Electronic Supplementary information for:

The First Atomic Layer Deposition Process for Fe_xN Films

*Liyong Du[a], Wei Huang[a], Yuxiang Zhang[a], Xinfang Liu[b], Yuqiang Ding[a]**

a. International Joint Research Center for Photoresponsive Molecules and Materials, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, 214122 (P. R. China), E-mail: yding@jiangnan.edu.cn;

b. Henan Key Laboratory of Function-Oriented Porous Materials, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934 (P.R. China)

Experimental Detail

1. Film Deposition

Anhydrous hydrazine (N_2H_4) was purified from hydrazine hydrate. Fe(^{t}Bu-amd)$_2$ and other chemicals were purchased from J&K Chemical and used as recieved. All films were deposited in a flow-type ALD reactor (MNT-f-150-212, Jiangsu MNT Micro and Nanotech Co., LTD, China). SiO_2(100)/Si wafer were used as substrates to study the deposition behavior. And these substrates were ultrasonically cleaned in acetone, isopropanol and deionized water in sequence prior to ALD. During ALD process, the heating temperature of Fe(^{t}Bu-amd)$_2$ was kept at 85 ^{o}C, and N_2H_4 at 40 ^{o}C. Besides, the working pressure was kept at 50-100 Pa under a flow of nitrogen (99.999%), which was used as both the carrier and purge gas. The substrate temperature was investigated at 215-315 °C. One typical ALD cycle included alternate pulses of Fe(^{t}Bu-amd)$_2$ and N_2H_4 for various time, separated by nitrogen purging. And the purge time was kept at 20 s for both Fe(^{t}Bu-amd)$_2$ and N_2H_4 during all ALD experiments.

The thickness of the films were measured by Bruker D8 X-ray reflection (XRR) and Hitachi S-4800 scanning electron microscopy (SEM) with the voltage of 3.0kV. The surface morphology were studied by SEM and a Bruker Multimode 8 atomic force microscopy (AFM, ScanAsyst Mode, three dimension scanning). The composition and the crystalline phase of the films were analysed using a Thermo ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) and a Bruker D8 X-raydiffraction (XRD).

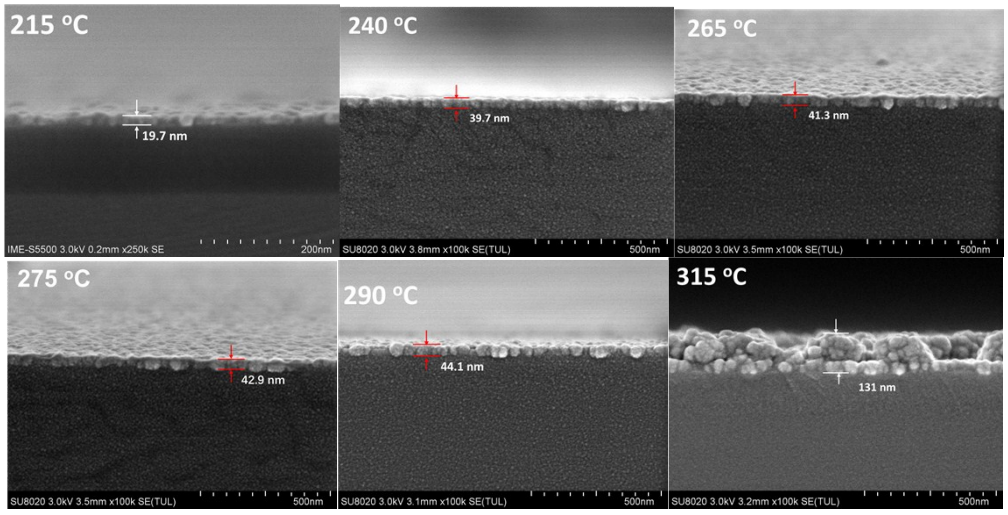


Figure S1 Cross-sectional SEM images of Fe_xN films deposited at varying temperatures using 6 s dose of Fe(^{t}Bu-amd)$_2$ and 0.6 s dose of N_2H_4 by 500 cycles.

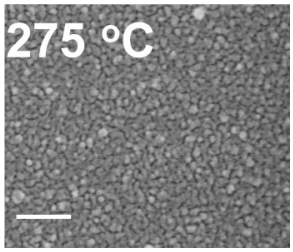


Figure S2 SEM images of 500-cycle Fe_xN films deposited at 275 °C.

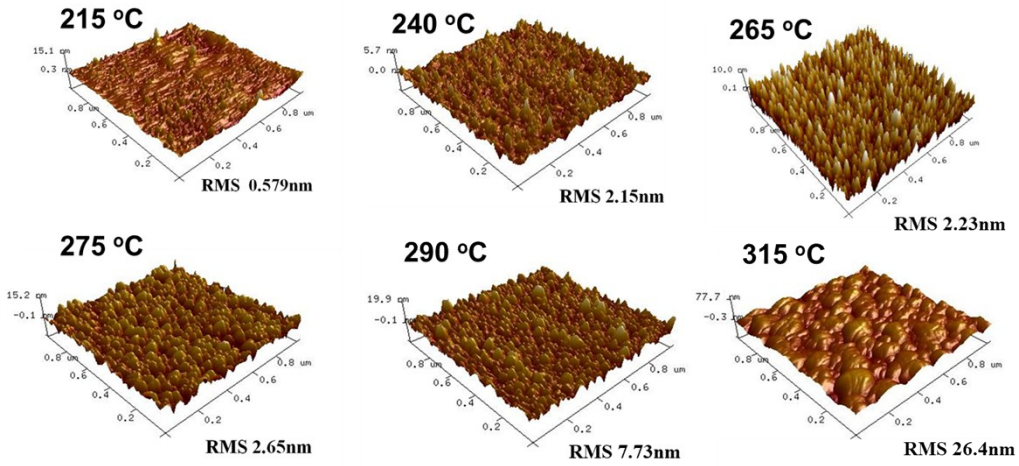


Figure S3 AFM images of Fe_xN films deposited at varying temperatures using 6 s dose of Fe(^{t}Bu-amd)$_2$ and 0.6 s dose of N_2H_4 by 500 cycles.

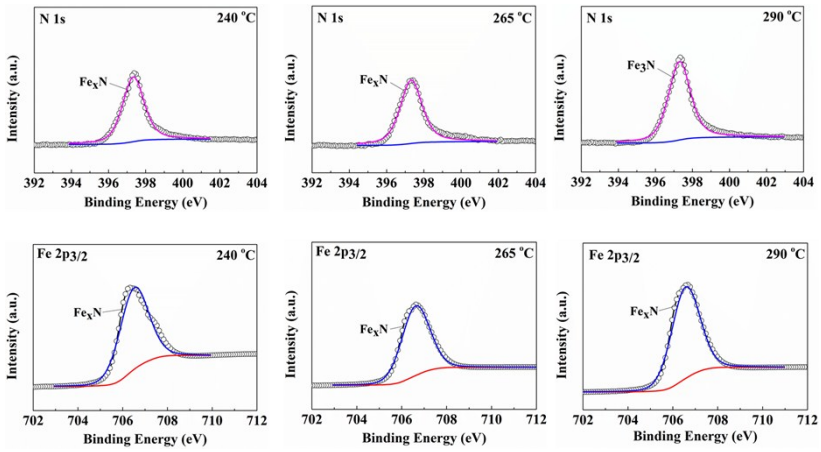


Figure S4 N 1s and Fe $2p_{3/2}$ XP spectra of film deposited at ALD window

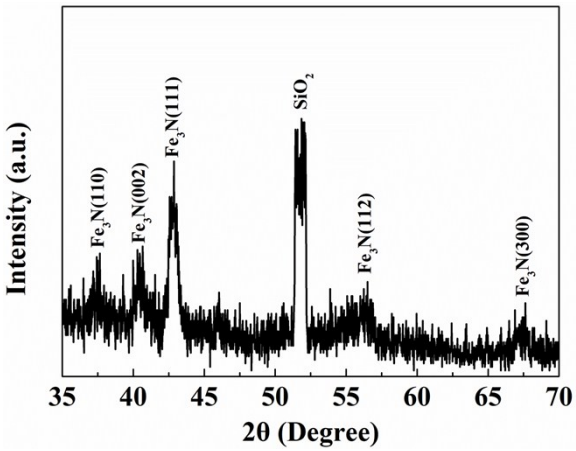
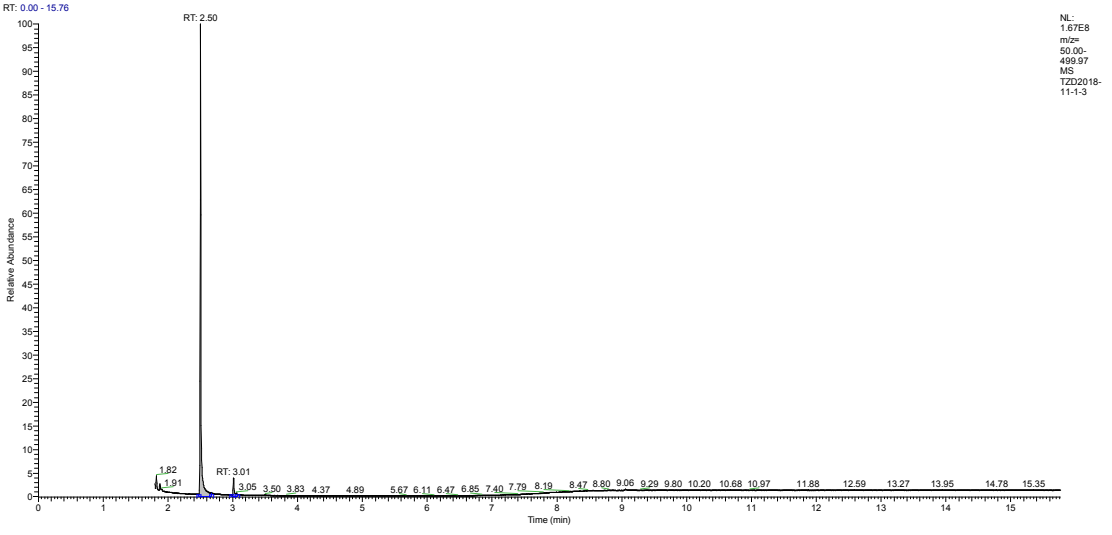


Figure S5 XRD of Fe_xN films deposited at 290 °C using 6 s dose of Fe(^{t}Bu-amd)$_2$ and 0.6 s dose of N_2H_4 by 500 cycles.

2. Mechanism Exploration

To a 100 mL Schlenk flask charged with Fe(^{t}Bu-amd)$_2$ (1 g) and toluene (30 mL), excess N_2H_4 was added at room temperature. Black precipitate and a large amount of gas generated immediately after N_2H_4 was added into Fe(^{t}Bu-amd)$_2$ solution. The gas was collected by a gas bag, which was pretreated through evacuation and argon purge for three times. After the reaction stirring for 10 minutes, the precipitate was filtered, then the filtrate was retained for analysis of possible by-products in solution. All operations were under the protection of argon. Besides, pale yellow liquid was trapped in the cold trap equipped between the ALD chamber and vacuum pump after above deposition processes, though gas by-products were difficult to collect. The collected gas, which was identified as a mixture of NH_3, N_2 and H_2, was analyzed by gas chromatograph equipped with a TCD detector (Agilent 6890A with 13X and Chromossorb 103 columns). The filtrate and pale yellow liquid were analyzed by GC-MS.



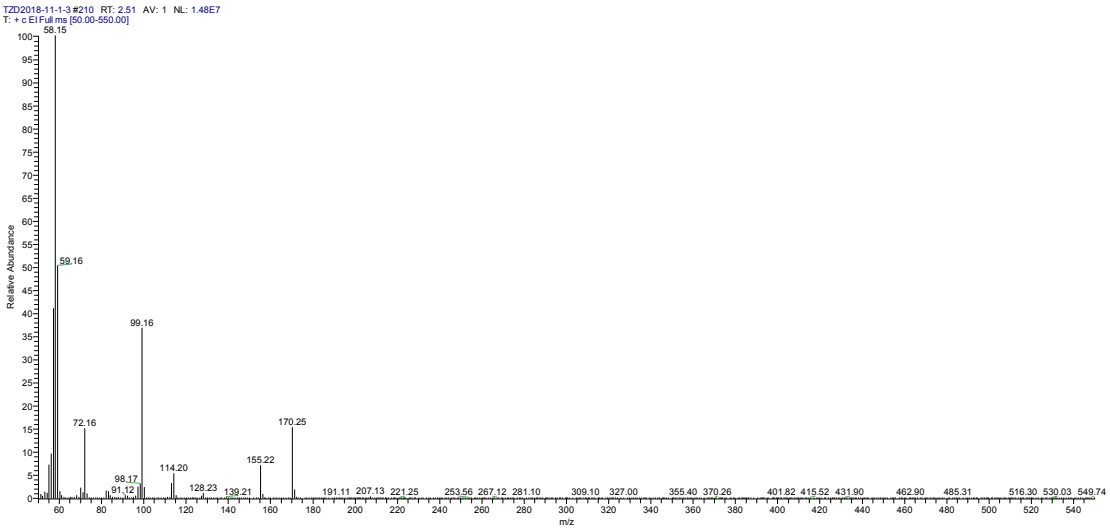


Figure S6 GC-MS result of the filtrate

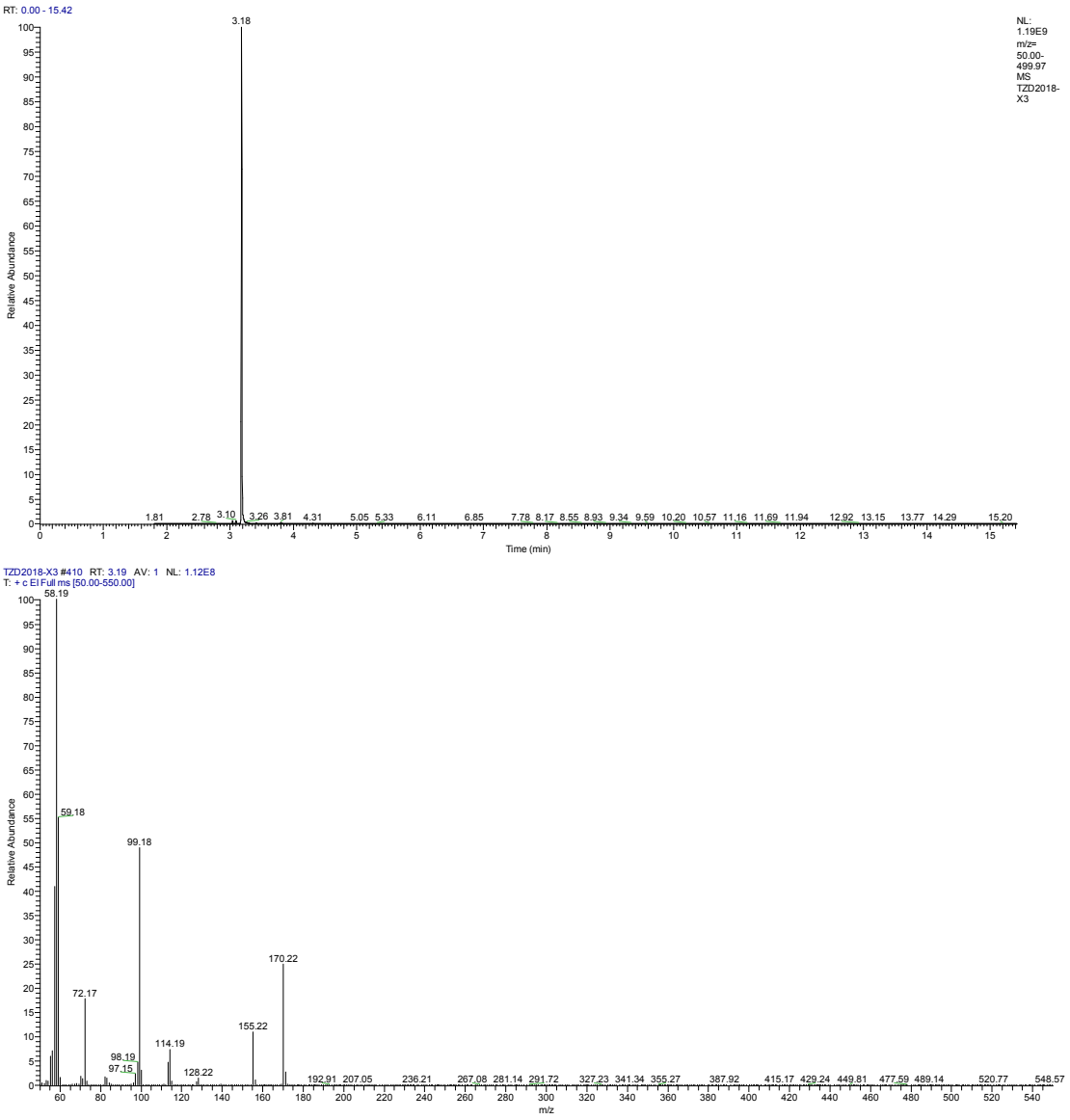


Figure S7 GC-MS result of the pale yellow liquid which was trapped in the cold trap equipped between the ALD chamber and vacuum pump