

## Insights into scanning probe high-field chemistry of diphenylgermane

Stephanie E. Vasko,<sup>ab</sup> Wenjun Jiang,<sup>d</sup> Renyu Chen,<sup>c</sup> Robert Hanlen,<sup>a</sup> Jessica D. Torrey,<sup>a</sup>  
Scott T. Dunham,<sup>dac</sup> and Marco Rolandi<sup>\*a</sup>

### Electronic Supplementary Information

#### Experimental Section

Si (100) substrates (Addison Engineering, B doped, resistivity  $\rho = 0.02 \text{ } \Omega \text{ cm}$ ) are cleaned by sonication in acetone, isopropyl alcohol, ethanol, deionized water, and annealing in Ar at  $900^\circ\text{C}$  for 10 min to remove any trace organics (oxide thickness *ca.* 3 nm). Diphenylgermane (Gelest) is filtered (Whatman, PTFE,  $0.2 \text{ } \mu\text{m}$ ) prior to use. Nanostructure direct-write is performed on a Veeco Multimode V AFM with a fluid cell operated in contact mode with Sb doped Si cantilevers from Nanoworld ( $\rho = 0.02\text{--}0.025 \text{ } \Omega \text{ cm}$ , spring constant  $k = 0.2 \text{ N m}^{-1}$ ). The fluid cell is purged of water vapor by flushing with dry nitrogen at a rate of  $4 \text{ L min}^{-1}$  for 30 minutes. Diphenylgermane vapor is introduced by bubbling nitrogen carrier gas at  $2 \text{ L min}^{-1}$  for one hour prior to the start of the experiments. A bias is applied to the tip ( $-20$  to  $20 \text{ V}$ ) via an Agilent 4155c Semiconductor Parameter Analyzer. The force setpoint is the same as for imaging in contact mode ( $\approx 1\text{--}10 \text{ nN}$ ). Patterning at lower or higher forces does not affect the patterns as long as contact with the sample is maintained during writing. After patterning, the samples are rinsed in acetone, methanol, and isopropanol. Tapping mode imaging is performed on the same AFM with Veeco Probes TESP Si Sb doped cantilevers ( $\rho = 0.01\text{--}0.025 \text{ } \Omega \text{ cm}$ ,  $k = 40 \text{ N m}^{-1}$ , resonant frequency  $\nu \approx 300 \text{ kHz}$ ).

Current was collected during writing at different voltages with the same 4155c Semiconductor Parameter Analyzer. Data at multiple times during the writing process for each voltage and averaged. Three such sets were collected and averaged. The error in the current value is a product of propagation of the error in the measurement (estimated as the noise peak to peak value during writing) as well as the standard deviation of the three measurements (Figure ESI 1). The overall data is in good agreement with the IV curve presented in Fig. 2 as well as the simulation at low voltages, but diverges (is lower) at higher voltages. Continuous change of tip shape during writing is likely responsible for these discrepancies at higher voltages.

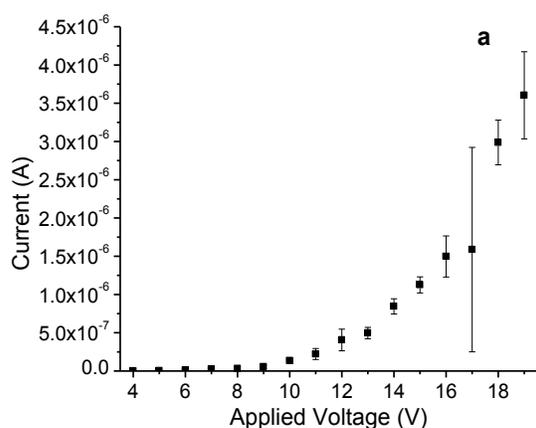
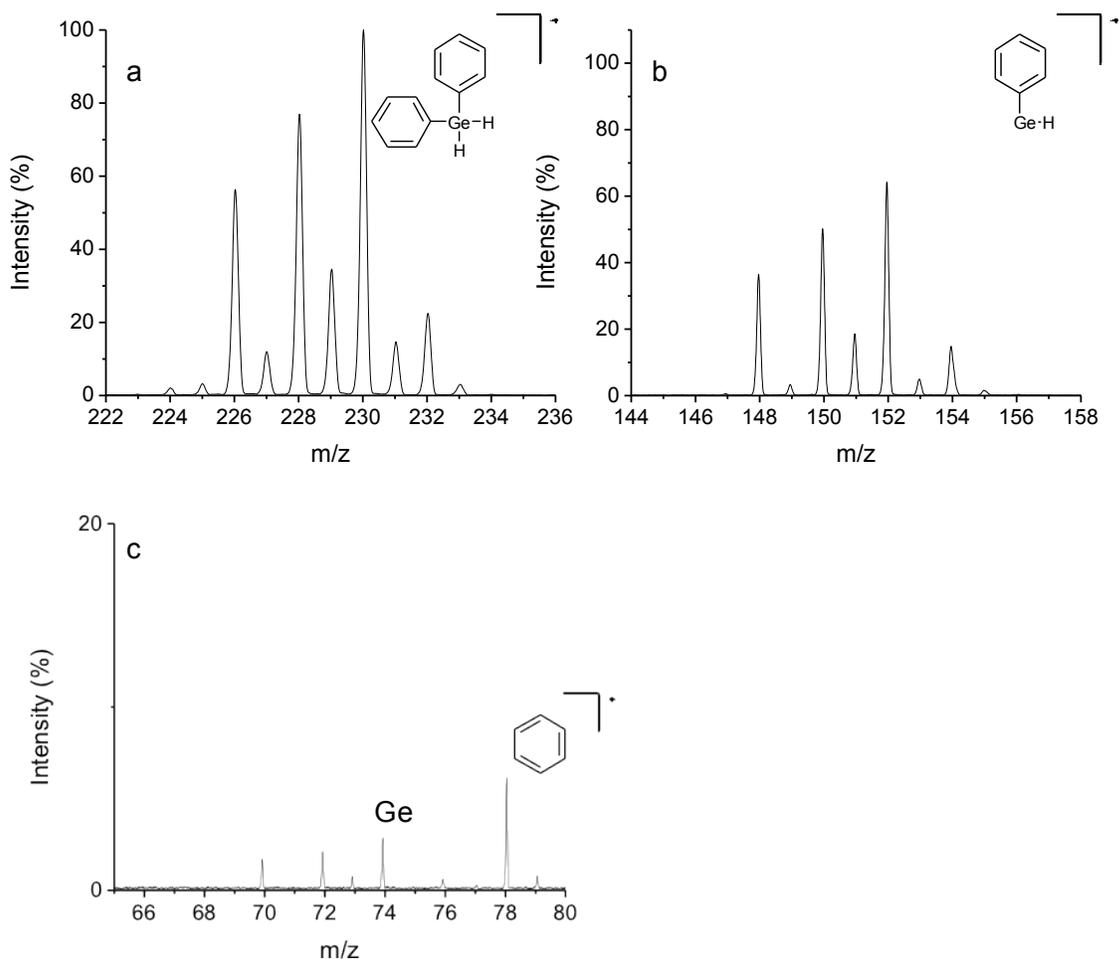


Fig. ESI1. Plot of current as a function of applied voltage acquired during writing.

Mass spectrometry of diphenylgermane was performed using a JEOL HX-110 magnetic sector mass spectrometer at the University of Washington Department of Chemistry Mass Spectrometry Facility. Small quantities of diphenylgermane liquid (Gelest) were introduced into the system via capillary tube. Negative ion spectra were collected in electron impact ionization mode with 17eV electrons. Electron ionization spectra were analyzed using the MASPECII32 data acquisition interface (Mass Spectrometry Services, Ltd., Manchester, UK).

Detailed spectra for the molecular fragments are presented below. The relative intensity and the position of the peaks is as expected when the isotopic abundance of Ge (20.5%, 70 amu; 27.4% 72 amu; 36.5 %, 74 amu; 7.8%, 76 amu) and C (98.9%, 12 amu; 1.1% 13 amu) as well as the loss of 1 H during ionization are included,



**Fig. ESI 2.** Detailed mass spectra data for diphenylgermane positive ion (a), phenylgermane positive ion (b), and Ge and benzene positive ions (c).

## Models and Simulations

Simulations of fields and currents in the tip/liquid/substrate system are conducted using the Sentaurus Device Simulator from Synopsys. The AFM tip is very heavily Sb doped ( $\sim 10^{20} \text{ cm}^{-3}$ ) n-type Si with a radius of curvature equal to 15 nm capped by a conformal 3.5 nm layer of  $\text{SiO}_2$ . The p-type silicon substrate is heavily B doped ( $\sim 10^{19} \text{ cm}^{-3}$ ) with a uniform 3.5 nm layer of  $\text{SiO}_2$ . The tip and substrate are nearly in contact (0.1 nm gap). The surrounding region is filled with the precursor liquid, which is modelled as a semiconductor with very low ionic mobility on the order of  $10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We utilize a phonon-assisted tunnelling model based on the work of Schenk et al.<sup>[1]</sup> and current continuity equations that are solved consistently with Poisson's equation. The simulations are based on a 2D system with a depth of 20 nm chosen based on the lateral current distribution used to calculate total tip current. The parameter values employed for DPG were permittivity of 2.5, electron affinity 0.01 eV, and bandgap of 9.25 eV.

The primary mechanism for current flow through the insulating  $\text{SiO}_2$  layer of the tip and substrate is expected to be quantum mechanical tunneling. The electric field at the tip (Fig. 1) is very large ( $> 10^7 \text{ V/cm}$  or  $10^9 \text{ V/m}$ ), requiring the use of the phonon-assisted band-to-band tunneling model used by Schenk et al.<sup>[1]</sup>:

$$R_{nset}^{bb} = AF^{\frac{1}{2}} \frac{\tilde{n}\tilde{p} - n_{i,eff}^2}{(\tilde{n} + n_{i,eff})(\tilde{p} + p_{i,eff}) \frac{[(F)_C^{\pm}]^{-\frac{3}{2}} \exp\left(-\frac{F_C^{\pm}}{F}\right)}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} + \frac{[(F)_C^{\pm}]^{-\frac{3}{2}} \exp\left(-\frac{F_C^{\pm}}{F}\right)}{1 - \exp\left(\frac{\hbar\omega}{kT}\right)}}$$

where the modified electron/hole densities can be expressed via Schenk density corrections:

$$\tilde{n} = n \left( \frac{n_{i,eff}}{N_{VC}} \right)^{\frac{\gamma_n |\nabla E_{F,n}|}{F}}$$

$$\tilde{p} = p \left( \frac{p_{i,eff}}{N_V} \right)^{\frac{\gamma_p |\nabla E_{F,n}|}{F}}$$

The critical field strengths are:

$$F_C^{\pm} = B(E_{g,eff} + \hbar\omega)^{\frac{3}{2}}$$

where the upper sign refers to tunneling generation ( $np < n_{i,eff}^2$ ) and the lower sign refers to recombination ( $np > n_{i,eff}^2$ ). The quantity  $\hbar\omega$  denotes the energy of the transverse acoustic phonon.

The dissociation energies of DPG are calculated using the VASP density functional theory (DFT) code<sup>[7]</sup> using the PW91 GGA functional<sup>[8]</sup>.

## Number of germanium atoms deposited per second estimate

We estimated the number of germanium atoms deposited per second by

$$N_{Geatoms} = \frac{V_{lines/second} \cdot \rho_{Ge} \cdot N_A}{A_{rGe}}$$

$$\rho_{Ge} = 5.32 \text{ g} \cdot \text{cm}^{-3}$$

$$N_A = 6.02 \cdot 10^{23}$$

$$A_{rGe} = 72.64 \text{ g / mole}$$

Number of electrons emitted per second was derived by  $N_e = I / e$ , where I = current, e = electron charge =  $1.6 \cdot 10^{-19}$  C. Volume of the lines was estimated by using line height \* FWHM \* length. Full width half maximum was used as an estimate of the width to minimize tip convolution effects.

References:

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