Effect of Silane Coupling Agent Chemistry on Electrical Breakdown across Hybrid Organic–Inorganic Insulating Films

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Effect of silane coupling agent chemistry on electrical breakdown across hybrid organic-inorganic insulating films

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Supplemental Information

A. SYNTHETIC MODIFICATION OF SILANE COUPLING AGENTS

Silane coupling agents (SCAs) that were not commercially available were modified synthetically using a chlorosilane to methoxysilane conversion based on a patent by Kotzsch and Vahlensieck,[1] involving the addition of anhydrous methanol to the chlorosilane under inert gas. Subsequent boiling of the resulting liquid removes hydrochloric acid, favoring the formation of methoxysilanes via the reaction

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$$RSi(Cl)_x(CH_3)_{3-x} + xCH_3OH \xrightarrow{\Delta} RSi(OCH_3)_x(CH_3)_{3-x} + xHCl , \qquad (1)$$
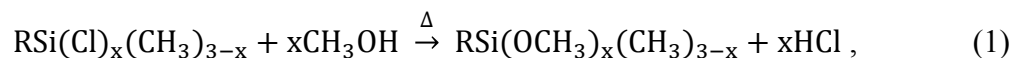
where R in this case is a fluorinated hydrocarbon chain of various length and x is an integer from one to three. In this investigation, tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (tDF-dMeC) was converted to tridecafluoro-1,1,2,2-tetrahydrooctyldimethylmethoxysilane (tDF-dMeM).

Chlorosilane to methoxysilane conversion

Two grams of SCA were quickly added to a flame dehydrated, three necked, 25 mL roundbottom flask connected to a Schlenk line under dry argon positive pressure. A stoichiometric amount of dry methanol was added in two stages. In the first stage, two thirds of the stoichiometric amount of dry methanol, freshly distilled over CaH_2, was injected over 10 mins into the flask using a dehydrated, dry argon filled syringe with a long-tipped stainless steel needle. The mixture was heated to 80°C in an oil bath for 40 mins while magnetically stirring to remove the HCl. In the second stage, the remaining third of the dry methanol was added in the same fashion over 5 mins, and the mixture was heated at 80°C for 1 hr. The liquid was passed through a 0.2 µm PTFE syringe filter and subjected to a rotary evaporator for 5 mins to remove residual HCl. Product quality was verified with ^{1}H nuclear magnetic resonance spectroscopy using deuterated chloroform as a solvent. The samples were then stored under dry argon until further use.

B. CALCULATION OF SELF-ASSEMBLED MONOLAYER INTERNAL ELECTRIC FIELDS

From classical electricity and magnetism,[2] the net electric field experienced by a material, E_{net}, is equivalent to the difference between the external applied field, E_o, and its induced field, $E_{induced}$, expressed as

$$E_{net} = E_0 - E_{induced} \tag{2}$$

which can be specified for the self assembled monolayer (SAM), depicted in Figure S1, as

$$E_{net,SAM} = E_0 - E_{induced,SAM} \tag{3}$$

Modeled as series parallel plate capacitor, Gauss' Law can be invoked, relating the total charge density on the electrodes, σ_{tot}, to the applied field

$$E_0 = \frac{\Delta V_0}{d_{tot}} = \frac{\Delta V_0}{d_{SAM}+d_{ox}} = \frac{\sigma_{tot}}{\varepsilon_0} \tag{4}$$

where d_{SAM} is the SAM thickness, d_{ox} is the oxide thickness, and d_{tot} is the total insulator thickness. Rearranging equation 3,

$$\sigma_{tot} = \frac{\Delta V_0 \varepsilon_0}{d_{SAM}+d_{ox}} \tag{5}$$

and the potential drop over the SAM is then

$$\Delta V_{SAM} = E_0 d_{SAM} \tag{6}$$

yielding an induced field within the SAM of

$$E_{induced,SAM} = \frac{\sigma_{induced,SAM}}{\varepsilon_0} = \left(\frac{\varepsilon_{r,SCA}-1}{\varepsilon_{r,SCA}}\right)\frac{\sigma_{tot}}{\varepsilon_0} \tag{7}$$
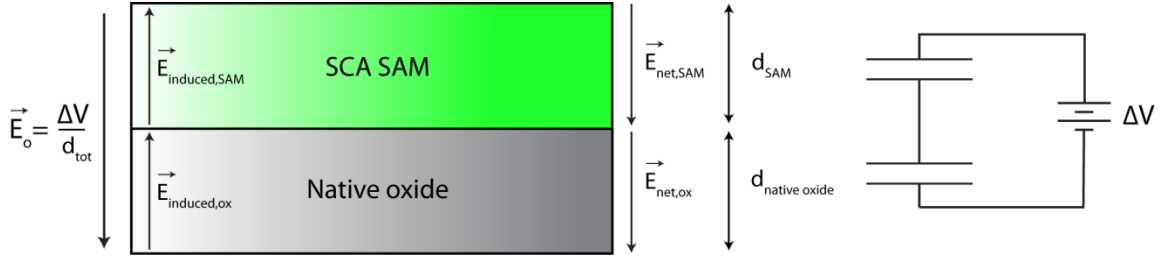
Substituting equation 4 into equation 6,

$$E_{induced,SAM} = \left(\frac{\varepsilon_{r,SCA}-1}{\varepsilon_{r,SCA}}\right)\frac{\Delta V_0}{d_{SAM}+d_{ox}} \tag{8}$$

and substituting equations 3 and 7 into equation 2,

$$E_{net,SAM} = \frac{\Delta V_0}{d_{SAM}+d_{ox}}\left(1 - \left(\frac{\varepsilon_{r,SCA}-1}{\varepsilon_{r,SCA}}\right)\right) \qquad (9)$$

the net electric field experienced by the SAM is found.

Figure S1. Schematic of parallel capacitor representation of C-AFM test.

The aforementioned calculation assumes that there are no field concentrations (i.e., the tip radius is large compared to the SAM thickness) and that the C-AFM tip does not protrude into the SAM, which is expected given the low force applied to the surface. Although it is noted that the SCA molecules are not isotropic, the difficulty in measuring the dielectric constant of the molecules themselves forces the authors to assume that the values are equivalent to the square of the bulk refractive index determined by the manufacturer. SCAs modified synthetically to change the binding groups are assumed to have the same refractive index as their precursor. The refractive index and assumed dielectric constant values for each SCA molecule are listed in Table S1.

Molecule	Abbreviation	Refractive Index	Dielectric Constant
Silicone oil	*n/a*	1.403	1.97
octyldimethylmethoxysilane	o-dMeM	1.423	2.02
n-octadecyldimethylmethoxysilane	oD-dMeM	1.444	2.09
tridecafluoro-1,1,2,2-tetrahydrooctyldimethylmethoxysilane	tDF-dMeM*	1.3453	1.81
tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane	tDF-dMeC	1.3453	1.81
tridecafluoro-1,1,2,2-tetrahydrooctylmethyldichlorosilane	tDF-MedC	1.35	1.82
heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane	hDF-tC	1.349	1.82
tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane	tDF-tC	1.3521	1.83
nonafluorohexyltrichlorosilane	nF-tC	1.36	1.85

Table S1. Refractive index and assumed dielectric constant values of SCA molecules. The silicone oil refractive index was obtained from Sigma Aldrich. Asterisk indicates assumed values as the binding groups of the molecule were synthetically modified and therefore not measured directly.

References

1. Kotzsch, H. J.; Vahlensieck, H. J., *US.Pat. No. 3985781*.

2. Serway, R. A.; Beichner, R. J., 5th ed.; Brooks/Cole Thomson Learning: USA, 2000; Vol. 2.