Title
Wafer-scale synthesis of WS$_2$ films with in-situ controllable p-type doping by atomic layer deposition

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Abstract
Wafer-scale synthesis of p-type TMD films is critical for its commercialization in next-generation electro/optoelectronics. In this work, wafer-scale intrinsic n-type WS$_2$ films and in-situ Nb-doped p-type WS$_2$ films were synthesized through atomic layer deposition (ALD) on 8-inch α-Al$_2$O$_3$/Si wafers, 2-inch sapphire and 1 cm$^2$ GaN substrate pieces. The Nb doping concentration was precisely controlled by altering cycle number of Nb precursor and activated by post-annealing. WS$_2$ n-FETs and Nb-doped p-FETs with different Nb concentrations have been fabricated using CMOS-compatible processes. X-ray photoelectron spectroscopy, Raman spectroscopy, and Hall measurements confirmed the effective substitutional doping with Nb. The on/off ratio and electron mobility of WS$_2$ n-FET are as high as $10^5$ and 6.85 cm$^2$V$^{-1}$s$^{-1}$, respectively. WS$_2$ p-FET with 15-cycle Nb doping, the on/off ratio and hole mobility are 10 and 0.016 cm$^2$V$^{-1}$s$^{-1}$, respectively. The p-n structure based on n- and p- type WS$_2$ films was proved with a $10^4$ rectifying ratio. The realization of controllable in-situ Nb-doped WS$_2$ films paved a way for fabricating wafer-scale complementary WS$_2$ FETs.
1. Introduction

As silicon-based CMOS technology is reaching its physical limits, two-dimensional transition metal dichalcogenides (TMDs) have been intensively investigated as potential ultra-thin channel materials for future electronics. TMDs show tunable bandgap, good air-stability and high carrier mobility, and can be applied in transistors, photodetectors, memory, RF and heterojunction synapse. However, there are still many challenges, including: (1) realization of large wafer-scale deposition, (2) a controllable p-type doping method for TMDs films, (3) reducing Schottky barrier induced Fermi level pinning at the metal/TMDs contacts, and (4) high quality high-k/TMDs interface. Chemical vapor deposition (CVD) is an effective way to synthesize single-crystalline TMDs films, but wafer-scale deposition and precisely-controlled thickness of TMDs films are difficult to achieve via CVD. Because TMD films are too thin for p-type doping by ion implantation, a variety of different approaches have been pursued, including charge transfer doping by physical adsorption of molecules or salts on surface, and metal oxides or metals induced inversion of WS₂ through interfacial interactions. However, it has proven difficult to precisely control the doping behaviors, and consequently electronic device performance.

Atomic layer deposition (ALD), a self-limiting process with precisely-controlled layer thickness, is an ideal technique to synthesize wafer-scale TMDs films. Niobium (Nb) has been demonstrated as an effective p-type dopant for WS₂. Halide-assisted CVD and low-pressure CVD have been utilized to insert Nb atoms into the WS₂ lattice, and pulsed laser deposition (PLD) can also achieve p-type WS₂ films using pre-melted Nb-doped targets, but without device demonstration. However, neither CVD or PLD are capable of in-situ and controllable doping. ALD has been demonstrated for synthesis of wafer-scale WS₂ films with WF₆ as W precursor and H₂S as S precursor. However, very few works have reported in-situ controllable p-type doped WS₂ FETs through ALD. NbS₂ can be synthesized by utilizing NbCl₅ and HMDST in ALD, similar to WS₂. In addition, the lattice constants of 2H-NbS₂ ((a, b, c) = (0.332, 0.332, 1.194) nm) are close to those of 2H-WS₂ ((a, b, c) = (0.316, 0.316, 1.247) nm), which facilitates substitutional doping of Nb atoms into the WS₂ lattice.

Here in this work, we demonstrate for the first time the wafer-scale synthesis of WS₂ films by ALD with controllable in-situ p-type doing, on 8-inch α-Al₂O₃/Si wafer, 2-inch sapphire wafers, and 1 cm² GaN substrate pieces. The growth mechanisms of ALD WS₂ and in-situ Nb doping were analyzed, and the doping concentration is shown to be controllable by altering Nb cycle numbers. Plan-view and cross-sectional TEM imaging reveals the layered structure of WS₂, and Hall effect measurements and TOF-SIMS confirms the effective incorporation of Nb dopants. Moreover, both WS₂ n-FETs and Nb-doped WS₂ p-FETs were fabricated by CMOS-compatible processes from as-prepared ALD-grown n-WS₂ and Nb-doped p-WS₂ films. The on/off ratio and electron mobility of WS₂ n-FET were up to 10⁵ and 6.85 cm²V⁻¹s⁻¹, while the on/off ratio and hole mobility of Nb-doped WS₂ p-FET were 10⁴ and 0.016 cm²V⁻¹s⁻¹, respectively. WS₂ FETs with different concentrations of Nb dopants were also investigated. Our work, by demonstrating in-situ controllable Nb-doped WS₂ films and consequently p-FETs, helps establish a path to fabricate complementary WS₂ FETs at wafer-scale volumes.

2. Results
Fig. 1. Illustration of ALD growth mechanisms and characterizations. (A) Idealized schematic of the mechanisms of the ALD process for WS$_2$ growth and in-situ Nb-doping. The doping concentration could be controlled by adjusting NbS$_2$ cycle numbers. (B) Photographs of 400-cycle WS$_2$ films deposited on 8-inch α-Al$_2$O$_3$/Si wafer, 2-inch sapphire wafer and pieced GaN substrates. (C) The Raman spectra of annealed WS$_2$ on Si/Al2O3, GaN, and sapphire confirm the successful synthesis of WS$_2$ on each substrate surface.

Growth mechanisms

Figure 1A illustrates the mechanisms of the ALD process for WS$_2$ growth and in-situ Nb-doping. The reactor temperature was 400 °C, while the WCl$_6$ (99.9 %), NbCl$_5$, and HMDST (98 %) were kept at 93 °C, 60 °C and room temperature, respectively. One cycle of WS$_2$ deposition includes 1s WCl$_6$ pulse, followed by 8s purge (Argon, 99.99 %), and 1s HMDST pulse, followed by 5s purge, sequentially. For Nb-doping, NbCl$_5$ and HMDST are used as precursors. One cycle of NbS$_2$ deposition includes 1s NbCl$_5$ pulse, followed by 8s purge (Argon, 99.99 %), and 1s HMDST pulse, followed by 5s purge. The growth rate of WS$_2$ film was calibrated to about 0.036 nm/cycle. To realize a controllable in-situ doping, WCl$_6$ pulses were replaced by NbCl$_5$ pulses, and the doping concentration could thus be adjusted by varying NbCl$_5$ pulse numbers. Fig. 1B showed photographs of wafer-scale 400-cycle WS$_2$ films deposited on 8-inch amorphous-Al$_2$O$_3$/Si wafer, 2-inch sapphire wafer and pieced GaN substrate with good uniformity. Raman spectra of 400-cycle annealed WS$_2$ films at 950 °C are shown in Fig. 1C, confirming that high quality WS$_2$ could be deposited on all these substrates except for Si with different thickness at 400 cycles. In view of this, we use sapphire as the substrate for this research.
Fig. 2. **Material characterizations of ALD grown WS₂ films without doping.** (A) The XPS fine spectra of W 4f and S 2p for as-deposited and annealed 400-cycle WS₂ film. Both WS₂ and WS₃ peaks were observed, with the W/S ratio of 1:2.7. Only WS₂ was observed in fine spectra of annealed WS₂, indicating the necessity of annealing and the W/S ratio was reduced to 1:2.1. (B) The Raman spectra of annealed WS₂ film, with differing thickness. The Raman peak separation increased with increasing film thickness. (C) The plane-view and cross-sectional TEM result of 400-cycle annealed WS₂ film, and the plane-view TEM result and statistical analysis of film grains by selected area electron diffraction (SAED) patterns. Layered structure was clearly observed in cross-sectional TEM. The average grain size of 259 WS₂ grains was 55 nm, with the maximum size up to 160 nm.

ALD-deposited WS₂ film. At the initial stage, the WCl₆ and HMDST vapor were exposed directly onto the sapphire substrates and WS₂ layers were formed laterally on sapphire substrates. The subsequent layers were deposited onto the initial WS₂ layer to connect the isolated flakes and form films. Considering this, a post-annealing process would be beneficial for improving film quality. The as-deposited WS₂ films were annealed at 950°C for 2h in sulfur atmosphere. The XPS spectra of as-deposited and annealed WS₂ films are shown in Fig. 2A. The fine spectra of as-deposited WS₂ contained two pairs of W 4f peaks, representing WS₃ and WS₂, respectively. The higher coordination number of W atom in WS₃ than in WS₂ results a shift towards higher binding energy, with the binding energies of W⁶⁺ 4f⁵/₂ and W⁶⁺ 4f⁷/₂ being 38.7eV and 36.68eV, and those of W⁴⁺ 4f⁵/₂ and W⁴⁺ 4f⁷/₂ being 35.22 eV and 33.08 eV, respectively. Similarly, the fine spectra of as-deposited WS₂ showed two pairs of S 2p peaks. The positions of the S₂ 2p⁵/₂ and S₂ 2p³/₂ peaks for W⁶⁺-S bonding were at 164.54 eV and 163.54 eV, while the positions of the S₁ 2p⁵/₂ and S₁ 2p³/₂ peaks for W⁴⁺-S bonding were at 164.02 eV and 163.04 eV, respectively. XPS analysis for as-deposited WS₂ films shows the films to be a mixture of WS₃ and WS₂, and the stoichiometric ratio of W/S was about 1:2.7. A post-annealing process in S atmosphere at 950°C for 2 hours improves film crystallinity. After annealing, the fine spectra of W 4f exhibited only one pair of W 4f⁵/₂ and W 4f⁷/₂ peaks, indicating WS₃ components decomposed to WS₂, along with a similar result for S 2p spectra, both without characteristic peaks indicative of W⁶⁺-S bonding. As a result, the stoichiometric ratio of W/S was reduced to 1:2.1, with the help of desulfurization and improved film crystallinity. The full spectra of as-deposited and annealed WS₂ are shown in Fig. S2. To further investigate the crystallinity of as-deposited and annealed WS₂ films, Raman
spectroscopy was performed. After annealing, the relative intensity of the $A_{1g}$ and $E_{12g}^{1}$ +2LA(M) peaks for annealed WS$_2$ was much higher than that of as-deposited WS$_2$ (Fig. S3), confirming the improved film crystallinity after annealing. Therefore, subsequent WS$_2$ films in this paper have undergone post-annealing process. In addition, when increasing WS$_2$ film thickness from 250 cycle to 500 cycle, the separation between the $A_{1g}$ and $E_{12g}^{1}$ +2LA(M) peaks increased from 64.2 cm$^{-1}$ to 69.5 cm$^{-1}$, demonstrating good thickness controllability for ALD grown WS$_2$, as shown in Fig. 2B. Plan-view and cross-sectional TEM imaging shown in Fig. 2C reveal a continuous planar film, without warpages or kink formation. The thickness of the annealed 400-cycle WS$_2$ film was 4.6 nm, and a cross-sectional TEM image of a 3.7 nm WS$_2$ film is shown in Fig. S4.

Preparing monolayer films is very challenging due to the growth mechanism of ALD TMDs films. From the plane-view TEM and SAED patterns results, out of 259 WS$_2$ analyzed grains, the average grain size was 55 nm (details of grain size were shown in Fig. S5), while the largest grain size was as high as 160 nm. The AFM image of 4.6 nm WS$_2$ film was shown in Fig. S6.

**In-situ Niobium-doped p-type WS$_2$ films.** Pure NbS$_2$ films were deposited by ALD using NbCl$_5$ and HMDST precursors, and the XPS results of as-deposited NbS$_2$ films are shown in Fig. S7. The Nb doping process is illustrated in Fig. S8 and Table S1. As-deposited and annealed 400-cycle WS$_2$ films with 30 cycles Nb doping were then investigated by XPS. In the fine spectra of W 4f peaks (Fig. 3A) of as-deposited Nb-doped WS$_2$ films, two pairs of characteristic peaks revealing both W$^{6+}$-S bonding and W$^{4+}$-S bonding were observed. However, different from the fine spectra of S 2p of as-deposited WS$_2$, a pair of characteristic peaks of Nb-S bonding was also observed, indicating successful Nb substitutional incorporation. The fine spectra of Nb 3d confirmed the presence of NbS$_2$ as well. After annealing, only W$^{4+}$-S bonding was observed in the W 4f fine spectra (see Fig. 3A), while W$^{4+}$-S bonding and Nb-S bonding were both observed in the S 2p fine spectra. The Nb 3d fine spectra proved the formation of NbS$_2$, indicating that Nb atoms were substituted into WS$_2$ lattice. The stoichiometric ratio of Nb/S was about 1:2.0, while that of W/S was 1:2.1. The full spectra of as-deposited and annealed Nb-doped WS$_2$ are shown in Fig. S9. The Raman spectra of annealed Nb-doped 400-cycle WS$_2$ films with Nb doping varying from 10 cycles to 100 cycles are shown in Fig. 3B. From the spectra, the blue shift of the $A_{1g}$ peaks was obvious, especially in the Nb-doped WS$_2$ film with 100 cycles Nb doping, which implies stiffening of the Nb-doped WS$_2$ lattice with Nb-S bonds. The annealing process was necessary for Nb atoms to be activated and incorporated substitutionally into the WS$_2$ lattice. The plan-view EDX mapping results are shown in Fig. S10, confirming successful Nb doping of the WS$_2$ film.
Fig. 3. Material characterization of Nb-doped p-type WS$_2$. (A) The XPS fine spectra of as-deposited and annealed 400-cycle WS$_2$ with 30-cycle Nb doping. WS$_2$, WS$_{2+x}$, and NbS$_2$ were all observed in as-deposited Nb-doped WS$_2$ film. After annealing, only WS$_2$ and NbS$_2$ were observed, indicating the effective doping. (B) The Raman spectra of 400-cycle WS$_2$ with Nb doping varying from 10 to 100 cycles. A blue shift of A$_{1g}$ peak was observed when increasing doping concentration, implying the stiffening of Nb-doped WS$_2$ lattice with Nb-S bonds. (C) The hall mobility and resistivity of WS$_2$ and Nb-doped WS$_2$ with 50 cycles Nb doping at temperature varying from 50K to 300K. (D) The mobility, resistivity and TOF-SIMS of WS$_2$ and Nb-doped WS$_2$ with Nb doping of 15, 20 and 100 cycles. After 15-cycle Nb doping, the carrier type changed from electrons to holes, and the mobility decreased one order of magnitude, while the resistivity increased 4 orders of magnitude. However, with increasing Nb doping, the mobility continued to decrease, while the resistivity started to decrease. The normalized Nb secondary ions intensity of Nb-doped WS$_2$ films indicated the occurrence of p-type doping.

Hall effect measurements of undoped WS$_2$ and Nb-doped WS$_2$ with 30 cycles Nb doping were performed at temperatures ranging from 50 K to 300 K. As shown in Fig. 3C, the carrier type of undoped WS$_2$ was electrons, while the carrier type of Nb-doped WS$_2$ film was holes, confirming the effective Nb-substitutional doping. The hall mobility of undoped WS$_2$ was up to 147.9 cm$^2$V$^{-1}$s$^{-1}$ at 50 K and 86.3 cm$^2$V$^{-1}$s$^{-1}$ at 300 K, while the hall mobility of Nb-doped WS$_2$ was 12.4 cm$^2$V$^{-1}$s$^{-1}$ at 50 K and 3.6 cm$^2$V$^{-1}$s$^{-1}$ at 300 K, respectively. The resistivity of Nb-doped WS$_2$ was 4 orders of magnitude higher than that of WS$_2$, which revealed the fact that the Nb atom was effectively doped to substitute W atom in WS$_2$ lattice.
As shown in Fig. 3D, the Hall mobility and resistivity of Nb-doped WS$_2$ films with Nb doping of 15, 20 and 100 cycles at 300 K and TOF-SIMS of pristine WS$_2$. Nb-doped WS$_2$ with Nb doping of 20 and 100 cycles were investigated as well. With increasing Nb concentration, the hall mobility decreased from 12.60 cm$^2$V$^{-1}$s$^{-1}$ to 5.73 cm$^2$V$^{-1}$s$^{-1}$, while the resistivity of 15-cycle Nb-doped WS$_2$ film was 3 orders of magnitude higher than that of 100-cycle Nb-doped WS$_2$ film. This result implied that 100-cycle Nb-doped WS$_2$ was heavily p-doped. Nb secondary ions intensity of pristine WS$_2$ film was normalized to 1, while the Nb intensity of Nb-doped WS$_2$ films with Nb doping of 20 and 100 cycles was normalized as 5.13 and 19.25. The increased normalized Nb intensity implied the rising doping concentration with the increase of Nb cycle number. Both hall effect results and TOF-SIMS gave evidence of in-situ controllable and substitutional Nb doping. Accurate quantitative value of concentration of Nb doping could not be obtained due to the poor detection accuracy and low atom collection efficiency. STEM is not applicable for ALD grown Nb-doped WS$_2$ films, due to the nature of polycrystalline films yielding only the statistical results within few layers. Raw data of Hall measurements of WS$_2$ and Nb-doped WS$_2$ with in Fig 3D were shown in Table S2.

**Electrical properties of WS$_2$ n-FET and Nb-doped WS$_2$ p-FET.** To characterize the electrical properties of 4.6 nm WS$_2$ n-FETs and Nb-doped WS$_2$ p-FETs, top-gate transistors were fabricated with 2 μm gate width on sapphire substrate. The CMOS-compatible process flow and the structure of top-gate FET were shown in Fig. 4A (detailed process was discussed in Method section). ALD Al$_2$O$_3$ films (20 nm) were used as high-k dielectrics. The equivalent oxide thickness was 13 nm. The transfer characteristic of 8-layer WS$_2$ n-FET was shown in Fig. 4B, with $V_d$ varying from 0.1 V to 0.5 V, while the output characteristics with $V_g$ varying from 1 V to 5 V. The transfer on-current of WS$_2$ n-FET reached as high as 0.4 μA/μm at $V_d$=0.5 V, and the on-off ratio was up to 10$^5$. The detailed mobility of 30 tested WS$_2$ n-FETs was also plotted in Fig. 4b. The maximum and minimum mobility of n-FETs were 6.85 cm$^2$V$^{-1}$s$^{-1}$ and 0.32 cm$^2$V$^{-1}$s$^{-1}$ respectively, while the median mobility was 3.58 cm$^2$V$^{-1}$s$^{-1}$. The mobility of over 70% of WS$_2$ n-FETs was in the range of 1 to 5 cm$^2$V$^{-1}$s$^{-1}$.
The transfer characteristic of a 4.6 nm Nb-doped WS₂ p-FET with 15-cycle Nb doping with $V_d$ varying from 0.1 V to 0.5 V and the output characteristics with $V_g$ varying from -2 V to -6 V are shown in Fig. 4C. Compared to the WS₂ n-FET, the carrier type changed from electron to hole, which proved the Nb substituted for W atom in WS₂ lattice. The on- and off-current of Nb-doped WS₂ p-FET was only $5 \times 10^{-2} \mu$A/μm, while the on/off ratio was $10^1$. For hall effect measurements, the resistivity of 15-cycle Nb-doped WS₂ was 5 orders of magnitude higher than that of undoped WS₂, and the mobility of 15-cycle Nb-doped WS₂ was far less than that of undoped WS₂ at 300 K. The field-effect mobility of WS₂ FETs was smaller than the Hall effect of WS₂, due to the influence of transistors’ electrical contacts on the underestimation of field-effect mobility. The Hall mobility was roughly estimated through field-effect mobility due to the nonlinear dependence of carrier concentration on gate voltage. Moreover, the stability of our process was inquired through measuring the on-current of Nb-doped WS₂ p-FET with gate length varying from 5μm to 50μm. (Fig. 4C). The distribution of $I_{on,sat}$ (@$V_g=-4V$, $V_d=0.5V$) amongst 132 Nb-doped WS₂ p-FET with 20-cycle Nb doping on the same die was summarized. With increasing gate length, $I_{on,sat}$ decreased, suggesting the fabrication process was well-controlled and uniform. To explore the controllability of Nb doping, the transfer characteristics of Nb-doped WS₂ FETs with Nb doping varying from 1 cycle to 20 cycles were measured (Fig. 4D). Nb-doped WS₂ FET did not show p-type behavior but with a decreased on- and off-current until reaching 15 cycles. When further increasing Nb concentrations, the current of p-FET increased and the on/off ratio decreased in that the resistivity and mobility of Nb-doped WS₂ film decreased, which was identical to the hall effect measurements. The WS₂ FET was heavily p-doped after 20 cycles Nb doping. These results proved the good controllability of in-situ Nb doping by ALD.

Due to the lack of dangling bonds at the surface of WS₂, it was difficult to deposit very high quality high-k dielectrics. Thus, the PBTI of WS₂ n-FET was carried out to analyze the reliability of Al₂O₃ high-k dielectric. The stress was applied to gate and biased at 5.5 V. DC transfer characteristics at $V_g=0.5$ V were measured right after the removal of PBTI stress at room temperature. As shown in Fig. 4E, after 1000s stress, the degradation of on-current was 3.5 %, while the $V_{th}$ shift was only 300 mV which was 6 % of max-applied gate voltage. The results implied the instability of high-k films indeed affected the electrical properties of WS₂ n-FET. Higher quality high-k dielectrics would improve the electrical property of WS₂ n-FET. To investigate the air-stability of WS₂ film, the WS₂ n-FET was placed in ambient, and the transfer characteristics were tested at $V_g=0.5V$ after 1 month, 3 months and 6 months, as shown in Fig. 4F. The on-current of WS₂ n-FET...
degraded slightly, while the degradation was within one order of magnitude even after 6-month exposure in air. However, despite the fact that the deterioration of off-current was hardly observed after 3-month exposure, the deterioration of off-current was almost one order of magnitude after 6-month exposure. Consequently, the on/off ratio decayed from $10^5$ to $10^4$ after 6 months in ambient. Furthermore, vertical p-n structure based on WS$_2$ and Nb-doped WS$_2$ films was fabricated. The electrical property of p-n structure with rectifying ratio of $10^4$ was shown in Fig. 4G, with an ideal factor of 2.3, indicating a conspicuous recombination of electron-hole.

Table 1 | Benchmark of p-type WS$_2$ transistors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method of p-type doping</th>
<th>Growth method</th>
<th>Controllable doping</th>
<th>Wafer scale synthesis</th>
<th>EOT (nm)</th>
<th>$I_{on}/I_{off}$ @4.6MV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our work</td>
<td>Nb</td>
<td>ALD</td>
<td>√</td>
<td>√</td>
<td>13</td>
<td>10$^1$</td>
</tr>
<tr>
<td>[20]</td>
<td>Nb</td>
<td>CVD</td>
<td>×</td>
<td>×</td>
<td>270</td>
<td>&lt;10</td>
</tr>
<tr>
<td>[36]</td>
<td>Nb</td>
<td>CVD</td>
<td>×</td>
<td>×</td>
<td>285</td>
<td>10$^2$</td>
</tr>
<tr>
<td>[39]</td>
<td>$\Phi_m$</td>
<td>ALD</td>
<td>×</td>
<td>√</td>
<td>15</td>
<td>10$^2$</td>
</tr>
<tr>
<td>[27]</td>
<td>$\Phi_m$</td>
<td>ALD</td>
<td>×</td>
<td>√</td>
<td>60</td>
<td>10$^4$</td>
</tr>
<tr>
<td>[28]</td>
<td>$\Phi_m$</td>
<td>CVD</td>
<td>×</td>
<td>×</td>
<td>5.16</td>
<td>10$^6$</td>
</tr>
<tr>
<td>[23]</td>
<td>CH</td>
<td>PECVD</td>
<td>×</td>
<td>×</td>
<td>32.5</td>
<td>10$^4$</td>
</tr>
</tbody>
</table>

$\Phi_m$ stands for adjusting metal work function. (Ti, W, et al.)

The benchmark of p-type WS$_2$ transistors was listed in Table 1, including various deposition doping methods. CVD method could yield the highest $I_{on}/I_{off}$ ratio by adjusting metal work function, but suffers from the difficulties of large volume synthesis on 8/12-inch wafers. For ALD approach, wafer scale deposition has been studied, however, our work was the first demonstration of p-type WS$_2$ films on large-scale wafers, with in-situ controllable doping.

4. Discussion

For the first time, we demonstrated the wafer-scale synthesis of WS$_2$ films by ALD with controllable in-situ p-type doing, on 8-inch $\alpha$-Al$_2$O$_3$/Si wafer, 2-inch sapphire wafer and pieced GaN substrates with post-annealing process. The plane-view and cross-sectional TEM indicated the successful synthesis of WS$_2$ film with the average grain size of 55 nm. The XPS spectra, hall effect and TOF-SIMS proved the substitutional doping of Nb. The Nb-doped WS$_2$ FETs with different Nb doping concentration were fabricated to demonstrate the controllable Nb doping. Furthermore, the p-n structure based on WS$_2$ and Nb-doped WS$_2$ films showed $10^4$ rectifying ratio, giving evidence to the realization of p-type WS$_2$. Our work realized the controllable in-situ Nb doping WS$_2$ films by ALD, which obviated the difficulty of p-type WS$_2$ film and paved a path to the fabrication of complementary WS$_2$ FETs and further applications on logic circuits.

5. Materials and Methods

Materials synthesis and characterization. The WS$_2$ and Nb-doped WS$_2$ film were deposited on 2-inch sapphire substrate by ALD (Beneq, TFS-200). Prior to the deposition, the sapphire substrate was cleaned by acetone, ethyl alcohol, diluted HF (1:50) and deionized water in order. For Nb doping, a typical cycle includes 1 s NbCl$_5$ pulse,
followed by 8 s purge (Argon, 99.99 %), and 1 s HMDST pulse, followed by 5 s purge. To achieve Nb-doped WS$_2$ film, the NbS$_2$ process was sandwiched into WS$_2$ process accordingly. Nb concentration was precisely controlled through altering NbS$_2$ cycle numbers. The cycle number of 4.6 nm WS$_2$ was 400. The as-deposited samples were put in a quartz boat placed in the center of Zone I and Zone II, and 0.5 g sulfur powder was placed in Zone III carried by a quartz boat. The samples were annealed for 2 h in a 4-inch quartz tube at the base pressure less than 0.4 Pa. The temperature of Zone I and Zone II were raised to 950 °C in 55 minutes, and the temperature of Zone III was raised to 350 °C in 55 minutes. The morphology and structure of WS$_2$ and Nb-doped WS$_2$ were characterized by XPS (Augerscan-PHI5300, monochromatic Al Kα anode at 9.97 kV and 14.7 mA as the source of X-Ray radiation, Pass energy was 112 eV, step was 0.1 eV, peak fitted using combined Gaussian and Lorentzian line shapes), Raman (LabRAM, 532 nm laser wavelength, 1mW x100_VIS), Hall effect measurements (Lakeshore 8400, van der Pauw, DC,4-probes), and HRTEM (Thermofisher Talos F200X, acceleration voltage was 200 kV, The sample was prepared by Thermofisher Helios G4 UX focus ion beam, and a protective layer of Pt was deposited on the surface of the sample by electron beam and ion beam).

**Device fabrication.** Top-gate FETs for WS$_2$ and Nb-doped WS$_2$ films were fabricated through CMOS-compatible processes. After annealing in S atmosphere, photolithography was used to define channel area, and was etched by CF$_4$/Ar (20/10 sccm) in RIE. Source and drain were patterned by photolithography, and metalized by Ti/Au (15/70 nm) for WS$_2$ n-FETs and Pt (70 nm) for Nb-doped WS$_2$ p-FETs by PVD (Kurt J. Lesker PVD75). A 20-nm Al$_2$O$_3$ gate oxide was deposited by ALD at 250 °C. The precursors for Al$_2$O$_3$ were TMA and H$_2$O respectively. After top-gate patterning, 15/70 nm Ti/Au was deposited by PVD.

**Device measurement.** All electrical properties of WS$_2$ n-FETs and Nb-doped WS$_2$ p-FETs were measured in ambient at room temperature by Agilent B1500A Semiconductor Device Analyzer in probe station (MPI-TS3000). The field-effect carrier mobility was extracted from the transfer characteristic using the equation $\mu=(\Delta I_d/\Delta V_g)\times L/(W C_{ox} V_d)$, and the $C_{ox}=2.656$ F/m$^2$ was the unit gate capacitance between channel and top-gate ($C_{ox}=\varepsilon_2/\varepsilon_0/d, \varepsilon_1=6, d=20$ nm for Al$_2$O$_3$ dielectric).

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**Author Contributions:** Y.W., C.T. and L.J. conceived and designed the experiments. Y.W., C.T., R.B. and H.J.Y. carried out the materials deposition, annealing and device fabrication. Y.W., C.T. and Z.C.W. carried out the I-V measurements and reliability measurements. S.H. and X.Z. contributed to material characterizations. All authors contributed to interpreting the data and writing the manuscript.

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Conflicts of Interest
The authors declare no competing financial interest.

Data Availability
All data needed to evaluate the conclusions in the paper are present in the paper or the Supplementary Materials.

Supplementary Materials
Fig. S1 Thickness of the 400-cycle WS$_2$ films as a function of HMDST and WCl$_6$ precursor pulse time.
Fig. S2. XPS full spectra of as-deposited and annealed WS$_2$ films
Fig. S3. Raman spectra of as-deposited WS$_2$ film
Fig. S4. Cross-sectional TEM of 3.7 nm WS$_2$ film
Fig. S5. Grain size analysis of WS$_2$ film
Fig. S6. WS$_2$ film images with different cycle numbers and AFM image of 4.6 nm WS$_2$ film
Table. S1. WS$_2$ film process cycles with different Nb doping concentrations
Fig. S7. XPS results of as-deposited NbS$_2$ film
Fig. S8. Schematic diagram of process cycle of Nb doped WS$_2$ film.
Fig. S9. XPS full spectra of as-deposited and annealed Nb-doped WS$_2$ films
Fig. S10. Plane-view EDX mapping of Nb-doped WS$_2$ film
Table. S2. Hall measurements of WS$_2$ and Nb-doped WS$_2$ with Nb doping of 15, 20 and 100 cycles.

References


