New frontier in printed thermoelectrics: Formation of $\beta$-Ag$_2$Se through thermally stimulated dissociative adsorption leads to high $ZT$

Md Mofasser Mallick$^1$*, Andres Georg Rösch$^1$, Leonard Franke$^1$, Andre Gall$^1$, Sarfraz Ahmad$^2$, Holger Geßwein$^2$, Andrey Mazilkin$^3$, Christian Kübel$^3$ and Uli Lemmer$^{1,4}$*

$^1$Light Technology Institute, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany
$^2$Institute for Applied Materials, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
$^3$Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany
$^4$Institute of Microstructure Technology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

Email: uli.lemmer@kit.edu, mofasser.mallick@kit.edu

Fig. S1: The room temperature XRD patterns of the printed films (1-x)Ag-xSe for x=0.20, 0.27 and 0.40, sintered at 473 K indicate the presence of orthorhombic $\beta$-Ag$_2$Se phase along with a small fraction of excess Ag or Se.
Fig. S2: EDS analysis results for both the non-sintered (a) and sintered (b) films for x=0.27 are given in the table.

Table S1: Wt % and At % of Ag and Se in the
Ag$_2$Se phase using EDS analysis

### Elements

| Elements | Non-sintered/Fig. (a) | Sintered/Fig. (b) |
|----------|-----------------------|-------------------|
|          | Weight % | Atomic %   | Weight % | Atomic %    |
| Ag       | 68.21    | 61.10       | 75.59    | 69.39       |
| Se       | 31.79    | 38.90       | 24.41    | 30.61       |

**Fig. S3:** The temperature dependent specific heat capacity ($C_p$) of the ink for $x=0.27$
Fig. S4: Schematic diagram of the ZT-chips. The TFA chip is used to measure TE parameters of the Ag$_2$Se films.

The thermal conductivity of a film on a microchip is measured by Linseis TFA (thin film analyser) system, which is developed by V. Linseis et. al. [Ref.35], based on the method presented by Völklein et. al.[Ref.36]. The TFA chip fabricated on a silicon wafer where two thin heater with a width < 5 µm are deposited on free standing Si3N4 membranes which is surrounded by and Au rim. The heaters are connected in a 4-wire configuration. A controllable
current (I) is applied to the heater, hence a heat flux is developed between the heater and surrounding silicon (heat sink). The thermal conductivity can be estimated by measuring temperature rise of the heater and applied heating power using heat flux model. The detail measurement procedure and mathematical models are described in Ref.35.

Fig. S5: Composition dependent $\kappa$ & L (a) and $\kappa_e$ & $\kappa_l$ (b) of the film with x=0.20, 0.27 and 0.40.
Fig. S6. The temperature dependent thermoelectric parameters (a) \( S \), (b) \( \sigma \) and (c) \( \kappa \) of the film for \( x=0.27 \) a day and a month from 300 to 450 K. (d) The Fig.-of-merit ZT of the printed film is found to be repeatable even after a month. A high average ZT value of \( \bar{ZT} \approx 0.94 \) is achieved in the film between 300 and 400 K (inset of d).

To check repeatability of the results, the temperature dependent TE parameters were measured after 1 month and its TE properties are studied in the temperature range from 300 to 450 K. The printed material is found to be exhibited similar TE performance. At lower temperatures, the electrical conductivity increases with increasing temperature up to 400 K, showing semiconducting behaviour. The electrical band gap can be estimated from the slope of \( \log(\sigma) \) vs 1/T curve. A value of \( \DeltaE \approx 0.03 \text{ eV} \) is found, indicating a rather narrow bandgap semiconductor.