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Electronic Supplementary Information for

Polygermane: Bandgap Engineering via Tensile Strain and Side-Chain Substitution

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In the supplementary information, computational details, computed electronic band structures of polygermanes and the strain-dependent band gap of poly(diphenylgermane) using the local-density approximation (LDA)[1] and generalized gradient approximation (GGA)[2] of exchange-correlation functional, as well as the hybrid HSE06 functional[3] are provided. GGA calculation results of polystannanes are also presented.

I. Computational details

Our numerical simulations were carried out within the Perdew-Burke-Ernzerholf (PBE) GGA implemented in the Vienna *ab initio* simulation package (VASP).[4] The projected augmented-wave (PAW) method[5] and a plane-wave cutoff energy of 520 eV were used. A three-dimensional periodic tetragonal supercell was chosen with polymers aligned along the z axis and sufficiently separated in the x-y directions by 25 Å. The supercell contains four Ge atoms to fully simulate the structural segments in the linear $\mathrm{Pr^i{}_3Ge(GePh_2)_4GePr^i{}_3}$. The Monkhorst-Pack k-point sampling scheme along the z axis was employed,[6] with a sufficient number of k points as determined by convergence tests. Since the effects of spin polarization on the structures and energies are negligible in chainlike polygermanes, the spin-restricted PBE calculation results were reported in the main text. To obtain the unstrained configuration, atomic position and z lattice parameter were optimized using a conjugate gradient algorithm. When applying mechanical strains, the strained cell is modeled by stretching/compressing the lattice vector to a fixed value in the z-direction while atoms were allowed to relax. The criterion of convergence for energy and force were set to be 10^{-6} eV and 0.02 eV/Å, respectively. We have also repeated some calculations by the spin-restricted LDA with the Ceperley-Alder exchange-correlation,[2] and found no qualitative differences between the LDA and GGA results (see Section II below). It is known that DFT with GGA or LDA tend to underestimate the bandgaps of semiconductors. Hybrid functionals that include a certain percentage of Hartree-Fock exchange or the many-body techniques usually give more accurate bandgaps compared with experiments.[3] Nevertheless, the trend of bandgap changes under different side-chain substituents or strains described here is qualitatively the same, confirmed by the hybrid HSE06 functional calculations (see below).

II. Comparison of LDA and GGA computational results

Both LDA and GGA exchange-correlation functionals are used to compute the electronic band structures of polygermanes and the strain-dependent bandgap of poly(diphenylgermane). As shown in Figs. S1 and S2, the LDA results are very similar to the GGA results, especially the general trend of strain-dependent bandgaps.

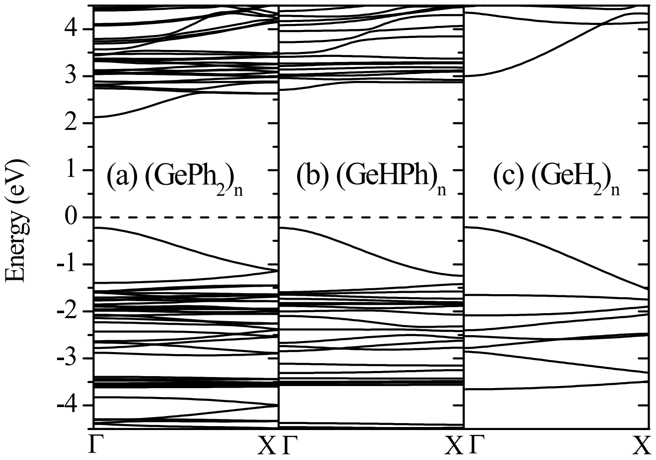

Figure S1. Computed band structures of (a) $(GePh_2)_n$, (b) $(GeHPh)_n$, and (c) $(GeH_2)_n$ in ideal chains, based on the LDA calculation.

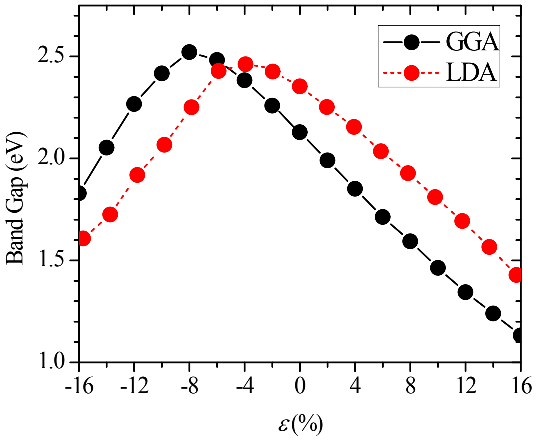

Figure S2. Uniaxial strain-dependent bandgaps of poly(diphenylgermane), based on the LDA and GGA calculations.

III. Results of hybrid HSE06 functional calculations

The HSE06 calculations are also performed for the three kinds of polygermanes with different side-chain substituents and their band structures are shown in Fig. S3. The overall trend in bandgap reduction with the increase of side-chain size is the same as that predicted from the PBE/GGA calculations. The HSE06 calculations confirm that the polygermanes considered here are low-dimensional semiconductors with a direct bandgap. For $(GeXY)_n$, the bandgap obtained from the hybrid HSE06 functional changes from 2.778, 3.455, to 3.827 eV, for XY = Ph_2, HPh, and H_2, respectively. Compared to the GGA's results of the bandgap change from 2.129, 2.724, to 3.033 eV, the HSE06 calculations predict the same trend of bandgap change although the HSE06 bandgaps are larger than the corresponding GGA ones.

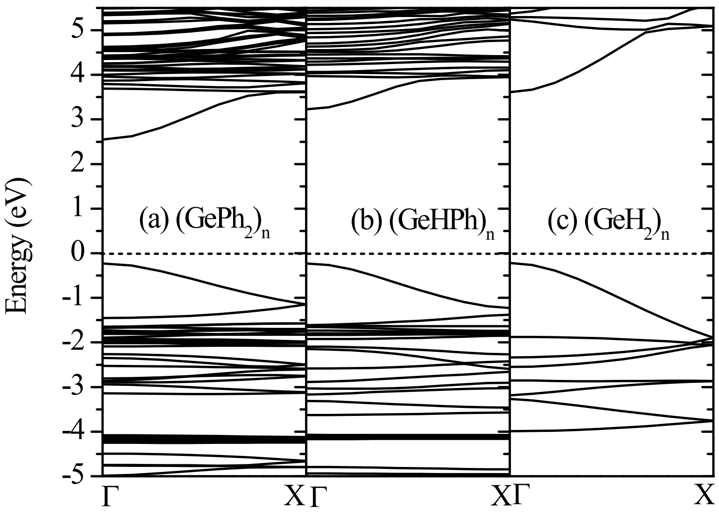

Figure S3. Computed band structures of (a) $(GePh_2)_n$, (b) $(GeHPh)_n$, and (c) $(GeH_2)_n$ in ideal chains, based on the hybrid HSE06 calculations.

IV. Additional calculation results of polystannanes

Using DFT calculations with a GGA exchange-correlation functional, we have also obtained structural and electronic properties of *polystannanes*. Polystannanes also exhibit the direct-bandgap character and their band-edge states are attributed mainly to skeleton Sn atomic orbital. Hence, although the bandgap of polystannane tends to be reduced when larger alkyl groups are substituted in side chains, the degree of reduction is not large, as in the cases of the Si- and Ge-containing polymers. For example, when the side-chain substituents vary from H_2 to HPh to Ph_2, the bandgaps of the three polystannanesare changed from 2.412 to 2.214 to 2.007 eV due to relatively weak electronic contribution from the side chains.

The bandgaps of polystannanes can be also tuned by applying mechanical strains, showing similar strain dependence of bandgap as polygermanes. Figure S4 presents computed relative energies and bandgaps of $(SnPh_2)_n$ with respect to uniaxial strain along the z-direction. Clearly, the tensile strain can reduce bandgap. The compressive strains can enlarge the bandgap up to -8%. Beyond -8% strain, the bandgap decreases with the strain due to induced variation of band-edge states.

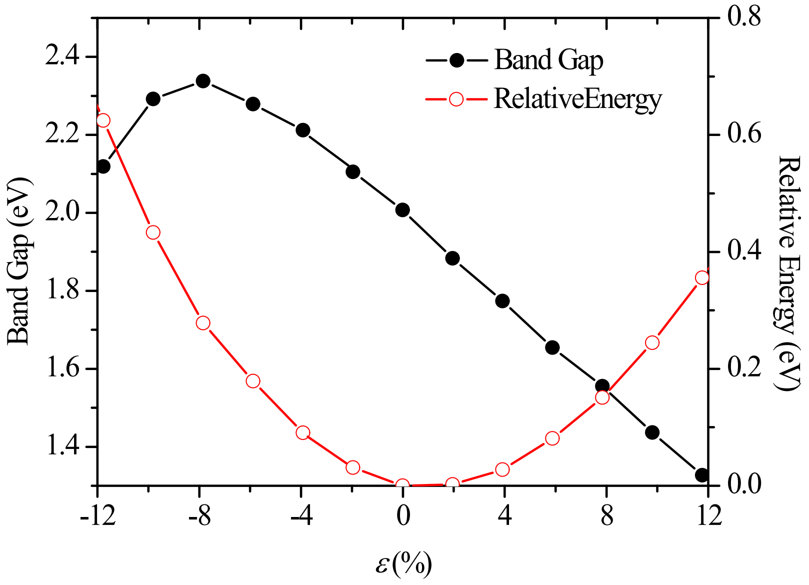

Figure S4. Computed bandgap and relative energy of poly(diphenylstannanes) with respect to strain, ε, which varies from -12 to 12%. Strain is applied to the optimized structure (ε= 0) through uniaxial deformation in z-direction; negative ε represents compressive strain and positive ε represents tensile strain.

ESI References

1 J. P. Perdew and A.Zunger, *Phys. Rev. B*, 1976, **23**, 5048-5079.

2 J. P.Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*,1996, *77*, 3865-3868.

3 J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber and J. G. Ángyán, *J. Chem. Phys.*, 2006, **125**, 249901.

4 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.

5 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.

6 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.