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Characterization of Chemical Bonding in Low-K Dielectric Materials for Interconnect Isolation: A XAS and EELS Study

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ABSTRACT

The use of low dielectric constant materials in the on-chip interconnect process reduces interconnect delay, power dissipation and crosstalk noise. To achieve the requirements of the ITRS for 2007-2009 minimal sidewall damage from etch, ash or cleans is required. In chemical vapor deposited (CVD) organo-silicate glass (OSG) which are used as intermetal dielectric (IMD) materials the substitution of oxygen in SiO_2 by methyl groups ($-CH_3$) reduces the permittivity significantly (from 4.0 in SiO_2 to 2.6-3.3 in the OSG), since the electronic polarizability is lower for Si-C bonds than for Si-O bonds.

However, plasma processing for resist stripping, trench etching and post-etch cleaning removes C and H containing molecular groups from the near-surface layer of OSG. Therefore, compositional analysis and chemical bonding characterization of structured IMD films with nanometer resolution is necessary for process optimization.

OSG thin films as-deposited and after plasma treatment are studied using X-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS). In both techniques, the fine structure near the C1s absorption or energy loss edge, respectively, allows to identify C-H, C-C, and C-O bonds. This gives the opportunity to differentiate between individual low-k materials and their modifications. The O1s signal is less selective to individual bonds. XAS spectra have been recorded for non-patterned films and EELS spectra for patterned structures. The chemical bonding is compared for as-deposited and plasma-treated low-k materials. The Fluorescence Yield (FY) and the Total Electron Yield (TEY) recorded while XAS measurement are compared. Examination of the C 1s near-edge structures reveal a modified bonding of the remaining C atoms in the plasma-treated sample regions.

INTRODUCTION

SiO_2 is mainly used as dielectric material for interconnect isolation in present semiconductor process technologies. Minimizing the capacitance between these interconnects can decrease power consumption and wire delay. This can be achieved by using materials with a dielectric constant ε_r (low-k materials) lower then that of SiO_2 (ε_r^{SiO2}=3.9). As replacement mate-

rial polymers [1], organo-silicate glass (OSG), and materials with artificially introduced voids (porous material) [3] are investigated. Additionally, the use of air-gaps with the ultimate dielectric constant of $\varepsilon_r=1$ are suggested by Gosset et al. in [4] for isolation of parts of the wires. Polymers exhibits inherently low dielectric constants which can be reduced additionally by using polymers with a very open structure, like polycyanurates [2] to create a void-rich and porous structure. In all these ultra-low-k materials voids and pores play a key role in decreasing ε_r. Therefore many investigations are dealing with problems like manufacturability [5] or pore-sealing (a survey can be found in [6]). Theoretical models are developed to estimate the stiffness as a function of the pore size and distribution [7].

In the OSG material discussed in this paper some Si-O bonds are replaced by $Si\text{-}CH_3$ bonds. On the one hand this leads to a less polar bonding. On the other hand the material gets nano-porous due to a more open structure. Both leads to a reduction of ε_r to values between 2.6 and 3.3. Oxygen plasma processes used to pattern the OSG leads to a decay of the $Si\text{-}CH_3$ bonds and to the formation of Si-OH groups [8]. This so-called sidewall damage will increase the dielectric constant ε_r and hence has to be minimized. With regard to the ITRS, which suggests materials for future semiconductor technology with $\varepsilon_r < 2.2$ and minimal sidewall damage, the minimization of the process-induced damage becomes even more important. This can only be achieved with porous ultra-low-k materials together with development of treatments which allow to avoid severe damage of the fragile ultra-low-k material. Therefore materials science is required, not only to investigate the mechanical properties of such materials (like presented in [9]), but also to study the chemical stability (like presented in this work). Motivated by ELNES experiments on patterned OSG using a TEM [10], our attempt here is to investigate the influence of plasma treatment on OSG by XAS, a method comparable to ELNES.

EXPERIMENTAL

The OSG layers investigated here were produced by PE-CVD processes from two different precursors, OMCTS and 3MS. The resulting layers have a thickness in the range of 180nm to 240nm. After deposition two different plasma treatments were applied. With helium plasma treatment a densification of the layer was achieved. This is obtained mainly by introducing cross-linking within the OSG material. Using oxygen plasma treatment the damage while plasma etch processes was simulated.

The XAS experiments were performed at the ALS in Berkeley/CA at the beamline 8.0.1. The energy resolution was better than 50meV. The Total Electron Yield (TEY) was measured on a wire biased with a positive voltage. At the same time the Fluorescence Yield (FY) was measured with a Canberra fluorescence detector. The spectra were normalized to the x-ray intensity I_0, measured on an Au mesh. Because the OSG is very sensitive, the radiation damage while measurement is a severe problem and has to be monitored carefully. Therefore the C1s XAS spectrum was measured at first and again at the end of a measurement cycle, and the change in the spectrum was taken in order to estimate the radiation damage. It was found that decreasing the beamline intensity by a factor of 1,000 (to a flux of approx. 10^9 photons per second) is sufficient to have a stable C1s signal.

For the TEM/ELNES experiments cross-sections of as-deposited and electron-beam or He-plasma-treated OSG films were prepared by grinding and Ar+-ion beam polishing. The

measurement was performed with a ZEISS LIBRA 200 TEM (200 keV primary electron energy) equipped with a monochromated Schottky field emitter electron gun and an in-column corrected 90° OMEGA electron energy filter. Sample regions with a thickness smaller than 60 nm were selected for the EELS/ELNES measurements. Spectra around the C-K (1s) electron energy-loss edge were recorded with an acquisition time of 60 s from circular areas with about 80 nm diameter, at an energy resolution of 0.15 eV. The analyzed areas were located in original OSG material and in modified OSG zones. The spectra were power-law background-subtracted.

RESULTS AND DISCUSSION

XAS results: Influence of the plasma treatment

XAS spectra around the adsorption edge of Si2p, C1s, and O1s were recorded for untreated OSG samples, and for He-plasma- and O_2-plasma treated samples. The Si2p- and C1s-spectra are given in figure 1 below. OSG with and without treatment show clear differences in the XAS spectra: C1s emissions around 287.3eV are attributed to excitations from the C1s core level into empty σ-states of the Si-<u>C</u>H_3 bond. Measurement of Ade et al. at organic materials containing different amounts of -CH_3 groups confirm that [11]. The plasma treatment leads to a vanishing of that emission around 287.3eV and emission around 285.2eV and 288.7eV appear. A reference measurement on HOPG (not shown here) reveals, that the emission around 285.2eV belongs to an excitation into the π^* orbital of graphite. The emission at 288.7eV indicates excitations into empty π-orbitals of a C=O bond [12].

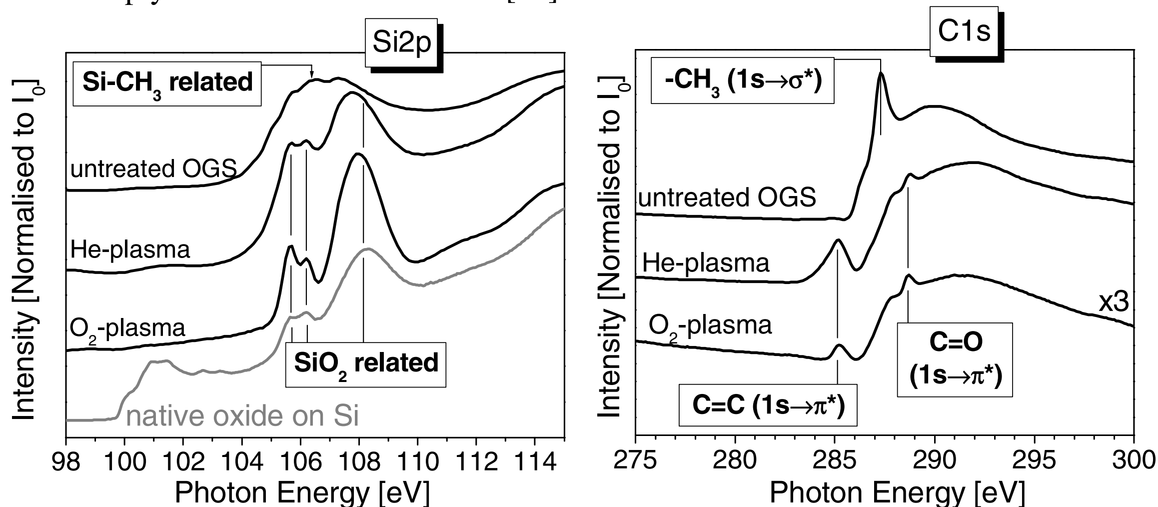

Figure 1: Si2p- (left) and C1s- (right) XAS spectra on untreated (top), He-plasma treated (middle) and O_2-plasma treated (bottom) OSG samples. The Si2p spectrum of native SiO_2 on Si (gray curve) is given for comparison.

The Si2p XAS spectra also show a clear influence of the plasma treatment. Although the emissions are not that clear separated like in the C1s spectra, one can identify a decay in the emission around 106.4eV. The remaining emissions around 105.6eV / 106.2eV (spin-orbit split-

ting in Si2p is 0.6eV) and 108.0eV are very similar to those on a SiO_2 layer on Si substrate. Therefore we attribute the emission around 106.4eV to excitations within a Si-CH_3 bond.

The differences between the He- and the O_2-plasma treatment are rather small. It is evident from the smaller graphite resonance that less graphite is formed on O_2-plasma treatment. Additionally, the C=O-resonance is more pronounced. The Si2p spectrum also exhibits a difference around 108.0eV and a more SiO_2-like appearance. In general one can summarize that plasma treatment leads to a decay of the -CH_3 groups and to oxidation of carbon and silicon. As a consequence the layer gets more SiO_2-like. A significant difference in the OSG layers prepared by the OMCTS and 3MS precursors could neither be detected in the untreated nor in the plasma treated samples.

XAS results: Comparison of electron and fluorescence yield

Together with the electron yield, fluorescence yield spectra were also recorded while XAS measurement. The signal-to-noise ratio is reduced because of the low intensity used to protect the OSG from radiation damage. In figure 2 are shown the fluorescence spectra of the untreated and the He-plasma treated sample. For comparison, the electron yield spectra are shown also.

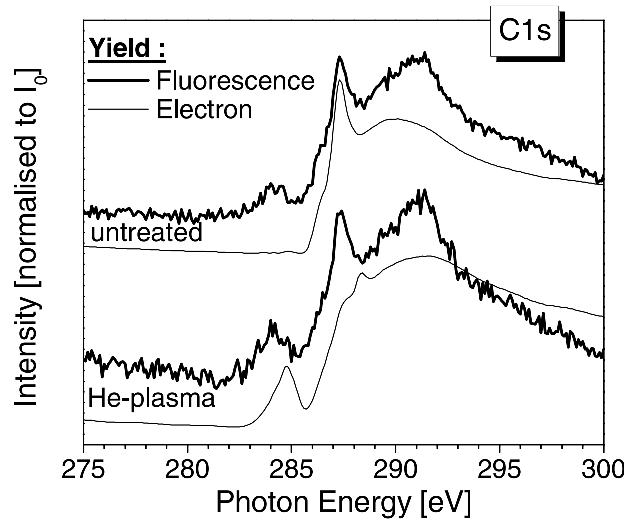

Figure 2: Total electron yield (TEY, thin line) and fluorescence yield (FY, bold line) spectra around the C1s absorption edge. Shown are the spectra for the untreated (top) and the He-plasma treated (bottom) OSG. O_2-plasma treatment exhibits very similar spectra, and therefore is not shown here.

The fluorescence spectra also exhibit an emission around 287.3eV, which belongs to a resonance into σ^*-orbitals of the Si-C**H**$_3$ bond. Contrary to the TEY spectra this emission also appears on the plasma treated samples. Nevertheless a small decay can be detected when comparing this resonance to the broad σ^*-resonance around 291.2eV. The emission from the graphite (around 284.2eV) is also present on both sample. This emission increases considerable with the He-treatment, indicating again a formation of graphite. Remarkable is a shift of the graphite emission of about 0.6eV towards lower photon energies in the FY compared to TEY spectra. Not visible in FY is the emission from C=O bonds around 288.4eV.

The results obtained from the comparison of TEY and FY can be understood with respect to the different depth sensitivity of TEY and FY: The electrons used to collect the electron yield are interacting much more intense with the sample than the fluorescence light. The electrons have an escape depth of several 10nm, whereas the fluorescence light can escape from depth in the range of µm. Therefore the TEY gives information about the surface of the OSG film. This is affected by the plasma treatment much more than the bulk material. Hence the decay in the Si-C**H**$_3$-resonances in the TEY spectra reflects the damage at the surface and the persistence of that emission in the FY shows the unaffected bulk OSG material. In that connection the appearance of emissions from graphite on the non-treated OSG could mean that graphite also exists on the non-treated OSG, but only in greater depth. A possible explanation would be formation of graphite at the beginning of the PE-CVD process. The absence of the emission from C=O bonds in the FY spectra can also be understood as a result of the higher bulk sensitivity of the fluorescence. But this emission can also be concealed by the noise because also in the TEY the signal is very weak. In general, the comparison of TEY and FY shows that the influence of the plasma treatment is restricted to the surface of the OSG.

ELNES results: Influence of treatment and comparison to XAS

Electron loss spectra around the C-K edge recorded on OSG films are shown in figure 3. The OSG was prepared from the OMCTS precursor and different treatment was applied: Beside the He-plasma treatment an electron treatment using 4keV of kinetic energy was applied. The ELNES measurements are discussed in more detail in [9] in this volume.

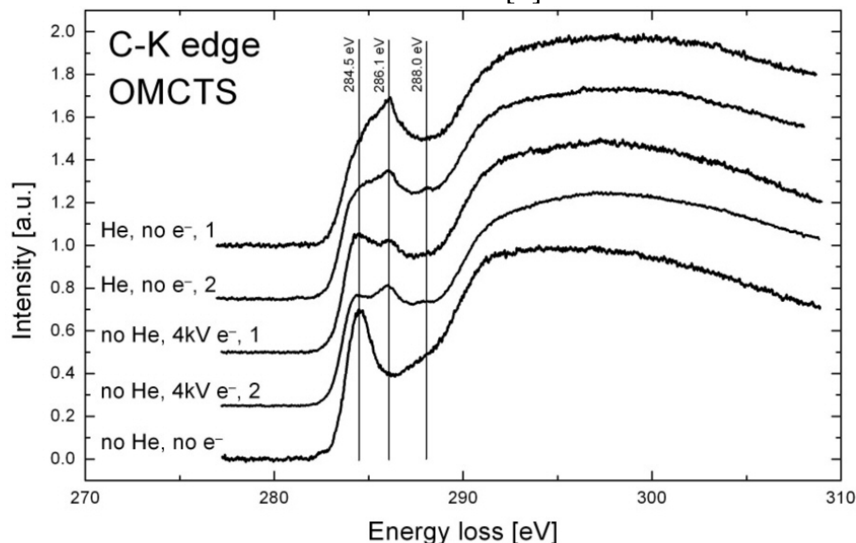

Figure 3: Electron Loss Near Edge Spectra (ELNES) around the C-K edge on OSG prepared by the precursor OMCTS. Spectra were recorded on as-prepared OSG (bottom), on electron beam treated samples (two sample sections: 2nd and 3rd curve from below), and on He-plasma treated OSG (also two sample sections: both top spectra).

The ELNES emission around 284.5eV is attributed to C=C bonding in graphitic carbon [9]. This is in agreement with the XAS spectra described above. Contrary to the findings in the XAS analysis the ELNES spectrum of the as-prepared OSG is dominated by this graphitic emission. The resonance appearing around 288.0eV can be explained as excitation into C=O bonds (also in agreement with XAS). The most prominent emission in the He-treated samples appears

around 286.1eV. In the XAS spectra a resonance at this energy was attributed to excitations into Si-$\underline{\mathbf{C}}H_3$ σ^* orbitals. This is not applicable in the ELNES case, because this emission here appears only after the treatment. If it would be connected to -$\underline{\mathbf{C}}H_3$ groups it should have its maximal intensity at the non-treated samples. More likely is the interpretation of that emission around 286.1eV as excitation into C-O (single) bonds, because it always appears in conjunction with the C=O resonance around 288.1eV. A reason why no excitations into σ^* orbitals of the Si-$\underline{\mathbf{C}}H_3$ bonds are visible in ELNES spectra could be, that a sigma resonance is less pronounced and very broad in ELNES, in general (compare emissions between 290eV and 300eV in the ELNES and XAS spectra). Another possible explanation could also be, that -CH_3 groups are already destroyed while TEM sample preparation or while measurement (due to electron beam damage). In XAS measurements this problems could only be solved by reducing the x-ray beam intensity by a factor of 1,000. This could also be an explanation for the occurrence of the graphite already on the non-treated samples. But also in fluorescence yield XAS some graphite was detected, and radiation damage could be ruled out because the TEY measured at the same time did not show any graphite. This points out that both methods, XAS and ELNES, can deliver comparable information, but also can give complementary results.

CONCLUSIONS

The influence of plasma treatment on OSG material was investigated by X-ray absorption spectroscopy. By using electron and fluorescence yield the decay of the Si-CH_3 bonds at the plasma-influenced surface could be detected. The OSG becomes more SiO_2-like. This is more pronounced at O_2-plasma treatment than at He-plasma treatment. Additionally graphitic carbon is formed by the plasma treatment and C=O bonds are created. Differences in the OSG depending on the precursor used in the PE-CVD process could not be detected by XAS.

A comparison of ELNES and XAS spectra show similar emissions, like from graphitic carbon (C=C bonds) and from C=O bonds. An open question is, why emissions from Si-CH_3 bonds are absent in ELNES spectra and why on the non-treated OSG graphite is visible already .

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