Reducing Agents for the Atomic Layer Deposition of WS\textsubscript{2} from the WF\textsubscript{6} and H\textsubscript{2}S Precursors

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Transition metal dichalcogenides (MX\textsubscript{2}, with M a transition metal and X a chalcogen) are inorganic two-dimensional (2D) materials with versatile properties that complement those of graphene. Single and few monolayers of semiconducting MX\textsubscript{2} (e.g. WS\textsubscript{2}, MoS\textsubscript{2}, WSe\textsubscript{2}, MoSe\textsubscript{2}) hold large promise as novel channel materials in field-effect transistors because of their large band gap values, lack of dangling bonds, structural stability and mobility comparable to Si. The concept has already been demonstrated using exfoliated MoS\textsubscript{2} monolayers\textsuperscript{1}, but industrial applications require MX\textsubscript{2} deposition on large area substrates. Atomic layer deposition (ALD) is promising because of its inherent growth control and low deposition temperature. However, only few publications of WS\textsubscript{2} and MoS\textsubscript{2} ALD exist\textsuperscript{2,3}, and it is currently not clear if and how one can grow fully continuous MX\textsubscript{2} monolayers with good 2D structure and crystallinity by ALD. In addition, the nucleation and reaction mechanisms are not yet understood. A particular challenge is the control of the oxidation state of the transition metal in MX\textsubscript{2} ALD, as in many commercially available precursors the Mo and W atoms are not in the +IV oxidation state. For example, for WF\textsubscript{6}, a partial reduction of W from the +VI oxidation state in WF\textsubscript{6} to the +IV oxidation state in WS\textsubscript{2} is required. ALD of crystalline WS\textsubscript{2} thin films from WF\textsubscript{6} and H\textsubscript{2}S has been demonstrated by adding Zn(Et)\textsubscript{2}\textsuperscript{3}, the latter presumably acting as reducing agent. However, the use of Zn(Et)\textsubscript{2} resulted in high levels of Zn-impurities in the WS\textsubscript{2} layers.

In this work, we investigate ALD processes for few and single monolayers of WS\textsubscript{2} from the WF\textsubscript{6} and H\textsubscript{2}S precursors. We have investigated these precursors without and with a number of reducing agents that have already been applied previously in W ALD and chemical vapor deposition (CVD), i.e. Si layers, TiN layers, H\textsubscript{2} and H\textsubscript{2} plasma. In line with\textsuperscript{3}, we did not find WS\textsubscript{2} deposition for sequential WF\textsubscript{6}/H\textsubscript{2}S exposures on several dielectric substrates (Al\textsubscript{2}O\textsubscript{3}, Si\textsubscript{3}N\textsubscript{4}, SiO\textsubscript{2}) in the temperature range 250-450°C, as indicated by Rutherford Backscattering Spectrometry (RBS). This suggests that a reducing agent is needed for WS\textsubscript{2} deposition, and/or that there are severe nucleation issues on these oxide substrates.

On the other hand, WS\textsubscript{2} deposition is enabled by using either Si layers or H\textsubscript{2} plasma as reducing agents. Si is introduced as a thin (0.7 – 2.5 nm) sacrificial layer on Al\textsubscript{2}O\textsubscript{3} layers, and monolayer controlled deposition of WS\textsubscript{2} is demonstrated by applying WF\textsubscript{6} and H\textsubscript{2}S exposures at 450°C. The deposition starts by the reaction “2 WF\textsubscript{6}(g) + 3 Si(s) \rightarrow 2 W(s) + 3 SiF\textsubscript{4}(g)”. The number of WS\textsubscript{2} monolayers is controlled by the thickness of the sacrificial Si layer, which is completely consumed by the reaction with WF\textsubscript{6}.

Also H\textsubscript{2} plasma enables the deposition of WS\textsubscript{2} layers on Al\textsubscript{2}O\textsubscript{3} substrates, in a plasma enhanced ALD (PEALD) process with WF\textsubscript{6}/H\textsubscript{2} plasma/H\textsubscript{2}S reaction cycles\textsuperscript{4}. In this case, the number of WS\textsubscript{2} monolayers is conventionally controlled by the number of PEALD reaction cycles. The process has a broad temperature window between 250 and 450°C.

Both deposition approaches yield monolayer content controlled deposition of WS\textsubscript{2} on 300mm wafers. The S/W ratio of the deposited layers is close to two (RBS). The formation of WS\textsubscript{2} with 2D structure is confirmed by X-ray Photoelectron, Raman spectroscopy (E\textsubscript{2g} and A\textsubscript{1g} modes characteristic of WS\textsubscript{2}) and X-Ray Diffraction (XRD). The as-deposited layers are polycrystalline with 2D structure. Still, the continuity and crystallinity of the as-deposited WS\textsubscript{2} layers needs further improvement, as evidenced by transmission electron microscopy (TEM).

\textsuperscript{1} B. Radisavljevic et al., Nature Nanotechnology, 6, 147 (2011).
\textsuperscript{4} B. Groven et al., ALD 2015 conference.