Structural Characterization of Porous Low-k SiOC Thin Films Using X-ray Porosimetry

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Abstract

A novel x-ray porosimetry measurement is used to characterize the structure and properties of porous low-k dielectric films after varying process conditions. We determine the film thickness, density depth profile, average density, wall density, and porosity. When the deposition temperature increases, the porosity and wall density increase. The low porosity of films deposited at 200 °C results in good mechanical properties with a dielectric constant as low as 2.5.

Introduction

As minimum device dimensions are reduced below 0.18 μm, the increase in propagation delay, cross-talk noise, and power dissipation of the interconnect structure become limiting factors for integrated circuits. To address these problems, new low dielectric constant (low-k) interlayer dielectric materials are being developed to replace the traditional silica. Among them, low-k thin films prepared by chemical vapor deposition (CVD) have attracted interest due to their physical rigidity, superior mechanical strength, and compatibility with current Si technology. Recently, new ultra low-k CVD films with voids demonstrate the potential of porous CVD films for implementation in the interconnect structure of future chips (1). If one can vary the porosity in a controlled manner, it should be possible to control the dielectric constant. Unlike traditional nonporous dielectric materials, the detailed structure of the porous network affects other properties crucial to the integrated chip. Therefore, it is critical to characterize the on-wafer structure of these porous thin films to understand, interpret and control the correlations between the processing conditions and the resulting physical properties (2-4).

In this work, we use unique x-ray porosimetry for on-wafer characterization of structural properties of porous carbon-incorporated silicon oxide (SiOC). These films are prepared at different deposition temperatures using a novel bis-trimethylsilylmethane (BTMSM) precursor (5). We illustrate the power of this new methodology by reporting critical structural information such as porosity, average film density, density profile, matrix material density, and film thickness. Specially, we identify correlations between the processing conditions and the structural characterization that are needed to control the dielectric properties.

Experimental

Porous SiOC thin films were prepared on p-type (100) Si substrates by plasma enhanced chemical vapor deposition (PECVD) using a BTMSM liquid precursor. Three deposition temperatures of 200 °C, 300 °C and 400 °C were used with RF powers and pressures ranging from 100 W to 400 W and from 13 Pa to 400 Pa, respectively. This PECVD system and the detailed deposition conditions are describe in elsewhere (5). After depositing, the samples were annealed in vacuum at 400 °C for 1 h to investigate the effects of the post anneal on the structural properties. The elemental composition of the films was determined using Rutherford backscattering spectrometry (RBS) for the silicon, carbon, and oxygen and forward recoil spectrometry (FRES) for the hydrogen. The dielectric constant at 1 MHz was measured on a C-V analyzer with a metal insulator semiconductor (MIS) structure. Nano-indentation was used to probe the mechanical properties. High-resolution specular x-ray reflectivity (SXR) experiments were performed at grazing incident angles on a modified θ–2θ x-ray diffractometer. The x-ray source is finely focused copper K_α radiation with a wavelength, λ, of 1.54 Å. Measurements were made both on samples in vacuum and under a saturated toluene vapor, where liquid toluene condensed in the interconnected pores. Evacuated samples were measured in a conventional manner reported elsewhere after evacuation for 2 h (6). The saturated environment is created by placing a container of liquid toluene inside the SXR chamber. The samples were saturated under a toluene atmosphere for 2 h before measuring the x-ray reflectivity.

Results and Discussion

Fig. 1 shows experimental SXR data and the best fit for a film deposited at 200 °C both under vacuum and in the saturated toluene vapor. The SXR data is presented as the logarithm of the reflected intensity (I_r/I_0) as a function of q ($q = (4\pi/\lambda)\sin\theta$), where θ is the grazing incident angle of the x-ray beam. At low q, the reflectivity is unity and the x-ray beam is totally reflected from the sample surface. The reflectivity drops sharply as the x-rays begin to penetrate the film above a critical value of q. This critical angle, in units of q_c^2 (Å^{-2}), is proportional to the film's average electron density. Given the elemental composition of the film, this electron density is easily converted into an average mass

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density. The elemental composition data are summarized in Table 1. The electron density for the sample in the vacuum sample shown in Fig. 1 is calculated to be (0.386 ± 0.005) electrons/Å^3, corresponding to an average mass density of (1.26 ± 0.01) g/cm^3 (7). Notice that a second critical angle occurs at slightly higher q values. This corresponds to the point at which the x-rays begin to penetrate the silicon substrate.

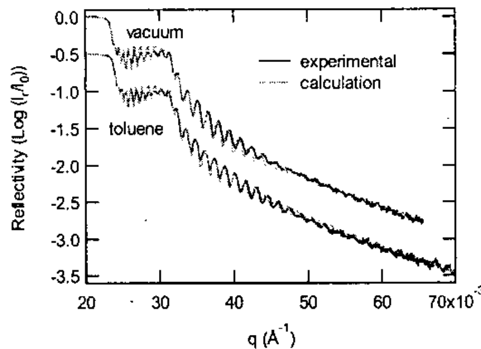

Fig. 1 SXR curves of a film depositied at 200 °C under vacuum and saturated toluene vapor. The data are presented the logarithm of the reflected intensity as a function of q. The solid and dotted curves indicate the experimental and calculated data, respectively.

(0.865 g/cm^3). Here, the porosity reflects only pores filled by the solvent.

By comparing the results of the sample in vacuum with the toluene results, one can calculate the amount of toluene adsorbed, and hence the number of pores. The two unknowns, wall material density and porosity, can be solved simultaneously from equation (1) and (2), providing a rigorous measurement of porosity and the average wall density. The wall density calculated by this method is an average of the wall material and any non-filled pores such as closed pores and pores smaller than the toluene molecules. From x-ray porosimetry, the porosity of the PECVD low-k thin films with varying process conditions ranges from 5 % to 12 %. The porosity and wall density results from these films are summarized in Table 1.

The SXR data are fit by comparing model electron density profiles to the experimental data using a least squares fitting routine based on the algorithm of Parrat (8). Multi-layer profiles with variable thickness, electron density and roughness are adjusted until the calculated reflectivity agrees with the data. Fig. 1 demonstrates the excellent agreement obtained between the calculated and experimental data. In Fig. 2, the density depth profiles corresponding to the best fit to the SXR data in Fig. 1 show a very uniform electron density profile with a thin, densified layer (approximately 300 Å) at the free surface of the film. The thickness increases due to swelling of the wall material with toluene is less than 3 %. There are only slight differences in the density profiles from samples under vacuum and saturated under toluene, primarily small increases in average density in the saturated toluene. These results demonstrate that the distribution of pores is uniform through the film.

Table 1. Structural properties of porous CVD thin films varying process condition

Sample	Dielectric Constant	Atomic Composition (Si: O: C: H, %)	Film Thickness (Å)	q_c^2 (E-4) (Å^{-2})	Average Density (g/cm^3)	Wall Density (g/cm^3)	Porosity (%)
Dep. @ 200 °C	2.5	21: 37: 17: 26	3680	5.47	1.26	1.33	5
Dep. @ 300 °C	3.0	27: 47: 11: 14	2320	6.00	1.39	1.53	9
Dep. @ 400 °C	4.1	27: 54: 8: 12	4410	6.43	1.50	1.71	12
Dep. @ 200 °C/ anneal	–	–	3610	5.43	1.25	1.33	6
Dep. @ 300 °C/ anneal	–	–	2240	5.99	1.40	1.55	10
Dep. @ 400 °C/ anneal	–	–	4280	6.45	1.50	1.74	13

The relative standard uncertainties of the atomic composition, film thickness, q_c^2, average density, wall density, and porosity are ± 5 %, 50 Å, 0.05 Å^{-2}, 0.05 g/cm^3, 0.05 g/cm^3 and 1 %, respectively.

Fig. 1 also indicates that the critical angle of the porous film moves to higher q in the presence of the saturated toluene vapor. This can be attributed to capillary condensation of the toluene inside the pores accessible to the solvent vapor such as pores interconnected to the free surface. The condensation of toluene into these pores decreases the effective porosity, which appears as an increase in the average density of the film. The average mass density of the film is related to the porosity and matrix density of the film through the rule of mixtures in equations (1) and (2).

$$\rho_{ave} = \rho_w \times (1-P) \quad (1)$$

$$\rho_{ave,\,toluene} = \rho_w \times (1-P) + \rho_{toluene} \times P \quad (2)$$

where ρ_w, P, $\rho_{ave,\,toluene}$, and $\rho_{toluene}$ are the density of the wall material between the pores, the porosity of the film, average mass density of porous thin film saturated under toluene vapor and average mass density of toluene solvent,

The SXR measurements for all of the remaining films under vacuum and saturated toluene are shown in Fig. 3 and Fig. 4. As expected, the critical angle of the film shifts to higher q as the deposition temperature increases, indicating an increase in the average film density. To determine the effects of the post anneal on the structural properties, we performed x-ray porosimetry measurements on films both before and after the 400 °C post anneal. Fig. 3 and 4, and Table 1, show that post anneal does not significantly change the average density of the films. These porous SiOC samples are stable even at a low deposition temperature, 200 °C. The thermal stability is likely due to the bonding

characteristics of the precursor material. BTMSM has been used for the epitaxial growth of silicon carbide at low temperature because of its strong $Si-CH_2-Si$ bond between silicon atoms (5).

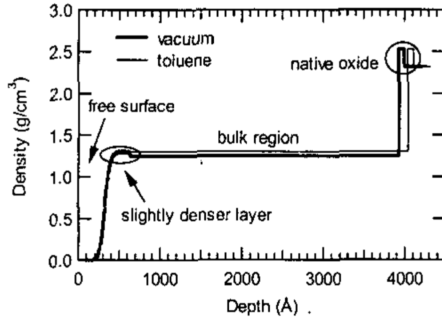

Fig. 2 Calculated density profile of the film deposited at 200 °C under vacuum and saturated toluene vapor. The free surface is located at the far left of the horizontal axis and the silicon substrate is located at the far right of the abscissa.

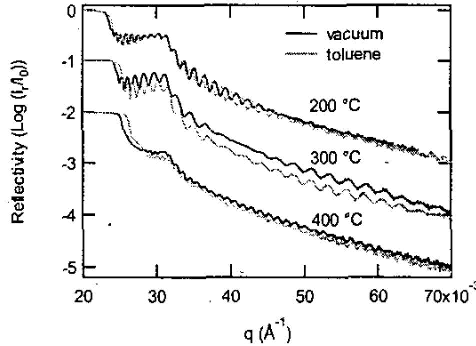

Fig. 3 SXR curves of the as-deposited SiOC thin films with different deposition temperature. Measurements were performed under vacuum and saturated toluene vapor.

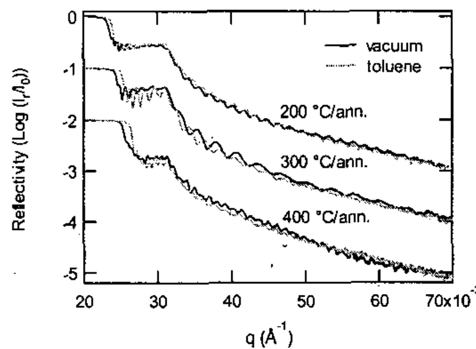

Fig. 4 SXR curves of films annealed at 400 °C for 1 h Measurements were performed under vacuum and saturated toluene vapor. Ann. represents post annealing step.

Fig. 5 shows the relationship between wall density and porosity of the as-deposited and post-annealed films as a function of the deposition temperature. Interestingly, both the porosity and the wall density increase with increasing deposition temperature. This can be described by the following. The volatilization of the alkyl (CH_3) groups in the film is considerably more difficult at the lower substrate temperature than at higher temperature. This results in a higher organic content of the wall material at low deposition temperatures. These are consistent with the ion scattering elemental compositions in Table 1. The lower organic content of the film deposited at higher temperature leads to denser walls. Even though the porosity of films deposited at higher temperatures is slightly higher than films deposited at lower temperatures, the average film density of films deposited at higher temperatures is higher due to its greater wall density.

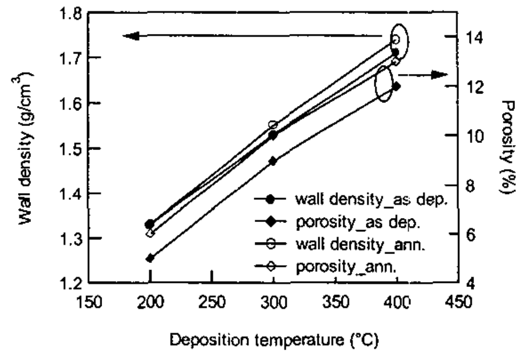

Fig. 5 Wall density and porosity of as-deposited (filled symbols) and annealed (open symbols) samples are shown as a function of the deposition temperature. The solid lines are solely intended to emphasize trends in the experimental data.

By controlling the deposition conditions, we have prepared porous low-k SiOC films at low temperature with very favorable properties. The as-deposited film at 200 °C had a dielectric constant of 2.5 with excellent mechanical properties. The elastic modulus and hardness of the SiOC film deposited at 200 °C were 7.6 GPa and 1.1 GPa, respectively. These results represent that low temperature CVD process are feasible for low-k dielectrics.

Conclusion

We have applied x-ray porosimetry as a novel non-destructive methodology to determine important structural and physical properties of BTMSM based porous CVD thin films with different deposition temperatures. We determine the film thickness, density depth profile, average film density, matrix material density, and porosity. The mechanism of film formation and mechanical properties are interpreted with this unique information.

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