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Pore sealing of *k* 2.0 dielectrics assisted by self-assembled monolayers deposited from vapor phase

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ABSTRACT

Self-assembled monolayers (SAMs) derived from 11-cyanoundecyltrichlorosilane precursor are deposited in vapor phase and characterized on ultra-low-*k* Chemical Vapor Deposition (CVD) dielectric films ($k = 2.0$) with open porosity up to 50% and pore diameter as large as 3.5 nm. Two surface preparation methods, such as Ar/H_2 and Ar/N_2 plasma pretreatments, are investigated and the pore sealing efficiency after SAM deposition is quantified from the experimental determination of open porosity and pore size measurements derived from toluene adsorption isotherms. In parallel, low-*k* damage is evaluated after surface preparation and SAM deposition by XPS depth profiling and by monitoring the change in refractive index, thickness and *k* value together with the $-CH_3$ and $-CH_2$ normalized FTIR peak areas vs. the pristine dielectric. Subsequently, a 10 nm HfO_2 thin film was deposited by Atomic Layer Deposition (ALD) in order to assess the pore-sealing capability of the proposed approach. When combining surface activation, SAM deposition and ALD, it was possible to accomplish a wide range of pore sealing. By adequate optimization, it was possible to obtain complete pore sealing after ALD, without precursor penetration into the porous low-*k* film, but at the expense of a 37% *k* increase for a 90 nm dielectric thickness.

1. Introduction

The introduction of porosity close to 50% and pore diameters as large as 3.5 nm and above in organo-silicate glass dielectric materials enables *k* values as low as 2.0. One of the major concerns with such porous materials (>2 nm diameter pores) is the fact that pores open to the surface and connected internally, are pathways for penetration of gases, liquids [1,2] and barrier deposition precursors [3,4]. Nevertheless, if from one side pore sealing to prevent penetration became a stringent requirement for the integration of porous dielectrics [5], from the other side minimizing the degree of damage to the low-*k* material is critical in maintaining the desired electrical, mechanical and chemical properties. The difficult balance needed between achieving sealed ultra-low-*k* materials and maintaining a low effective *k* value remains one of the primary integration challenges. Leveraging synergies across the breadth of existing processes such as plasmas, wet chemical treatments, surface functionalization layers and/or interactions with the precursors used in the following deposition steps is one of the most promising routes [6,7]. In particular, self-assembled monolayers (SAMs) deposited on the pre-activated low-*k* materials may provide an interesting solution because they can be easily engineered in order to achieve a sub-3 nm dense film which acts as a sealant coating without penetrating into the pore structure. SAMs are commonly deposited through either liquid- or vapor-based methods. Due to the existing need to make the deposition processes simpler and more reliable, to reduce the generation of contaminated effluents and polymerized products, and to lower the production costs [8], processes which utilize vapor phase deposition can eliminate some of the problems that are seen in liquid-based deposition and also make themselves amenable to be used in batch and microelectronics-compatible processes [9,10]. In these vapor phase processes, the precursor chemistry is easily controlled and efficient mass transport ensures coating of patterned surfaces and high aspect ratio structures. Moreover, it has been shown that the performance of SAM coatings grown in vapor phase is comparable or superior to the one of SAMs that are grown in liquid phase [11], and the vapor phase methods can be more easily applied at the wafer scale level than to the liquid phase methods [12]. Vapor-phase deposition of trichlorosilane SAMs with a variety of terminal functional groups has been achieved on oxide surfaces previously [13–18]. Nevertheless, these tri-functional silanes are also known to polymerize in either aqueous or vapor phase deposition methods over a wide range of temperatures and environmental conditions [19–23]. Consequently, high

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quality monolayer formation may require optimized processing conditions.

In this paper, we report the results of our investigation on the pore sealing efficiency of vapor phase deposited SAMs derived from 11-cyanoundecyltrichlorosilane precursor. The SAMs barrier performance vs. metal ALD precursor penetration in the bulk of the porous low-*k* material is evaluated against plasma surface activation pretreatments.

2. Experimental

2.1. Sample preparation

On 300 mm (100) Si wafers, a 1.5 nm thermal SiO_2 was grown followed by the deposition by chemical vapor deposition (CVD) of a ca. 90 nm 2.0 low dielectric constant thin film. Then the wafer was cleaved in 3 × 3 cm coupons and SAMs derived from 11-cyanoundecyltrichlorosilane (from Sikemia) were deposited from the vapor phase. Chemically grown native Si oxide films on Si substrates were used as a reference and cleaned by 15 min exposure to UV-ozone treatment. Different low-*k* surface activations were investigated including Ar/H_2 and Ar/N_2 plasma based treatments. All the plasmas were applied on 300 mm wafers in a capacitively coupled plasma (CCP) reactor, with a powered upper electrode and the wafer lying on the grounded bottom electrode which was kept at a fixed temperature of 350 °C. Table 1 summarizes all the tested plasma conditions referred to the pristine material for which a *k* value of 2.02 and a water contact angle of 103° were measured. The cleaned SiO_2 reference and low-k substrates were placed together with 15 µl of the silane precursor in a vacuum oven at 140 °C for 1 h and 4 h. A schematic of the oven is shown in Fig. 1.

2.2. Analysis

The different pretreatments were evaluated in terms of low-*k* damage and surface hydrophilization. To this purpose, the *k* value, water contact angle (CA) and mass loss after plasma treatment on 300 mm wafers were compared. The mass difference was determined with an accuracy better than 0.05 mg through in-line mass measurements.

Before and after SAMs and/or ALD HfO_2 deposition, the Si oxide reference and low-*k* films were characterized by water CA, ellipsometric porosimetry (EP), X-ray refractivity (XRR), Fourier transform infrared spectroscopy (FTIR), Rutherford Backscattered Spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS) measurements. EP, using toluene, determined the open porosity of the different films and the average pore size. The error on the results is typically ±2% for the open porosity and ±0.1 nm for the pore radius. XRR was used to determine thicknesses of the different films in the film stacks. XPS and FTIR were used to study chemical modifications caused by the plasmas and by the SAM deposition. The ALD process consisted of repeated cycles where the precursor molecules tetrakis(ethylmethylamino)hafnium (TEMAH) were introduced in the chamber, followed by purging and H_2O, and again purging at a reactor temperature of 215 °C. A thickness of 10 nm Hf oxide was deposited as measured by ellipsometry. The ALD processes were performed on coupons, containing either a pristine film or a plasma treated film before and after SAM deposition. The choice of the TEMAH precursor was dictated by process availability on coupon scale and by the higher sensitivity of the RBS technique towards heavier elements such as Hf. Dense SiO_2 substrates were used as a reference for the ALD deposition on high density SAM. Prior to deposition, the oxide substrates were cleaned in a UV-Ozone Cleaner for 15 min. RBS was used to determine the amount of the deposited Hf. The thickness of the layers was deduced from spectra taken with a scattering angle of 170° and a sample tilt of 11°. The amount of penetration of Hf into the pores was derived from spectra taken in the glancing exit angle geometry that is optimized for depth resolution. The latter geometry is characterized by a scattering angle of 135° and a sample tilt of 35°, corresponding to a glancing exit angle of 10°. With this technique, it was possible to determine the penetration of Hf into the low-*k* film with an accuracy of approximately ±8%. Thickness and refractive index (RI) of the films were measured by spectroscopic ellipsometry (SE). Finally, the dielectric constant was measured by *C–V* measurements [24].

3. Results and discussion

The pristine low-*k* materials are intrinsically hydrophobic in order to prevent moisture uptake which would drastically increase the *k* value. Nevertheless, the presence of –OH groups is needed on the surface in order to anchor the silane precursors during SAMs formation. Therefore, Ar/H_2 and Ar/N_2 plasma based low-*k* treatments were screened with the aim of maximizing the density of surface hydroxyl groups in order to form as dense as possible SAMs while minimizing the depth of damage in the bulk low-*k* material. The plasma treatments decreased the water contact angle values from 110° to values in the range 10–30°. A clear correlation between the increase in the observed *k* values and the mass loss after the plasma treatments is shown in the plot in Fig. 2a. Nevertheless,

Table 1
Summary of the investigated plasma conditions and correspondent measured mass loss and *k* values. The plasmas selected for the silanization experiments are highlighted in bold.

Sample	Power (W)	T (°C)	Gas partial pressure	*t* (s)	Mass loss after plasma (g)	*k* Value	Water CA (degrees)
1	200	150	0.89 H_2	20	4.6E-05	2.19	15
2	200	150	0.89 H_2	60	3.7E-05	2.25	22
3	25	150	0.89 H_2	20	8.2E-05	2.07	67
4	25	150	0.89 H_2	60	2.6E-05	2.12	30
5	25	150	0.89 H_2	240	19.5E-05	2.36	19
6	100	150	0.89 H_2	60	7.4E-05	2.28	23
7	25	150	0.09 H_2	60	4.8E-05	2.18	34
8	25	150	0.09 H_2	240	12.8E-05	2.24	21
9	200	250	0.89 H_2	60	7.0E-05	2.35	24
10	**200**	**350**	**0.89 H_2**	**60**	**3.0E-06**	**2.17**	**26**
11	**200**	**350**	**0.89 H_2**	**120**	**1.6E-05**	**2.24**	**22**
12	25	350	0.89 H_2	60	8.6E-05	2.16	29
13	200	350	0.24 H_2	60	21.7E-05	2.37	24
14	200	350	0.09 H_2	60	19.9E-05	2.46	27
15	**100**	**350**	**0.09 N_2**	**60**	–	**2.27**	**18**
16	Pristine low-*k* substrate (90 nm)				–	2.02	103