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Alkoxysilane layers compatible with Cu deposition: Towards new diffusion barriers?

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ABSTRACT

Self-assembled monolayers (SAMs) deposited on SiO_2 and on a porous dielectric material using a supercritical CO_2 ($SCCO_2$) process are investigated by X-ray reflectivity (XRR) and neutron reflectivity (NR). Monolayers of MPTMS and AEAPTMS were successfully grown on SiO_2, whereas APTMS leads to thicker polycondensed films. The ability of these layers to receive Cu deposits is also examined. Most of these layers cannot endure PVD Cu deposition, leading to copper diffusion penetration into the porous dielectric material. Interestingly enough, AEAPTMS seems to successfully withstand PVD deposition, and could be compatible with this process. An important result of this study is that all silane layers remain intact after MOCVD Cu deposition, and prevent copper diffusion penetration into the dielectric material during metallization. Therefore, MPTMS and AEAPTMS monolayers can be considered as promising candidates as new barriers against copper diffusion.

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1. Introduction

Self-assembled monolayers (SAMs) are being actively investigated in semiconductor devices [1]. Extremely thin monolayers of mercapto- and amino-silane formed by silanization reaction could replace metallic barriers against copper diffusion [2–4]. Such layers have been shown to successfully passivate porous low-k materials commonly used in the fabrication of copper-based interconnect structure [5]. Recently, good adhesion properties between a monolayer of mercaptopropyltrimethoxysilane and copper have been demonstrated [6]. During the silanization reaction, the silane precursor is hydrolyzed by water contained in the medium, and then condenses with the sample surface to form the SAM. Alternatively, a dimerization reaction may occur within the liquid phase, eventually leading to the adsorption of a thick polycondensed layer. To prevent this, anhydrous organic solvents are generally employed.

In this work, we have used instead supercritical CO_2 ($SCCO_2$) as already proposed by other authors [7]. $SCCO_2$ is inexpensive, non-toxic, inert, non-flammable and recyclable. Its zero surface tension facilitates the access to small structures. Its high diffusion and auto-diffusion coefficients allow a fast transfer of matter, and its viscosity and density can be simply adjusted by varying pressure and temperature. In most of the literature, SAMs are grown on SiO_2 [4,8]. For this study, alkoxysilane films have also been deposited on a porous dielectric material and coated with copper using physical vapor deposition (PVD) and metal organic chemical vapor deposition (MOCVD) [9]. The morphological and structural characteristics of the alkoxysilane layers and their ability to receive Cu deposits are investigated by two techniques particularly interesting to thin layer characterization: X-ray reflectometry (XRR) and neutron reflectometry (NR). Both techniques are based on the detection of interference fringes resulting from the reflection of the incident beam by a multilayered sample. The characteristics of these fringes depend on physical (density) and morphological (thickness, roughness, ...) properties of each layer in the stack. However, both techniques are complementary, as they respond to different physical properties. X-ray radiation is sensitive to electronic density in the sample, whereas neutrons interact with atomic nuclei.

2. Experimental

For initial testing, cleaned and polished Si (1 0 0) samples were treated with O_2 plasma (800 W, 47 °C) to form 1 nm thick layers of hydrophilic SiO_2. In other experiments, samples were cut from a 300 mm silicon wafer coated with a 400 nm thick porous SiOCH ultra-low k material (ULK, $k = 2.5$) deposited by Plasma-enhanced Chemical Vapor Deposition (PECVD) in an Applied Material Producer SE equipped with a UV-assisted thermal chamber (400 °C under He). The dielectric surface was modified by pure O_2 plasma to form a hydrophilic surface.

Three alkoxysilanes with various chemical headgroups were used: aminopropyltrimethoxysilane (APTMS), mercaptopropyltri-

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methoxysilane (MPTMS), and aminoethylaminopropyltrimethoxysilane (AEAPTMS). $SCCO_2$ silanization was performed by placing 0.2 g of alkoxysilane directly in the chamber nearby the sample. The CO_2 was pumped into the chamber and pressurized up to 100 bars. The temperature was adjusted to 60 °C. Then, the system was closed and maintained under pressure and temperature during 15 min. The sample was rinsed with $SCCO_2$ during 5 min. Finally, the chamber was depressurized to ambient pressure during 1 min.

Non-collimated Physical Vapor Deposition (PVD) was used to deposit a 10 nm thick Cu film on the silanized samples in an ENDURA 5500 instrument from Applied Materials. Deposition was performed at 20 °C, applying 2000 W for 4 s. In the same equipment, 40 nm of Cu was deposited by Metal–Organic Chemical Vapor Deposition (MOCVD) from the Cupraselect Cu(hfac)(TMVS) precursor at 200 °C, with a chamber pressure of 1.5 Torr for 30 s [9]. Both processes were applied without preliminary degassing in order to preserve the alkoxysilane films.

XRR measurements were performed in a laboratory X-ray diffractometer installed on a rotating anode source (Cu $K_{\alpha 1}$, λ = 0.154056 nm). Standard θ–2θ scans from 0° to 3° with a 0.002° angular resolution were performed. Reflectivity curves were fitted using the Firefx4c_6 software [10]. NR measurements were performed on the D17 reflectometer at the Institut Laue-Langevin in time-of-flight mode. Two angles of incidence were used to cover a q range from 0.01 to 0.24 $Å^{-1}$ with a 0.003 $Å^{-1}$ resolution. The reflectivity curves were fitted using the Parratt 32 1.5 software [11].

Transmission Fourier Transform Infrared (FTIR) spectra were collected using a Bruker IFS 55 FTIR spectrometer. Water contact angle measurements were carried out using Krüss DSA 100 equipment. Finally, samples were characterized by X-ray Photoelectron Spectroscopy (XPS) with a SSI S-Probe spectrometer using monochromated, microfocused Al K_α radiation ($h\nu$ = 1486.6 eV), and an overall energy resolution of 0.6 eV. The collection angle was 35°, ensuring a photoelectron escape depth of about 5 nm.

3. Results and discussion

3.1. Formation of the organic layers on SiO_2

In a first series of experiments, APTMS, AEAPTMS and MPTMS were deposited on SiO_2 and characterized by XRR (Fig. 1). By comparison with the reference (bare) sample, the curves all exhibit a similar fringe at higher q values, which was successfully simulated with the simple addition of a superficial organic layer whose thickness depends on the precursor. While AEAPTMS and MPTMS lead to thin layers (1.1 nm and 1.4 nm, respectively), the film formed with APTMS is significantly thicker (2.2 nm). Accordingly, water contact angle increases from 12° (bare sample) to 60° (AEAPTMS), 67° (MPTMS) and 81° (APTMS). At last, a peak is clearly observed by XPS in the N1s region after silanization with APTMS (Fig. 2). All these results suggest that AEAPTMS and MPTMS form monolayers. In the case of APTMS, the decomposition of the N1s peaks in Fig. 2 shows the contribution of two distinct chemical states of nitrogen, NH–C at 399.8 eV and C–NH_3^+ at 401.5 eV. The latter is ascribed to the proton exchange with remaining surface hydroxyl groups [12]. Also, the water contact angle value of 81° is slightly higher than expected for a surface having –NH_2 head group, around 63° [13]. Both observations suggest that some of the –NH_2 head groups are oriented towards the SiO_2 surface, exposing the alkyl chains. Hence, APTMS seems to form polycondensed adsorbed layers. This is consistent with other reports from solvent-based processes which show that APTMS is prone to form polycondensed layers, especially in concentrated solutions [14]. In fact, it seems

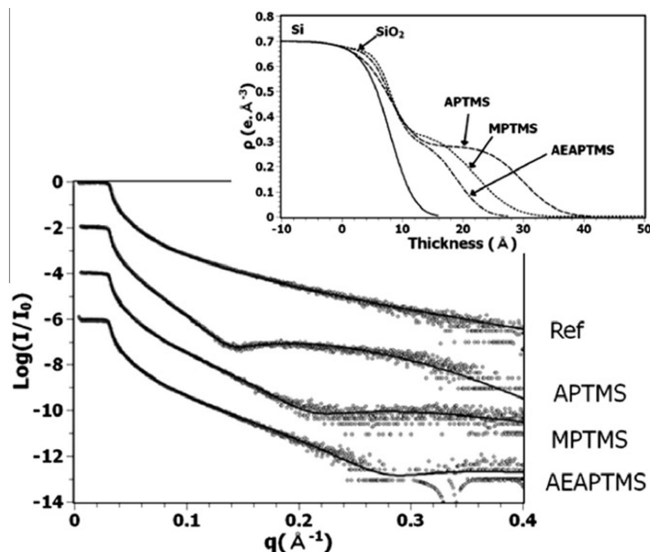

Fig. 1. Experimental and simulated X-ray reflectivity curves of the samples before and after silanization on SiO_2. The corresponding electron density profiles are given in the inset.

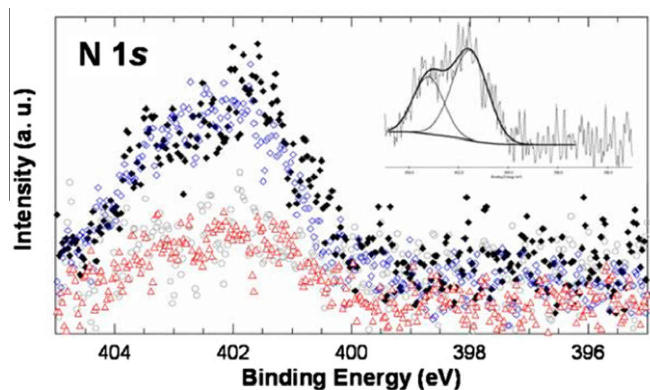

Fig. 2. XPS N1s core-level spectrum of samples before and after deposition of APTMS on SiO_2.

that this behavior holds in $SCCO_2$. Up to 9 nm thick APTMS layers were obtained when the precursor was first dissolved in a co-solvent (acetone) to increase its solubility, and when $SCCO_2$ was dispensed in a dynamic mode (i.e. flowed through the chamber) during process.

3.2. Formation of the organic layers on porous SiOCH

Substrates with O_2-treated porous SiOCH were characterized by XRR and NR before alkoxysilane deposition. Narrow fringes are detected by NR (see reference sample in Fig. 4). This curve was successfully simulated using the following stack: 44 nm of porous SiOCH buried under 316 nm of denser material. This denser layer is the result of the partial oxidation of the SiOCH material under O_2 plasma. By contrast, X-ray reflectivity curves (not shown here) only exhibit a monotonic decrease of intensity, with no visible fringe. The oxidized zone is too thick and has insufficient electronic contrast with the non-modified material to be detected in our experimental conditions. In the remainder of this study, the dielectric film was considered to be a monolithic substrate for X-ray reflectivity curve simulations. For NR analysis, the thicknesses of the partially oxidized and non-modified zones were fixed, and

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