Hot wire technique as a radical source for atomic layer deposition of metal and metal nitride films

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Atomic layer deposition (ALD) of metal and metal-nitride films has triggered significant interest in semiconductor and optoelectronic industries, owing to its characteristic in depositing ultra-thin (a-few-nm) films [1, 2]. The thermal activation of precursors in conventional ALD processes has been complemented by plasma- and other means of (gaseous) radical production. For example, in order to sustain the film growth for a number of ALD processes, the dissociation of ammonia (NH_3) into radicals is necessary [3, 4]. In parallel, generation of atomic hydrogen radicals can be essential for the deposition of metallic films [5, 6]. A hot-wire (heated W) filament can serve as a highly controllable, ion- and UV-free source of radicals [7]. In this premise, we have: (i) characterized the *hot-wire (HW) technique* for generation of atomic hydrogen (at-H) radicals from both molecular hydrogen (H_2) and NH_3 precursors, (ii) explored the feasibility of HW to generate N-containing radicals (N-rad) from the dissociation of NH_3, and (iii) studied the effects of the so-generated N-rad in the deposition of aluminium nitride (AlN) and boron nitride (BN) films.

The *generation of at-H and N-rad* by HW action was investigated, respectively by: (i) etching of sputtered tellurium (Te) films into the formation of volatile hydrogen telluride (H_2Te) on exposure to at-H (to note: H_2 itself cannot sustain this reaction [6]), and (ii) nitridation of Si(100) wafers by N-rad. Additionally, the mechanism of *delivery of these radicals* to the wafer was studied by placing the HW both out and in the line-of-sight with the wafer, and also by altering the distance between them. All experiments were monitored in real-time by in-situ spectroscopic ellipsometry (SE). Ex-situ characterization was performed by X-ray photoelectron spectroscopy (XPS) and grazing incidence angle X-ray diffraction (GIXRD) techniques.

Fig. 1(left) demonstrates that at-H could be produced and delivered from the dissociation of both H_2 and NH_3; the latter precursor however exhibited a reduced Te etch rate. This was attributed to a possible lower dissociation efficiency of NH_3 and/or a shorter lifetime of at-H due to several gas-phase reactions. Further, the effect of increasing the reactor pressure, resulting in recombination of at-H, and thereby leading to reduced etch rates, is demonstrated in Fig. 1 (center). In terms of delivery of at-H, no observable difference in etch rates was observed on changing the HW position from in- to out of line-of-sight of the wafer.

The generation, delivery and distribution of the N-rad was studied from its nitridation action on H-terminated Si wafers. In-situ SE monitoring indicated the formation of a nitride (SiN_x) film *only* upon placing the HW in the *line-of-sight* of the wafer (Fig. 1; right). Furthermore, increasing the reactor pressure suppressed nitride formation due to recombination of the N-rad (same figure). To be noted: there was no film growth when argon (instead of NH_3) was supplied through the HW (Fig. 2; left), suggesting that the film was indeed from nitridation (over oxidation) of Si. XPS survey scans finally confirmed the formation of SiN_x (Fig. 2; center). The highest concentration of nitrogen (from the N_{1s} signal) was observed at the wafer-center, corresponding to the direct line-of-sight with the HW (Fig. 2; right). The reduction in nitrogen concentration from the wafer-center to the wafer-edge indicated a gradual recombination (and depletion) of N-rad.

The action of N-rad in HW-deposited AlN and BN films was observed from changes in the film properties. In case of AlN, HW-action resulted in a change of crystallinity: although both thermal- and HW-deposited AlN films were hexagonal (wurtzitic), the ratio of the (002)- to the (101) peak intensity (I_{002}/I_{101}) underwent significant reduction in case of HW-deposited AlN. However, deposition at a higher pressure caused this ratio to approach that of thermal-AlN (Fig. 3; left). This observation was in agreement with the decreasing amount of N-rad at higher pressures. In case of BN, only by the contribution of N-rad (i.e., from the HW) could BN films be deposited; thermal-deposition resulted in B-rich (i.e., N-deficient) films. This is apparent from XPS survey scans (Fig. 3; right) which revealed the shift of the B_{1s} peak position from B to BN on increasing the HW temperature (an action which possibly increased N-rad production). Our presentation will contain a detailed discussion on the above-mentioned effects accompanied with additional HW-deposition results.

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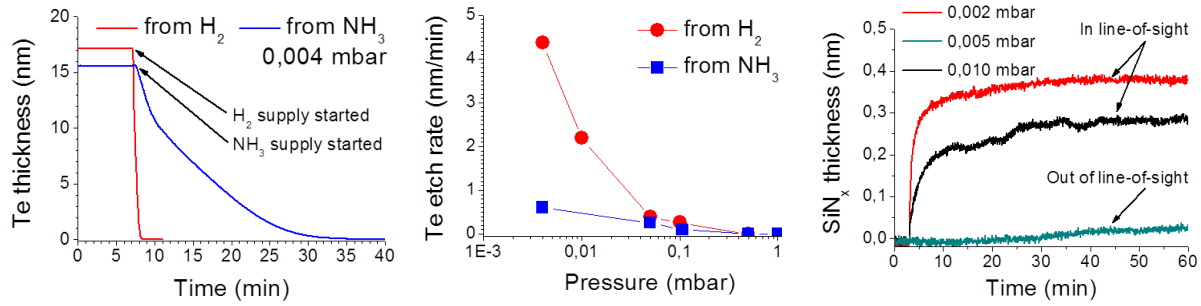

Figure 1. (Left, Center) – Etching of Te films by at-H from the dissociation of H_2 and NH_3 on HW at 1800 ^oC. (Right) – Nitridation of (H-terminated) Si wafers under different pressures by N-containing radicals, as generated from HW-dissociated NH_3. Further, nitridation in- and out of line-of-sight-of-HW were compared.

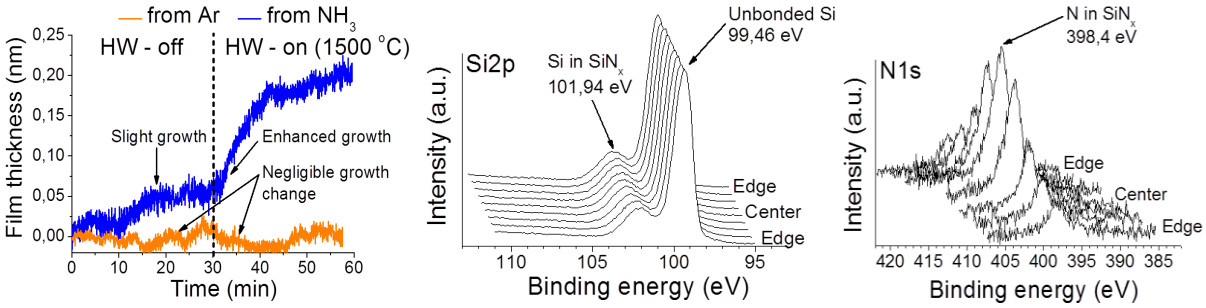

Figure 2. (Left) – Replacing NH_3 by Ar showed no film growth (orange) hence indicating film formation by Si-nitridation over Si-oxidation by HW-dissociated NH_3 (blue). (Center, Right) – XPS survey scans confirmed the formation of SiN_x with the highest N-concentration at the center of the wafer (i.e. in the line-of-sight).

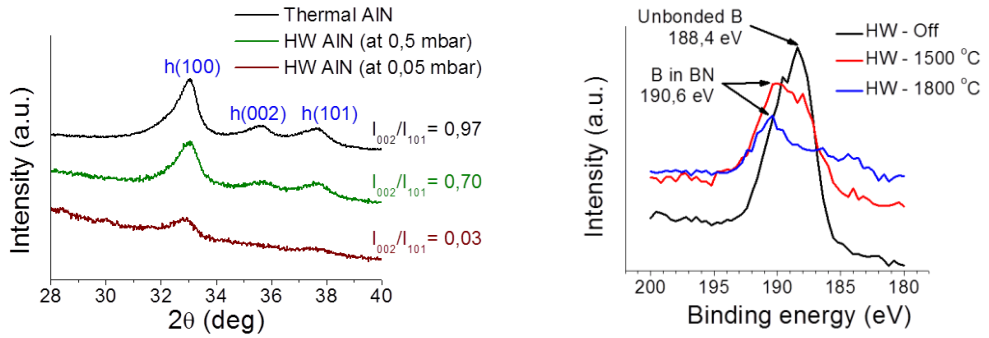

Figure 3. (Left) – GIXRD scans of thermal- and HW-deposited AlN: although both are hexagonal, the action of N-rad in HW-AlN lowered the I_{002}/I_{101} value. (Right) – Shift of the Boron 1s XPS peak with increasing HW temperature, indicating the transition from B-rich (N-deficient) films to BN films.