Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

High-Performance Field Emission Based on Nanostructured Tin Selenide for Nanoscale Vacuum Transistors

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Chemical synthesis of tin selenide

Tin selenide nano-flower (SnSe NF) was synthesized by added $SnCl_4 \cdot 5H_2O$ (0.4mmol, 140 mg), SeO_2 (0.4 mmol, 44 mg), and oleylamine (OAM, 20 mL) into a three-neck flask at room temperature. The flask was then sealed and the mixture is stirred continuously for five minutes. Afterwards, the mixture was sonicated for 30 minutes at room temperature. The mixture was degassed with pure N_2 then aged at 150^{o}C for 10 minutes while being stirred continuously under N_2 atmosphere. Finally, the mixture was slowly heated to 350^{o}C at rate ~10^{o}C/min and aged at 350^{o}C for 15 to 20 minutes. After this process, SnSe NF was extracted and cleaned with excess ethanol. SnSe NF is then dried and stored for following characterizations.

Single-crystal (SC) SnSe was synthesized by chemical vapor transport method. High quality of Sn and Se powder (99.999% purity, from Alfa Aesar) were mixed together and placed into the quartz tube. The quartz tube is evacuated and flame sealed under high vacuum (10^{-5} torr). We place quartz tube on the multi-zone furnace. Temperature was set the 950 ^{o}C and 900 ^{o}C as a reaction temperature for hot zone and cold zone, respectively. Temperature of furnace was slowly heated from room temperature to reaction temperature for 12 hours and hold on 96 hours at reaction temperature, and slowly cool down to the room temperature.

Electrical measurement

The electrical measurement was performed in air at room temperature and ambient pressure. The SnSe cathode is grounded and the anode voltage was increased at 0.01 V per step using a Precision Source/Measure Unit (SMU) (Keysight 2902A). The emission current was measured and averaged with every five measurements.

Data analysis

The Fowler-Nordheim (FN) equation is given as

$$I = A\frac{aV^2\beta^2}{h^2\varphi}exp\left(-\frac{b\varphi^{1.5}h}{V\beta}\right) \quad \text{(S1)}$$

where I is emission current, A is emission area, V is operating voltage, h is vacuum channel length between anode and cathode emitter, φ is emitter's work function, β is field enhancement factor, a and b are constant with $a = 1.54 \times 10^{-6}\ AeV/V^2$ and $b = 6.83\ \times 10^{9}\ eV^{-1.5}Vm^{-1}$. The field enhancement factor β is extracted from eq. S1 by rewrite eq. S1 as:

$$\frac{d\left(\ln\left(\frac{I}{V^2}\right)\right)}{d\frac{1}{V}} = \frac{\mathrm{d}\ ln\left(\int\int\frac{\beta^2}{h(x,y)^2}exp\left(-\frac{b\varphi^{1.5}h(x,y)}{V\beta}\right)dxdy\right)}{\mathrm{d}\frac{1}{V}} \quad \text{(S2)}$$

The 3D tip geometry and channel length of NF emitters are determined using AFM and SEM images (for example, Figure 1e and 2c in main text). The tip profile is fitted using a parabolic equation. We extract the linear slope from FN plot (for example, see Figure 3b in main text) and calculate field enhancement factor of NF using eq. (S2).

For the single crystal (SC) emitters, eq. S2 is simplified as:

$$\frac{d\left(\ln\left(\frac{I}{V^2}\right)\right)}{d\frac{1}{V}} = -\frac{b\varphi^{1.5}h}{\beta} \quad \text{(S3)}$$

The left-hand-side of eq. (S3) represents the linear slope extracted from FN plot (Figure 3b in main text) which is used to calculate the field enhancement factor.