Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Defects-engineered $Si_{1-x}Ge_x$ alloy under electron beam irradiation for Thermoelectrics

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There exists a fundamental governing relationship in rhombohedral epitaxy, i.e. the growth of [111]-oriented cubic crystals on the basal *c*-plane of trigonal sapphire crystals. The problem with this epitaxy relationship is that two crystal structures tend to be formed that exhibit a twin relationship. The epitaxial layer affords two possible in-plane alignments shown in the top view in Figure S1(b). The two orientations of cubic crystals in Figure S1(b) are coexisting twins with one rotated by 60° in the (111) plane. This twin defect has proven to be a major problem with rhombohedral epitaxy and has hindered further applications. In this study, we report on the temperature dependence of the crystalline growth by twinning of $Si_{1-x}Ge_x$ thin films on sapphire (0001) substrates.

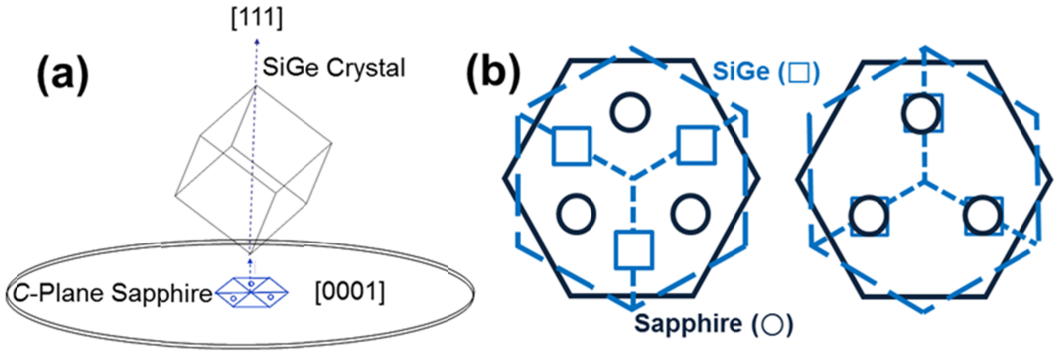

Figure S1. (a) Rhombohedrally aligned $Si_{1-x}Ge_x$ on *c*-plane sapphire, [111] direction of cubic crystal is aligned with the [0001]-direction of trigonal substrate, and (b) two possible in-plane azimuthal alignments ($Si_{1-x}Ge_x$) inside rhombohedral alignment (*c*-plane sapphire).

The XRD results of $Si_{1-x}Ge_x$ on *c*-plane sapphire before electron-beam irradiation is presented in Figure S2 where (a) show θ-2θ scans of the sample in the direction perpendicular to the surface. The peaks (i) to (iv) correspond to $Si_{1-x}Ge_x$ (111), sapphire (0006), $Si_{1-x}Ge_x$ (113), and sapphire (00012) respectively. The strong $Si_{1-x}Ge_x$ (111) peak indicates that the majority of the $Si_{1-x}Ge_x$ layer was grown in the [111]-orientation on the substrate. The majority peaks are noted as (I) in graph (b). The minority primary-twin crystal peaks rotated by 60° are noted as (II) in (b). The ratios between majority single crystal and minority twin crystal are 99.6:0.4. The (220) peaks of the majority crystal are aligned with the (1 0 -1 4) peaks of sapphire.

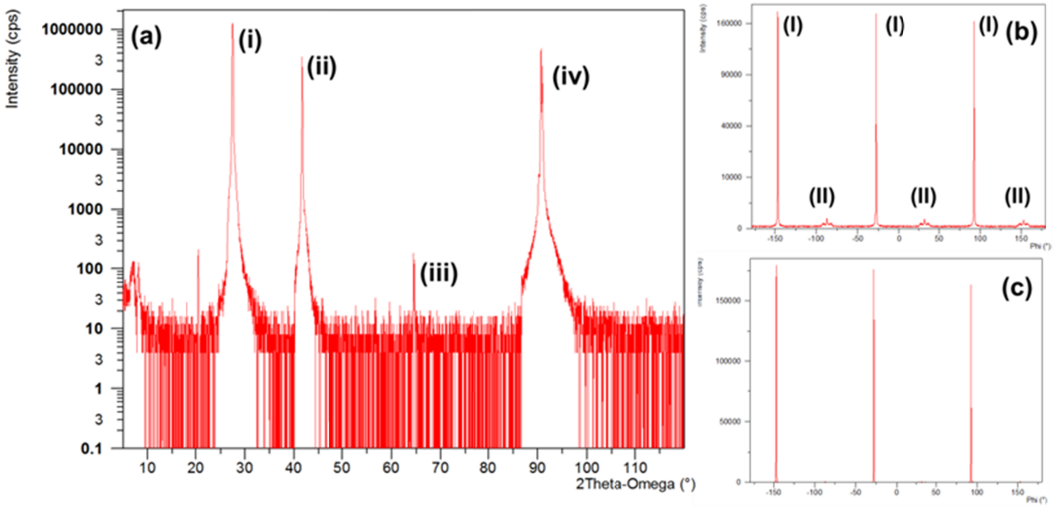

Figure S2. X-ray diffraction measurement of $Si_{1-x}Ge_x$ on *c*-plane sapphire before electron-beam irradiation. Plot (a) shows *θ-2θ* scan in the direction normal to the surface, graph (b) shows phi scan of $Si_{1-x}Ge_x$ (220) peaks, and graph (c) shows phi scan of sapphire (1 0 -1 4) peaks for the relative atomic alignment. Graph (a) is in square root scale to show tiny twin peaks.

The electrical conductivity of $Si_{1-x}Ge_x$ is increased after E-beam irradiation with increasing x. The increasing of x from 0.85 (before E-beam irradiation) to 0.88 (after E-beam irradiation) was confirmed by the $Si_{1-x}Ge_x$ profile obtained from energy-dispersive x-ray spectroscopy (EDS) measurements in the TEM.

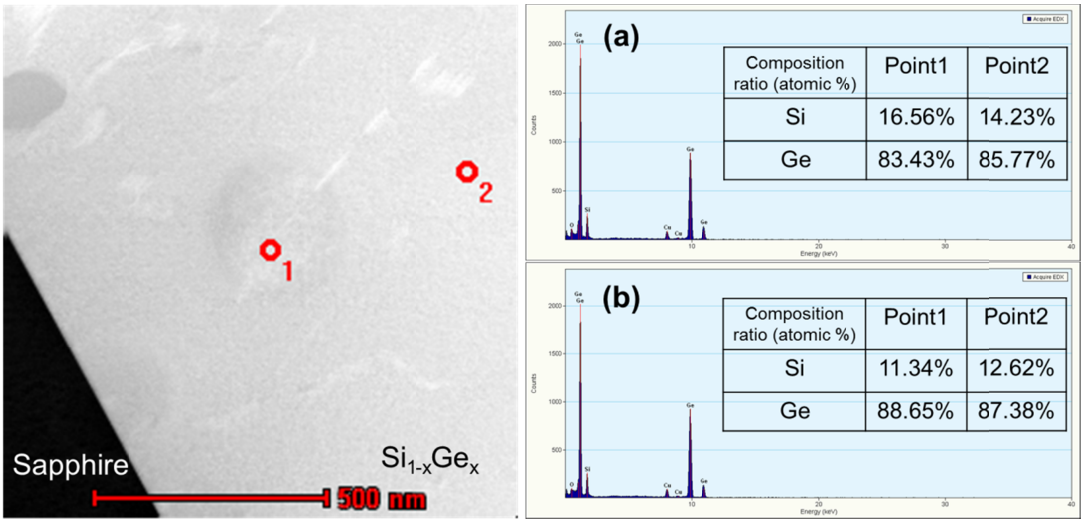

Figure S3. EDS spectra obtained from (a) $Si_{1-x}Ge_x$ film before E-beam irradiation and (b) $Si_{1-x}Ge_x$ film after E-beam irradiation using a flood electron gun.

In order to understand the effect of twinning on the thermal properties of $Si_{1-x}Ge_x$, we have to consider the phonon dispersion in the reciprocal lattice of diamond structure. The unit cell of the reciprocal lattice is the First Brillouin Zone as shown in Figure S4. The name of each crystal orientation is given with Miller indices. Note that the [111]-direction is called the L-point,[100]-direction is called the X-point, and [110]-direction is called the K-point. Similarly, halfway to L-point is Λ-point, halfway to X-point is Δ-point, and halfway to K-point is Σ-point.

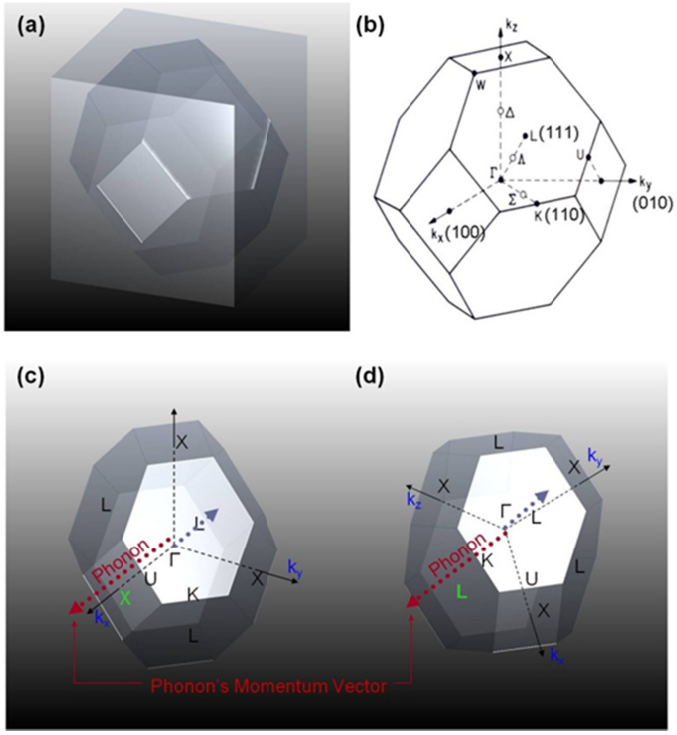

Figure S4. (a) First Brillouin Zone of diamond structure, (b) orientation names and Miller indices in the First Brillouin Zone [2], (c) relative orientation of First Brillouin Zones in diamond crystal, and (d) twin crystal made by stacking faults.

Now consider the effect of twin crystal made by stacking faults. The twin crystal is rotated by 60 degree in the (111)-plane from the underlying crystal. Therefore, the First Brillouin Zone inside the twin crystal is rotated by 60 degree in the (111)-plane as shown in Figure S4 (c), (d). The traveling phonon in the [111]-direction, i.e. L-point, is drawn as the blue dotted vector. The length of this vector is the momentum of the phonon. In the twin crystal's First Brillouin zone, the blue phonon travels the same direction (L-point) as the original crystal. On the other hand, the traveling phonon (red dotted vector) in X-point in the original crystal will be headed into a new orientation, the L-point in the twin crystal made by stacking fault. Therefore when a phonon near the X-point in the original crystal enters the twin crystal, it will go into L-point phonon bands of the twin crystal by the conservation of momentum. However, the phonon band in L-point in twin crystal has different energy from the X-point phonon band in the original crystal. Therefore, the phonon in the twin crystal

cannot propagate as it did in the original crystal. In order to conserve the momentum and energy of the traveling phonon in X-point of the original crystal, the phonon will be scattered. Thus, the stacking fault and twin in this new material design can cause phonon scattering without breaking the electrical connection. Because stacking faults and twinning are atomic size phenomenon, a high degree of scattering with in-situ / ex-situ E-beam irradiation of $Si_{1-x}Ge_x$ films can be created.

List of references

[1] J. M. O. Zide, D. Vashaee, Z. X. Bian, G. Zeng, J. E. Bowers, A. Shakouri, A. C. Gossard, *Phys. Rev. B*. 2006, **74**, 205335.

[2] N. W. Ashcroft, N. D. Mermin, *Solid State Physics*, Harcourt College Publishers, **1976**.