Supplementary Information

Current-Induced Thermal Tunneling Electroluminescence via

Multiple Donor-Acceptor-Pair Recombination

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Temperature distribution mapping of HC-GZO microrod

In ZnO, the frequency-dependent renormalization of phonon energy caused by the thermal expansion of lattice resulted in a Raman shift for phonon modes. The lattice temperature *T* can therefore be estimated by peak shift (Δ_T) of *Ehigh* 2mode (437 cm⁻¹ at room temperature), where the lattice distortion by Ga doping was ignored. The Δ_T regulated by *T* is expressed as [40]

$$\Delta_T = -\omega_0 \gamma \int_0^T \left[\alpha_c(T) + 2\alpha_c(T) \right] dT$$
(S1)

where $\omega_0 = 440 \text{ cm}^{-1}$ and $\gamma = 2.02$ are Grüneisen parameters of *Ehigh 2*mode; $\alpha_c(T)$ and $\alpha_a(T)$ are the temperature-dependent thermal expansion coefficients along the parallel and perpendicular directions with respect to the *c*-axis, respectively. The thermal expansion coefficients are estimated by [S1]

$$\begin{cases} \alpha_c(T) = 5.2042 + 0.522 \times 10^{-5}T + 12.13 \times 10^{-9}T^2 \\ \alpha_a(T) = 3.2468 + 0.623 \times 10^{-5}T + 12.94 \times 10^{-9}T^2 \end{cases}$$
(S2)

PL spectra of HC-GZO microrods



Figure S1. PL spectra of HC-GZO microrods at room temperature, where the deep level defect-related emission (DLE) was red-shifted with O₂ pressure ratio increasing during growth.

Simplified dynamics model for electron transitions

The schematic of electron excitation and radiative recombination in a HC-GZO microrod for EL emission is shown in Figure S2, in which the non-radiative recombination and fine energy of V_0 and V_{Zn} are ignored.



Figure S2. Schematic of electron excitation and recombination in a HC-GZO microrod for EL emission.

For the simplified energy level system, the rate equations are described as

$$\begin{cases} \frac{dn_{e}}{dt} = -\kappa_{eA}n_{e} - \kappa_{eD_{1}}n_{e} - \kappa_{eD_{2}}n_{e} + \kappa_{Ae}n_{A} \\ \frac{dn_{A}}{dt} = -\kappa_{Ae}n_{A} + \kappa_{eA}n_{e} + \kappa_{D_{1}A}n_{D_{1}} + \kappa_{D_{2}A}n_{D_{2}} \\ \frac{dn_{D_{1}}}{dt} = -\kappa_{D_{1}A}n_{D_{1}} + \kappa_{eD_{1}}n_{e} \\ \frac{dn_{D_{2}}}{dt} = -\kappa_{D_{2}A}n_{D_{2}} + \kappa_{eD_{2}}n_{e} \end{cases}$$
(S3)

where n_A is the concentration of electron at the acceptor level (V_{Zn}); κ_{eA} and κ_{Ae} are the transition rates of excitation and FA recombination, respectively. For a steady-state EL emission, the dynamic equilibrium of electron transitions is expressed as

$$\frac{dn_e}{dt} = \frac{dn_A}{dt} = \frac{dn_{D_1}}{dt} = \frac{dn_{D_2}}{dt} = 0$$
(S4)

According to Equations (S3) and (S4), we can get

$$\begin{cases} \kappa_{D_{1}A} n_{D_{1}} = \kappa_{eD_{1}} n_{e} \\ \kappa_{D_{2}A} n_{D_{2}} = \kappa_{eD_{2}} n_{e} \end{cases}$$
(S5)

References:

[S1] Iwanaga H, Kunishige A, Takeuchi S. Anisotropic thermal expansion in wurtzitetype crystals. J Mater Sci 2000, 35 (10): 2451-2454.