Investigation of N_2 Plasma Effects on the Depth Profile of Hydrogen Silsesquioxane Thin Films Using High Resolution Specular X-ray Reflectivity

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Abstract. Non-destructive, specular X-ray reflectivity (SXR) measurements were used to investigate N_2 plasma effects on the density depth profile of hydrogen silsesquioxane (HSQ) thin films. The SXR data indicate that the density profile of an HSQ film without plasma treatment is not uniform with at least four layers with different electron densities. When the HSQ film is treated with increasing plasma power or time exposed to the plasma, oscillations present in the SXR profile of the as-cured HSQ film decrease in amplitude and the absolute value of the reflectivity rapidly decreases. These changes in the reflectivity data are due to increases in the film roughness. Additionally, a layer denser than the rest of the film was observed at the film/air interface of each HSQ film. The thickness of the densified layer increased with plasma power and plasma exposure time. An HSQ film treated with N_2 plasma at 200 W for 60 s had an HSQ layer almost fully densified to SiO_2 and was approximately 14 nm thick. When the plasma power was 600 W and the exposure time was 60 s, the entire HSQ film (around 400 nm thick) was affected by the plasma.

INTRODUCTION

As the device dimensions continue to shrink below 0.25 μm, interconnect delay (RC delay) becomes a limiting factor to the improved performance of integrated circuit (IC) devices. Because RC delay is a simple product of the resistance between the metal lines and the capacitance of the inter-layer dielectric (ILD) material, there are two ways to reduce RC delay. One solution is to lower the resistance of the metal line and the other solution is to lower the dielectric constant of ILD material.

Recently, many new ILD materials with low dielectric constant (low-k) have been developed to replace conventional silicon dioxide. Among these materials, HSQ has been used in IC production for its excellent planarization and gap fill capabilities. In addition, many researchers are developing new processes with HSQ to address technical issues such as reducing copper diffusion, decreasing the leakage current, suppressing water uptake, and avoiding damage during patterning [1-5].

Many of these issues can be addressed through processes that increase the surface density of the film. The development of an accurate analytic technique to measure the thickness of the densified dielectric layer is essential. However, few experimental techniques able to measure the density profile of dielectric thin films that are several thousands angstrom thick with high depth resolution. In this work, we demonstrate the use of specular X-ray reflectivity (SXR) as a powerful technique to measure the depth profile of plasma treated HSQ films. SXR is a non-destructive measurement and current instruments are now capable of angstrom resolution for films up to 1.2 μm thick. We use high resolution SXR to present the first measurements of the density depth profile of HSQ thin films after various N_2 plasma treatments.

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EXPERIMENT

Samples were prepared by spin-coating HSQ films onto 200 mm silicon wafers, then baked, sequentially on separate hot plates at 150 °C, 200 °C and 350 °C for 1 min, and finally cured in the furnace at 400 °C for 1 h. Samples were prepared with two different thicknesses, 300 nm for HSQ film without plasma treatment and 400 nm for films undergoing plasma treatments. Several kinds of N_2 plasma post-treatments were applied to the cured HSQ films to determine the effect of the plasma power and time on the film densities. In one series of treatments, the samples were placed in the plasma for 60 s while the plasma power was varied from 200 W to 600 W. Second, the plasma power was maintained at 400 W while the time in the plasma was varied from 50 s to 80 s.

Specular X-ray reflectivity measurements were performed using a modified high-resolution X-ray diffractometer with a tube source using Cu K_α radiation (λ = 1.54 Å) capable of measuring films up to 1.2 μm thick. The reflected intensity was collected as a function of the grazing incident angle equal to the detector angle. The measured angular range was from 0.1 ° to 0.6 °.

When the grazing incidence angle, θ, of the X-ray beam is smaller than the critical angle of the film, θ_c, the X-ray beam is almost completely reflected. The critical angle is directly related to the density of the film through the equation: $\theta_c = \lambda(\rho_e r_e/\pi)^{1/2}$, where λ is the wavelength of the incident radiation, ρ_e is the electron density, and r_e is the classical electron radius, 2.818 fm. The momentum transfer in the film thickness direction (Q_z) is also related to the incident angle and is defined as $Q_z = (4\pi/\lambda)\sin\theta$. From these relationships, the precise measurement of the critical angle is important to the determination of the electron density of the film.

The SXR data were analyzed by fitting model electron density depth profiles to the experimental data using a least square fitting routine based on the algorithm of Parratt [6,7]. The theoretical basis of the deconvolution of the SXR data is described elsewhere [8]. The depth profile of the electron density of the film was modeled as a series of layers each characterized by an electron density, thickness, and interfacial width or roughness. The reflectivity was then calculated for a model profile and compared with the experimental data. The model electron density profile was then numerically adjusted until the calculated reflectivity agrees well with the data.

RESULTS AND DISCUSSION

Figure 1 shows the SXR curve for the cured HSQ film presented as the logarithm of the ratio of the reflected beam intensity (I) to the incident beam intensity (I_o) versus magnitude of the momentum transfer in the film thickness direction (Q_z). Two critical edges are observed in the reflectivity data; one at Q_z = (0.0255 ± 0.0005) Å^{-1} due to the dielectric thin film and one at Q_z = (0.031 ± 0.0006) Å^{-1} due to the silicon substrate [12]. Constructive and destructive interference between radiation reflected from the air/film interface and the film/silicon interface results in oscillations in the SXR curve. The thickness of the film is easily determined from the spacing of the interference fringes in the SXR data because the periodicity of the oscillations is proportional to the thickness (thickness = 2π/fringe spacing) [6]. At low Q_z near the critical edge of silicon, the relationship between film thickness and the periodicity of the interference fringes is affected by multiple scattering. However, multiple scattering contributions to the reflectivity signal are less than 1 % of the reflected intensity when the reflectivity is less than 10^{-2}. In this work, the film thickness of HSQ was determined from the spacing of the fringes in the Q_z region ranging from 0.053 Å^{-1} to 0.092 Å^{-1}. The resulting thickness was (316 ± 1) nm.

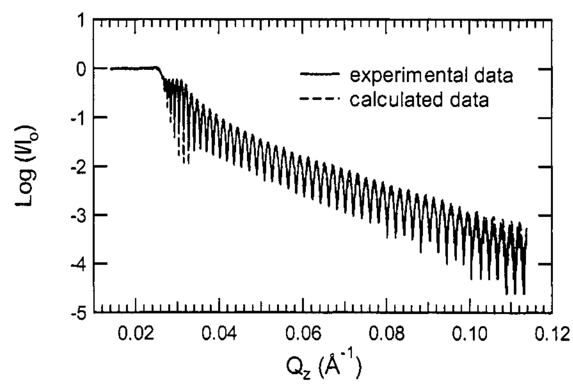

FIGURE 1. Specular X-ray reflectivity curve of HSQ film without plasma treatment as represented as the logarithm of the ratio of the reflected beam intensity (I) to the incident beam intensity (I_o) versus magnitude of the momentum transfer in the film thickness direction (Q_z). The dotted and solid curves represent the experimental and calculated data with four dielectric layers, respectively.

The best fit to the experimental data of HSQ film is also shown in figure 1. We found that the HSQ film without plasma treatment required at least four distinct layers to adequately fit the data. Figure 2 shows the density profile from the best fit to the HSQ reflectivity data. This profile includes a dense top layer about

5nm thick as well as a layer that is slightly denser than pure HSQ about 51 nm thick. The density of the top layer is approximately 92 % of the density of quartz (Q_c^2 = 1.14E-3 Å^{-2}), suggesting that this layer has been nearly transformed into a structure similar to silicon dioxide. The density of the second layer is approximately 3% higher than the third layer (pure HSQ). This densification is expected to be due to the loss of Si-H bonds and some film oxidation during the bake and cure processes. Interestingly, there is also a less dense layer, approximately 6 nm thick, near the silicon substrate with a density 91 % that of the pure HSQ layer.

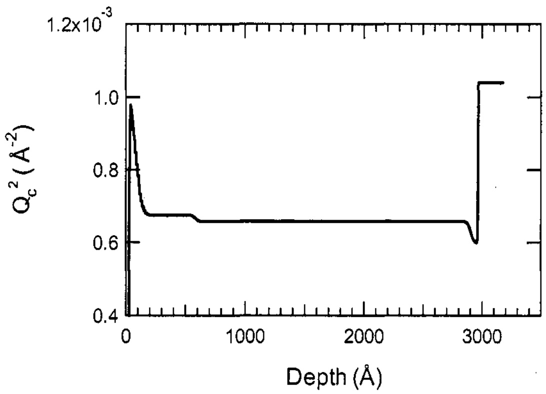

FIGURE 2. Electron density depth profile of the film shown in Fig. 1. The free surface is located at the far left of the horizontal axis the silicon substrate is located at the far right of the abscissa.

Figures 3 and 4 show the SXR data of HSQ films after treatments under varying plasma conditions. It is clear that the amplitude of the oscillations observed in the as-cured HSQ film decrease and the specular reflectivity drops more quickly beyond critical edge than the pure HSQ data with increasing plasma power or plasma exposure time. These characteristics in the SXR data represent increasing film roughnesses with plasma treatment. When the roughness of the film increases, the specular reflectance at angles beyond critical angle falls faster than those values calculated for an ideal smooth interface using the Fresnel equations [8-10]. When the plasma power and plasma exposure time increase, a new longer wavelength oscillation appears and the critical edge of the HSQ film moves to higher values, indicating the formation of a denser layer. These SXR data were analyzed using the same methods used for the pure HSQ film and the results are shown in Figures 5 and 6. To describe these plasma treated samples, up to seven distinct thin film layers as well as the silicon substrate layer were required to adequately fit the SXR data.

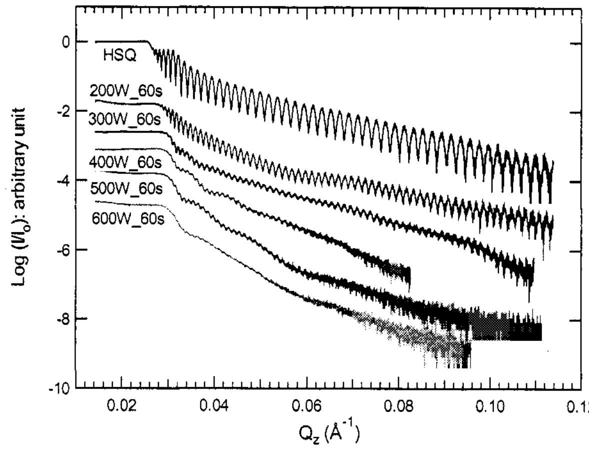

FIGURE 3. Specular X-ray reflectivity curves of plasma treated HSQ films with different plasma powers presented as the logarithm of the ratio of the reflected beam intensity (I) to the incident beam intensity (I_o) versus the magnitude of the momentum transfer in the film thickness direction (Q_z).

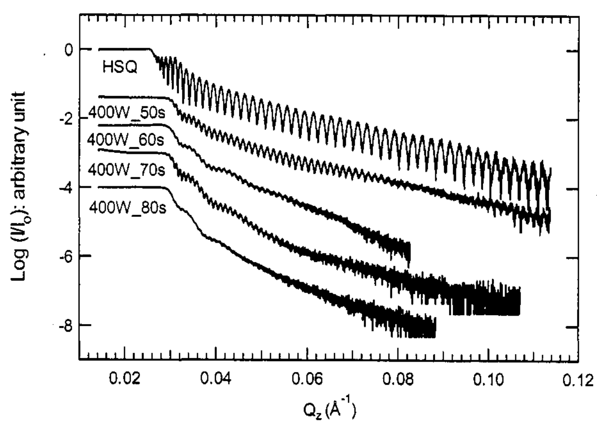

FIGURE 4. Specular X-ray reflectivity curve of plasma treated HSQ films with different plasma exposure times presented as the logarithm of the ratio of the reflected beam intensity (I) to the incident beam intensity (I_o) versus magnitude of the momentum transfer in the film thickness direction (Q_z).

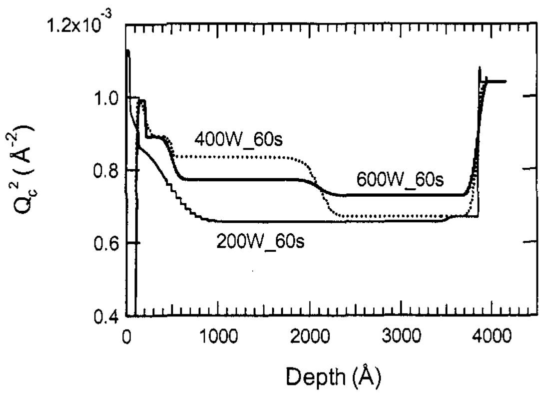

FIGURE 5. Electron density depth profiles of HSQ films treated with different plasma power for 60 s.

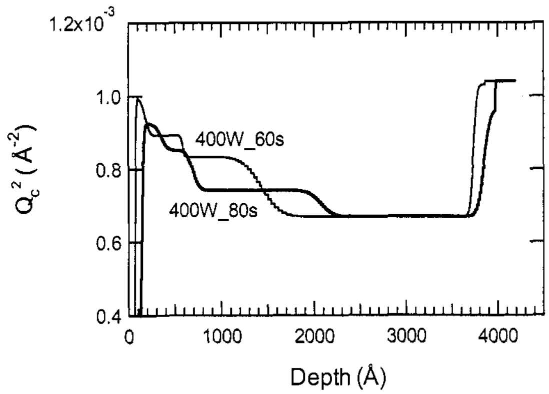

FIGURE 6. Electron density depth profiles of HSQ films treated at 400 W of power for 60 s and 80 s.

The electron densities of fully densified quartz and plasma enhanced chemical vapor deposition (PECVD) tetraethoxysilane (TEOS) dioxide are reported to be $1.14\text{x}10^{-3}$ Å^{-2} and $0.887\text{x}10^{-3}$ Å^{-2} [11]. We define a fully densified film as film with a density larger than the density of PECVD TEOS oxide. An HSQ film treated with N_2 plasma at 200 W for 60 s shows an almost fully densified layer approximately 14 nm thick. In general, the thickness of the densified layer by plasma treatments increases with plasma power and plasma exposure time. When the exposure time was fixed at 60 s, the thicknesses of the densified layers were around 45 nm, 63 nm, 137 nm, and 265 nm, for plasma powers of 200 W, 300 W, 400 W, and 500 W, respectively. When the plasma power was 600 W and the exposure time was 60 s, the entire HSQ film (around 400 nm thick) was affected by the plasma. The thickness of densified HSQ film was around 194 nm at 400 W and 80 s.

SUMMARY

The density profiles of the HSQ films after different N_2 plasma treatments were measured using high resolution SXR. The best-fit model profile for the SXR data from an as-cured HSQ film had at least four distinct layers with different electron densities. Plasma treated HSQ films required up to seven separate layers to adequately fit the data. A densified HSQ layer was observed for all films studied here. Both the thickness of the densified layer and the film roughness at the film/air interface increased with increasing plasma power and plasma exposure time. In summary, we have demonstrated that the SXR technique is a unique and promising method to obtain detailed information about the density profile of films after different plasma processing conditions.

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12. All data in the text and in the figures are presented with the standard uncertainty (±) associated with the measurement.