Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Materials

Supplementary Note 1:

The optical properties of the GA_switch and GA_Ferro structures were computed. When these structures are fully relaxed the difference in n and k across the visible spectrum is negligible. However, if we take the relaxed GA_switch structure and heat the material using density functional molecular dynamics, we find that premelt disordering of the Ge-Te-vdW gap occurs at 1260 K, whist the other atoms remain in their crystallographic positions. Relaxing this structure, and then computing the optical properties leads to a 10 % lower optical reflectivity, see Supplementary Figure S1. This is consistent with the experiments reported in the supplementary information of [1]. Again, these simulations agree with our model that the Ferro-type transition is the starting point for a remelt disordering process. And the disordering, which breaks resonant bonds, is necessary for the optical contrast.

Model Notes.

- The DFT-MD was carried out in VASP 5.3.3 [2] with with PAW-pseudopotentials [3] , PBE exchange-correlation functional [4], 3 fs timesteps, and an NVT ensemble
- The starting structure was a 3 by 3 by 1 supercell of the 18-atom GA_switch structure (162 atoms)
- The cutoff energy for the plane wave basis set was 180 eV. An energy tolerance of 10^{-4} eV at the gamma point was used to stop the self consistent field loops.
- The GA_switch structure was heated from 400 K to 1600 K at a rate of 20 K/ps.
- We took the structure at 1260 K, which had a disordered Ge-Te-vdW layer, and performed a BFGS relaxation of the atomic coordinates using Castep [5] with OTFG ultrasoft pseudo potentials and a plane wave cutoff energy of 395 eV. The SCF loops were terminated when the DFT energy changed by <5.6 eV/atom at the gamma-point. The BFGS relaxation was terminated when forces on the atoms was <100 eV/A.
- Due to computational resource limitations, the band structure for comparing the optical properties was also calculated at the gamma-point. The band energy tolerance was 10^{-5} eV. Then the refractive index was computed by first calculating the absorption spectra by summing over the bands assuming (001) polarised light, and then using a Kramers-Kronig transformation to get the refractive index real part.

Supplementary Figure S1

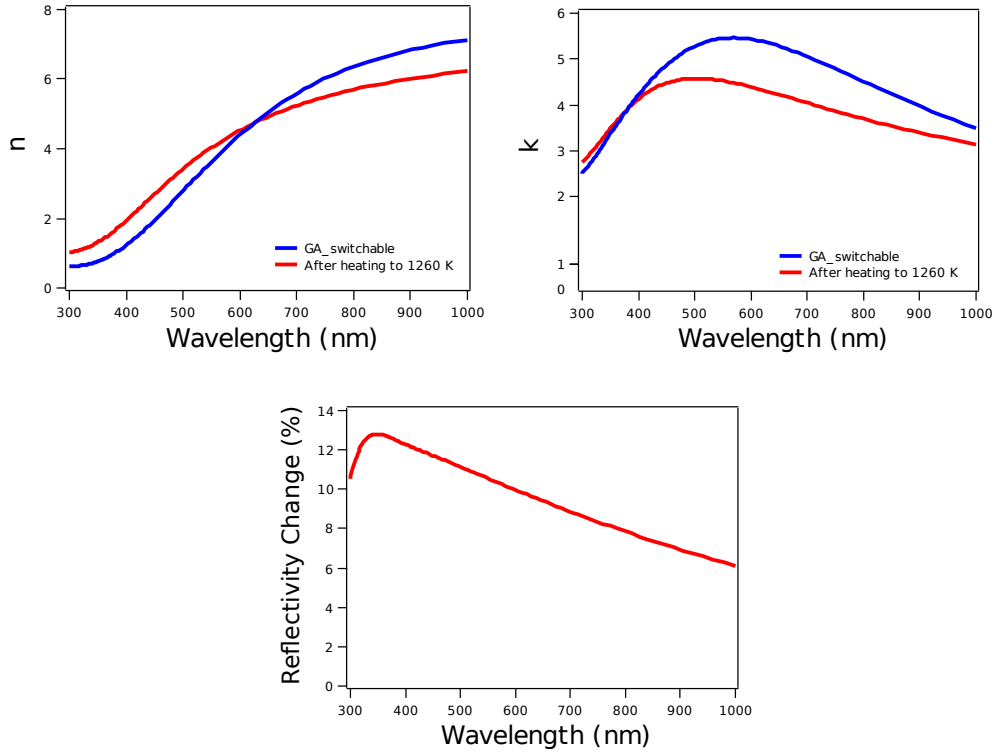

Figure S1: Optical contrast after Ferro-type Ge switching and subsequent disordering

Supplementary References

1. Kalikka et al. Nat. Commun., 7(11983):–, 2016
2. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).
3. Kresse, G. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).
4. Perdew, J., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
5. M. Segall et al. First-principles simulation: ideas, illustrations and the CASTEP code. J. Phys. Cond. Mat., 24(11):2717–2743, 2002.