Microelectronic Engineering 167 (2017) 32–36

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Research paper

Optimization and upscaling of spin coating with organosilane monolayers for low-k pore sealing

Yiting Sun [a,b,*], Ainhoa Romo Negreira [c], Johan Meersschaut [a], Ilse Hoflijk [a], Inge Vaesen [a], Thierry Conard [a], Herbert Struyf [a], Zsolt Tokei [a], Juergen Boemmels [a], Mansour Moinpour [d], Steven De Feyter [b], Silvia Armini [a]

[a] imec, Kapeldreef 75, B-3001 Leuven, Belgium
[b] KU Leuven, Department of Chemistry, 3001 Heverlee, Belgium
[c] Tokyo Electron Europe Ltd, Kerkenbos 1015, Unit C, 6546 Nijmegen, The Netherlands
[d] Logic Technology Development, Intel Corporation, Hillsboro, OR, 97124, United States

ARTICLE INFO

Article history:
Received 29 June 2016
Received in revised form 26 September 2016
Accepted 17 October 2016
Available online 18 October 2016

Keywords:
Low-k
Self-assembled monolayer
SAM
Spin coating
Pore sealing

ABSTRACT

For porous low-k film to be integrated into the next generation of interconnects, the pores need to be sealed against metal ions and barrier precursors. Self-assembled monolayers (SAMs) from organosilane precursor are spin coated onto 300 mm k = 2.2 low-k wafers. Two solvents, propylene glycol monomethyl ether acetate (PGMEA) and methanol with different dielectric constant of 8.3 and 20.1, are evaluated in terms of SAMs layer quality and sealing efficiency at coupon level. SAMs deposited from PGMEA show better sealing than SAMs deposited from methanol and therefore are selected for upscaling. Full wafer spin coating results show that a concentration of 0.05 mM or below results in a partial coverage and a tilt angle as high as 70° from the backbone to the normal. Aggregation is observed for all tested concentrations and is worse for higher concentrations, which is possibly induced by the non-negligible presence of water in PGMEA solvents. In order to test the sealing efficiency of the SAMs layer against metal barrier precursors, MnN films by chemical vapor deposition (CVD) and TaN_x/Ta (TNT) films by physical vapor deposition (PVD) are deposited on SAM coated low-k wafers. HfO_2 is also deposited by Atomic layer deposition (ALD), which is not considered as a barrier but to test the sealing against ALD precursors. Depth profiling Rutherford Backscattering Spectrometry (RBS) measurements indicate an effective sealing of SAMs against CVD and ALD precursors but not against PVD barrier.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Porous low-k films are developed for the ultra large scale integration (ULSI) devices. Those films can reduce resistance-capacitance (RC) delay, dynamic power consumption, and cross-talk noise [1–3]. For porous low-k materials to be integrated into the next generation of ULSI interconnects, the pores have to be sealed in order to prevent the diffusion of barrier precursors and metal ions. Two strategies have been made in order to seal the low-k materials: plasma induced pore densification and add-on sealing layer [4–6].

As one type of add-on sealing layer strategy, SAMs have been identified as promising sealing materials due to their selective deposition nature and their ability to facilitate subsequent metal barrier formation [7,8]. Feasibility of sealing with SAMs has already been demonstrated by beaker-scale immersion coating at coupon level and vapor deposition [9,10]. The beaker deposition, however, is difficult to scale up to full wafers due to the high volume consumption of precursor and solvents, the difficulty to control bath quality, and the lack of control over concentration profile (wafer homogeneity). Vapor phase deposition is easy to integrate and compatible with most back end of line processing. However, not all SAM precursors could be successfully evaporated. Therefore in this work we are investigating the SAM deposition technique by spin coating on a full wafer scale. Compared with beaker deposition, spin coating is faster and consumes less solvent and precursor. In spin coating, the bath lifetime can be controlled in an easier way and fresh solution could be prepared and used immediately. The biggest challenge of SAM spin coating is to deposit SAM in a very short time since the chains might not have enough time to arrange in a dense and packed array.

Previous work of SAMs spin coating is mainly focused on organo phosphonic acids or polymers [11–13]. The spin coating of organosilane onto low-k or SiO_2 wafers are not investigated in detail yet.

In this work, we spin coated SAMs onto a mesoporous low-k material. Two solvents have been compared in terms of SAMs quality and sealing efficiency. Also, the influence of the concentration on the SAMs coverage and quality have been studied. After finding the proper

* Corresponding author.
E-mail address: Yiting.Sun@imec.be (Y. Sun).

http://dx.doi.org/10.1016/j.mee.2016.10.011
0167-9317/© 2016 Elsevier B.V. All rights reserved.

parameters for SAM spin coating on low-k film, metal nitride and metal oxide layers were deposited on top and the metal precursor diffusion was evaluated with RBS.

2. Experimental

Low-k films were deposited from a sol of organosilica precursors and polyethylene oxide containing non-ionic surfactant. The sol was spin-coated on top of 300 mm Si wafers with 1 nm of thermally grown SiO_2. The oxide films were subjected to a 2 min soft bake at 150 °C and then hard-baked for 2 h at 400 °C in N_2 atmosphere. The films had a thickness of approximately 90 nm, a pore radius of 1.4 nm, a porosity of 40% and a dielectric constant of 2.26. The wafer was then etched for 6 s with CF_4 plasma in a capacitively coupled plasma (CCP) chamber and the thickness was reduced to around 80 nm after etching. A 3 s CO_2 plasma treatment was then applied to the wafers to increase the hydrophilicity [14]. Immediately before the SAM deposition, the wafer was annealed under N_2 atmosphere at 150 °C to remove physically absorbed water. SAMs were spin coated onto the low-k film from a solution of 0.005–0.5 mM (3-trimethoxysilylpropyl)diethylenetriamine (DETA) precursor [Fig. 1] in PGMEA or methanol solution at low spin-speed RPM on a TEL CLEAN TRACK ACT™ 12.

The precursor solution was dispensed from a small volume dispensing unit onto the wafer. The wafers were rinsed using the same solvent right after the application of the precursor solution and annealed at 120 °C for 15 min in N_2 atmosphere in order to remove solvents residual and to allow for chain re-ordering. The sealing efficiency against metal barrier precursors was evaluated by depositing MnN and TNT films on the wafers. To test if SAM could seal against ALD precursors, HfO_2 film was also deposited but it is not considered as a metal barrier since it is a high-k material. A 3 nm MnN barrier was deposited by $(EtCp)_2Mn$ CVD in a 300 mm AMAT Endura platform [15]. Before the CVD, the wafers were degassed at 110 °C or 300 °C under vacuum. A 10 nm HfO_2 was deposited by firstly degassing the coupons to 250 °C in vacuum followed by repeated cycles of ALD where the precursor molecules tetrakis(ethylmethylamino)hafnium (TEMAH) were introduced in the chamber, succeeded by purging and exposing to H_2O, and again purging at a reactor temperature of 250 °C. A 10 nm TaN_x/Ta metal diffusion barrier was deposited by physical vapor deposition (PVD).

The macroscopic properties of the deposited SAMs were monitored using water contact angle (WCA) measurements. The static WCA of deionized water droplets dispensed on the sample surface was measured in the air using a software-controlled Video Contact Angle System. The k-value was extracted from capacitance measured on a structure formed by evaporating Pt dots in the range from 0.09 to 9 mm^2 on the surface of the sample, and applying a gallium-indium paste as back side contact. The capacitance was measured at 100 kHz on samples biased in accumulation [16]. The thickness and refractive index of the samples were measured by a SENTECH 801 spectroscopic ellipsometer (SE). A one layer model based on the Cauchy approximation was applied on the spectra collected in the wavelength range of 400–800 nm. The pore structure of the films was analyzed by ellipsometric porosimetry using toluene as an adsorbate [17]. Rutherford backscattering spectrometry (RBS) with He^+ ion beam accelerated to 1.523 MeV was used to get information about penetration of $(EtCp)_2Mn$ precursor inside the pores of low-k dielectric layer. All samples were measured with a glancing exit angle to improve depth resolution. To extract depth information, the analysis was performed using a 3-layer model: one layer on the top and two buried layers representing various diffusion depths from the metal into the low-k material. The 2 × 2 μm^2 surface morphology images measured by AFM were recorded by the Agilent 5100 AFM/SPM microscope in tapping mode. The XPS measurements were carried out in angle resolved mode using a Theta300 system from Thermo Instruments. The measurements were performed using a monochromatized Al Kα X-ray source (1486.6 eV) and a spot size of 400 μm^2.

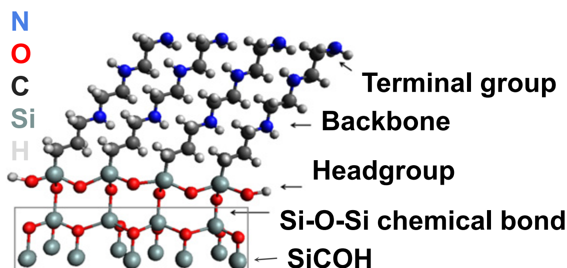

Fig. 1. Chemical structure of DETA precursor.

3. Results and discussion

It has been reported that for the liquid phase deposition of aminosilane, the polarity of solvents would influence the morphology of SAMs layer by affecting the solvolysis of the precursors [18]. Rozlosnik et al. found that solvents with different water content might result in monolayer/multilayer formation [19]. Therefore the pore sealing efficiency of DETA in two different solvents, methanol and PGMEA, are evaluated. Fig. 2 shows the pore size distribution (PSD) measured from porosimetry on low-k samples after SAM's spin coating from the two solvents. In porosimetry measurements, the free volume (V) and pore radius (R_p) are calculated from the psi and delta change with toluene vapor pressure. The pore size distribution (PSD) is obtained from the desorption isotherm applying the Barrett–Joyner–Halenda (BJH) and Dubinin–Radushkevich models within pressure ranges corresponding to mesopores and micropores, respectively. Assuming a monomodal and symmetric PSD, the mean pore radius corresponds to the maximum of the pore radius distribution curve $dV/dR_p = f(R_p)$.The surface sealing is achieved when the pore neck size at the top surface decreased, which results in the decrease in the toluene diffusion rate through the sealing layer [17,20]. Both solutions are prepared at a concentration of 0.5 mM. It is shown that the original low-k pristine is a mesoporous material with a pore neck radius of 1.42 nm and a certain concentration of micropores. After deposition from methanol, low-k pore neck radius is still close to that of pristine. While after deposition from PGMEA, low-k pore neck radius decreased significantly. Therefore from the perspective of low-k pore sealing, PGMEA outperforms methanol and therefore was selected for further

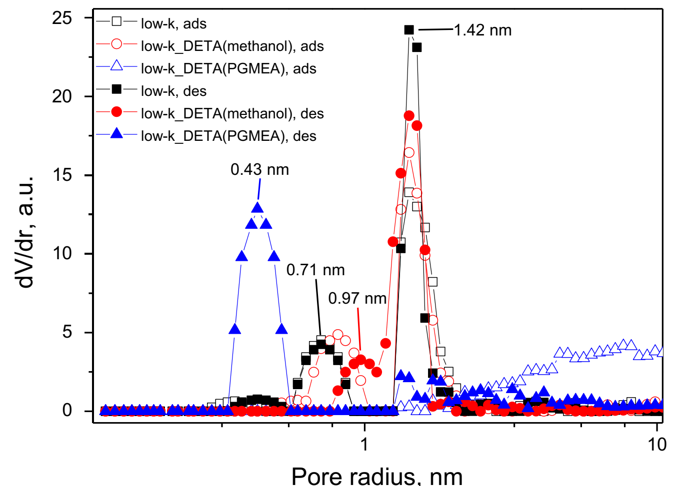

Fig. 2. Influence of solvents on pore size distribution of low-k film (calculated from adsorption and desorption isotherm): SAMs solution in PGMEA seals the pores partially.

Download English Version:

https://daneshyari.com/en/article/4971046

Download Persian Version:

https://daneshyari.com/article/4971046

Daneshyari.com