Thin Solid Films 575 (2015) 103–106

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

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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ARTICLE INFO

Available online 12 October 2014

Keywords:
HWCVD
SiOC:H
Ellipsometric porosimetry
FTIR
XRR
SIMS
Porous ultra low-k

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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http://dx.doi.org/10.1016/j.tsf.2014.10.033

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.

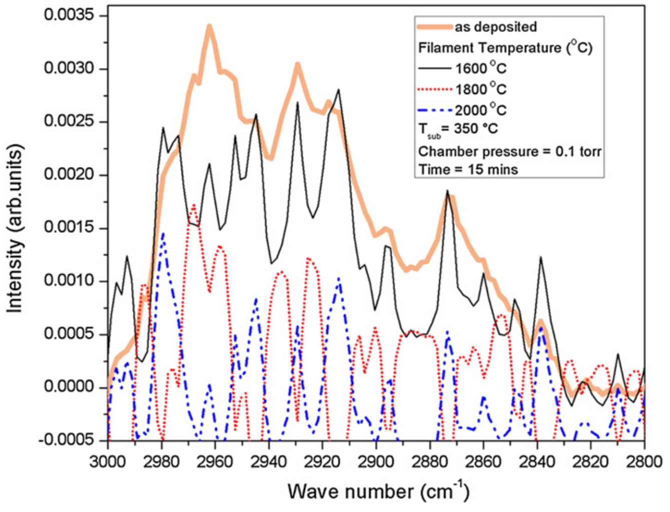

Fig. 1. FTIR spectra (for 1600,1800 and 2000 °C) in the region 2800–3000 cm^{-1} showing the influence of the filament temperature on the concentration of remaining C – CHx groups after a 15 minute atomic H treatment of the SiOC:H film.

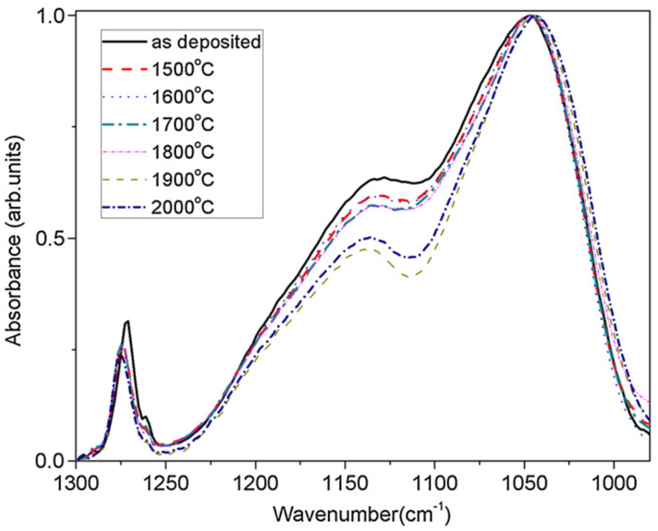

Fig. 2. FTIR spectra of the Si – O, and $Si-CH_3$ bonds in the region 1000–1300 cm^{-1} showing the influence of the filament temperature of a 15 minute atomic H treatment of the SiOC:H film.

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

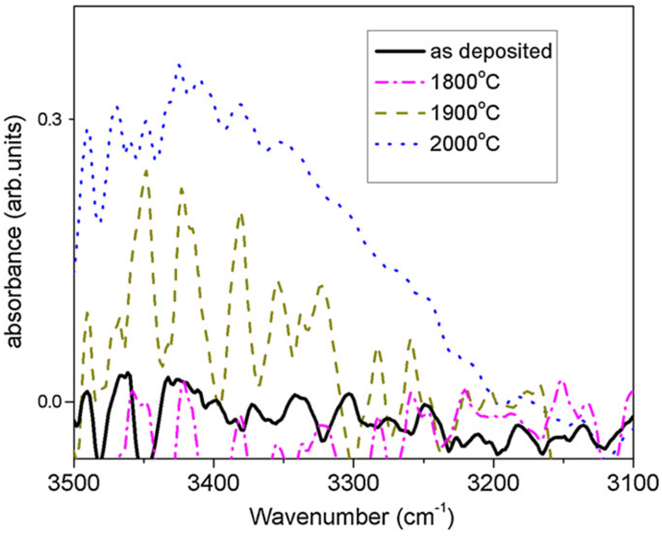

Fig. 3. FTIR spectra of – OH bonds in the region 3100–3500 cm^{-1} for samples treated at filament temperature of 1800, 1900 and 2000 °C.