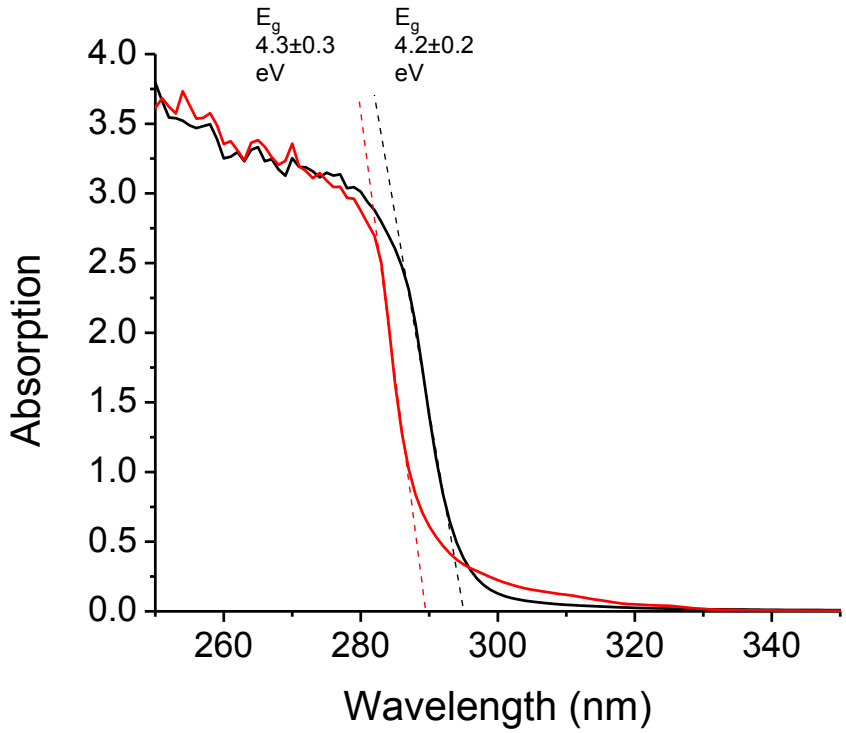
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

High-field chemistry of organometallic precursors for direct-write of germanium and silicon nanostructures

Stephanie E. Vasko,[ab] Wenjun Jiang,[cd] Haoyu Lai,[d] Martin Sadilek,[b] Scott Dunham,*[acd] and Marco Rolandi [*a]

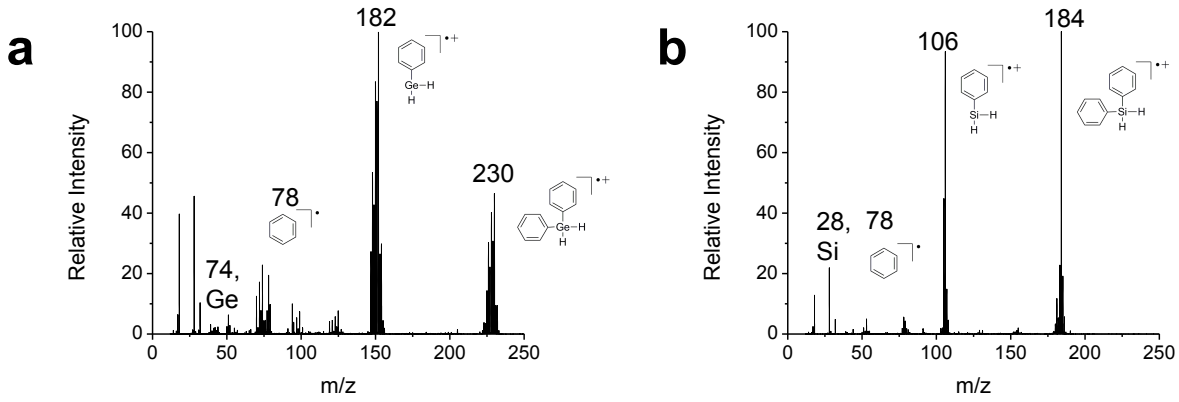
Electronic Supplementary Information

Experimental Section



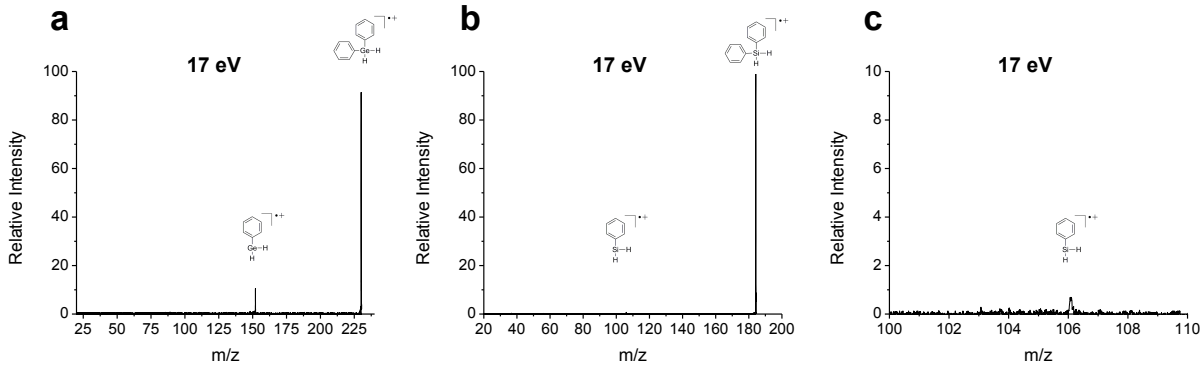
ESI Figure 1: UV-Visible Spectra of DPG and DPS

UV-vis spectra diphenylgermane (black) and diphenylsilane (red) with linear trend lines



ESI Figure 2: Electron-impact mass spectra for DPG and DPS at 70 eV. The 70 eV EI-MS for diphenylsilane matches previously published results at this acceleration voltage.[1]

[1] *Silane, diphenyl-*, <http://webbook.nist.gov/cgi/cbook.cgi?ID=C775122&Units=SI&Mask=200 - Refs> (2011).



ESI Figure 3: Electron Ionization Mass Spectrometry: Collision Induced Decay Data

Collision induced dissociation (CID) data acquired from liquid diphenylgermane (a) and diphenylsilane using 17 eV (b,c) ionization electrons. The most isotopically abundant molecular ion was chosen for DPG (230 amu) and DPS (184 amu). CID indicates that these molecular ions both fragment by losing one neutral phenyl.

Modeling and Simulations

Simulations of fields and current in the tip/liquid/substrate system are conducted using the Sentaurus Device Simulator ® from Synopsys. The AFM tip is very heavily Sb doped (10^{20} cm^{-3}) n-type Silicon with a radius of curvature equal to 15 nm capped by a conformal 2 nm layer of SiO_2. The p-type silicon substrate is heavily boron doped (10^{19} cm^{-3}) with a uniform 2 nm layer of SiO_2. The tip and substrate is nearly in contact (3 Å). The surrounding region is filled with the precursor liquid, which is modeled as a semiconductor with very low ionic mobility on the order of 10^{-6} $cm^2/(V \cdot s)$. We utilize a phonon-assisted tunneling model based on the work of Schenk *et al*, non-local tunneling model for negatively charged ions in the liquid, together with current continuity equations that are solved consistently with Poisson equation. The simulations are based on a 2D system with a depth of 20 nm chosen based on the lateral current distribution used on calculate total tip current. The parameter values employed for DPG/DPS are $\varepsilon_{DPG} = \varepsilon_{DPS} = 2.5$, $\chi_{DPG} = 4.0$ eV, $\chi_{DPS} = 4.0$ eV, $Eg_{DPG} = 4.2$ eV, $Eg_{DPS} = 4.3$ eV.

The primary mechanism for current flow through the insulating SiO_2 layer of the tip and substrate is expected to be quantum mechanical tunneling. The electric field at the tip is very large (> 10^9 V/m), requiring the use of the non-local tunneling model, based on WKB tunneling probability:

$$\begin{cases} \kappa_{C,v}(r,\varepsilon) = \frac{1}{\hbar}\sqrt{2m_C(r)\left|E_{C,v}(r)-\varepsilon\right|}\,\Theta\left[E_{C,v}(r)-\varepsilon\right] \\ \kappa_{V,v}(r,\varepsilon) = \frac{1}{\hbar}\sqrt{2m_V(r)\left|\varepsilon-E_{V,v}(r)\right|}\,\Theta\left[\varepsilon-E_{V,v}(r)\right] \end{cases}$$

where m_C is the conduction-band tunneling mass and m_V is the valence-band tunneling mass, $E_{C,v}$ and $E_{V,v}$ are the conduction and valence bands energies. So the tunneling probability between positions l and u>l for a particle with energy ε can be written as:

$$\begin{cases} \Gamma_{CC,v}(u,l,\varepsilon) = T_{CC,v}(l,\varepsilon)\exp\left(-2\int_{l}^{u}\kappa_{C,v}(r,\varepsilon)dr\right)T_{CC,v}(u,\varepsilon) \\ \Gamma_{VV,v}(u,l,\varepsilon) = T_{VV,v}(l,\varepsilon)\exp\left(-2\int_{l}^{u}\kappa_{V,v}(r,\varepsilon)dr\right)T_{VV,v}(u,\varepsilon) \end{cases}$$

which $T_{CC,v}(l,\varepsilon)$ and $T_{VV,v}(l,\varepsilon)$ are the interface transmission coefficients happened at conduction band and valence band.

The DFT calculations are done using the Vienna *Ab initio* Simulation Package (VASP) with generalized-gradient approximation (GGA). The supercell size is 2.5nm x 2.5nm x 2.5nm with only one k-point sampling at Γ point. The INCAR file is as following:

PREC = Accurate

ISPIN = 2

ISMEAR = 0

SIGMA = 0.01

LREAL = Auto

ALGO = Fast

IBRION = 1

NELMIN = 4

NSW = 500

NELM = 160

EDIFF = 1e-5

EDIFFG = -0.01

For calculations with E-field, the following lines are added to the INCAR file:

EFIELD = -0.4

IDIPOL = 3

LDIPOL = .TRUE.