Low-Temperature Deposition of High-Quality, Nanometer-Thick Silicon Nitride Film in Electron Cyclotron Resonance (ECR) Plasma-Enhanced CVD System

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ABSTRACT

Ultra-thin silicon nitride films were deposited in an electron cyclotron resonance (ECR) plasma-enhanced chemical vapor deposition (PECVD) system. High quality films with low leakage current, high dielectric strength, and nanometer-scale thickness were achieved at deposition temperatures below 150°C. The study showed that, among all deposition parameters, ECR power played a dominant role in determining film quality.

Keywords: nanometer dielectric films, electron cyclotron resonance, low temperature PECVD, silicon nitride films

INTRODUCTION

One of the challenges facing nanofabrication is to deposit dielectric films with thicknesses compared to the critical dimension of devices under fabrication, typically in a range of a few nanometers, for purposes such as gate dielectrics, surface passivation layers, diffusion barriers, charge isolation gaps, etc. In addition, many applications use a variety of substrates that require deposition temperatures below 200ºC. Although low-temperature physical vapor deposition, such as plasma sputtering, has been studied [1, 2], plasma enhanced chemical vapor deposition (PECVD) is more attractive due to its ability of achieving high quality films [3-5]. However, to our knowledge, these studies were carried out at a temperature range of 300 – 400ºC.

On the other hand, it has been demonstrated that electron cyclotron resonance (ECR) can produce high-density plasmas with low ion energy at low chamber pressure, allowing the deposition of high-quality films at relatively low temperatures [6]. In this work, we demonstrate the feasibility of using ECR-PECVD method to deposit ultra-thin (nanometer scale) silicon nitride films at temperatures below 150ºC.

EXPERIMENT

Silicon nitride films were deposited in an ECR-PECVD system equipped with a helium-cooled chuck whose temperature was controlled between -15 to 80°C. Substrate surface temperature was measured using OMEGA Irreversible Temperature Indicators, which are placed on the top surface of a sample. The system is integrated with a loadlock that allows fast system pumping-down and low base pressure (~ 10^{-7} Torr).

3% SiH_4 and N_2 were used as the active gases in this study. The typical deposition conditions are listed in Table 1. SiH_4 flow rate, microwave and rf power, and chamber pressure were eventually optimized to improve film properties, such as film dielectric breakdown voltage. The temperatures on substrate surfaces were controlled below 150°C throughout the entire study.

Table 1 Typical deposition conditions

Parameter	Value
Microwave power (W)	265
RF bias (W)	0
Pressure (mTorr)	10
3% SiH4 flow rate (sccm)	55
N2 flow rate (sccm)	5.8
Ar flow rate (sccm)	20
He backside cooling pressure (Torr)	10

Si was chosen for this study simply because it is the most popular substrate used today. In particular, n-type, low-resistivity substrates were used. The low resistance substrate also served as one of the electrodes used for leakage current and breakdown voltage measurements. However, there is a drawback in using Si substrate, caused by its native oxide. Since the thickness of the films under study is comparable to that of the native oxide, its impact on film properties and, most importantly, the accuracy of estimating the film dielectric strength have to be addressed carefully.

WVASE32 Variable-Angle Spectroscopic Ellipsometer was used to measure film thickness. X-ray photoelectron spectroscopy (XPS) is an ideal tool for analyzing chemical bonding structures in nanometer-scale thin films. In this study, Surface Science SSX-100 XPS system with Al Kα x-ray source was used.

After deposition, 0.7μm-thick aluminum pads with different areas were fabricated on the top of the just-deposited films. The Al metal film, silicon nitride film, and low-resistive Si substrate form Metal-Insulator-Si (MIS) capacitors. Leakage current density and breakdown voltage were measured using these capacitors with a Keithley 2400 source meter.

RESULTS AND DISCUSSION

In order to determine the impact of the native oxide, two types of substrates were prepared. One was directly from as-purchased Si wafers, but cleaned in acetone then methanol solutions. The other type was additionally dipped in buffed HF solution for 20 seconds before immediately loading into the deposition chamber.

Fig. 1 shows the Si 2p XPS spectrum of a silicon nitride film deposited on the acetone/methanol cleaned substrate with deposition conditions shown in Table 1. A strong chemically shifted Si 2p peak at the binding energy of 102.0 eV, resulting from silicon nitridation, was observed. Since the thickness of the silicon nitride film is thinner than the escape depth of photoelectrons from the native oxide and Si substrate, a Si-O peak at 103.0 eV contributed by the native oxide and a Si-Si peak at 98.9 eV contributed by the Si substrate were also observed. The N 1s spectrum of the sample is shown in Fig. 2. A small amount of N-H bonds exist in the film, as indicated by the peak at 400.7 eV, caused by H^+ from the SiH_4 gas.

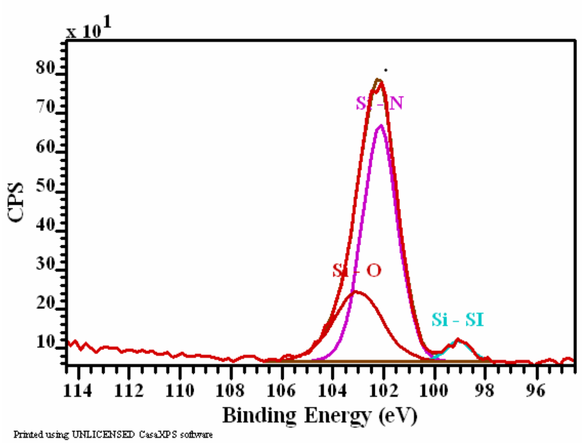

Fig. 1 Si 2p XPS spectrum from a sample deposited on Si substrate cleaned with acetone/methanol

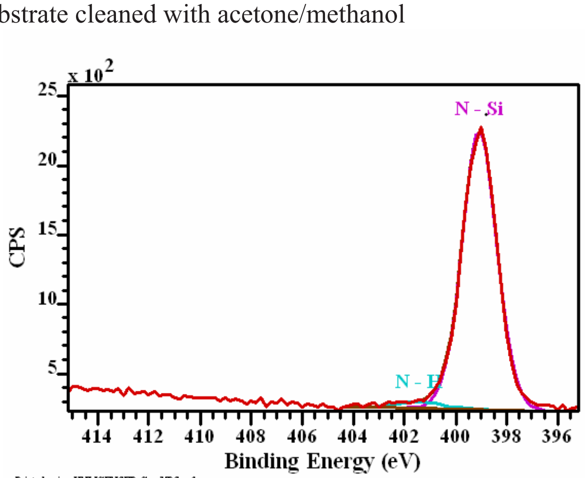

Fig. 2 N 1s XPS spectrum of the silicon nitride film shown in Fig. 1

The Si 2p XPS spectrum of the nitride film deposited on a Si substrate with HF dip is shown in Fig. 3. The deposition conditions are the same as the one shown in Fig 1. A Si-O peak still exists but its intensity is much smaller than the one in Fig. 1, indicating thin oxide still exists on the Si substrate. It is well known that, in the atmosphere, native oxide grows immediately on a Si substrate after dipped in HF. It is a challenge to accurately measure the thickness of such a thin layer using Ellipsometry. However, its thickness can be estimated using the core level ratio of the Si-O peaks shown in Figs. 1 and 3. Later, we will show that the native oxide thickness on a substrate without HF dip is 3.0 – 3.5 nm. Using this number, we estimated the native oxide thickness on a Si substrate with HF dip is between 0.6 to 0.7 nm.

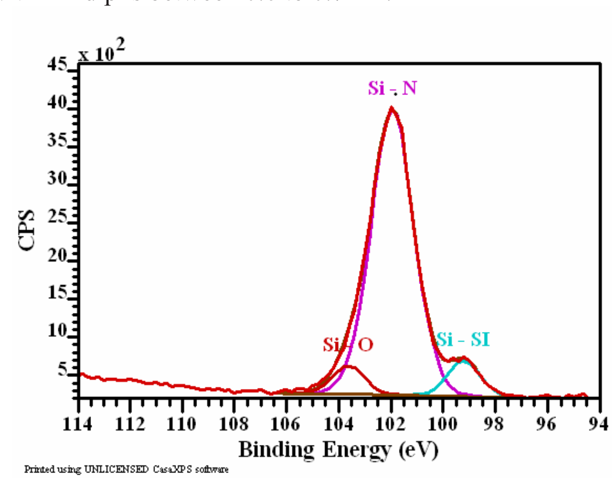

Fig. 3 Si 2p XPS spectrum of silicon nitride film on Si substrate cleaned with HF dip

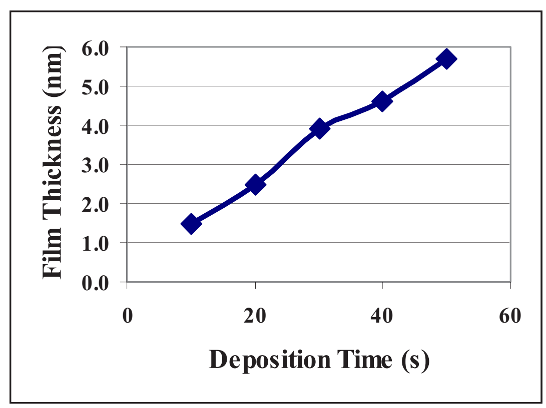

Fig. 4 Silicon nitride film thickness as a function of deposition time determined using ellipsometry

Film thicknesses were controlled by deposition time. The spectroscopic ellipsometer was then used to determine the thicknesses of both silicon nitride films and the native oxide as well. The dependence of silicon nitride thickness on deposition time is shown in Fig. 4. Film thickness increases linearly with deposition time at a deposition rate of 0.11 nm/s. On the other hand, as shown in Fig. 5, the native oxide on substrates without HF dip are 3.0 – 3.5 nm thick, independent from the deposition time. It is understandable since no oxygen existed in the deposition chamber during the deposition.

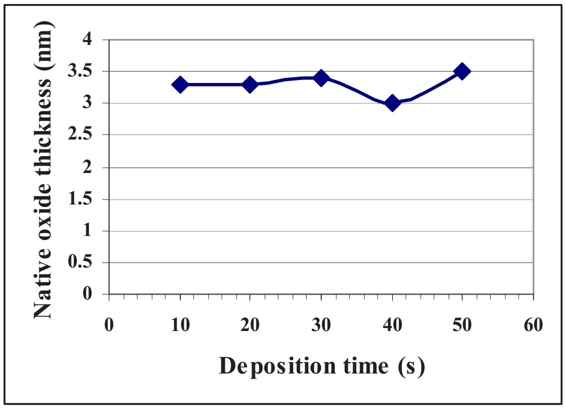

Fig. 5 Native oxide thickness vs. nitride deposition time

Fig. 6 shows the curves of current density vs. voltage (J-V curves) for the nitride films deposited with different ECR powers. The deposition time of these films was 30 s, corresponding to a nitride thickness of 3.8 nm, as shown in Fig. 4. In this case, Si substrates were not dipped in HF. As expected, ECR power played a significant role in determining the film quality. When the ECR power was greater than 265 W, the films with high breakdown voltage and low leakage current were obtained. With lower ECR power, a high percentage of MIS capacitors failed at very low bias voltage. It also shows that when the quality of the silicon nitride films is poor, the quality of the entire film stack, native oxide plus the nitride film, is also poor. It confirmed the well known fact that the electric strength of the native oxide is poor. In addition, since the dielectric constant of silicon nitride is almost twice of that of silicon oxide, the electric field in the native oxide is much higher than in the nitride film during the test. Therefore, the native oxide is expected to breakdown at much lower voltage than the nitride film does. Thus, the excellent dielectric strength at high ECR power is mainly a contribution of the silicon nitride layer.

Fig. 7 shows the J - V curves of the samples deposited with different SiH_4 flow rates. The deposition time for these samples was 40 s with an ECR power of 265 W. When the flow rate increased from 55 to 65 sccm, slight increase in leakage current and decrease in breakdown field were observed. A flow rate of 55 sccm resulted in a breakdown field of 8.5 MV/cm, comparable to the published results on the nitride films deposited at much higher temperature [3]. Similarly, the leakage current density is also low, about 1.0×10^{-5} A/cm^2 at an electric field of 5 MV/cm, within the same magnitude of silicon nitride film formed at much higher temperatures [3].

The breakdown voltage as a function of the capacitor area was measured and is shown in Fig. 8. The breakdown voltage decreases from 6.2 to 4.3 V when the capacitor area increases from 7.5×10^{-3} to 1.0 mm^2, indicating weak spots exist in the deposited films, which are the places where dielectric breakdown starts. As the capacitor area increases, the number of weak spots in the capacitor also increases, causing the average breakdown voltage to drop. However, even for the largest capacitor, the breakdown field still remained at ~ 6.0 MV/cm, indicating the ultra-thin films are continuous and pinholes absent.

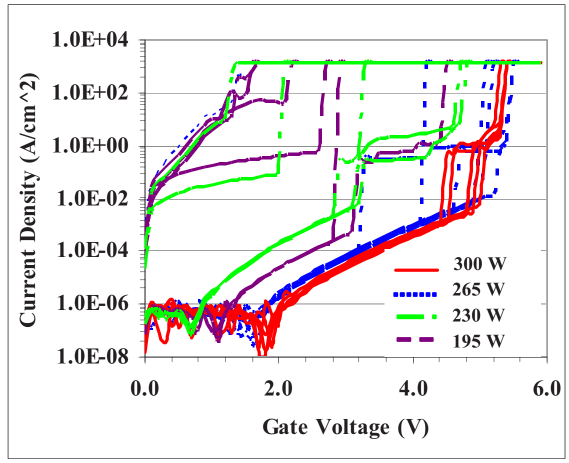

Fig. 6 Current density vs. voltage for the samples deposited at different ECR powers

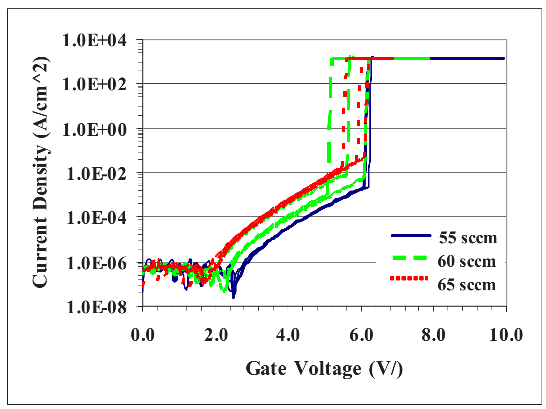

Fig. 7 J – V curves of silicon nitride films deposited at 265W ECR power, but different SiH_4 flow rates. The deposition time was 40 s for all the films.

The breakdown voltages of two groups of samples, prepared with and without HF substrate dip, are compared in Fig. 9. Nitride films on the substrates dipped in HF did show lower breakdown voltages compared with that on the substrates without dipping in HF. Two possible reasons are attributed to the observations. First, the additional native oxide reduces the electric field in the nitride film significantly because of the large difference in their dielectric constant. As a result, a larger voltage is needed in order to break down the nitride film when a thicker native oxide exists. Second, the quality of films on substrates with and without HF dip may be different. In fact, calculations showed that the dielectric strength of the films deposited on HF dipped substrates is actually slightly higher than that deposited on the acetone/methanol cleaned substrates.

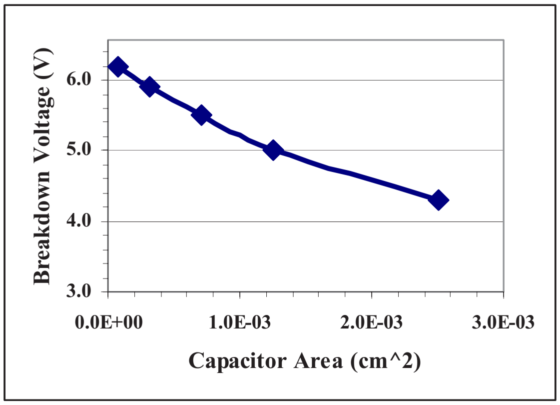

Fig. 8 Breakdown voltage as a function of capacitor area

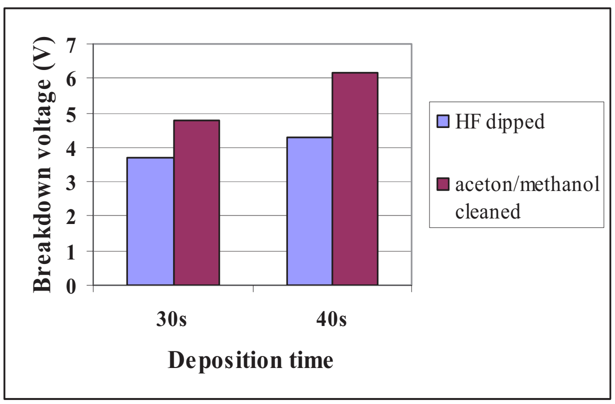

Fig. 9 Breakdown voltage comparison between silicon nitride films deposited on silicon substrates with and without HF dip

Electric strength of the films with different thicknesses but same deposition conditions was also compared. Fig. 10 shows the breakdown fields of ultra-thin (4.6 nm thick) and thin (50 nm) films deposited at optimized conditions. Breakdown fields decreased from 10 to 8.5 MV/cm when the film thicknesses decreased from 50 to 4.6 nm. The two reasons for this are: first, at the initial phase of deposition, equilibrium plasma conditions are not yet established. As a result, the first several atomic layers of the film are not stoichiometrically optimized, which degrades the integrity of the film, particularly when the film is only several nanometer thick. Second, as discussed previously, the impact of the native oxide is more profound in thinner film than in thicker film. Nevertheless, the data shows that the quality of the ultra-thin nitride films is comparable to that of the much thicker ones.

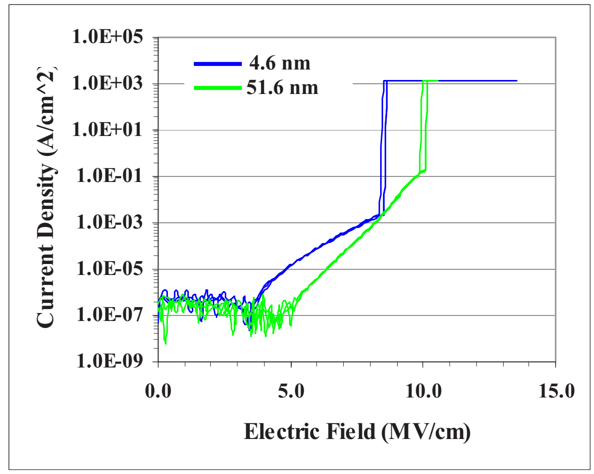

Fig. 10 Breakdown field comparison between ultra-thin and thin nitride films deposited with the same condition

SUMMARY

Ultra-thin silicon nitride films were deposited at temperatures below 150°C using an ECR-PECVD system with $SiH_4/N_2/Ar$ gases. Through deposition condition optimization, high quality films with thickness only several nanometers were achieved. Electrical characterization indicated that the leakage current and dielectric strength of the films are comparable to that of those films deposited at much higher temperatures. Analysis also indicated that no pinholes exist in such thin films.

REFERENCES

[1] R.D. Gould, S.A. Awan, "Dielectric properties of RF-sputtered silicon nitride thin film with gold electrodes", Thin Solid Films 433 (2003) 309 – 314

[2] M. Vila, C. Prieto, R. Ramirez, "Electrical behavior of silicon nitride sputtered thin films", Thin Solid Films 459 (2004) 195 – 199.

[3] K. Sekine, Y. Saito, M. Hirayama, and T. Ohmi, "Highly robust ultrathin silicon nitride films grown at low-temperature by microwave-excitation high-density plasma for giga scale integration', IEEE Transaction on Electron Devices, Vol, 47, No. 7, July 2000.

[4] I. Hallakoun, I. Toledo, J. Kaplun, G. Bunin, M. Leibovitch, Y. Shapira, "Critical dimension improvement of plasma enhanced chemical vapor deposition silicon nitride thin films in GaAs devices", Materials Science & Engineering B102 (2003) 352 – 257.

[5] D. Criado, I. Pereyra, and M.I. Alayo, "Study of nitrogen-rich silicon oxynitride films obtained by PECVD", Materials Characterization 50 (2003) 167 – 171.

[6] S. Sitbon, M,C. Hugon, and B. Agius, "Low temperature deposition of silicon nitride films by distributed electron cyclotron resonance plasma-enhanced chemical vapor deposition," J. Vac. Sci. Tech., A13(6) (1995), 2900.