**Supporting Information**

# Self-catalyzed VLS Growth of PbSe wires with SignificantlySuppressing the VS Process

Chao Fan, Xing Xu, Yushuang Zhang, Tianren Chen, Songyang Wang, Chi Zhang, Qinglin Zhang*

*Key Laboratory for Micro-Nano Physics and Technology of Hunan Province,School of Physics and Electronics, Hunan University, Changsha, 410082, China*

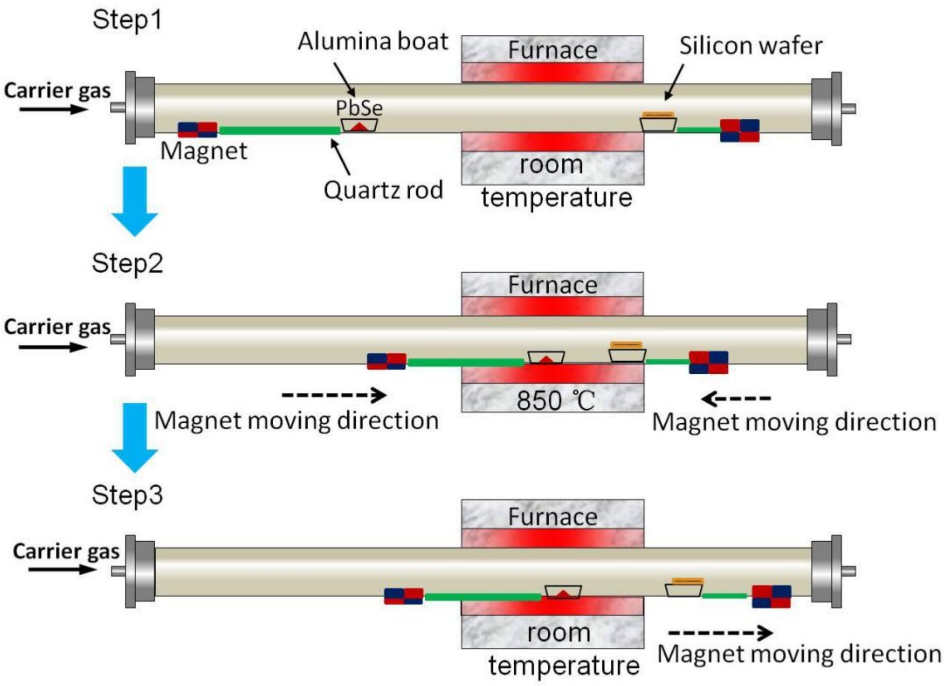


**Fig. S1. The setup schematic for the growth of PbSe wires.**

**Step 1**, the system is flushed with 200 sccm carrier gas for 30 min to purge the oxygen, and the alumina boats loaded with the precursor and Si substrates are located away from heating zone. **Step 2**, when the center temperature reach the pre-set temperature of 850 °C, the PbSe precursor and Si substrates are respectively inserted into the center and low temperature (410 °C) areas via amagnetic loading rod. **Step 3**, when samples are grown for a given time, the Si substrates are pulled out from the heating zone.

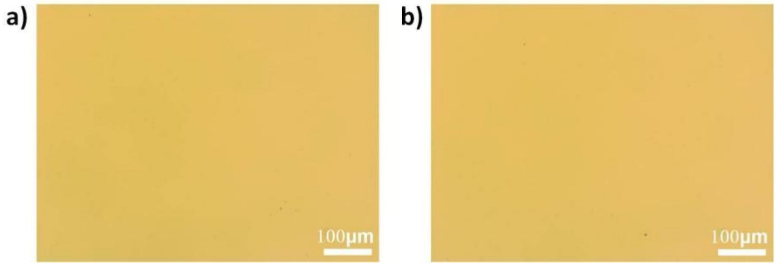


**Fig. S2.** a) and b) are optical microscope images of the substrate before and after growing for 6 min, with 100 sccm carrier gas of pure $N_2$ and other conditions unchanged.

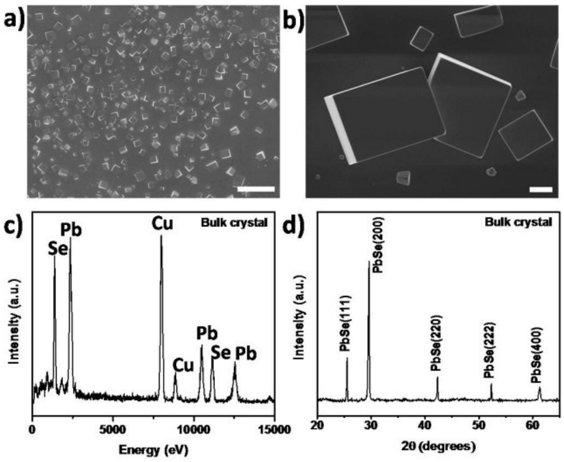


**Fig.S3.** a) The SEM image of PbSe bulk crystals on the Si(100) substrate (40 sccm, pure $N_2$); b) The amplified SEMimage; c) The EDS result of the PbSe bulk crystal; d) XRD result of PbSe bulk crystals. Scale bars are (a) 10 μm, (b) 2 μm.

**The surface energy increasing by per PbSe supplied:**

According to the SEM, TEM and XRD results, we have known that the PbSe wire growth along one direction, while the PbSe bulk crystal have six equivalent growth surfaces, and both the wire and bulk crystal are surrounded by the (200) surfaces.

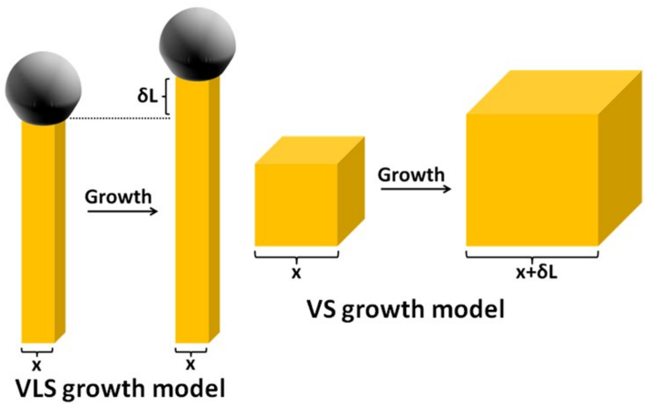


**Fig. S4.** The growth models of the PbSe wire and bulk crystal.

For VLS growth, the changes in the surface area and the number of atoms are related to the increase of wire length δL:

$$\delta S = 4x\delta L \; ; \; \delta N = \frac{x^2 \delta L}{\Omega}$$

Therefore:

$$\frac{\sigma \delta S}{\delta N}^{VLS} = \frac{4\sigma\Omega}{x}$$

Similarly, for VS growth:

$$\delta S = 6\left[(x + \delta L)^2 \text{ - } x^2\right] ; \; \delta N = \frac{(x + \delta L)^3 - x^3}{\Omega}$$

Therefore:

$$\frac{\sigma \delta S}{\delta N}^{VS} = \frac{\sigma(6\delta L^2 + 12x\delta L)\Omega}{\delta L^3 + 3x\delta L^2 + 3x^2\delta L}$$

δL is far less than x, so:

$$\frac{\sigma \delta S}{\delta N}^{VS} \cong \frac{12\sigma x \delta L \Omega}{3x\delta L^2 + 3x^2\delta L} = \frac{4\sigma\Omega}{\delta L + x} \cong \frac{4\sigma\Omega}{x}$$

**$p_\infty$ in the VS and VLS growth:**

The VLS wires growth is the result of the precipitation of PbSe solid from the molten Pb particles. According to the PbSe phase diagram (Fig S5) [1], PbSe wires can grow from Pb catalyst when the atomic percent of selenium up to 0.2% at 410°C. While VS growth is due to the transformation from the vapor-phase to the solid-phase of the evaporated PbSe source.Therefore, the $p_\infty$ for the VLS and the VS growth are estimated by the vapor pressure of lead selenide in the Pb rich Pb-PbSe system (the lowest reported content of PbSe 0.05) and in the PbSe system from theprevious report[2], respectively (see the Table S1).At the deposition temperature of 683.15 K, the $p_\infty$ for the VS and the VLS growth are~$2.6 \times 10^{-4}$ Pa and~$1.9 \times 10^{-5}$ Pa, respectively.

**Table 1**. Temperature dependence of lead selenide vapor pressure in the Pb-PbSe system

| | PbSe content in the Pb-PbSe system | A1 | B1 |
|---|---|---|---|
| For VLS growth | 0.05 | 26.148±1.421 | 25199±1512 |
| For VS growth | 1 | 27.420±1.357 | 24091±1192 |

$A_1$ and$B_1$ are the coefficients in the equation for the temperature dependence of lead selenide vapor pressure: $\ln p_{PbSe}[Pa]=A_1-B_1/T$

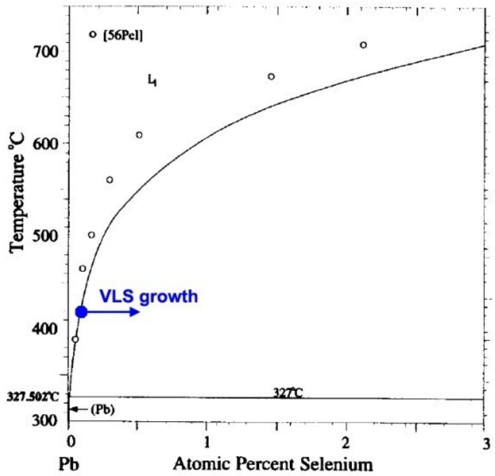


**Figure S5:** the locally magnified phase diagram of Pb-Se[1].


[1] J. C. Lin, R. C. Sharma and Y. A. Chang, *J. Phase Equilibria*,1996, **17**, 253-260.

[2] V. N. Volodin, N. M. Burabaeva and S. A. Trebukhov, *Russ. J. Phys. Chem. A+*, 2016, **90**, 572-574.