Wafer-Scale Synthesis of WS₂ Films with In Situ Controllable p-Type Doping by Atomic Layer Deposition

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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 WS₂ films and in situ Nb-doped p-type WS₂ films were synthesized through atomic layer deposition (ALD) on 8-inch α-Al₂O₃/Si wafers, 2-inch sapphire, and 1 cm² GaN substrate pieces. The Nb doping concentration was precisely controlled by altering cycle number of Nb precursor and activated by postannealing. WS₂ 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 WS₂ n-FET are as high as 10⁵ and 6.85 cm² V⁻¹ s⁻¹, respectively. In WS₂ p-FET with 15-cycle Nb doping, the on/off ratio and hole mobility are 10 and 0.016 cm² V⁻¹ s⁻¹, respectively. The p-n structure based on n- and p-type WS₂ films was proved with a 10⁴ rectifying ratio. The realization of controllable in situ Nb-doped WS₂ films paved a way for fabricating wafer-scale complementary WS₂ 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 ultrathin channel materials for future electronics. TMDs show tunable bandgap, good air-stability, and high carrier mobility and can be applied in transistors [1–4], photodetectors [5], computing technologies [6, 7], memory [8, 9], RF [10–12], and heterojunction synapse [13, 14]. However, there are still many challenges, including (1) realization of large wafer-scale deposition, (2) a controllable p-type doping method for TMD films, (3) reducing Schottky barrier-induced Fermi level pinning at the metal/TMDs contacts, and (4) high-quality high-k/TMD interface. Chemical vapor deposition (CVD) is an effective way to synthesize single-crystalline TMDs films [15–17], 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 [18–21], a variety of different approaches have been pursued, including charge transfer doping by physical adsorption of molecules or salts on surface [22–25], and metal oxides (MoO₃) [26] or metal-induced inversion (Tungsten) [27, 28] 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 TMD films [29–32]. Niobium (Nb) has been demonstrated as an effective p-type dopant for WS₂ [33–35]. Halide-assisted CVD and low-pressure CVD have
been utilized to insert Nb atoms into the WS₂ lattice [20, 36], and pulsed laser deposition (PLD) can also achieve p-type WS₂ films using premelted Nb-doped targets, but without device demonstration [18]. However, neither CVD nor PLD is capable of \textit{in situ} and controllable doping. ALD has been demonstrated for the synthesis of wafer-scale WS₂ films with WF₆ as a W precursor and H₂S as a S precursor [37, 38]. However, very few works have reported in situ controllable p-type-doped WS₂ FETs through ALD [39]. NbS₂ can be synthesized by utilizing NbCl₅ and HMDST vapor onto the initial WS₂ layer to connect the isolated flakes and form films. Considering this, a postannealing 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 Figure 2(a). 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 that in WS₂ results a shift towards higher binding energy, with the binding energies of W⁴⁺4f⁵/² and W⁶⁺4f⁷/² being 38.7 eV and 36.68 eV and those of W⁴⁺4f⁵/² and W⁶⁺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 S₁ 2p⁵/² and S₂ 2p⁹/² peaks for WS₂ bonding were at 164.54 eV and 163.54 eV, while the positions of the S₁ 2p⁵/² and S₂ 2p⁹/² peaks for WS₃ 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 WS₂ and WS₃, and the stoichiometric ratio of W/S was about 1:2.7. A postannealing process in S atmosphere at 950°C for 2 hours improves film crystallinity. Afterannealing, the fine spectra of W 4f exhibited only one pair of W 4f⁵/² and W 4f⁹/² peaks, indicating WS₂ 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 A₁g and E₁g²₂g+2LA(M) peaks for annealed WS₂ was much higher than that of as-deposited WS₂ (Fig. S3), confirming the improved film crystallinity after annealing. Therefore, subsequent WS₂ films in this paper have undergone a postannealing process. In addition, when increasing WS₂ film thickness from 250 cycle to 500 cycle, the separation between the A₁g and E₁g²₂g+2LA(M) peaks increased from 64.2 cm⁻¹ to 69.5 cm⁻¹, demonstrating good thickness controllability for ALD grown WS₂, as shown in Figure 2(b). Plan-view and cross-sectional TEM imaging shown in Figure 2(c) reveal a continuous planar film, without warpages or kink formation. The thickness of the annealed 400-cycle WS₂ film was 4.6 nm, and a cross-sectional TEM image of a 3.7 nm WS₂ film is shown in Fig. S4. Preparing monolayer films is very challenging due to the growth mechanism of ALD TMD films. From the plane-view TEM and SAED patterns results, out of 259 WS₂ analyzed grains, the average grain size was 55 nm (details of grain size were shown...
Figure 1: Illustration of ALD growth mechanisms and characterizations. (a) Idealized schematic of the mechanisms of ALD process for WS₂ growth and in situ Nb doping. The doping concentration could be controlled by adjusting NbS₂ cycle numbers. (b) Photographs of 400-cycle WS₂ films deposited on 8-inch α-Al₂O₃/Si wafer, 2-inch sapphire wafer, and pieced GaN substrates. (c) The Raman spectra of annealed WS₂ on Si/Al₂O₃, GaN, and sapphire confirm the successful synthesis of WS₂ on each substrate surface.

Figure 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 WS₂+x 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 films with varying 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. A 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.
in Fig. S5), while the largest grain size was as high as 160 nm. The AFM image of 4.6 nm WS2 film is shown in Fig. S6.

2.1.2. In Situ Niobium-Doped p-Type WS2 Films. Pure NbS2 films were deposited by ALD using NbCl5 and HMDST precursors, and the XPS results of as-deposited NbS2 films are shown in Fig. S7. The Nb doping process is illustrated in Fig. S8 and Table S1. as-deposited and annealed 400-cycle WS2 films with 30-cycle Nb doping were then investigated by XPS. In the fine spectra of W 4f peaks (Figure 3(a)) of as-deposited Nb-doped WS2 films, two pairs of characteristic peaks revealing both W6+-S bonding and W4+-S bonding were observed. However, different from the fine spectra of S 2p of as-deposited WS2, 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 NbS2 as well. After annealing, only W4+-S bonding was observed in the W 4f fine spectra (see Figure 3(a)), while W6+-S bonding and Nb-S bonding were both observed in the S 2p fine spectra. The Nb 3d fine spectra proved the formation of NbS2, indicating that Nb atoms were substituted into WS2 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 WS2 are shown in Fig. S9. The Raman spectra of annealed Nb-doped 400-cycle WS2 films with Nb doping varying from 10 cycles to 100 cycles are shown in Figure 3(b). From the spectra, the blue shift of the A1g peaks was obvious, especially in the Nb-doped WS2 film with 100-cycle Nb doping, which implies stiffening of the Nb-doped WS2 lattice with Nb-S bonds [18]. The annealing process was necessary for Nb atoms to be activated and incorporated substitutionally into the WS2 lattice. The plan-view EDX mapping results are shown in Fig. S10, confirming successful Nb doping of the WS2 film.

Hall effect measurements of undoped WS2 and Nb-doped WS2 with 30-cycle Nb doping were performed at temperatures ranging from 50 K to 300 K. As shown in Figure 3(c), the carrier type of undoped WS2 was electrons, while the carrier type of Nb-doped WS2 film was holes, confirming the effective Nb-substitutional doping. The hall mobility of undoped WS2 was up to 147.9 cm2 V−1 s−1 at 50 K and 86.3 cm2 V−1 s−1 at 300 K, while the hall mobility of Nb-doped WS2 was 12.4 cm2 V−1 s−1 at 50 K and 3.6 cm2 V−1 s−1 at 300 K, respectively. The resistivity of Nb-doped WS2 was 4 orders of magnitude higher than that of WS2, which revealed the fact that the Nb atom was effectively doped to substitute W atom in WS2 lattice.

As shown in Figure 3(d), the Hall mobility and resistivity of Nb-doped WS2 films with Nb doping of 15, 20, and 100 cycles at 300 K and TOF-SIMS of pristine WS2 and Nb-doped WS2 with Nb doping of 20 and 100 cycles were investigated as well. With increasing Nb concentration, the hall mobility decreased from 12.60 cm2 V−1 s−1 to 5.73 cm2 V−1 s−1, while the resistivity of 15-cycle Nb-doped WS2 film was 3 orders of magnitude higher than that of 100-cycle Nb-doped WS2 film. This result implied that 100-cycle Nb-doped WS2 was heavily p-doped. Nb secondary ion intensity of pristine WS2 film was normalized to 1, while the Nb intensity of Nb-doped WS2 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. An 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 WS2 films, due to the nature of polycrystalline films yielding only the statistical results within few layers. Raw data of Hall measurements of WS2 and Nb-doped WS2 with in Figure 3(d) are shown in Table S2.

2.1.3. Electrical Properties of WS2 n-FET and Nb-Doped WS2 p-FET. To characterize the electrical properties of 4.6 nm WS2 n-FETs and Nb-doped WS2 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 are shown in Figure 4(a) (detailed process was discussed in Materials and Methods). ALD Al2O3 films (20 nm) were used as high-k dielectrics. The equivalent oxide thickness was 13 nm. The transfer characteristic of 8-layer WS2 n-FET is shown in Figure 4(b), with Vg varying from 0.1 V to 0.5 V, while the output characteristics with Vg vary from 1V to 5V. The transfer on-current of WS2 n-FET reached as high as 0.4 μA/μm at Vg = 0.5 V, and the on/off ratio was up to 105. The detailed mobility of 30 tested WS2 n-FETs is also plotted in Figure 4(b). The maximum and minimum mobilities of n-FETs were 6.85 cm2 V−1 s−1 and 0.32 cm2 V−1 s−1, respectively, while the median mobility was 3.58 cm2 V−1 s−1. The mobility of over 70% of WS2 n-FETs was in the range of 1 to 5 cm2 V−1 s−1.

The transfer characteristic of a 4.6 nm Nb-doped WS2 p-FET with 15-cycle Nb doping with Vg varying from 0.1 V to 0.5 V and the output characteristics with Vg varying from -2 V to -6 V are shown in Figure 4(c). 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 × 10−2 at Vg = 0.5 V, far less than that of WS2 n-FET. However, the hole mobility of Nb-doped WS2 p-FET was 0.016 cm2 V−1 s−1, while the on/off ratio was 105. 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 n-FETs was smaller than the Hall effect of WS2 due to the influence of transistors’ electrical contacts on the under-estimation 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 [41]. Moreover, the stability of our process was ensured through measuring the on-current of Nb-doped WS2 p-FET with gate length varying from 5 μm to 50 μm. (Figure 4(c)). The distribution of Id, saturation (at Vg = −4 V, Vd = 0.5 V) amongst 132 Nb-doped WS2 p-FET with 20-cycle Nb doping on the
same day was summarized. With increasing gate length, $I_{d,sat}$ decreased, suggesting the fabrication process was well-controlled and uniform. To explore the controllability of Nb doping, the transfer characteristics of Nb-doped WS$_2$ FETs with Nb doping varying from 1 cycle to 20 cycles were measured (Figure 4(d)). Nb-doped WS$_2$ 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 WS$_2$ film decreased, which was identical to the hall effect measurements. The WS$_2$ FET was heavily p-doped after 20-cycle 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 WS$_2$, it was difficult to deposit very high quality high-k dielectrics. Thus, the PBTI of WS$_2$ n-FET was carried out to analyze the reliability of Al$_2$O$_3$ high-k dielectric. The stress was applied to gate and biased at 5.5 V. DC transfer characteristics at $V_d = 0.5$ V were measured right after the removal of PBTI stress at room temperature. As shown in Figure 4(e), after 1000 s 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 WS$_2$ n-FET. Higher quality high-k dielectrics would improve the electrical property of WS$_2$ n-FET [42]. To investigate the air stability of WS$_2$ film, the WS$_2$ n-FET was placed in ambient atmosphere, and the transfer characteristics were tested at $V_d = 0.5$ V after 1 month, 3 months, and 6 months, as shown in Figure 4(f). The on-current of WS$_2$ 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 $10^4$ is shown in Figure 4(g), with an ideal factor of 2.3, indicating a conspicuous recombination of electron-hole.

The benchmark of p-type WS$_2$ transistors is listed in Table 1, including various deposition doping methods. The 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 WS₂ films on large-scale wafers, with in situ controllable doping.

3. Discussion

For the first time, we demonstrated 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 wafer, and pieced GaN substrates with a postannealing process. The plane-view and cross-sectional TEM indicated the successful synthesis of WS₂ 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 WS₂ FETs with different Nb doping concentrations were fabricated to demonstrate the controllable Nb doping. Furthermore, the p-n structure based on WS₂ and Nb-doped WS₂ films showed 10⁴ rectifying ratio, giving evidence to the realization of p-type WS₂. Our work realized the controllable in situ Nb doping WS₂ films by ALD, which obviated the difficulty of p-type WS₂ film and paved a path to the fabrication of complementary WS₂ FETs and further applications on logic circuits.

4. Materials and Methods

4.1. Material Synthesis and Characterization. The WS₂ and Nb-doped WS₂ 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 NbCl₅ pulse, followed by 8 s purge (Argon, 99.99%), and 1 s HMDST pulse, followed by 5 s purge. To achieve Nb-doped WS₂ film, the NbS₂ process was sandwiched into a WS₂ process accordingly. Nb concentration was precisely controlled through altering NbS₂ cycle numbers. The cycle number of 4.6 nm WS₂ 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 WS₂ and Nb-doped WS₂ were characterized by XPS (Augerscan-PH5300, 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, 1 mW x100_VIS), Hall effect measurements (Lakeshore 8400, van der Pauw, DC,4-probes), and HRTEM (Thermo Fisher Scientific Talos F200X; acceleration voltage was 200 kV; the sample was prepared by Thermo Fisher Scientific 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).

4.2. Device Fabrication. Top-gate FETs for WS₂ and Nb-doped WS₂ films were fabricated through CMOS-compatible processes. After annealing in S atmosphere, photolithography was used to define channel area and was etched by CF₄/Ar (20/10 sccm) in RIE. Source and drain were patterned by photolithography and metalized by Ti/Au (15/70 nm Ti/Au was deposited by PVD. From the transfer characteristic using the equation μ = (ΔI_d/ΔV_g) × L/(W C_{ox} V_d), and the C_{ox} = 2.656 F/m² was the unit gate capacitance between channel and top-gate (C_{ox} = ε₁ε₀/d, ε₁ = 6, and d = 20 nm for Al₂O₃ dielectric).

4.3. Device Measurement. All electrical properties of WS₂ n-FETs and Nb-doped WS₂ p-FETs were measured in ambient room temperature by the Agilent B1500A Semiconductor Device Analyzer in probe station (MP1-TS3000). The field-effect carrier mobility was extracted from the transfer characteristic using the equation μ = (ΔI_d/ΔV_g) × L/(W C_{ox} V_d), and for Al₂O₃ the C_{ox} = 2.656 F/m² was the unit gate capacitance between channel and top-gate (C_{ox} = ε₁ε₀/d, ε₁ = 6, and d = 20 nm for Al₂O₃ dielectric).

Table 1: Benchmark of p-type WS₂ transistors.

| Reference | Method of p-type doping | Growth method | Controllable doping | Wafer scale synthesis | EOT (nm) | I_off/I_on at 4.6 MV/cm |
|-----------|-------------------------|---------------|---------------------|-----------------------|---------|------------------------|
| Our work  | Nb                      | ALD           | √                   | √                     | 13      | 10¹                    |
| [20]      | Nb                      | CVD           | ×                   | ×                     | 270     | 10²                    |
| [36]      | Nb                      | CVD           | ×                   | ×                     | 285     | 10⁴                    |
| [39]      | Φₘ₉                    | ALD           | ×                   | ×                     | 15      | 10²                    |
| [27]      | Φₘ₉                    | ALD           | ×                   | ×                     | 60      | 10⁶                    |
| [28]      | Φₘ₉                    | CVD           | ×                   | ×                     | 5.16    | 10⁶                    |
| [23]      | CH                      | PECVD         | ×                   | ×                     | 32.5    | 10⁴                    |

Φₘ₉ stands for adjusting metal work function (Ti et al.).

Conflicts of Interest

The authors declare no competing financial interest.

Authors’ 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 material 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. Hanje Yang, Yang Wang, Xingli Zou, and Li Ji contributed equally to this work.

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Supplementary Materials

Fig. S1: thickness of the 400-cycle WS2 films as a function of HMDST and WCl6 precursor pulse time. Fig. S2: XPS full spectra of as-deposited and annealed WS2 films. Fig. S3: Raman spectra of as-deposited WS2 film. Fig. S4: cross-sectional TEM of 3.7 nm WS2 film. Fig. S5: grain size analysis of WS2 film. Fig. S6: WS2 film images with different cycle numbers and AFM image of 4.6 nm WS2 film. Fig. S7: XPS results of as-deposited NbS2 film. Table S1: WS2 film process cycles with different Nb doping concentrations. Fig. S8: schematic diagram of process cycle of Nb-doped WS2 film. Fig. S9: XPS full spectra of as-deposited and annealed Nb-doped WS2 films. Fig. S10: plane-view EDX mapping of Nb-doped WS2 film. Table. S2: hall measurements of WS2 and Nb-doped WS2 with Nb doping of 15, 20, and 100 cycles. (Supplementary Materials)

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