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Electronic Supplementary Information

Tuning the Field Emission Properties of AlN Nanocones by Doping

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Detailed experimental

The CVD growth of doped AlN nanocones was carried out in a three-zone tubular furnace (see Fig. S1). For synthesizing Mg-doped AlN nanocones, anhydrous $MgCl_2$ was used as a new kind of dopant. Typically, about 0.5 g of anhydrous $AlCl_3$ and $MgCl_2$ were separately placed at the precursor-loaded zones I and II and a Si(100) substrate at the deposition zone III. After evacuating and Ar flushing the sealed alumina tube for several times, the three zones were heated to 125, 700 and 750 ºC, respectively, under the protection of Ar gas. Flowing Ar of 300 mL min^{-1} was then introduced to transport the $AlCl_3$ and $MgCl_2$ vapours to zone III, where they mixed and reacted with NH_3 gas (20 mL min^{-1}) for 3 h. After the system was cooled down to ambient temperature, AlN nanocone arrays with Mg doping were obtained. If a Mo grid with the diameter of 8 mm was covered on the Si substrate during the growth, patterned arrays of Mg-doped AlN nanocones were gotten by disposing of the Mo grid mask. The preparation procedure for the Si-doped AlN nanocones was quite similar except that the dopant source was SiH4 in this case. Briefly, anhydrous $AlCl_3$ and Mo grid-covered Si(100) substrate were loaded at zone I and zone III, respectively. The temperatures of the three zones were also set to be 125, 700 and 750 ºC though zone II was nothing-loaded in this synthesis. When the furnace reached the desired temperature, 300 mL min^{-1} of Ar, together with 1.5 mL min^{-1} of SiH_4/Ar (SiH_4, 5 vol%), were introduced into the system. After 3 hours of CVD growth, Si-doped AlN nanocone arrays with patterned distribution were synthesized by in situ doping.

The products were examined by X-ray diffraction (XRD, Philips X'pert Pro X-ray diffractometer), scanning electron microscopy (SEM, Hitachi S-4800) attached with an energy dispersive X-ray spectroscopy (EDS, SHIMADZU-SEDX), and high resolution transmission electron microscopy (HRTEM, JEM-2100). FE properties were tested using a parallel-plate diode configuration with a cathode-anode distance of 100 μm in a vacuum chamber of 8×10^{-5} Pa. Before the data recording, the field emission of the sample was carried out for 2 hours under high voltage (~3000 V) for desorbing gaseous species on the nanocone surface and stabilizing the emission.

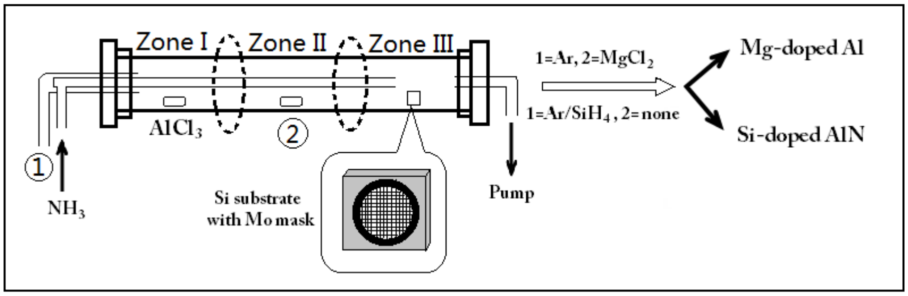

Fig. S1. Schematic of three-zone tubular furnace and the synthetic procedure of the AlN nanocone arrays.

Table S1. Doping amount of Mg in the AlN nanocones obtained at different vaporization temperature of $MgCl_2$.

Vaporization temperature of $MgCl_2$ (°C)	700	800	900	1000
Mg content (at.%)	0.50	0.63	0.71	0.81

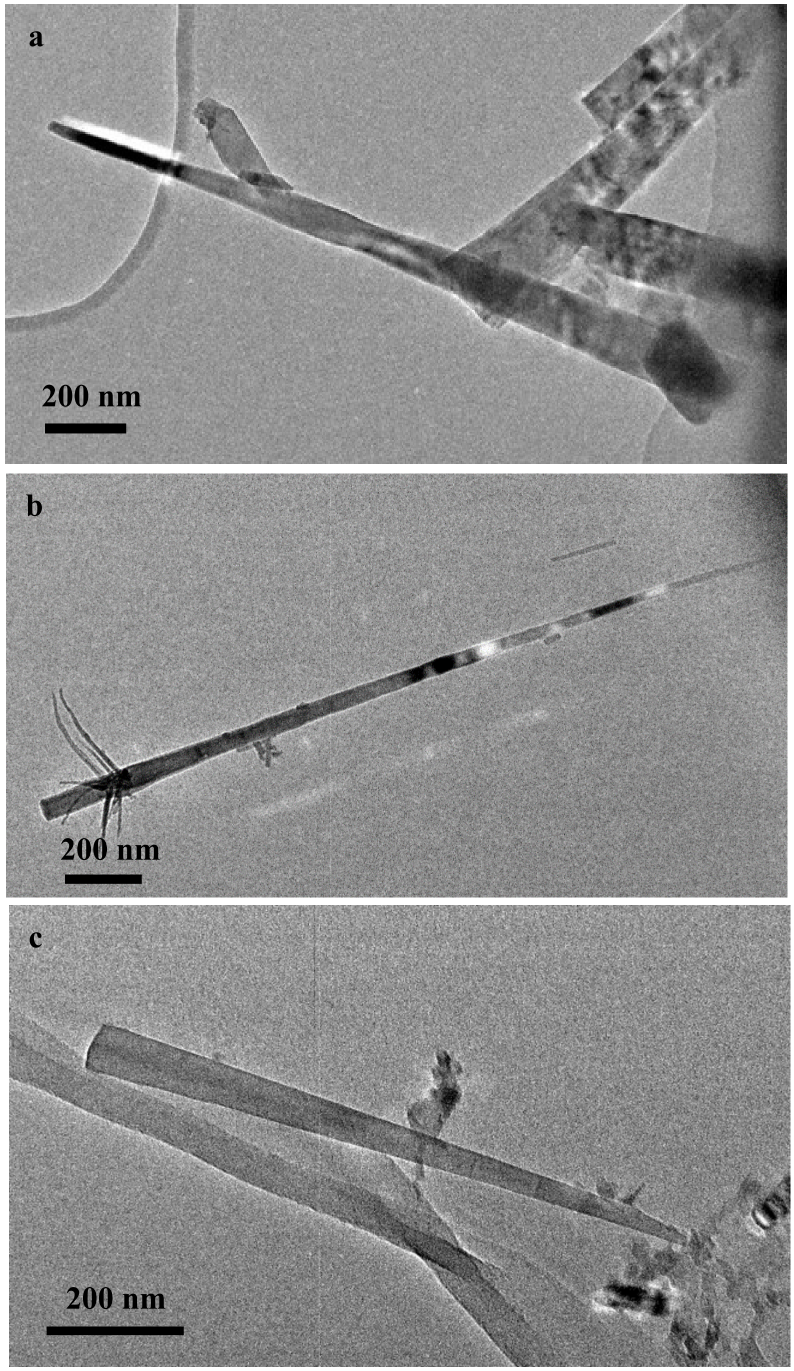

Fig. S2. Typical TEM images of the Si-doped (a), Mg-doped (b) and undoped (c) AlN nanocones. It is shown that the AlN samples have conelike morphologies with the length up to 1~2 micrometer and the diameter of 5~20 nm at the tips and ~50 nm at the roots.

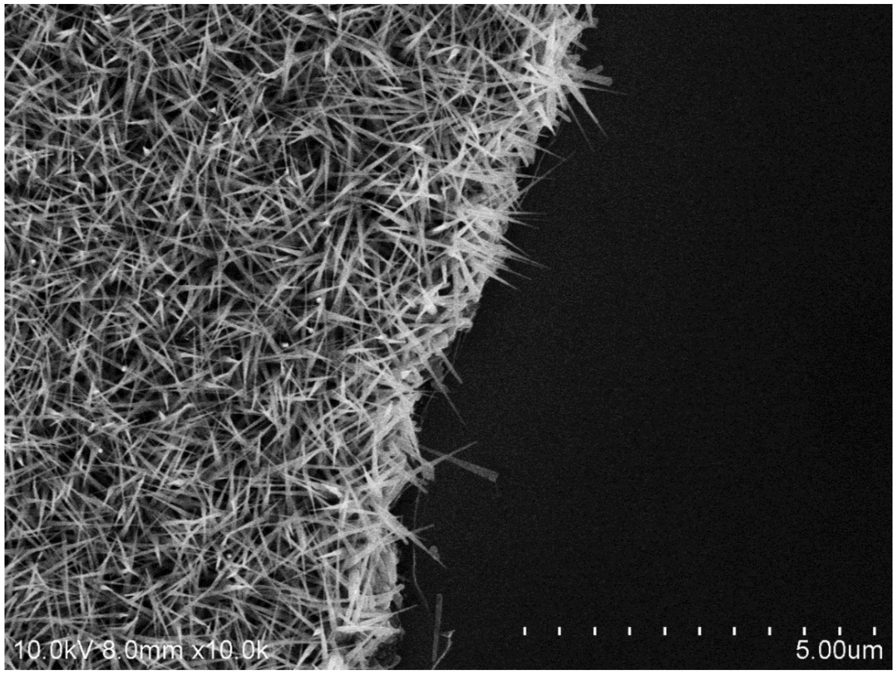

Fig. S3. SEM image of Mg-doped AlN nanocones. It is seen that the nanocones are quasi-aligned.

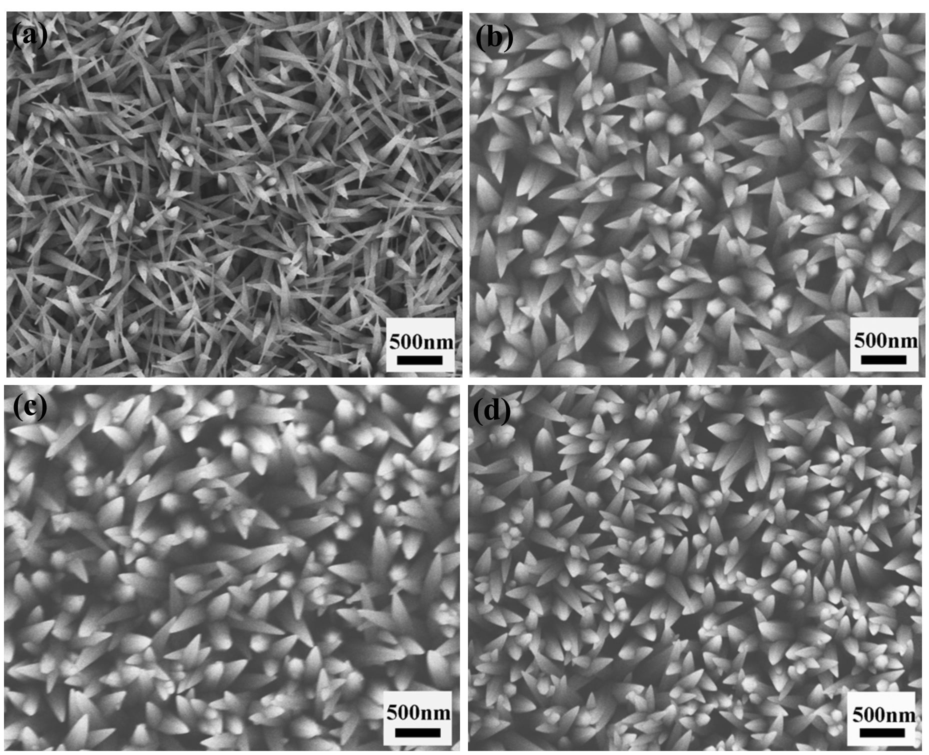

Fig. S4. SEM images of the Si-doped AlN nanocones synthesized at different flow rate of SiH_4/Ar gas: (a) 1 mL min^{-1}, (b) 2 mL min^{-1}, (c) 5 mL min^{-1}, (d) 10 mL min^{-1}.

From (a) to (d), the Si doping amounts were 2.5, 1.2, 1.0 and 0.7 at.% respectively. Meanwhile, the sharpness and length of the nanocones decreased with increasing the flow rate of SiH_4/Ar gas. It is learned that high concentration of SiH_4 was unfavorable for the growth of AlN nanocones, probably owing to the formation of Si_3N_4 species via vapor phase reaction. To obtain Si-doped AlN nanocones with suitable aspect ratio and doping amount, a flow rate of 1.5 mL min^{-1} was preferred.

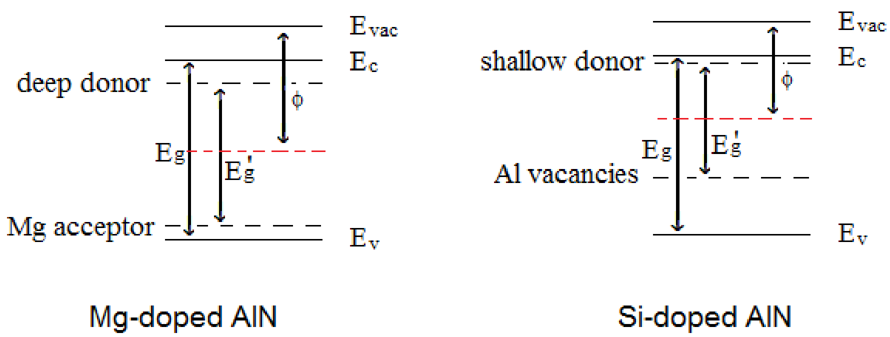

Fig. S5. Sketch of energy levels for AlN. Here, E_c, E_v and E_{vac} are conduction level, valance level and vacuum level, respectively. E_g is the energy gap between E_c and E_v, and E_g' is the energy gap between the donor and acceptor levels.

The work function can be estimated according to the literature results. Many reports have demonstrated that the Mg-doping could induce the light emission band at 4.70 eV originating from the donor-acceptor pair transition involving V_N^{3+} donor (~0.90 eV below the conduction band E_c) and Mg acceptor (~0.51 eV above the valence band E_v) [1,2]. The Si-doping could result in an enhancement of the Al vacancies in the AlN, and thus PL band at 3.50-4.0 eV could be observed, which could be assigned to recombination from a shallow donor (60±20 meV below the E_c) to $(V_{Al}\text{-complex})^{2-}$ and V_{Al}^{3-} (~2.5 eV above the E_v) [3,4]. The work function of semiconductor could be estimated as the sum of half of the band gap ($E_g/2$) and the electron affinity (χ, i.e., the energy gap between E_c and vacuum energy level E_{vac}) [5]. Here, the E_g should be replaced by E_g', i.e., the energy gap between the donor and acceptor levels, because the electron transitions in the doped AlN occurred indeed between these two energy levels. Based on above analysis, the ϕ of the Si-doped AlN is smaller than that of the Mg-doped sample.

References

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