Supporting information

Revealing the nature of low-temperature photoluminescence peaks by laser treatment in Van der Waals epitaxially grown WS_2 monolayers

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I. STRUCTURAL CHARACTERIZATION OF VAN DER WAALS EPITAXIALLY (VDWE) GROWN MONOLAYERS

In this section, we present additional characterization results which demonstrate the large-scale uniformity of our Van der Waals epitaxially (VdWE) grown WS_2 monolayers. Figure S1(a), Figure S1(b), and Figure S1(c) show a photo, an optical microscope image, and a SEM image, respectively, of samples grown on 300 nm SiO_2 on a Si wafer. Figure S1(d) shows a picture of a WS_2 monolayer grown on quartz substrate. The images present no color variation/pattern and/or structural non-uniformity, thus demonstrating the large-scale homogeneity of the thin films. The samples are also homogeneous over larger scales such as 35 by 30 mm. As observed in Figure S1(a), the films on SiO_2/Si have a purple-ish colour which is due to optical contrast with the substrate. When the monolayer WS_2 is grown on quartz or c-plane sapphire substrates, the colour of the monolayer on these transparent substrates is usually light-yellow, as observed in previous reports[1,2]. This is shown in Figure S1(d) for a monolayers grown on quartz.

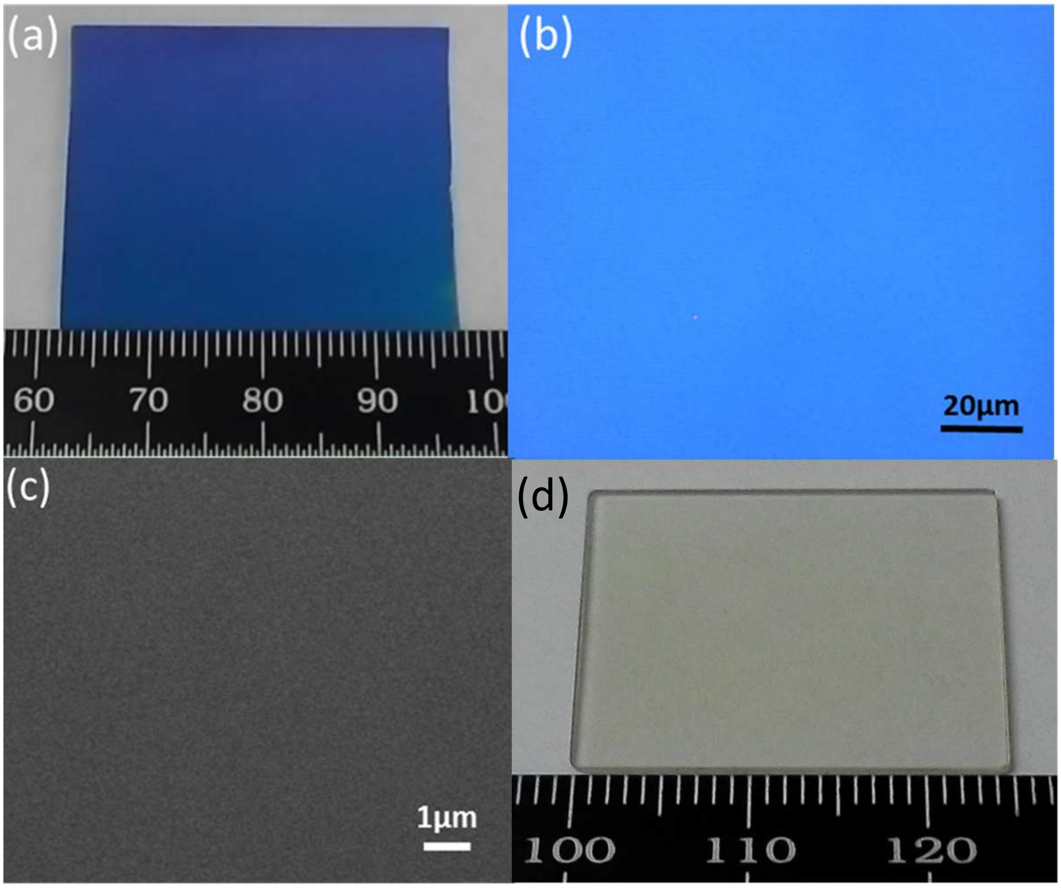

FIG. S1: (a) A photo of VdWE-grown WS_2 monolayer on large-scale (35 mm by 30 mm) 300 nm SiO_2/Si wafer. (b) An optical microscope image of VdWE-grown WS_2 monolayer shown in (a). (c) A top view SEM image of VdWE-grown WS_2 monolayer shown in (a). (d) A photo of typical VdWE-grown WS_2 monolayer grown on quartz.

Figure S2 shows Raman spectroscopy characterization of the samples. Figure S2(a) illustrates Raman spectra (excited at 514.5 nm) obtained in VdWE-grown monolayer on SiO_2/Si substrates. We can clearly observe the two main Raman modes of WS_2 monolayers, namely the 2LA+ E^1 (356 cm^{-1}) and A'(418.5 cm^{-1}) modes[3]. The inset in Figure S2(a) shows Raman spectra measured at 3 different positions separated by 6 mm along the surface of one of the samples. As it can be seen, the shape of the spectra and peak position do not vary with position on such scale. Figure S2(b) presents the intensity of the 2LA+ E^1 mode (excited at 532 nm) obtained in a two-dimensional Raman mapping over an area of 4 mm by 5 mm. We observe relatively small variations in peak intensity over such large scale, which demonstrates the structural homogeneity of our WS_2 monolayer films. Figures S2(c) and (d) show Raman spectra (excited at 514.5 nm) of monolayer and few monolayers WS_2 grown on quartz, respectively. Figure S2(c) shows that the Raman spectra of monolayers on quartz subtrates agree with the ones shown in Figure S2(a) for SiO_2/Si substrates. Comparing Figures S2(c) and (d), we observe an inversion of the relative intensity between the 2LA+ E^1 and A' peaks. This is a characteristic behavior of the Raman spectra of WS_2 when one goes from monolayer to more than one monolayer. Due to change in the band structure, the 2LA+ E^1 mode scattering is a resonant process for monolayer samples for excitation at 514.5 nm, which makes the intensity of this peak higher than the A'[3].

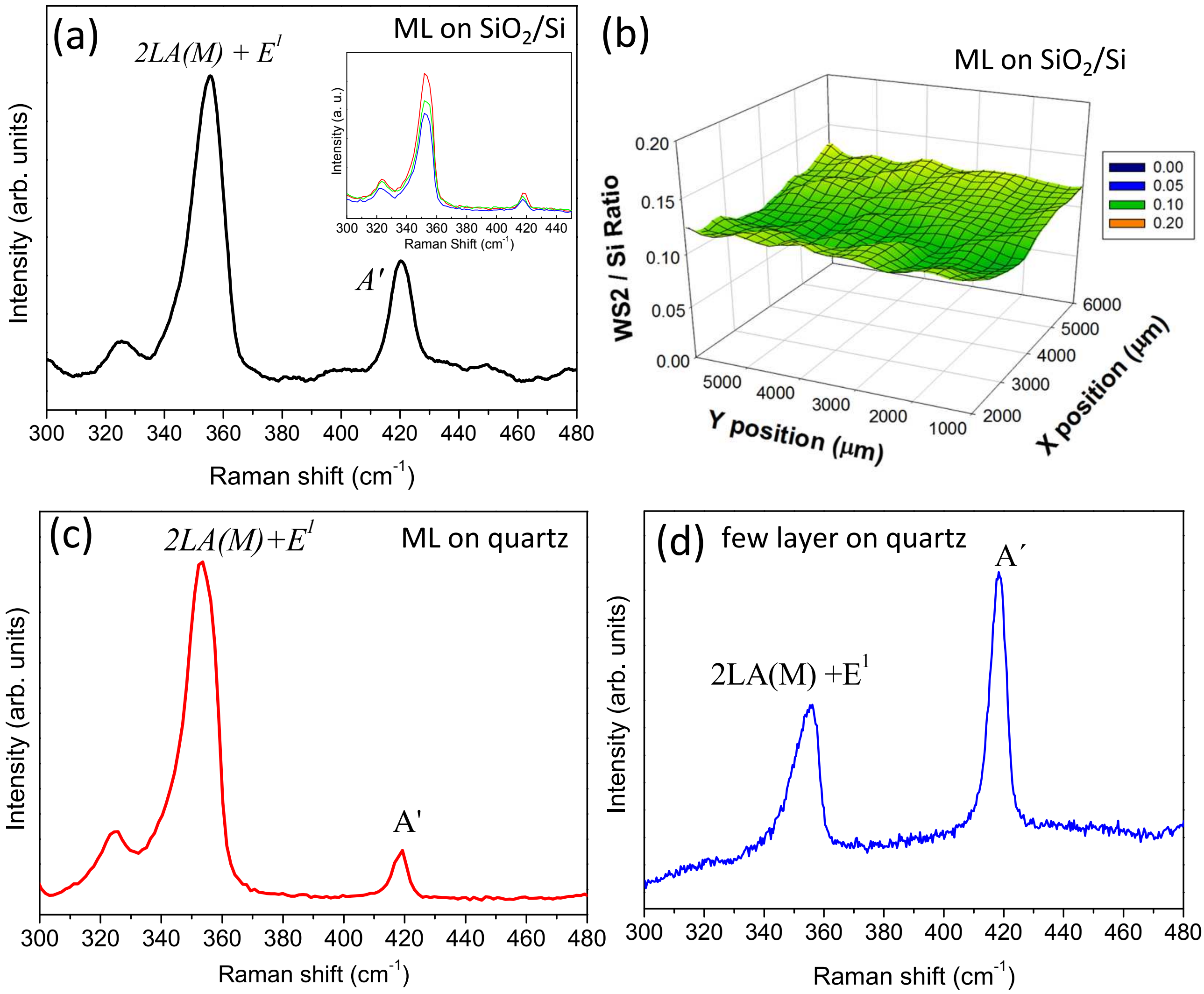

FIG. S2: (a) Raman spectrum of VdWE-grown monolayer WS_2 on SiO_2/Si at 300K using 514.5 nm excitation with low laser power. The inset shows the Raman spectra at different positions on a different piece of the wafer. (b) Raman of VdWE-grown WS_2 monolayer on quartz. (c) Room temperature Raman spectra mapping of VdWE-grown monolayer WS_2 on 300nm SiO_2/Si substrate corresponding to the intensity ratio of WS_2 (2LA+E1) peak to Si peak over the area of 4 mm by 5 mm using 532 nm laser excitation. (d) Typical Raman spectrum of few monolayers of VdWE-grown WS_2 on quartz at 300K using 514.5 nm laser excitation.

Figure S3 presents the photoluminescence (PL) characterization of our samples at room temperature measured with 532 nm laser excitation. Figure S3(a) shows the PL of a monolayer grown on SiO_2/Si. The PL peak position at approximately 2.01 eV is in good agreement with previous literature reports[4]. Figure S3(b) shows the PL mapping at 2.009 eV over an area of 4 mm by 5 mm (the same area probed in Figure S2(b)), demonstrating good homogeneity in PL intensity over such scale in our VdWE samples. Figure S3(c) compares the emission energy position between a monolayer and a few monolayers WS_2 on quartz. As can be seen, the recombination energy decreases by approximately 27 meV as additional layers are grown on the system, which is consistent with the bandgap decrease expected for such situation[5].

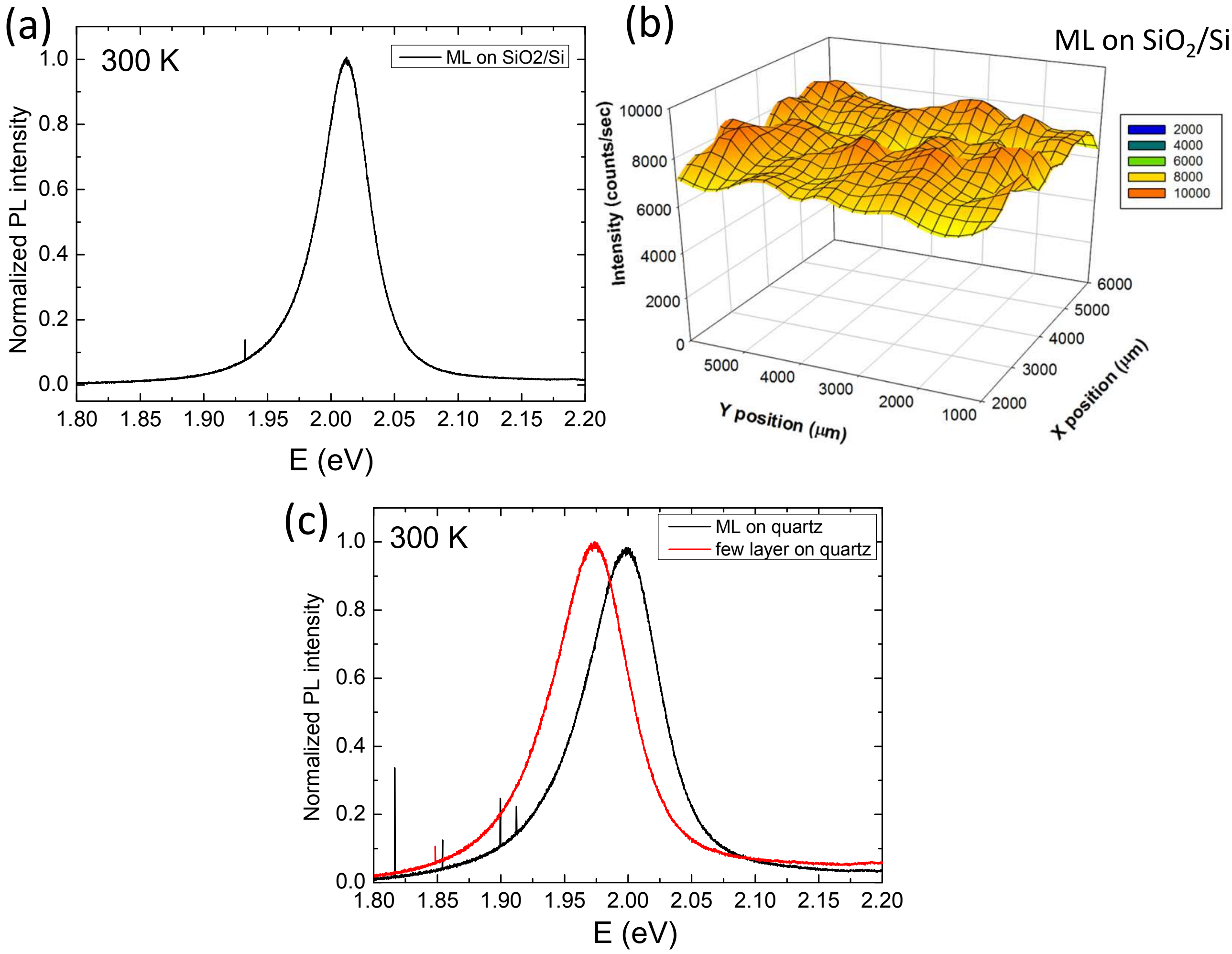

FIG. S3: (a) Typical room temperature PL spectrum of VdWE-grown monolayer WS_2 on SiO_2 using 532 nm laser line as excitation. (b) 300K PL spectra mapping at 2.009eV of VdWE-grown monolayer WS_2 on 300nm SiO_2/Si substrate using 532 nm laser excitation for the same area on the sample shown in Figure S2(c). (c) PL spectra at 300K using 532 nm excitation at low laser power of monolayer and few monolayers of WS_2 on quartz substrate.

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