MS15-P26 Fluorous low-dielectric-constant materials: non-porous coordination polymers *vs*. metal-organic frameworks

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Identifying novel low-dielectric-constant (low-κ) materials for integrated circuit (IC) use is a main concern for the microelectronics industry.

Metal-organic frameworks (MOFs) and functional non-porous coordination polymers (FN-PCPs) are studied as alternatives to currently applied low-κ dielectrics: their properties can be modulated through a sensible choice of nodes and spacers, with the added value of the high thermal stability imparted by *N*-donor struts. Compared to MOFs, FN-PCPs possess *i*) higher material density, granting a higher density of functionally-active centers; and *ii*) lower sensitivity to high-κ species, such as water (κ ~80), due to lack of porosity. Nevertheless, few reports, regarding exclusively MOFs, have appeared to date on dielectric properties.

Here we report on two classes of related CPs:

1. Tetrazolate-based CPs: These include FN-PCP-1 (Ag_2(FBTB), FBTB = 1,4-bis-(tetrazol-5-ate)tetrafluorobenzene) and FMOF-3 (Cu(FBTB)), which are isostructural to Ag_2(BTB) [1] and Cu(BTB) [2], respectively. As demonstrated by VT-PXRD, fluorination enhances thermal stability: FN-PCP-1 and FMOF-3 decompose in air at 260 and 400 °C, respectively (*vs.* 380 °C T_{dec} for Ag_2(BTB); 100 °C $T_{phase\ change}$ for Cu(BTB)). Fluorination and lack of porosity favour water stability: contact angles up to ~75° were measured for FN-PCP-1 (*vs.* ~50° for Ag_2(BTB); FN-PCP-1 is recovered intact after 1 month exposure to water vapours while FMOF-3 undergoes a phase change after 24 h. Fluorination reduces κ_{RT} values to 2.59(3) for FN-PCP-1 and 2.44(5) for FMOF-3 (*vs.* 3.79(4) for Ag_2(BTB)). After 72 h exposure to water vapours FN-PCP-1 κ increases to only 2.63(5).

2. Triazolate-based CPs: These include FMOF-1 ($Ag_2(Ag_4Tz_6)$, Tz = 3,5-bis(trifluoromethyl)-1,2,4-triazolate) [3] and its polymorph FN-PCP-2 ($Ag_7(Tz)_7$). FMOF-1 is stable, under N_2, up to 380 °C. DFT simulations show that both FMOF-1 and FN-PCP2 possess non-polar building blocks. Measured contact angles up to ~160° for FMOF-1 suggest superhydrophobicity. A record low-κ_{RT} is obtained from preliminary studies that remain ongoing.

Work is in progress to complete this case study and exploit other metal-ligand combinations, maintaining the above promising properties yet increasing the thermal stability up to the ~450 °C needed for practical IC application.

References

[1] A.Maspero *et al.* Inorg.Chim.Acta 2009, 362, 4340.

[2] M.Dincă *et al.* J.Am.Chem.Soc. 2006, 128, 8904.

[3] C.Yang *et al.* J.Am.Chem.Soc. 2007, 129, 15454.

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