Synthesis of uniform single layer WS$_2$ for tunable photoluminescence

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Two-dimensional transition metal dichalcogenides (2D TMDs) have gained great interest due to their unique tunable bandgap as a function of the number of layers. Especially, single-layer tungsten disulfides (WS$_2$) is a direct band gap semiconductor with a gap of 2.1 eV featuring strong photoluminescence and large exciton binding energy. Although synthesis of MoS$_2$ and their layer dependent properties have been studied rigorously, little attention has been paid to the formation of single-layer WS$_2$ and its layer dependent properties. Here we report the scalable synthesis of uniform single-layer WS$_2$ film by a two-step chemical vapor deposition (CVD) method followed by a laser thinning process. The PL intensity increases six-fold, while the PL peak shifts from 1.92 eV to 1.97 eV during the laser thinning from few-layers to single-layer. We find from the analysis of exciton complexes that both a neutral exciton and a trion increases with decreasing WS$_2$ film thickness; however, the neutral exciton is predominant in single-layer to single-layer. The binding energies of trion and biexciton for single-layer WS$_2$ are experimentally characterized at 35 meV and 60 meV, respectively. The tunable optical properties by precise control of WS$_2$ layers could empower a great deal of flexibility in designing atomically thin optoelectronic devices.

Atomic layer two-dimensional transition metal dichalcogenides (2D TMDs) have garnered many interests for their unique electrical and optical properties including excellent electron mobility, high photoluminescence, semiconductor at atomic scale, and tunable band gap$^{4,5}$. Recent studies have shown that single-layer TMDs exhibit direct band gap property that is accompanied by strong photoluminescence (PL) emission and large exciton binding energy; thus, they are promising materials for fundamental studies as well as next-generation ultra-thin opto-electronic devices$^{4,5}$. Among the 2D TMDs, most researches have focused on MoS$_2$ in hopes of finding new properties and potential applications; however, little attention has been paid to WS$_2$. Single-layer WS$_2$ has a direct band gap of 2.1 eV$^6$ and a strong quantum yield of ~6% (single-layer MoS$_2$ yields ~0.1%)$^7$, whereas few-layer WS$_2$ is an indirect band gap semiconductor with a bandgap of 1.35eV$^8$. Few attempts have been made to synthesize large scale single-layer WS$_2$ film. Song et al.$^9$ presented fabrication of layer-controlled WS$_2$ by sulfurization of WO$_3$ film using atomic layer deposition (ALD), and Yun et al.$^{10}$ reported centimeter-scale single-layer WS$_2$ on gold foil by using chemical vapor deposition (CVD). However, their PL spectra within the single-layer WS$_2$ film were spatially nonuniform. In our previous report$^{11}$, we demonstrated centimeter scale WS$_2$ film by the two-step process of tungsten deposition followed by sulfurization in a low-pressure CVD. Despite the successful synthesis of the large scale WS$_2$ film, the film exhibits both single- and few-layer of WS$_2$; also, the single-layer WS$_2$ does not show uniformity. Thus, several post-treatment approaches were attempted to control the number of layers for any 2D TMDs. For example, Castellanos-Gomez et al.$^{12}$ reported the thinning of exfoliated few-layer MoS$_2$ film down to a single-layer by using a focused laser beam. Venkatakrishnan et al.$^{13}$ reported a laser thinning of WS$_2$ flake down to single-layer with revealing improvement of the fluorescence emission intensity and micro-encryption by surface modification. Ni et al.$^{14}$ used a plasma technique for layer by layer etching of mechanically exfoliated MoS$_2$ film; however, this technique requires physical mask for selective etching on TMDs film. No systematic study for fabrication of uniform single-layer WS$_2$ and its related opto-electronic properties have been reported.

One of the peculiar features of single-layer TMDs is strong excitonic effect caused by their absence of inter-layer coupling and the lack of inversion symmetry, which mostly account for the interesting PL emission property$^{15,16}$. The excitons are generated by electron-hole pairs in a single-layer TMDs that has the large binding energy. The exciton complexes, such as neutral exciton, bi-exciton, and trion, thus become important for optoelectronic devices$^{17}$. As the number of layers of a TMD decreases, both a neutral exciton and a trion increase in intensity$^{18}$. The excitons are generated by electron-hole pairs in a single-layer TMDs that has the large binding energy.

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energies ranging from 0.3 to 1.0 eV, which is attributed to their strong Coulomb attraction between charged particles. In particular, photoexcitation in 2D TMDs leads to the formation of multi-carrier bound states because excitons can interact with free electrons. Such interaction forms the exciton complexes including trions, a localized excitons consists of three charged quasiparticles (e.g., a negative trion consists of two electrons and one hole and a positive trion consists of two holes and one electron). The interaction of charged carriers and excitons controls the optical properties of TMDs. Hence, the first step is to understand the behavior of exciton complexes in WS₂ for practical applications in opto-electronic devices as well as for the fundamental physics of emergent new materials. Furthermore, the exact values for the binding energy of the excitons in WS₂ are still debated and the behavior of exciton complexes with respect to the WS₂ layers remains unexplored.

In this regard, we have employed high-power laser processing to fabricate a uniform single-layer WS₂ from the few-layer WS₂ synthesized by a scalable two-step CVD method. Atomically uniform single-layer WS₂ was successfully synthesized by the two-step CVD method followed by a laser thinning method. The behavior of exciton complexes with the number of WS₂ layer was investigated during the laser thinning process. We found that the PL intensity has increased linearly (up to 6 times higher) as the number of WS₂ layer decreased. In particular, the dominant exciton in single-layer WS₂ is neutral exciton, while trion is dominant in few-layer WS₂ as analyzed by PL spectrum. These changes of exciton intensity contribute largely to the PL spectra of WS₂ film; such phenomenon is invaluable to engineer the opto-electronic properties of 2D WS₂.

**Results**

**Synthesis and characterization of few-layer WS₂.** The synthesis of uniform few atomic layer 2D TMDs was presented in our previous report by the two-step method. Here we introduce a large-scale single-layer WS₂ film synthesis by using the two-step method followed by a laser thinning process. Schematic of the overall process and optical images of the sample in each step are presented in Fig. 1.

The synthesized WS₂ film was characterized by AFM, Raman spectroscopy, PL, and XPS. The optical image of as-synthesized few-layer WS₂ film on a SiO₂/Si substrate indicates uniform and large-scale growth of WS₂ film (Fig. 2a). The thickness of WS₂ film is estimated to be ~3.78 nm (Fig. 2b), which is 4–5 layers of WS₂, as confirmed by the AFM in the previous studies. Figure 2c presents the Raman spectrum of as-synthesized few-layer WS₂ film (measured at 514 nm excitation laser line). The Raman spectrum is governed by the first-order modes: E₁^2g (Γ) at 369.1 cm⁻¹ and A₁g (Γ) at 434.0 cm⁻¹; however, the intensity of the second order mode of 2LA (M) at 363.5 cm⁻¹ is also very high for WS₂. Even though the 2LA (M) mode is overlapped with the E₁^2g mode, the peak is separated their individual contributions by the Lorentzian fitting. The frequency difference (Δk) between 2LA (M) and A₁g as well as E₁^2g and A₁g modes are 70.5 cm⁻¹ and 64.9 cm⁻¹, respectively. Thus, it is confirmed that the as-synthesized film is 4–5 layers of WS₂. We also characterized the WS₂ film using XPS (Fig. 2d). The 4f core-level spectrum represents three peaks at 32.6, 34.8, 38.2 eV corresponding to the W 4f₁/₂, W 4f₃/₂, and W 5p₃/₂ states, respectively. Based on the XPS data, an excellent stoichiometry of the atomic WS₂ film is realized by the calculated S (66.7%) to W (33.3%) ratio of 2.25.

**Characterization of single-layer WS₂ fabricated by laser thinning method.** The as-synthesized WS₂ film was irradiated by a scanning laser to thin the few-layer WS₂ down to a single-layer. Inset of Fig. 3a shows the optical image of WS₂ film after laser irradiation for 10 seconds; the image represents the laser covering 5 μm × 5 μm area. Color contrast is observed for the laser irradiated region (A) showing uniform and reduced thickness. The relative thickness difference after the laser irradiation (Fig. 3a) is ~2.88 nm; thus, the thickness of laser irradiated region is ~0.9 nm which corresponds to a single-layer WS₂. The detailed surface profile of laser irradiated region is investigated by AFM (Fig. 3b). Remarkably, the laser beam can etch up to ~2.92 nm uniformly over the as-synthesized ~3.78 nm thick WS₂ film. It should be noted that the edge of the sidewalls is not flat. This is attributed to the Gaussian intensity profile of the confocal laser. The sidewall could be removed by overlapping the irradiated laser spots. After laser irradiation, Raman and PL measurements were performed with a reduced laser power of 200 μW to the irradiated area of 5 μm × 5 μm (Fig. 3c). The Raman spectra show the 2LA (M), E₁^2g (Γ), and A₁g (Γ) modes at 366.6 cm⁻¹, 369.6 cm⁻¹, and 432.1 cm⁻¹, respectively.
Figure 3d presents the 2LA (M) and A_{1g} modes of both laser irradiated (A) and non-irradiated (B) regions on WS_{2} film. The frequency differences (\Delta k) between two modes changed from 70.5 cm\(^{-1}\) to 65.5 cm\(^{-1}\); also, the relative intensity of I_{2LA}/I_{A1g} increased from 0.77 to 1.1. Berkdemir et al.\(^{6}\) reported that frequency differences (\Delta k) and the intensity ratios investigated by Raman spectra (\lambda_{exc}=514 nm) for thin WS_{2} film are modifiable by the number of layers. Particularly, single-layer WS_{2} shows a \Delta k of 65.2 cm\(^{-1}\) and I_{2LA}/I_{A1g} of 2.1; those values are slightly different from the results of our single-layer WS_{2} fabricated by laser irradiation. The differences are attributed to the unetched few-layer WS_{2} as illustrated in the height profile (Fig. 3b). Figure 3e indicates PL intensities for both regions A (laser-irradiated) and B (non-irradiated) in Fig. 3a. After laser irradiation, PL intensity increases substantially up to 6 times; in addition, the PL peak position is shifted from 1.92 eV to 1.97 eV. The 1.97 eV PL peak position corresponds to single-layer WS_{2}\(^{26,27}\). Based on this approach, wafer scale laser-thinned single-layer WS_{2} film could be readily fabricated by using a scanning laser beam irradiation. We employed in situ confocal PL and Raman spectroscopy to investigate the variation in the PL and Raman spectra with respect to the laser irradiation time. Figure 4a depicts the PL spectra of the WS_{2} film measured with laser irradiation times (from 0 to 7 seconds) under ambient conditions. The PL intensity increases steadily as a function of the laser irradiation time of up to 7 seconds in which the PL intensity reaches maximum; as a result, the PL peak position is shifted from 1.92 eV to 1.97 eV, (dotted line in Fig. 4a). Thus, the precise thinning of the as-synthesized few-layer WS_{2} film by the laser irradiation is evidenced by the increase in PL peak intensity and the shift in position. Figure 4b indicates Raman spectra of WS_{2} film recorded at different laser irradiation time. The relative intensity (I_{2LA}/I_{A1g}) is gradually changed from 0.8 for 1 second to 1.1 for 7 seconds; also, the frequency difference between 2LA (M) and A_{1g} (\Gamma) modes is reduced to 65.5 cm\(^{-1}\) for 7 seconds of irradiation time. The constant change of PL and Raman spectra with laser irradiation time reveals that the few-layer WS_{2} film is continuously thinned with the laser time. The Raman peak position shift in A_{1g} mode shows an interesting phenomenon with regard to self-limited etching behavior. Figure 4c shows the A_{1g} mode shift as a function of laser irradiation time (from 0 to 25 seconds). It is noted that there exist two regimes: the region exposed for 0–7 seconds shows larger slope than the region exposed for 8–25 seconds. As a result, it is expected that the top WS_{2} layers are etched entirely by the laser irradiation of 7 seconds, whereas the bottom single-layer WS_{2} remains unetched even after 7 seconds laser irradiation. The lower slope of the A_{1g} mode after 7 seconds is attributed to the local strains or disorders caused by the continuous laser irradiation\(^{28,29}\). PL and Raman spectra (Fig. 4a and b) verify that the single-layer WS_{2} film is already achieved after laser irradiation for 7 seconds; thus, the etching rate of WS_{2} film is \sim0.42 nm/sec calculated by etched thickness (2.92 nm in Fig. 3b) and laser irradiation time (7 seconds).

To demonstrate the fabrication of single-layer WS_{2} film with high uniformity, PL mapping with a PL peak position is carried out on the laser irradiated area (Fig. 4d–f). It is observed that the PL peak variation is uneven for 2 and 5 second irradiation time. However, the spatial uniformity increases significantly after laser irradiation for 10 seconds as shown in Fig. 4f. This uniform PL peak position demonstrates that the formation of uniform single-layer WS_{2} film was achieved by the laser irradiation; also, further undesirable damage after forming the single-layer WS_{2} film was prevented\(^{30}\). Once the normally incident laser is absorbed on WS_{2} layers, the WS_{2}...
layers produce local heating on the plane. Gastellanos-Gomez et al.\textsuperscript{12} reported that the generated thermal energy mostly dissipate through the planer direction to the TMDs layers rather than the perpendicular direction which is bonded by weak van der Waals forces. Similarly, as reported by Han et al.\textsuperscript{30}, the generated heat by light absorption is mainly accumulated on the upper graphene layers when a laser is induced on the film, while the SiO\textsubscript{2}/Si substrate plays an important role as a heat reservoir for the single-layer graphene to remain unetched. It is also reported that the heat conduction across 2D crystals-substrate interface is not negligible\textsuperscript{31}. Initially, the heat propagates mostly along the basal plane of WS\textsubscript{2} film due to higher thermal conductivity of the basal plane (124 W/mK) than the c-axis of WS\textsubscript{2} (1.7 W/mK)\textsuperscript{32}. When the thickness is getting reduced by the laser irradiation, the heat conduction across WS\textsubscript{2}-SiO\textsubscript{2}/Si substrate becomes dominant, and the SiO\textsubscript{2}/Si substrate plays a role as a heat sink. Therefore, the flat and uniform single-layer WS\textsubscript{2} film could be produced by laser irradiation.

Investigation on behavior of exciton complexes. The change of PL spectra was reported to be associated with a transition from indirect band gap (few-layer WS\textsubscript{2}) to direct band gap (single-layer WS\textsubscript{2}). Because the origins of variation in relative contributions of exciton complexes (\textit{i.e.} neutral exciton (A\textsubscript{X}), trion (A\textsubscript{T}), and biexciton (AA)) to PL emission have not been studied, we investigate the behavior of the exciton complexes depending on the numbers of WS\textsubscript{2} layer. First, we analyze the PL intensities of exciton complexes as a function of laser power to determine the transition and binding energies of the exciton complexes (Fig. 5a and b) as per the definition of the energies\textsuperscript{21}. These plots reveal that the estimated transition energies for A\textsubscript{X}, A\textsubscript{T}, and AA are 1.971, 1.936, and 1.911, respectively; also, the binding energies for AT, and AA are 35 meV and 60 meV, respectively. Those binding energies are consistent with the computationally simulated results of WS\textsubscript{2}\textsuperscript{33–35}. Each excitons indicates different values of slope (m) regarding the increase of PL intensity with respect to laser power (Fig. 5b). Based on previous studies, the exponent of \(m = 1.2\)–1.9 is a typical value for AA\textsuperscript{36,37}; in other words, AA has super-linear slopes because of the kinetics of excitation recombination and formation\textsuperscript{38}. It is also important to note that there is an indication for the exponent of the A\textsubscript{X} (\(m = 0.66\)) is half the value of the AA (\(m = 1.26\))\textsuperscript{39}. Therefore, the sub-linear values of \(m = 0.66\) and \(m = 0.91\) for A\textsubscript{X} and A\textsubscript{T}, respectively, and the super-linear value of \(m = 1.26\) for AA can verify the types of exciton for WS\textsubscript{2}\textsuperscript{40}. Figure 5c and d indicates the PL spectra obtained from representative irradiation times of 1–7 seconds by decomposing them into A\textsubscript{X}, A\textsubscript{T}, and AA. For the increased laser irradiation of up to 7 seconds, the predominant exciton of the PL spectrum is changed from A\textsubscript{T} to A\textsubscript{X} (Fig. 5c). It is noted that the steady intensity of AA disappeared at 3 seconds of irradiation time; thus, only A\textsubscript{X} and A\textsubscript{T} increases as the number of WS\textsubscript{2} layers decrease by the longer laser.
irradiation time. The increased rate in the intensity of $A^X$ is higher than $A^T$ (Fig. 5d); therefore, the PL spectrum is shifted up to 1.97 eV for the single-layer.

We expect that the intensity variation for both $A^T$ and $A^X$ is affected by the addition of charge carriers (either by an electron or hole) absorbed by oxygen molecule during laser irradiation; also, it is assumed that the variation of charge carriers can directly modify the intensity of both $A^T$ and $A^X$ [41,42]. Oh et al. [43] reported the intensity of exciton complexes for single-layer MoS$_2$ with various laser irradiation time under ambient conditions; here, the intensity of $A^X$ increases dramatically in the first few minutes of laser irradiation due to the charge transfer of MoS$_2$ to the adsorbed oxygen group induced by laser irradiation. Another report also presented a single-layer MoS$_2$ treated by oxygen plasma that shows much improved PL spectrum because of the charge transfer from MoS$_2$ to oxygen molecule on the sulfur vacancy [44].

To confirm the charge transfer effect, full width at half-maximum (FWHM) of the $A_{1g}$ mode is measured with laser irradiation time (0–25 seconds) (Fig. 6a). The reduced FWHM of the $A_{1g}$ mode during the WS$_2$ film thinning is the evidence of p-doping (electron is moved from WS$_2$ to oxygen molecule) [45]; otherwise, FWHM of the $E_{1g}$ mode is not widely variable as a function of laser irradiation time (Fig. 6b). Therefore, the charge transfer from WS$_2$ to oxygen molecule induced by laser irradiation contributes to the increased ratio of $A^X$ to $A^T$ with the thinning of WS$_2$. Interestingly, we observed the blue-shift of ~50 meV for the exciton peak as the thickness is reduced from few- to single-layer (Fig. 5c). Based on the previous experimental and theoretical studies, the quasi-particle band gap in 2D WS$_2$ is expected to increase with thinning of WS$_2$, also, the binding energy of exciton complexes is predicted to increase with the thinning of WS$_2$ film due to the enhanced electron-hole interaction by weak dielectric screening [46–50]. The increase in quasi-particle band gap and the exciton binding energy affects the exciton peak position; thus, the shift of exciton complexes is negligible with the decreasing number of WS$_2$ layer. The blue-shifting of the exciton peak (measured ~50 meV) during the laser thinning process is consistent with the previous report [15].

**Discussion**

Precise control of WS$_2$ layers is achieved by using two-step CVD synthesis method followed by a laser-thinning. The scalable synthesis of uniform single-layer WS$_2$ film is confirmed by AFM thickness measurement (~0.9 nm), Raman frequencies difference (65.5 cm$^{-1}$), and PL peak position (1.97 eV). Based on the variation of PL and Raman spectra with respect to laser irradiation time, the optimum laser irradiation time for the synthesis of a
single-layer WS$_2$ film is found to be 7 seconds. It is also realized that the single-layer WS$_2$ is retained with additional laser irradiation time, which is attributed to the thermal energy dissipated through the substrate. The intensity of both neutral exciton and trion increases with the reduction of WS$_2$ thickness; however, the biexciton appears to have no noticeable change. In particular, dominant exciton component in PL spectrum for the few-layer and single-layer WS$_2$ is trion and neutral exciton, respectively. The observed binding energies of the exciton complexes for single-layer WS$_2$ are 35 meV (trion) and 60 meV (biexciton). The tunable optical properties
by precise control of WS₂ layers and the understanding of their exciton complexes would lead to the design of novel optoelectronic devices.

**Methods**

**Preparation of wafer scale thin WS₂ film.** Large-scale few-layer WS₂ film was synthesized on a p-type silicon substrate (Boron doped; 0.001–0.005 Ω·cm) with 300 nm thick SiO₂ by using two-step method involving magnetron sputtering for deposition of tungsten (W) film and chemical vapor deposition (CVD) for sulfurization of W film. For the first step, 99.99% purity W target (Plasmamaterials) was used to deposit thin film of W. Sputtering W film was carried out for 10 seconds at room temperature. Subsequently, the W film was sulfurized in the CVD for 1 hour at 600 °C to transform the film into WS₂. During sulfurization, the sulfur powder was heated separately at ~250 °C, and argon was used as a carrier gas to convey sulfur (S) vapor species toward the W films.

**Characterization of the WS₂ film.** Thickness and surface analysis of as-synthesized WS₂ film were performed by atomic force microscopy (AFM) (Parks system, NX-10 model). X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, ESCALAB250 model) was used for the chemical binding energies of W and S orbitals. A lab-made spectrometer combined with 514 nm wavelength and 200 μW power of a solid-state confocal laser microscope was used for PL and Raman spectroscopy measurements. A 0.9 NA objective was used to focus the laser light which the lateral resolution was set at approximately 300 nm. Scattered light was gathered by the 0.9 NA objective and directed to a 50 cm long monochromater equipped with a cooled CCD.

**Condition of laser thinning process.** A scanning laser from a lab-made spectroscope (laser wavelength of 514 nm with 2.5 mW power and 300 nm lateral resolution) was used to thin few-layer WS₂ film down to single-layer by moving the laser over the WS₂ film laterally by 300 nm for the next exposure. The total number of exposures is 256 times for 5 × 5 μm area, and the exposure time is 15 seconds for each laser irradiation. For a detailed study of exciton complexes variation depending on layer numbers, we used the same laser with increased laser exposure time from 0 to 25.6 seconds and measured the individual PL spectrum per each 0.2 second (total 128 measurements) under ambient conditions.

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**Author Contributions**

J.P. performed the synthesis of WS2, film and characterization. J.P. and W.C. wrote the manuscript. M.K. worked on PL measurement and exciton complexes analysis. E.C. conducted device fabrication and prepared figures. J.K. and W.C. contributed to the overall guidance, data analysis and manuscript editing. All authors discussed the results and commented on the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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