Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Validity and limitations of the comparison

Despite clear differences between 3-stage co-evaporation and sequential processing, it is acknowledged that Na hampers In/Ga interdiffusion in both cases. However, the configuration of the experiments performed with the epitaxial films is different. The experiment is designed to resemble a diffusion couple, as a sandwich of Ga source (GaAs) and sink (CIS) components. The subsequent annealing treatments are crafted with the intent to assess purely the effect of Na on the extent of Ga migration into the initially Ga-free CIS (01). Sodium doping is effected via the gas phase by mixing Na_2Se and elemental selenium. A blank experiment in the presence of just selenium is performed in order to account for interdiffusion induced by the thermal treatment itself (i.e. not by Na).

(01) $CuInSe_2 + GaAs \rightarrow Cu(In_{1-x}Ga_x)Se_2 + (Ga_{1-x}In_x)As$

Where x is the Ga mole fraction. The enthalpy H of reaction (01) is computed from tabulated data assuming a linear relationship between H and x, while the entropic TΔS term is calculated based on a pure configurational contribution, taking into account the occupancy probability over the In and Ga sublattices. To this end, Boltzmann's relationship is used, approximated by Stirling's series (02), where k_B is Boltzman's constant, N_A is Avogadro's constant, $W_{i,f}$ are the configurational probabilities of initial and final states and R is the universal gas constant.

(02) $\Delta S = k_B N_A \ln (W_f/W_i) \sim R\,[x \ln(x) – (1\text{-}x) \ln(1\text{-}x)]$

The calculated -ΔG and TΔS functions *versus* x are shown in Fig. SI1, revealing that process (01) is thermodynamically spontaneous for $0 < x \leq 1$, regardless of whether Na is present or absent during the thermal annealing. An alternative chemical process potentially occurring during the doping experiments is the reaction between Na_2Se (or sodium polyselenides) and GaAs, to form Na_3As (sodium arsenide) and Ga_2Se_3 (gallium selenide) (03).

(03) $3Na_2Se_{(s)} + 2GaAs_{(s)} \rightarrow Ga_2Se_{3(s)} + 2Na_3As_{(s)}$

Depending on the energetics of (03), the formation of gallium selenide could potentially account for the enhanced Ga diffusion into the epitaxial CIS film. The absence of reported thermochemical properties for Na_3As does not allow to compute the free energy of reaction (03). No traces of Na_3As were observed in the samples after the doping experiments, but this compound was reported to decompose at high temperature (see P. Hafner and K.-J. Range, *Journal of Alloys and Compounds*, 1994, 216, 7–10). Therefore, Fig. SI1b provides the thermochemical assessment of process (03) and subsequent decomposition of $Na_3As_{(s)}$ into gaseous sodium and arsenic (04) (Born-Haber).

(04) $3Na_2Se_{(s)} + 2GaAs_{(s)} \rightarrow Ga_2Se_{3(s)} + 6Na_{(g)} + {}^{2}/_{n}\, As_{n(g)}$

Process (04) is thermodynamically unfavourable. Process (03) may be thermodynamically favourable only if the Gibbs free energy of Na_3As formation is sufficient to offset the very large energy gap in Fig. SI1b. Experimental thermochemical measurements are needed in order to obtain this information.

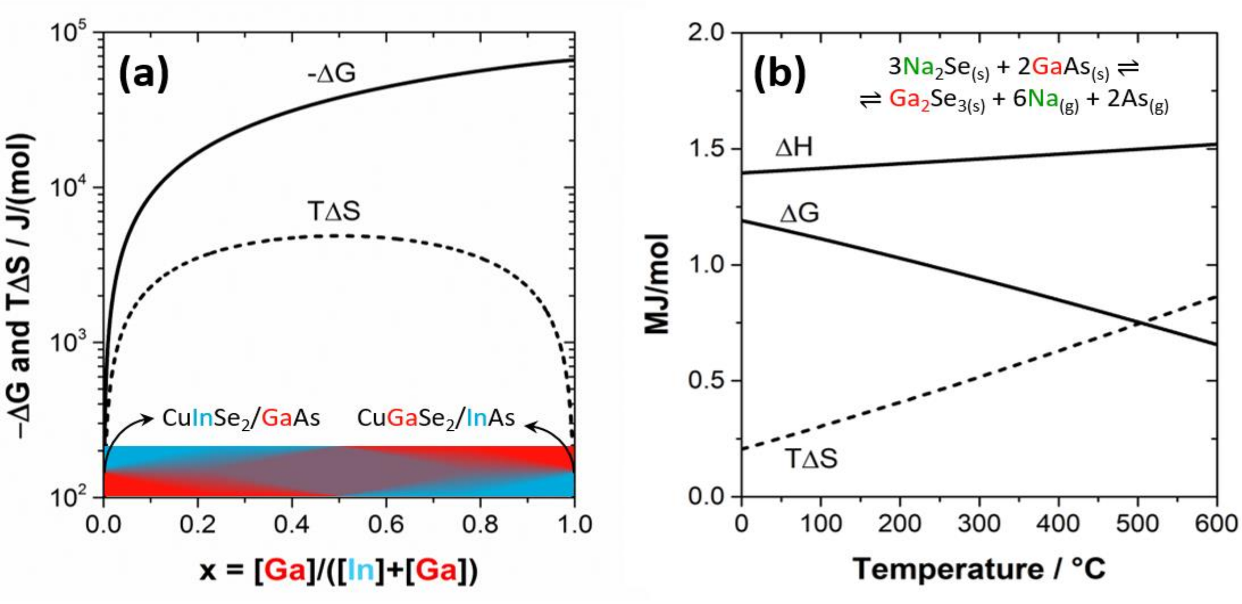

Fig. SI1 (a) Gibbs free energy and entropic term of a geometrically symmetric $CuIn_{1-x}Ga_xSe_2/In_xGa_{1-x}As$ diffusion couple as a function of Ga mole fraction x, calculated at 570 °C. **(b)** Gibbs free energy, enthalpic and entropic terms for the reaction between sodium selenide and gallium arsenide to form gallium selenide and the decomposition products of sodium arsenide (gaseous sodium and arsenic). Thermochemical data taken from Knacke-Kubashewski Springer, Berlin (1991) ISBN:0-387-54014-8.