Supporting Information

Compression Induced Deformation Twinning Evolution in Liquid-Like Cu_2Se

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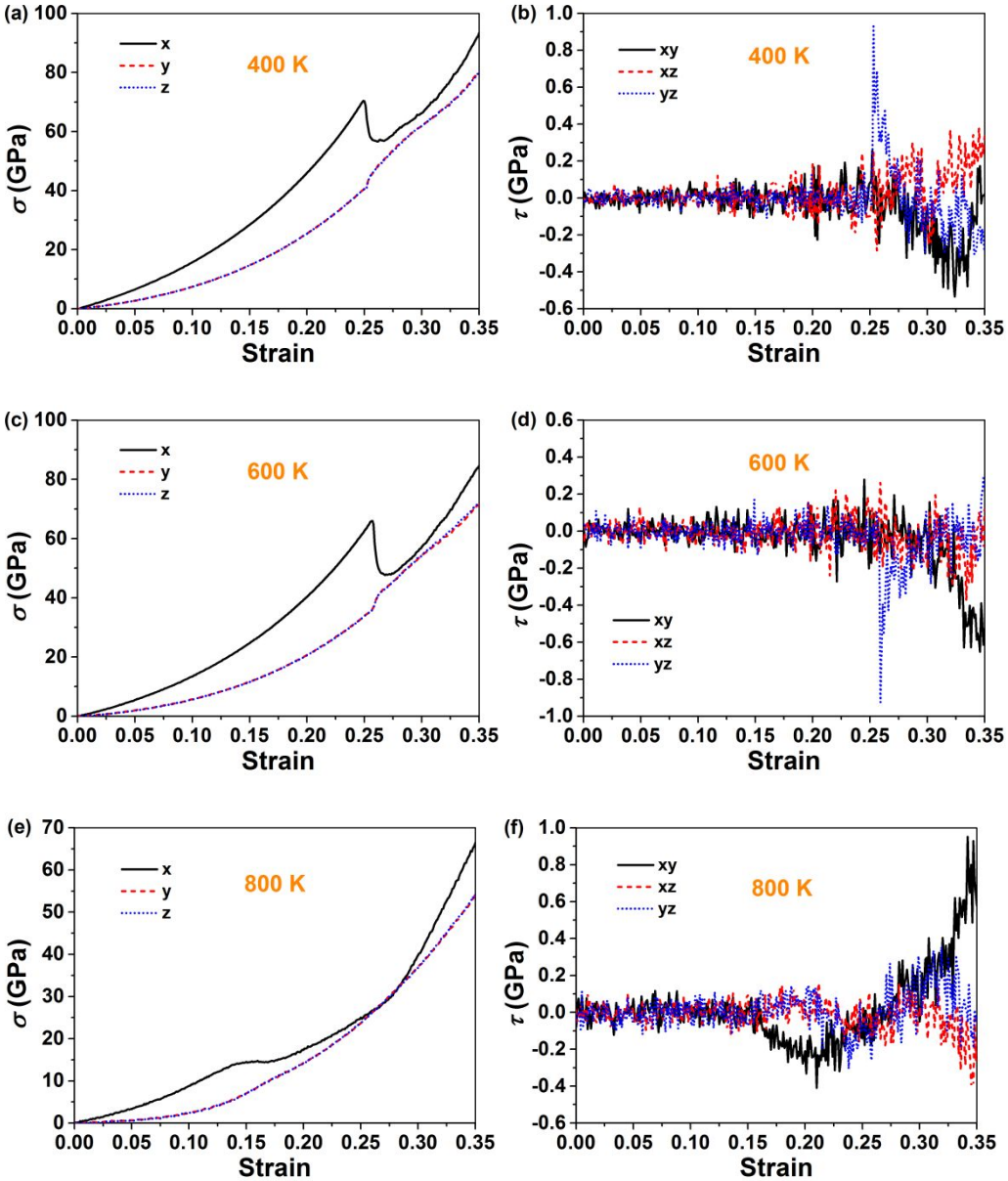
SI. Stress

For the compressed Cu_2Se at given temperature, the pressure stress (σ) and the shear stress (τ) with strain are shown in Figure S1. Compared to the solid models at low temperature such as 400 and 600 K, the liquid-like models at high temperature above 800 K tend to achieve normal stress homogenization and activated shear stress, which can also be measured by the corresponding standard deviation or average in the manuscript (Figure 2). Moreover, this will be promoted with increasing temperature because of more liquid-like components of highly mobile Cu ions.



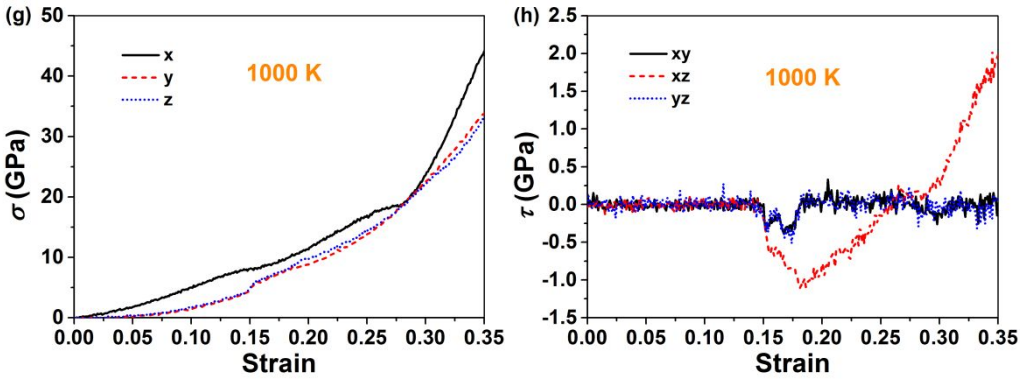


Figure S1. The stress-strain relationship including pressure stress (σ) and shear stress (τ) of compressed Cu_2Se at (a)-(b) 400 K, (c)-(d) 600 K, (e)-(f) 800 K and (g)-(h) 1000 K.

SII. Structure

Figure S2 and S3 show the configurations and the atomic strain distribution of the compressed solid model at 600 K. As discussed in the manuscript (Figure 6), there is no obvious deformation heterogeneity until large strain of about 0.25 with massive defect evolution or structural instability/failure. Therefore solid Cu_2Se exhibits a quite monotonic deformation mode.

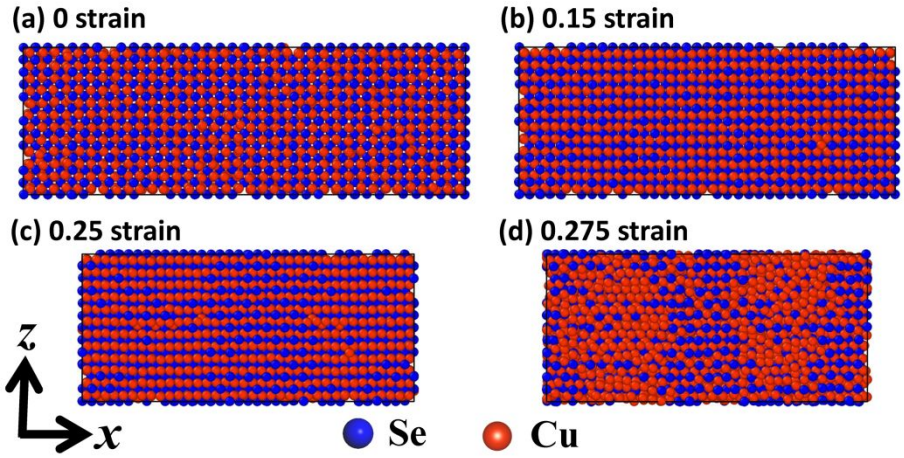


Figure S2. The atomic configurations of compressed solid Cu_2Se at 600 K: (a) initial structure without strain, (b) atomic structure at 0.15 strain, (c) atomic structure at 0.25 strain, before the structural instability and (d) unstable structure at 0.275 strain.

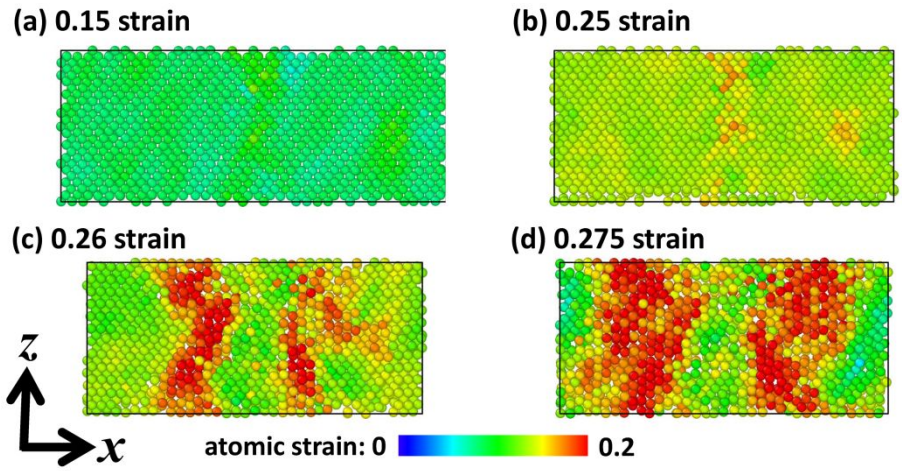


Figure S3. The atomic strain of compressed solid Cu_2Se at 600 K: (a) uniform distribution at 0.15 strain and (b)-(d) localization process caused by Cu migration above 0.25 strain.

On the other hand, owing to the Cu migration at high temperature, liquid-like Cu_2Se provides a complex mode comprising compression and shear as well as a restructuring process in term of twinning. However, the point defect evolution of Cu migration will inevitably cause localized deformation that hampers the analytical approach of stress/strain for twinning evolution (Figure S4). For example, liquid-like Cu_2Se at 1000 K achieves a large local strain of 0.5 even without loads (e.g. at 0 strain), while the dense twins inside at 0.195 strain can hardly be identified by this atomic strain distribution. Alternatively, changes of micro-structure especially the thermally stable Se sub-lattice (Figure S5) and the bond-load response should be concerned to uncover the deformation twinning mechanism.

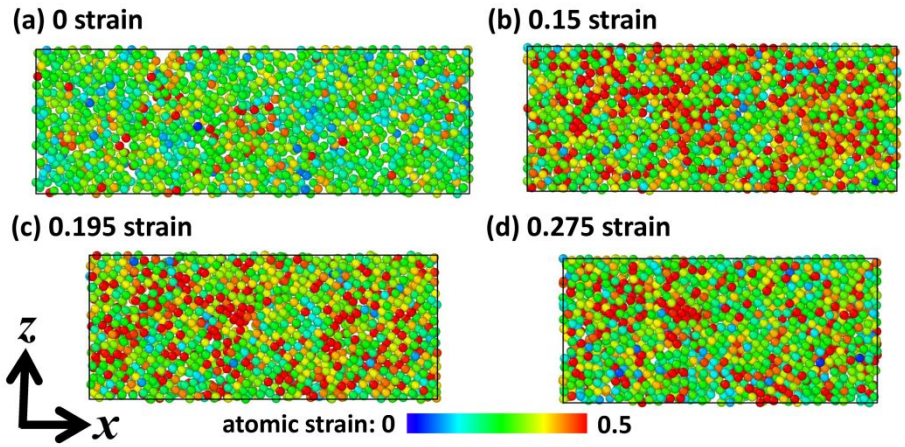


Figure S4. The atomic strain of compressed liquid-like Cu_2Se at 1000 K: (a) localized deformation even without strain, nonuniform distributions that are almost indistinguishable during (b)-(c) deformation twinning and (d) detwinning.

To reveal the role of load in Cu_2Se deformation twinning, only Se ions in fcc sub-structure are shown in the molecular dynamics (MD) configurations (Figure S5b from S5a). During twinning evolution, the faulted Se can be verified by the centro-symmetry parameter (CSP)[1] with large positive values, for example, about 12 for deformation twins (DT) at 0.195 strain (Figure S5c). The twinned Se sub-lattice is extracted and shown in Figure S5d, which is in line with the result from the cross section in Figure S5b. It can be verified from the configurations that twins form in {111} plane that is also the slip plane of fcc structure. For better observation of this twinning process, we show the cross section of Se sub-lattice with CSP in the manuscript (Figure 3).

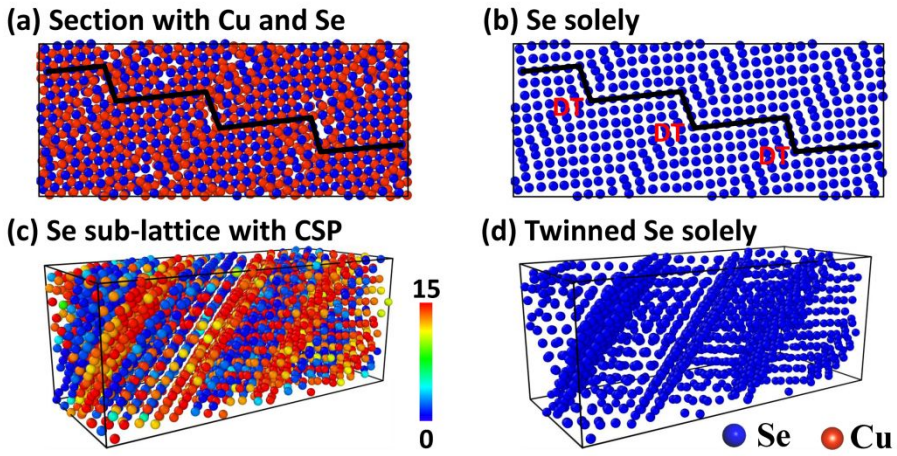


Figure S5. Deformation twin (DT) identification in liquid-like Cu_2Se at 0.195 strain and 1000 K: cross section of the atomic structure (a) with and (b) without showing Cu ions, (c) the centro-symmetry parameter (CSP) of Se sub-lattice and (d) the twinned Se structure that is extracted from (c) according to the large CSP.

With focus on deformation twinning mechanism in liquid-like Cu_2Se, we prefer a small MD model for dense twins during compression. For instance, at 0.195 strain and 1000 K, there are 52.7% faulted Se ions that can be verified as the twinned structure with the adopted model size of 105 Å×35 Å×35 Å (Figure 1c in the manuscript), while only 15.3% with a larger size of 246 Å×82 Å×82 Å (Figure S6a,b). In addition, for the solid simulations below 600 K, no twins can be observed in this larger model, which agrees with our conclusion about the monotonic deformation mode.

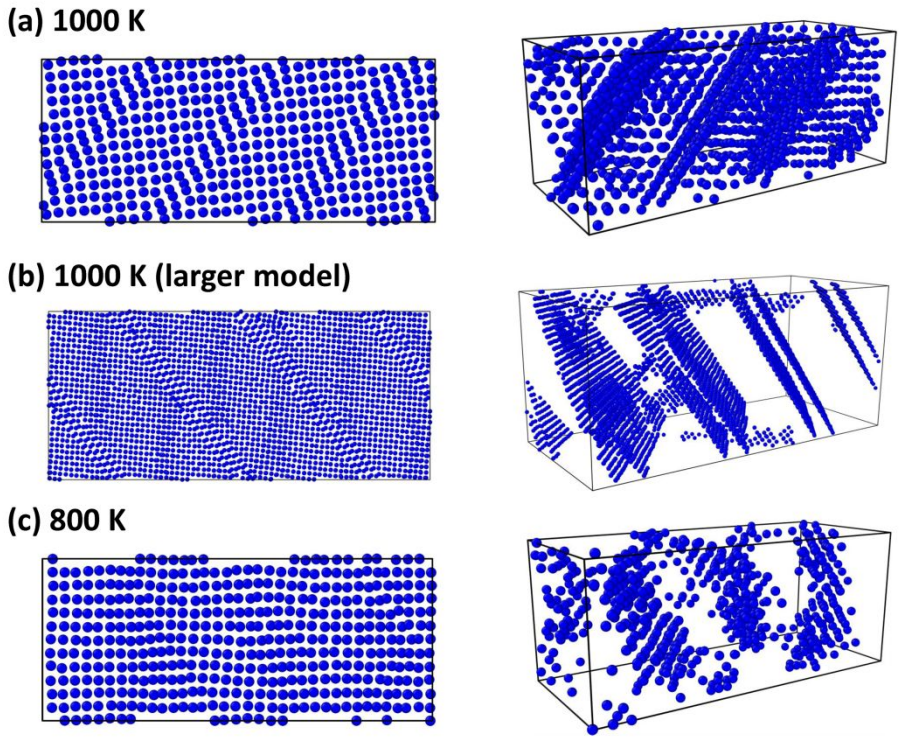


Figure S6. Twinned structures in liquid-like Cu_2Se at 0.195 strain with different model size or temperature: (a) 105 Å×35 Å×35 Å model at 1000 K, (b) 246 Å×82 Å×82 Å at 1000 K and (c) 105 Å×35 Å×35 Å model at 800 K.

Likewise, liquid-like simulation at higher temperature is preferable for higher density of twins. As discussed in the manuscript (Figure 4-5), due to the temperature dependence of diffusion-induced deformation accommodation and adaptive neighbor relationship in Cu_2Se hybrid structure with dynamical bonding, it is elevated temperature that promotes deformation twinning. At 1000 K, the calculated Cu diffusion coefficient (D_{cu}) is $2.6 \times 10^{-5} \mathrm{cm}^2/s$, which is much larger than that at 800 K (e.g. $6 \times 10^{-6} \mathrm{cm}^2/s$). With increasing strain to 0.15 where twins begin to form, there is a change of bond number ratio (BNR) of about 0.25, while only about 0.16 during 0-0.13 strain at 800 K. As a consequence, compare to the twin network at 1000 K, the twin growth at 800 K is inadequate with a smaller faulted Se ratio of 25.2% at 0.195 strain (Figure S6a,c).

The average length of Cu-Cu pairs are shown in Figure S7 as the complementary result of the bonding information studied in the manuscript (Figure 5). For the solid models at low temperature, Cu-Cu bonds are by and large along the Cartesian primary axes as the initial simulation setup. During deformation, only 1/3 of them bear the load in *x* axis. The normalized bond length (BL) of Cu-Cu pair along the loading direction of *x*

axis decreases monotonically until structural instability, while the rest along non-loading directions (*y* or *z* axis) remains unchanged. Hence the average BLs below 600 K can reduce linearly and share a constant slope in decline. Due to Cu migration and dynamical bonding in liquid-like Cu_2Se above 800 K, more Cu-Cu bonds of the kinetically disordered Cu ions bear the uniaxial load and accommodate local deformation compared to that in solid simulation. There is a non-linear tendency of Cu-Cu length reduction with a smaller slope, indicating the homogenization of this deformed hybrid structure.

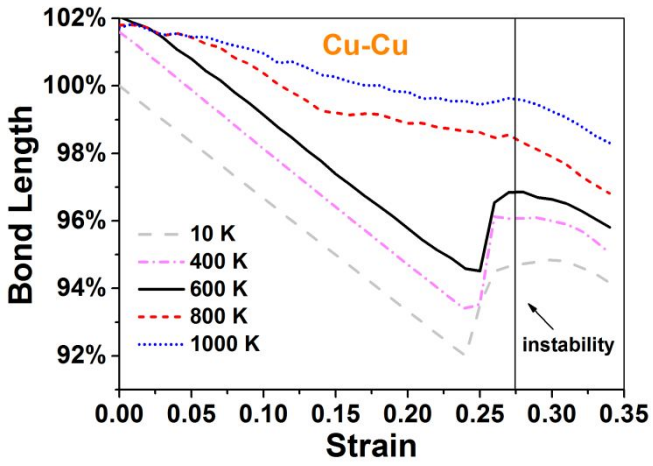


Figure S7. Average bond length of Cu-Cu pairs in compressed Cu_2Se at different temperature.

REFERENCES

(1) Kelchner, C. L.; Plimpton, S. J.; Hamilton, J. C., Dislocation nucleation and defect structure during surface indentation. *Phys. Rev. B* **1998,** 58, (17), 11085-11088.