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Study of porogen removal by atomic hydrogen generated by hot wire chemical vapor deposition for the fabrication of advanced low-k thin films

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ABSTRACT

In order to obtain low-k dielectric films, a subtractive technique, which removes sacrificial porogens from a hydrogenated silicon oxycarbide (SiOC:H) film, has been used successfully by different groups in the past. In this paper, we report on the porogen removal from porogenated SiOC:H films, using a hot wire chemical vapor deposition (HWCVD) equipment. Molecular hydrogen is dissociated into atomic hydrogen by the hot wires and these atoms may successfully remove the hydrocarbon groups from the porogenated SiOC:H films. The temperature of the HWCVD filaments proved to be a determining factor. By Fourier transform infrared spectroscopy, X-ray reflectivity (XRR), secondary ion mass spectrometry (SIMS), ellipsometric porosimetry and capacitance-voltage analyses, it was possible to determine that for temperatures higher than 1700 °C, efficient porogen removal occurred. For temperatures higher than 1800 °C, the presence of OH groups was detected. The dielectric constant was the lowest, 2.28, for the samples processed at a filament temperature of 1800 °C, although porosity measurements showed higher porosity for the films deposited at the higher temperatures. XRR and SIMS analyses indicated densification and Tungsten (W) incorporation at the top few nanometers of the films.

1. Introduction

One of the targets of microelectronic industry is to reduce the dielectric constant of the intermetal dielectric to 2.0–2.1 by the year 2016, in order to decrease RC delay and power consumption, increase signal to noise ratio etc. Porous hydrogenated silicon oxycarbide (SiOC:H) has attracted ultra low-k researchers' interest thanks to its properties [1,2]. For example, these films are chemically resistant during process integration while maintaining their low dielectric constant [3]. Porous SiOC:H films are obtained through either a structural or a subtractive way. The structural method employs a single process step and film properties depend mainly on precursor and deposition scheme [4]. The subtractive method requires at least two process steps: 1) co-deposition of a SiOC:H precursor and a sacrificial porogen (CH_x) precursor [5], and 2) removal of porogen. This removal can be done by several techniques, of which a remote plasma treatment [6,7] and a ultraviolet (UV) cure [8,9] are the most common. The UV cure treatment also may raise skeleton cross linking and enhance film mechanical properties [7] and may be, therefore, used as a third step in the subtractive method, when the second process step is a remote plasma [7,10]. Atomic hydrogen generated by hot wire chemical vapor deposition (HWCVD) has been used for etching residual oxide and to passivate surface defects [11,12].

HWCVD based porogen removal has some potential advantages towards plasmas, as there is no plasma involved which may cause unintentional changes of film or wafer surface properties. This technique also enjoys the benefit to be able to generate high amounts of hydrogen atoms. Considering these characteristics, a HWCVD based subtractive process is potentially interesting for the porogen removal of porous SiOC:H films. This paper reports on a series of tests of HWCVD based atomic hydrogen treatments for a porogen removal process.

2. Experimental details

An alkylsilane gas which was responsible to produce the SiOC:H network and a cyclic, hydrocarbon gas which created the porogen material, were used for the co-deposited film on 300 mm diameter wafers. The film thickness was around 100 nm with within wafer non-uniformity of less than 10%. The film deposition conditions were detailed elsewhere [9,10]. The second process step was the removal of porogen. This was carried out on coupons, using a 200 sccm H_2 flow in a HWCVD reactor

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with a tungsten (W) filament. The distance between the filament and sample was set at 5 cm. Atomic hydrogen was applied to all samples at chamber pressure of 0.1 torr for 15 min. In this set-up, the temperature of the sample remained constant at approximately 350 °C. Single coiled type filaments were used for all the treatments. Other details of this system were described elsewhere [13,14].

Fourier Transform Infrared (FTIR) spectra were recorded in absorption mode with a resolution better than 1 cm^{-1}, within the 400 to 4000 cm^{-1} range, in a nitrogen atmosphere. Ellipsometric porosimetry (EP) with in situ spectroscopic ellipsometry was used for porosity and pore size distribution measurements. X-ray reflectivity (XRR) spectra were recorded with an incident angle of 1500 s for an omega-2 theta range of 200 s to 10,000 s. The fitted results were used to evaluate layer thickness and to indicate density modifications caused by the treatments. Secondary ion mass spectrometry (SIMS) depth profiling analysis was performed with a Cameca IMS-6F ion microprobe. In order to reduce the so-called "matrix effect", we applied cesium ion sputtering of the sample surface while over with monitoring of CsM^+ secondary cluster ions (where M = Si, C, O, H and W). Quantification of experimental intensities was performed by using experimental Relative Sensitivity Factors found for Si. The dielectric constant (k) was extracted from capacitance–voltage (C–V) curves, measured at 100 kHz, using a metal-insulator-semiconductor structure. In this case platinum dots were used as front contacts and a Ga–In alloy was used as a backside ohmic contact. Only capacitors with a dissipation factor less than 0.1 were used for k-value extraction.

3. Results

There are an extensive number of reports on HWCVD based atomic hydrogen processes and on the influence of process parameters like filament temperature, substrate temperature etc. [15,16]. These process parameters were optimized for passivating c-Si surfaces or removal of residual oxide. However, in this study, the removal of porogens from a SiOC:H film is targeted and at the same time minimizing any kind of damage. Our approach for the process development included optimization of filament temperature to remove the porogen while targeting an ultra low-k value. Porogen removal has been generally analyzed with FTIR by observing the peak area of the C – CH_x bending bonds (2800–3000 cm^{-1}) [9].

Fig. 1 shows FTIR spectra of the remaining C – CH_3 and C – CH_2 groups in the 2800 cm^{-1} to 3000 cm^{-1} range [9] as a function of filament temperature, for a H_2 treatment for 15 min. In the 1500 °C to 1800 °C range, at higher temperatures more porogens have been removed. For temperatures higher than 1800 °C, the influence of the filament temperature did not significantly change the C–CH_x content.

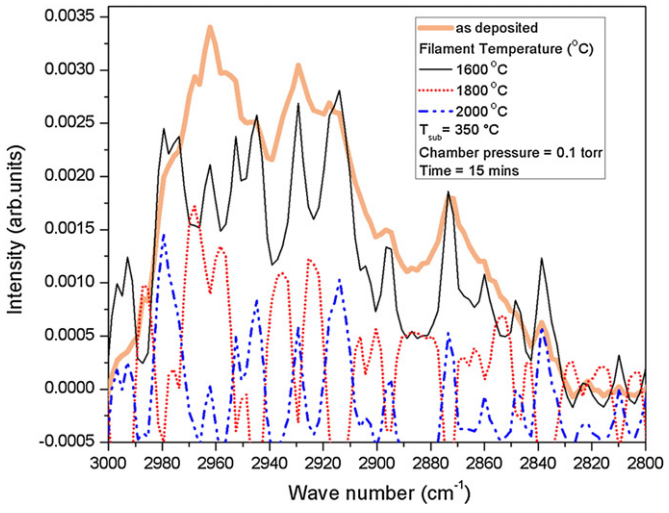

Fig. 1. FTIR spectra (for 1600,1800 and 2000 °C) in the region 2800–3000 cm^{-1} showing the influence of the filament temperature on the concentration of remaining C – CHx groups after a 15 minute atomic H treatment of the SiOC:H film.

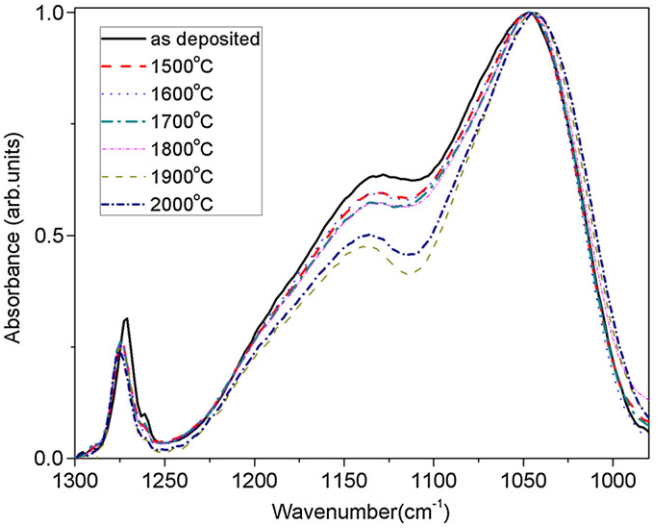

Fig. 2. FTIR spectra of the Si – O, and Si – CH_3 bonds in the region 1000–1300 cm^{-1} showing the influence of the filament temperature of a 15 minute atomic H treatment of the SiOC:H film.

Fig. 2 shows the broad absorption band in the region of 980–1250 cm^{-1} which is the result of at least four Si – O type overlapping bonds and the Si – $(CH_3)_x$ region around 1280 cm^{-1}. Fig. 3 shows the – OH region in the 3000–3500 cm^{-1} region [12]. No Si – H peaks (around 2170 cm^{-1}) were observed. The evolution of the amplitude of the Si – CH_3 peak is similar to the C – CH_x peaks. The single most interesting feature of the broad absorption band in the region of 980–1250 cm^{-1}, is that the highest Si – O peak retained its maximum at approximately the same wave number, independent of the filament temperature. This is a strong indication that there was little transition from cage and suboxide types of Si – O bonds to network bonds, different from when the as deposited films were treated by a UV cure, as reported in [9]. The FTIR spectra in the 3000–3500 cm^{-1} region indicate that there is some water incorporation in the films when they were treated at temperatures higher than 1800 °C.

Fig. 4 shows SIMS depth profiles for the as deposited film and films after H treatments at 1500 °C, 1800 °C and 2000 °C. The very first

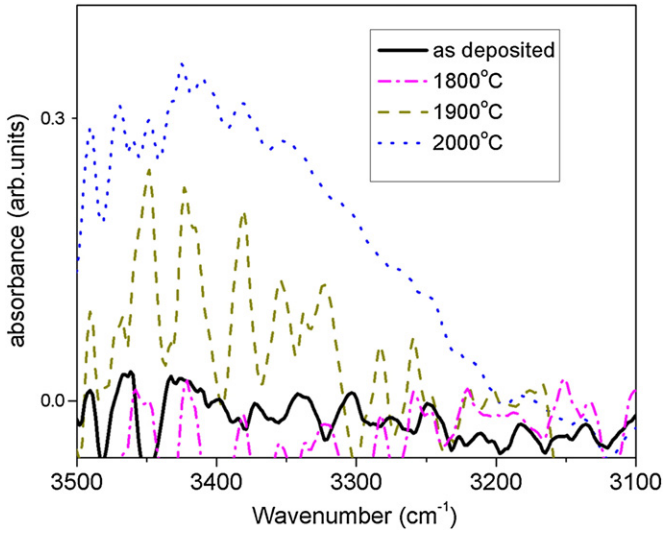

Fig. 3. FTIR spectra of – OH bonds in the region 3100–3500 cm^{-1} for samples treated at filament temperature of 1800, 1900 and 2000 °C.

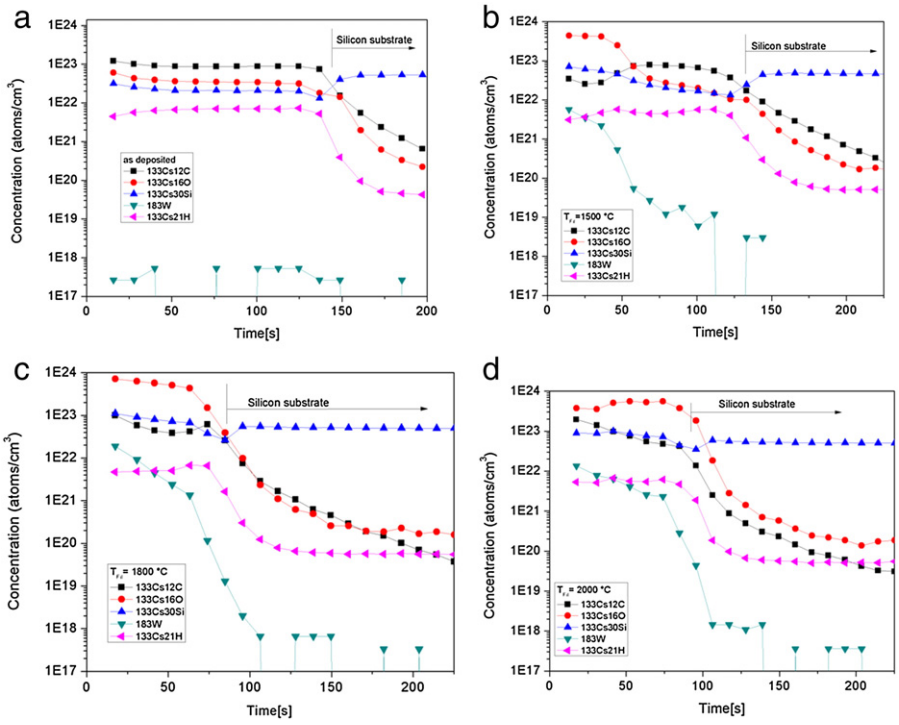

Fig. 4. SIMS profile of the elements Si, O, C that compose the SiOC:H film, also W (coming from the W wires) profile for 4 conditions : (a) as deposited films, (b) after atomic H treatment at filament temperature 1500 °C, (c) after atomic H treatment at filament temperature 1800 °C, (d) after atomic H treatment at filament temperature 2000 °C.

point of the spectra gives an indication of the situation at the surface of the wafer, which is often quite different from the situation of the bulk of the film. The as-deposited film has a very good depth uniformity of the composition of the film. After the 1500 °C treatment, C and H have been partially removed from the film: the bottom two thirds of the film retained its chemical composition. At the same time, a considerable amount of W can be found, mainly at the surface of the film. From the profile of the 1800 °C treated sample, the C and H have been removed quite uniformly from nearly the complete depth of the film. Only near the SiOC:H–Si interface a slight increase of C and H content can be found. For the 2000 °C film, one may say that the C and H have been quite uniformly, partially removed from the film. On the other hand, these figures also show clearly that there is a higher W contamination for the higher temperatures and that this W also diffused into the SiOC:H films.

Table 1 shows the results of XRR analyses of the resulting films: this table also shows the results of the analysis when remote plasma was applied to the film. This was the standard remote plasma, described in [7, 9]. In order to be able to fit the XRR spectra, it was necessary to divide the total film into up to 5 different layers, all with different densities. On the other hand, there was always 1 layer which is much thicker than the others, with a low density. This layer (layer 2 in the table) is, of course, the most relevant. The data in parentheses show that the density of layer 2 decreased with filament temperature, up to 1900 °C, after which it increased again somewhat for the 2000 °C sample. Data in Table 1 show that there was some shrinkage of the film, but much less than when remote plasma was applied.

Using the sum of the thicknesses of all the layers as the total thickness of the film and C–V measurements, the dielectric constant of the films was determined and the results are shown in Fig. 5, together with the porosity of the different films, as determined by EP. The EP results clearly show that the open porosity increased with filament temperature: at 1500 °C, the open porosity is still low, while at 2000 °C it has the same level as for the remote plasma treated low-k film. The dielectric value shows a steep decrease from the 1500 °C sample (2.78) to the 1800 °C sample (2.28), but k increased again for the higher filament treated samples. This paradox between porosity and dielectric constant will be discussed in the next section.

4. Discussion

From all these results, it is clear that at too low filament temperatures, the H treatment is not efficient enough. Gathering e.g. the results

Table 1
Thicknesses of different sub-layers as fitted from XRR analyses (layer with the lowest number is nearest to the Si substrate), for differently treated SiOC:H films. Densities of different sub-layers as fitted from XRR analyses are shown in parentheses.

	Thickness-nm (Density — g/cm^3)							
Layer	As grown	1500 °C	1600 °C	1700 °C	1800 °C	1900 °C	2000 °C	After plasma (reference)
Layer 1			0.6	0.7	1.4	0.6	0.5	1.2
			(0.9051)	(0.9957)	(0.9014)	(0.9842)	(0.9679)	(0.9858)
Layer 2	107.0	93.9	93.5	97.4	92.6	95.2	94.2	85.4
	(1.3685)	(0.9574)	(0.8584)	(0.8727)	(0.8174)	(0.7025)	(0.7483)	(0.7725)
Layer 3		1.5	2.1	1.9	1.5	1.0	1.1	1.3
		(1.2025)	(2.5874)	(3.8433)	(2.7645)	(7.2556)	(6.1824)	(1.4498)
Layer 4		2.1	2.4	1.8	1.8	1.8	1.8	
		(1.7818)	(4.7788)	(6.9936)	(6.0848)	(9.6205)	(9.9925)	
Layer 5		2.0		2.3	1.6	2.8	2.9	
		(4.0056)		(5.0864)	(5.256)	(4.8148)	(5.1352)	

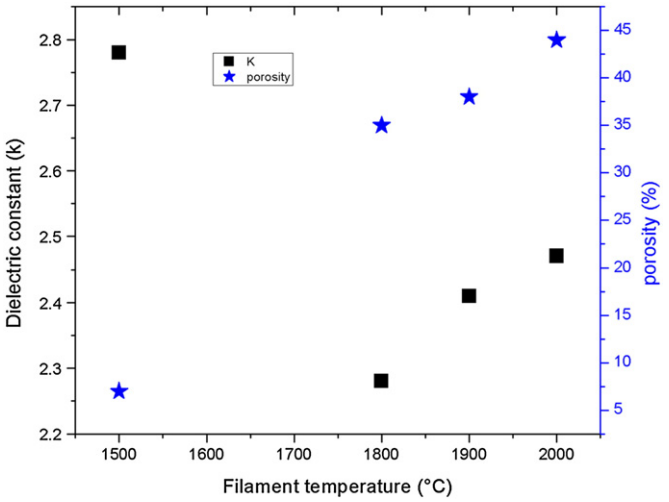

Fig. 5. Effect of filament temperature on dielectric constant (k) and porosity (%).

for the sample treated at 1500 °C, one may conclude that a certain amount of porogen had been removed (from FTIR, XRR, EP, SIMS, C–V), but only from a relatively thin, upper part of the film (SIMS), while the lower part still remained full of porogen (SIMS), resulting in an overall higher density (XRR), lower porosity (EP) and higher k (C–V). However, the results at 1500 °C already indicated that the technique of removing porogen by hot wire dissociation of H_2 molecules as such, can be a viable technique to remove porogens from a SiOC:H film. From former experiments and from these analyses, there are strong indications that the higher concentration of atomic hydrogen, formed at the higher filament temperature, is the main cause for the more efficient removal of porogen in this system.

The explanation of the results of the different analyses for the temperatures between 1800 °C and 2000 °C is less trivial. Firstly, it is necessary to discuss in more detail the SIMS results. Firstly, one may clearly see that W is incorporated in the top of the SiOC:H films. This incorporation may explain the high densities of the top layer in the XRR analyses: In general, the higher the filament temperature, the higher the density and the thicker the modified top layers [17]. The overall sputter rate (and sputter yield) strongly depends on the composition of the film. During the SIMS depth profiling tungsten showed a strong relation to oxygen due to the so called "matrix effect". For all these reasons, it is not trivial to obtain quantitative analysis results from SIMS data. However, we believe that the trends that were deduced from these spectra, as commented in the Results section, are correct. It can be observed from XRR measurements that there is no W diffusion into our film; the observed "tail" in W depth distribution, measured by SIMS, can be explained by a porous structure of the processed films. During the SIMS depth profiling tungsten showed a strong relation to oxygen due to the so called "matrix effect".

From the FTIR spectra, it is possible to conclude that the H treatment removed preferentially the C – CH_x compounds and to a much lower degree the Si – CH_3 groups. Too much removal of the Si – CH_3 groups would lead to a more hydrophilic film, with inferior characteristics [7]. Unfortunately, the FTIR spectra for the samples treated at 1900 °C and 2000 °C show an increase of the OH groups in the film. As the dielectric constant of water = 80, this absorption has an impact of the final k value of the film. Hence, even with a higher porosity at 1900 °C and 2000 °C than at 1800 °C, the final k value is higher for the higher temperatures. Other factors for this k-value increase are the higher density and higher W incorporation for the films treated at the highest temperatures.

In order to optimize further the porogen removal by this technique, it will be necessary to find a compromise between enough porogen removal in order to create a high porosity, and the incorporation of W and water into the low-k film.

5. Conclusions

The removal of porogens from a SiOC:H film by hydrogen treatments in a HWCVD system has been studied. The temperature of the filaments plays an important role in the removal of the porogens: in general, the higher the temperature, the higher the removal and the higher the open porosity of the resulting films. Unfortunately, after the treatments at the highest temperatures, there was also some water incorporated into the film and at the surface there was tungsten incorporation and some densification of the film. For these reasons, the lowest k-value was found at an intermediate filament temperature of 1800 °C, resulting in a k-value of 2.28.

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