

Supporting information

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Table 1: Compositions in at. % of $\text{Ge}_x\text{Se}_{1-x}$ layers used in Raman screening in Figure 1

Element	a	b	c	d	e	f
Ge	35	42	51	55	60	100
Se	65	38	49	45	40	/

In Fig. 1 several peaks of interest could be identified using a combination of sources containing studies of both chalcogenide thin films and bulk glasses.¹⁻⁸ The broad peak I, centred around 175 cm^{-1} , can be attributed to Ge-Ge modes in ethane-like $\text{Ge}_2(\text{Se}_{1/2})_6$ structural units as illustrated in the molecular representation. Peaks II and III, centred around 197 cm^{-1} and 217 cm^{-1} are related to GeSe_4 tetrahedra that can be connected by sharing Se atoms. Peak II corresponds to the symmetric stretching of Ge-Se-Ge linkages that are corner-shared (CS) whilst peak III corresponds to the breathing mode of a pair of Se atoms that are edge-shared (ES). Peak IV, at 250 cm^{-1} corresponds to the modes of a third structural unit that is difficult to observe for Ge rich layers. This broad peak, that overlaps partially with peak V, corresponds to stretching of Se-Se chains. Finally, peak V indicates a broad band stretching from $225\text{-}325\text{ cm}^{-1}$ that can be easily observed in all but

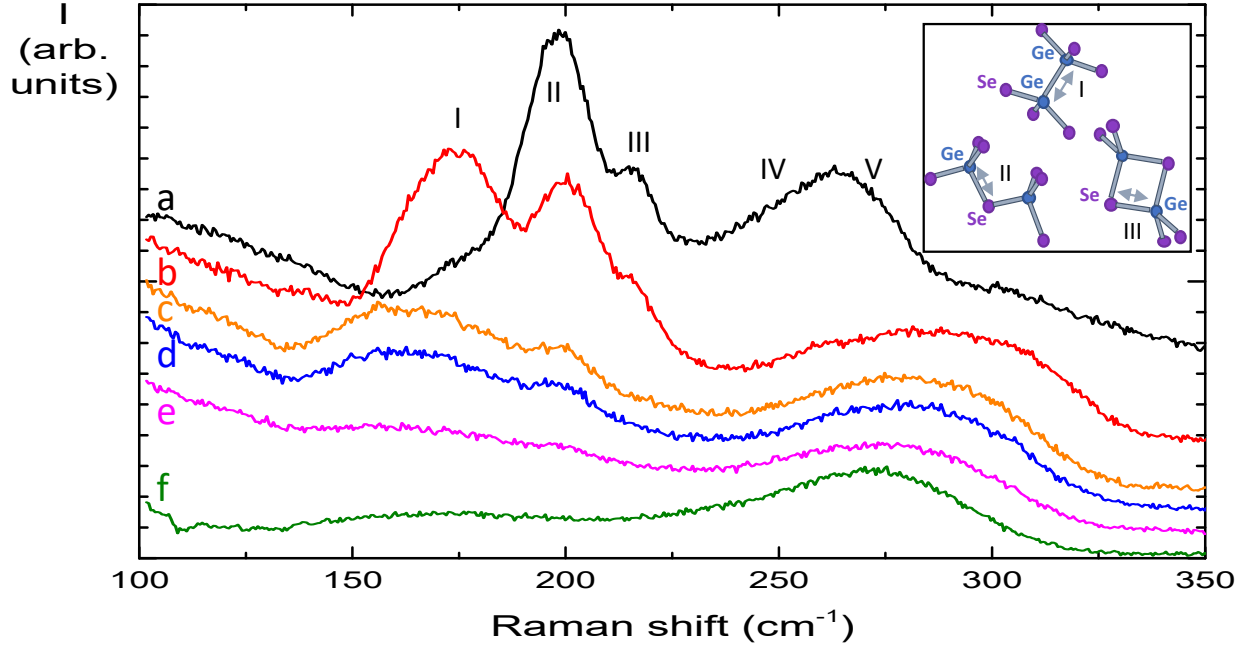


Figure 1: Raman spectra of $\text{Ge}_x\text{Se}_{1-x}$ layers a-f with resolved peaks I-V. The inset shows a molecular representation of the configuration modes corresponding to peaks I-III

the Ge-poorest layers. Specifically, this peak is also present in a pure Ge layer and is not dependent on the substrate material.

It can be observed that peak intensity varies greatly between compositions. For composition a, peaks II and III are the most intense. This is expected as this composition is closest to the 1-2 ratio of Ge-Se that make up the structural unit that is responsible for these peaks. Even still there are other peaks noticeable. The shoulder peak I indicates that some structural units contain an excess of Ge-Ge bonds, likewise the high intensity in region IV denotes the presence of pure Se chains. From this it can be deduced that the glass is not in perfect chemical equilibrium. This is a consequence of the PVD deposition process which results in thin films with a higher degree of disorder compared to their bulk glass alternatives. For composition b the shoulder at I greatly increases as here the composition has a moderate excess of Ge. Pure Se chains become near non-existent but the broad peak V, also observed in pure Ge remains, indicating a presence of pure Ge clusters in the Ge-Se matrix. As the compositions become richer in Ge, peaks I-III become less and less intense as all of these

are related to Se containing structural units and only the amorphous Ge peak remains. The fact this peak is present in all layers may suggest the presence of Ge clusters across all compositions which can explain findings on the bandgap and leakage current of GeSe.⁹⁻¹¹

References

References

- (1) Baudet, E.; Cardinaud, C.; Girard, A.; Rinnert, E.; Michel, K.; Bureau, B.; Nazabal, V. Structural analysis of RF sputtered Ge-Sb-Se thin films by Raman and X-ray photoelectron spectroscopies. *Journal of Non-Crystalline Solids* **2016**, *444*, 64–72.
- (2) Zhang, R.; Ren, J.; Jain, H.; Liu, Y.; Xing, Z.; Chen, G. In-Situ Raman Spectroscopy Study of Photoinduced Structural Changes in Ge-rich Chalcogenide Films. *Journal of the American Ceramic Society* **2014**, *97*, 1421–1424.
- (3) Edwards, T.; Sen, S. Structure and relaxation in germanium selenide glasses and supercooled liquids: a Raman spectroscopic study. *The Journal of Physical Chemistry B* **2011**, *115*, 4307–4314.
- (4) Boolchand, P.; Bresser, W. The structural origin of broken chemical order in GeSe₂ glass. *Philosophical Magazine B* **2000**, *80*, 1757–1772.
- (5) Jackson, K.; Briley, A.; Grossman, S.; Porezag, D. V.; Pederson, M. R. Raman-active modes of a- GeSe₂ and a- GeS₂: A first-principles study. *Physical Review B* **1999**, *60*, R14985.
- (6) Ikari, T.; Tanaka, T.; Ura, K.; Maeda, K.; Futagami, K.; Shigetomi, S. Raman spectra of P-, Sb-, or Bi-doped Ge_xSe_{1-x} bulk glasses. *Physical Review B* **1993**, *47*, 4984.

- (7) Pan, R.; Tao, H.; Zang, H.; Zhao, X.; Zhang, T. Annealing effects on the structure and optical properties of GeSe₂ and GeSe₄ films prepared by PLD. *Journal of Alloys and Compounds* **2009**, *484*, 645–648.
- (8) Wihl, M.; Cardona, M.; Tauc, J. Raman scattering in amorphous Ge and III–V compounds. *Journal of Non-Crystalline Solids* **1972**, *8*, 172–178.
- (9) Valery Afanas'ev, N. S. A.; Goux, L.; Kar, G. S.; Houssa, M.; Stesmans1, A. Electron States in Ovonic Switching Ge_xSe_{1-x}(0.4<x<0.72) Films. 2018 48th IEEE Semiconductor Interface Specialists Conference. 2018.
- (10) Clima, S.; Govoreanu, B.; Opsomer, K.; Velea, A.; Avasarala, N. S.; Devulder, W.; Shlyakhov, I.; Donadio, G. L.; Witters, T.; Kundu, S.; Goux, L.; Afanasiev, V.; Kar, G. S.; Pourtois, G. Atomistic investigation of the electronic structure, thermal properties and conduction defects in Ge-rich Ge_xSe_{1-x} materials for selector applications. 2017 IEEE International Electron Devices Meeting (IEDM). 2017; pp 4.1.1–4.1.4.
- (11) Clima, S. et al. Ovonic Threshold-Switching Ge_xSe_y Chalcogenide Materials: Stoichiometry, Trap Nature, and Material Relaxation from First Principles. *physica status solidi (RRL) – Rapid Research Letters* **2020**, *14*, 1900672.