Effects of oxygen, nitrogen and fluorine sources on the formation of α- and β-phase Tungsten films by hot-wire assisted ALD

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Atomic layer deposition (ALD) of metals has attracted a considerable attention in view of ultra-large-scale integrated circuit manufacturing. Plasma-enhanced ALD (PEALD) has been proposed as a suitable technique to grow a number of metals. Deposition of metals often requires generation of reactive species such as e.g. atomic hydrogen (at-H). In our previous work we have demonstrated an alternative and a technically easier approach to create at-H by replacing plasma with a heated (up to 2000 ^{o}C) tungsten (W) wire. This so-called hot-wire assisted ALD (HWALD) has been successfully utilized to deposit W films using alternating pulses of WF_6 gas and at-H [1-2].

It is known that W can be formed in either low-resistivity α- or higher-resistivity β-crystalline phases [3]. The former is clearly more attractive for applications in electronics. In our deposition system we have been able to selectively grow both phases of W by HWALD, depending on the actual reactor design and deposition conditions. Factors leading to the preferential formation of one of the phases over the other are still to be confirmed. For example, β-phase can be formed (i) via an intermediate oxidation state (further reduced to pure W by at-H) due to the presence of background oxygen source in the system (note that base pressure of 10^{-7} mbar still gives roughly a flux of 0.1 ML/s to the substrate) or (ii) because of other impurities (e.g. fluorine). To clarify the occurrence of β-phase, we have investigated the effects of adding reactive gases such as N_2O, O_2, NH_3 and H_2O on HWALD of W. All processes were in-situ monitored in real time by spectroscopic ellipsometry (SE).

To study the influence of oxidants on growth rate per cycle (GPC), HWALD W layers were first grown to a thickness of 0.5-2.2 nm and then exposed to a continuous flow of N_2O or O_2 in the same reactor, resulting in oxidation of the layers as shown in Fig. 1. Co-existent with the growth of tungsten oxide, a decrease in W thickness was observed. With the next series, HWALD W films were deposited up to roughly 6 nm in thickness; the process then continued with giving additional pulses of either N_2O or O_2 after every three full HWALD cycles. In Fig. 2, one can see that the GPC is suppressed by these additional pulses and decays with increasing the pulse duration. The negative GPC seen in Fig. 2 (center) for O_2 pulses longer than 0.5 s can be interpreted in terms of dominating oxidation, thereby reducing the W film thickness. An exposure to N_2O gas is less effective in reducing the GPC (Fig 2 left), which can be explained by the lower surface reactivity of N_2O compared to O_2. Importantly, the X-ray photoelectron spectroscopy still reveals the high purity of as-grown W films (Fig 3 left), almost without oxygen, indicating a sufficient reduction of the tungsten oxide by at-H. The X-ray diffraction pattern clearly shows α-W (Fig 3 center). Giving additional H_2O pulses, instead of N_2O or O_2, could reduce the GPC in a similar manner (Fig 2 right).

To note, in case of an exposure to H_2O or O_2 it was possible to recover the original GPC after removing the oxidants and applying a 20-min reduction in at-H containing ambient at the same temperature. This was however not the case for N_2O gas, as the growth of W films could be entirely terminated by an exposure to a constant flow of N_2O for 5 min. This suggested a possible nitridation of the W surface, playing a crucial role. To further investigate this, N_2O was replaced by NH_3. An NH_3 treatment could indeed entirely terminate the HWALD process, confirming the nitridation as the cause. Finally, we investigate the effects of WF_6 overdose, resulting in a long-term fluorine excess in the reactor. The data seen in Fig. 3 (right) demonstrate that increasing the WF_6 pulse time leads to decreasing GPC. The surplus of fluorine-containing gas appeared to be crucial for the process: in many cases this further led to the formation of β-phase W instead of α-phase with a memory effect

lasting for several deposition runs. Extra fluorine species present in the reactor were thus identified as the potential cause of β-phase formation.

In our presentation, we will give more details on the formation of α- and β-phase W by HWALD and further discuss the effects of adding the mentioned gases on film's growth and crystallinity.

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[2] M. Yang et al. Phys. Status Solidi A 212, 7, 1607–1614 (2015).

[3] E. Lassner and W. D. Schubert, *Tungsten: Properties, Chemistry, Technology of the Elements, Alloys, and Chemical Compounds* (Springer Science & Business Media, New York, 1999)

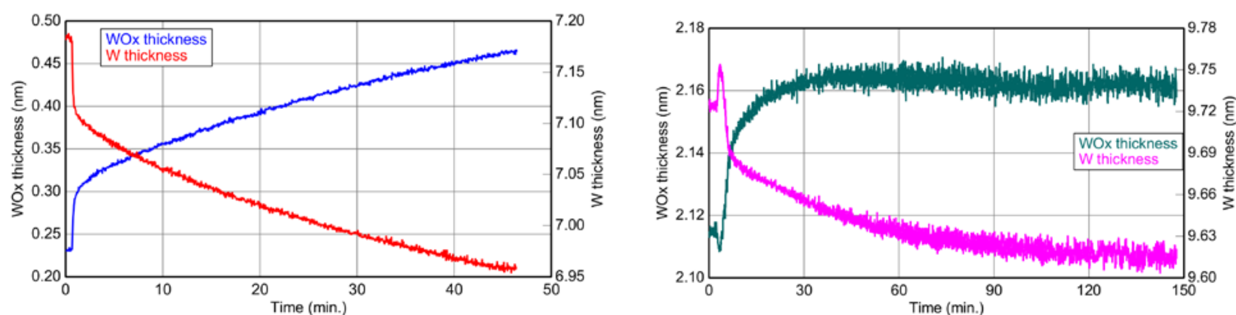

Figure 1. Oxidation measured by in-situ SE while exposing thin as-grown HWALD W films to a continuous 3 sccm flow of O_2 (left) or N_2O (right) at 275 ºC and a pressure of 0.05 mbar. Hot wire was turned off.

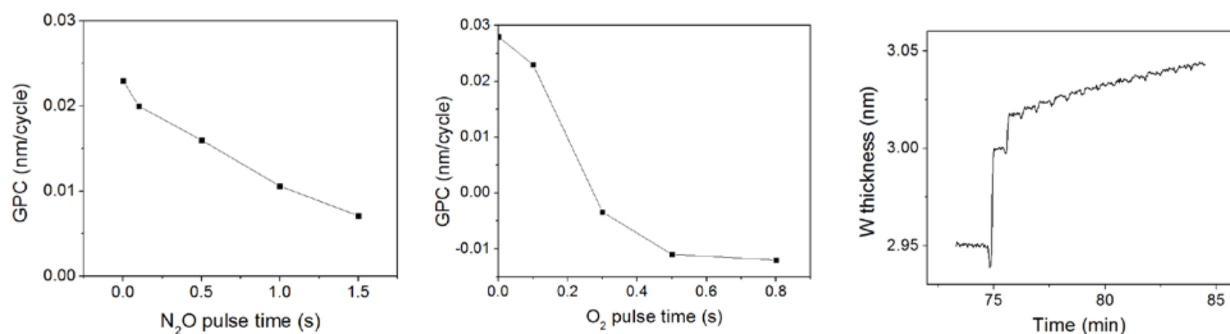

Figure 2. In-situ SE measurements performed at 275 ºC and a pressure of 0.05 mbar. A decrease of GPC of HWALD W films while giving additional N_2O (left) and O_2 (center) pulses after each 3 standard ALD cycles with a 7s-Ar purge in between. The negative growth rate observed for O_2 pulses corresponds to in-situ oxidation shown in Fig. 1. (Right) – the effect of decreasing GPC due to additional H_2O-vapor pulses of 5 s (followed by a purge of 10 s) inserted after each standard ALD cycle (steps = individual ALD cycles).

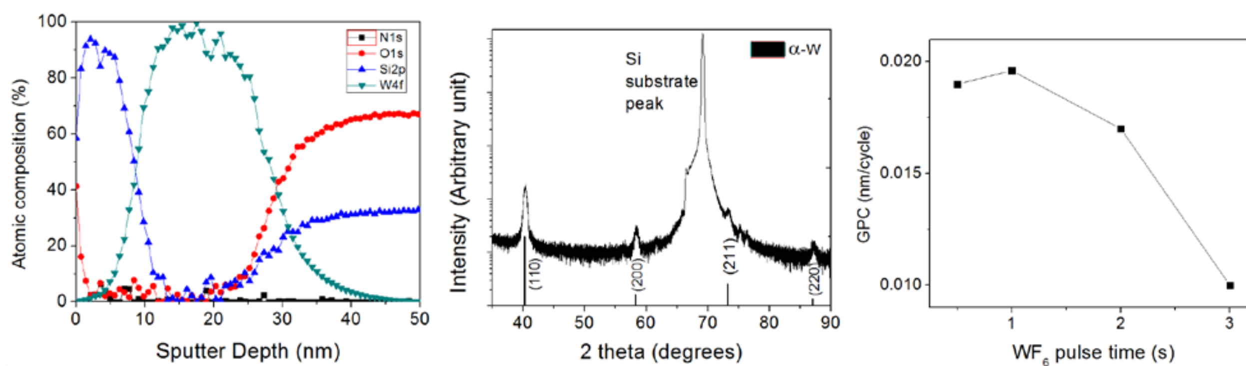

Figure 3. (Left) - X-ray photoelectron spectroscopy depth profile of a 15-nm W film grown by HWALD with additional O_2 pulses (0.1 s of O_2 + 7 s extra purge after each 3 standard ALD cycles). No increased concentration of oxygen in the layers is observed compared to an oxygen-free process. Note the a-Si layer on top of W, in-situ deposited to prevent oxidation of W film in air. (Center) - X-ray diffraction pattern of the same film showing α-phase W. (Right) – A decay of GPC versus WF_6 (10 sccm) pulse time at 275 ºC and a pressure of 0.05 mbar, showing a negative effect of fluorine-containing gas on the process. Excess fluorine species are further identified as the potential cause of β-phase formation.