C and/or 150°C.

 $\zeta$  Electrode area (mm<sup>2</sup>).

# Statistic parameters for goodness of fitting [8].

Effect of Plasma Treatment on the

Microstructure and Electrical Properties of Thin Film MIM Capacitors (Journal of Materials Science: Materials in Electronics) Effect of Size and Plasma Treatment and the Application of Weibull Distribution on the Breakdown of Thin Film Capacitors (Microelectronics Reliability)