Band Structure of Germanium Carbides for Direct Bandgap Photonics

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***Abstract*— Ab-initio simulations of dilute germanium carbides (Ge:C) using hybrid functionals predict a direct bandgap with <1%C. Growth of dilute Ge:C shows reduced direct gap consistent with the model, with no structural defects detected. Ge:C may enable lasers and compact modulators on Si.**

***Keywords*- germanium carbides, direct bandgap, silicon photonics, ab initio, band structure**

I. INTRODUCTION

A direct bandgap material on Si would enable strong optical coupling for compact integrated lasers, modulators, and detectors. Although Ge and C both have indirect bandgaps, an alloy of $Ge_{1-x}C_x$ with $x \approx 1\%$ may offer a strongly direct bandgap with $E_{CL}-E_{C\Gamma} > 0.2$ eV. This work presents ab-initio simulations and growth of dilute $Ge_{1-x}C_x$ to study the expected band structure of this alloy for optical applications.

II. AB INITIO CALCULATIONS

The Vienna Ab-initio Software Package (VASP) was used to calculate crystal and band structures of $Ge_{0.9922}C_{0.0078}$ using HSE06 hybrid functionals.[1,2] Although Ge and C have the same valence, C is much more electronegative than Ge and strongly perturbs the crystal and band structures. The Ge-C bond is 14% shorter than Ge-Ge (93 pm vs. 108 pm), as shown in Fig. 1. Electrons are localized near the C atom with roughly spherical symmetry, similar to the direct bandgap conduction band gap at Γ (*k*=0). This splits the conduction band (CB) into E+ and E- bands, while preserving the s-like character of the CB at Γ (Fig. 2). The new CB minimum $E_{G\Gamma} = 0.285$ eV is at least 0.2 eV below the L valley, so most electrons will populate the Γ valley. It is also less than the split-off band energy of 0.31 eV calculated from smaller supercells.

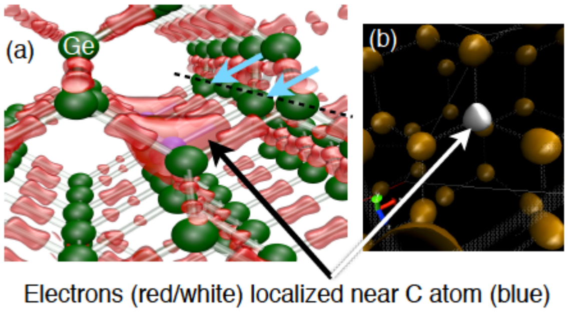

Fig 1. Simulated crystal structure and electron density equipotential surfaces showing electrons localized near C atoms. (a) Looking along a <111> column (upper left). Ge atoms are green, electron density in red (equipotential surface with isosurface=0.44 e-/cell). Blue arrows highlight two Ge atoms pulled out of Ge lattice positions (dashed line) by adjacent C atoms. (b) Closer view of a single C atom with isosurface=1.39 e-/cell. Regions of high electron density (white) approach s-like spherical symmetry around C atom.

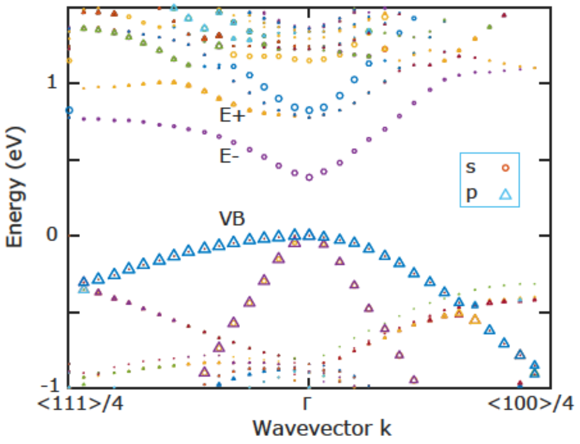

Fig 2. Decomposition of $GeC_{0.0078}$ folded band structure (without spin-orbit coupling) into *s* and *p* orbital weights. Marker size represents fraction of each type of orbital character at each point.

III. GROWTH AND CHARACTERIZATION

To prevent surface segregation and formation of undesirable C-C bonds, we grew Ge:C using a precursor molecule with a C atom already tetrahedrally bonded to four GeH_3 groups.[3] During growth by molecular beam epitaxy, H thermally desorbs, and the CGe_4 core is buried and diluted by Ge from a conventional Ge Knudsen cell. Local strain inhibits C atoms from moving closer than second-nearest neighbors.

Secondary ion mass spectroscopy showed the C to be approximately 0.2%, too small for a direct bandgap. However, no graphitic clusters or C-C bonds were visible in Raman spectroscopy, and nuclear reaction analysis Rutherford backscattering spectroscopy (NRA RBS) showed excellent crystallinity with no detectable interstitial C. Contactless electroreflectance (CER, Fig. 3) showed a reduction in direct bandgap of 0.14±0.1 eV/%C, comparable with dilute nitrides. Transitions to the E+ band in CER were obscured by Franz-Keldysch oscillations.

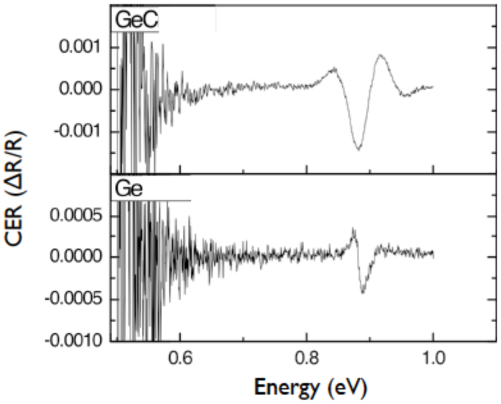

Fig. 3. Contactless electroreflectance of Ge:C sample and a bare Ge substrate. Transitions occur at lower energy in Ge:C.

IV. DISCUSSION

The strongly direct bandgap predicted here holds promise for a laser material. It is expected that the bandgap can be tuned by adding Si and/or Sn. Also, the calculated band structure is not well described by a simple band anticrossing model,[4] except perhaps near Γ, warranting further study. The electron effective mass was found to be nearly the same as pure Ge.

Mid-IR quantum well lasers often suffer from high Auger recombination. For Ge:C, $E_{G\Gamma} < E_{SOH}$, which suppresses Auger recombination. Future modeling will study transition rates between the E+ and E- conduction bands.

The small fraction of C in the experimental growth makes extraction of optical parameters uncertain. Growth of Ge:C with higher C content would reduce these uncertainties.

V. CONCLUSION

Ab-initio simulation of Ge:C predicts a strongly direct bandgap for 1% C. Growth of $Ge_{0.9922}C_{0.0078}$ was demonstrated with no structural defects detectable, and the reduction in direct bandgap agreed with simulated results. Growth with higher C content is needed to reach a direct bandgap and extract optical properties.

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REFERENCES

[1] C. A. Stephenson, W. A. O'Brien, M. Qi, M. Penninger, W. Schneider, M. A.Wistey, "Band Anticrossing in Dilute Germanium Carbides Using Hybrid Density Functionals," J. Electronic Materials, vol. 45, no. 4, p. 2121-6, April 2016. doi: 10.1007/s11664-015-4300-9

[2] C. A. Stephenson, W. A. O'Brien, M. Penninger, W. Schneider, M. Gillett-Kunnath, J. Zajicek, K. M. Yu, R. Kudrawiec, R. A. Stillwell, M. A.Wistey, "Band Structure of Germanium Carbides for Direct Bandgap Silicon Photonics," submitted to J. Appl. Phys.

[3] J. Kouvetakis, A. Haaland, D.J. Shorokhov, H.V. Volden, G. V Girichev, V.I. Sokolov, and P. Matsunaga, J. Am. Chem. Soc. 7863, 6738 (1998).

[4] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. 82, 1221 (1999).