EFTEM analysis of the interaction of Co with a fluorinated organic dielectric


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Summary: Cobalt fluoride as a barrier in an organic low-k dielectric and Cu metallization scheme is studied by means of Energy Filtered Transmission Electron Microscopy (EFTEM). It is shown that Co reacts with the fluorinated organic dielectric and forms a cobalt fluoride layer at the interface.

1. Introduction.
Low-k dielectric materials have a lower dielectric constant in comparison with traditionally used SiO₂ so that the interline capacitance in the high density interconnect structures in ULSI devices can be reduced. The use of porous dielectric materials or fluorinated materials allows to decrease the dielectric constant even further [1]. Cobalt fluoride is a possible barrier material between the metal and the dielectric. In this work the reaction of Co with a fluorinated low-k dielectric is studied by energy filtered transmission electron microscopy.

The investigated organic low permittivity material (SILK™, Dow Chemical) is not fluorinated and has a refractive index of 1.63. Fluorination is done by an afterglow plasma treatment at 100°C (60% NF₃/He for 5s). The refractive index and therefore the dielectric constant changes [2] after the plasma treatment to 1.42 ± 0.01. Afterwards, a cobalt layer is sputtered on top of the fluorinated dielectric. One specimen received an additional heat treatment (10s at 300°C). The TEM samples are prepared with a FIB wedge milling technique for which the surface is protected with a sputtered glass and a Pt layer.

Energy-filtered images are taken with a Philips CM30 FEG microscope (300 keV) equipped with a Gatan Imaging Filter. For image calculation and processing Gatan's software Digital Micrograph is used.

3. Results.
EFTEM is used in this study to complement the results obtained with other analysis techniques (XPS, ellipsometry, AFM, RBS, AES, AGM). These techniques require an etch-back of the cobalt to investigate the reaction of the cobalt with the fluorinated low-k dielectric. The advantage of TEM is that the samples can be studied without an etch-back. Fig. 1a shows a cross-section of the sample before the heat-treatment and fig. 1b shows the sample after the heat treatment which is intended to stimulate the formation of the cobalt fluoride layer.

From the TEM-images, it is possible to distinguish the different layers. On top of the cobalt layer (24 nm), the protective glass layer is visible. Underneath the cobalt, the low-k dielectric can be observed. At the interface, two distinct features show up, the clearest one is the appearance of voids (25 nm) underneath the cobalt layer. These voids are due to the fluorination process and are more pronounced in the sample that received the heat-treatment. The second feature that is clearly seen is a brighter layer (6 nm) in between the Co and the voids. EFTEM-analysis is used to characterise these features. First, a relative thickness map is calculated from the logarithmic ratio of an unfiltered and zero-loss filtered image [3] as shown in fig. 2. The voids clearly appear in the low-k dielectric resulting in a smaller thickness. To understand the nature of the layer in between
the cobalt and the low-k polymer, energy filtered images of oxygen (fig. 3a), fluorine (fig. 3b) and cobalt (fig. 3c) are acquired.

![Cross-sectional TEM image of a) the sample without heat-treatment and b) the sample after the heat-treatment. The voids are more clear in the latter case. Also the thin layer in between the voids and the cobalt is visible.](image1)

![Relative thickness map for the sample with the heat-treatment (fig 1b). The layer with voids shows up darker, indicating a lower mean thickness.](image2)

![Elemental distribution maps for a) oxygen b) fluorine and c) cobalt for the sample without heat treatment.](image3)

![Quantification profiles over the interface layers for a) the sample without heat-treatment and b) the sample with the heat-treatment (left = low-k polymer; right = glass layer).](image4)

Quantification profiles (fig. 4) are formed by calculating atomic ratio images and multiplying with ionisation cross-section ratios [4] (carbon, which is the major element in the polymer, is not considered in this case). These profiles indicate the presence of a cobalt fluoride layer that is formed after the cobalt sputtering. This layer is wider after the heat treatment. The second feature that shows up in the EFTEM-images are the voids. In the cobalt elemental map, brighter areas below the cobalt layer indicate that cobalt has drifted into the voids in the low-k polymer which is an undesirable effect. Also a higher concentration of fluorine is detected in the voids.

4. Conclusion.

We have studied the fluorination of cobalt sputtered on a fluorinated low-k polymer. All investigated samples reveal from cross-section EFTEM-images a fluorinated cobalt layer with a thickness of 6 nm in between the cobalt and the low-k polymer. This layer is wider when the samples received a heat-treatment to improve the fluorination.

It is shown that the use of EFTEM on cross-section specimens allows the direct identification of the thin fluorinated layer without the need to etch-back the Co as is necessary for other analysis techniques and which might introduce artefacts due to the etching. Relative thickness maps allow the detection of voids in the upper part of the polymer layer. With EFTEM the presence of Co and F in the void region is shown.

5. Acknowledgements.

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6. References.