

Unintentional carbide formation evidenced during high-vacuum magnetron sputtering of transition metal nitride thin films



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ABSTRACT

Carbide signatures are ubiquitous in the surface analyses of industrially sputter-deposited transition metal nitride thin films grown with carbon-less source materials in typical high-vacuum systems. We use high-energy-resolution photoelectron spectroscopy to reveal details of carbon temporal chemical state evolution, from carbide formed during film growth to adventitious carbon adsorbed upon contact with air. Using *in-situ* grown Al capping layers that protect the as-deposited transition metal nitride surfaces from oxidation, it is shown that the carbide forms during film growth rather than as a result of post deposition atmosphere exposure. The XPS signature of carbides is masked by the presence of adventitious carbon contamination, appearing as soon as samples are exposed to atmosphere, and eventually disappears after one week-long storage in lab atmosphere. The concentration of carbon assigned to carbide species varies from 0.28 at% for ZrN sample, to 0.25 and 0.11 at% for TiN and HfN, respectively. These findings are relevant for numerous applications, as unintentionally formed impurity phases may dramatically alter catalytic activity, charge transport and mechanical properties by offsetting the onset of thermally-induced phase transitions. Therefore, the chemical state of C impurities in PVD-grown films should be carefully investigated.

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Transition metal (TM) nitride-based thin films with applications, ranging from protective layers on high-speed cutting tools [1,2] to diffusion barriers in electronics [3–5], are typically grown by physical vapour deposition (PVD). Low homologous temperatures ($T_s/T_m < 0.3$, where T_s and T_m stand for the substrate and the melting temperature, respectively) together with extremely high cooling rates (on the order of 10^{13} K/s) during the vapour condensation on the film surface, result in growth conditions far from thermodynamic equilibrium [6]. This allows for synthesis of metastable phases with unique properties which paves the ground for heavily researched field [7].

The presence of carbon impurities is regularly confirmed during surface analysis by X-ray photoelectron spectroscopy (XPS) in binary and ternary TM nitride films grown by PVD techniques such as magnetron sputtering [8–14], or cathodic arc evaporation [15–20]. Often this is attributed to the post deposition atmosphere exposure and labeled as adventitious carbon adsorbed at the surface and/or at grain boundaries, hence, excluded from the discussion of microstructure – property relationships of the as deposited thin films. C 1s core-level signal is only used (if at all) for binding energy (BE) scale calibration [9,12,13,17,19,20], and spectra are published only occasionally [8], typically with a rather poor signal-to-noise ratio that prevents complete chemical state identification. Here it is shown that in addition to adventitious carbon another previously overlooked carbon population exists.

Direct evidence for unintentional and, at the same time, unexpected carbide formation during high-vacuum (HV) growth of

group IVb transition metal nitride thin films by magnetron sputtering is presented. Layers are deposited in Ar/N₂ atmosphere using typical industrial sputter-deposition system under process conditions that are commonly employed for nitride growth. High-energy-resolution XPS analyses combined with the *in-situ* Al-capping technique [21] are used to trace the temporal evolution of C chemical state starting from film growth, through venting and air exposure, to storage in the lab atmosphere. The signature of carbides formed during film growth is masked by the presence of adventitious carbon contamination, appearing as soon as samples are exposed to atmosphere, and eventually disappears after one week-long storage in lab atmosphere. Possible source of incorporated carbon during film growth is residual gas and/or target impurities. The reaction may be triggered by gas ion bombardment that leads to recoil implantation and forward sputtering of adsorbed C species. This finding is relevant for numerous applications, as even small amounts of foreign (unintentional) phases may dramatically alter catalytic activity, charge transport or even mechanical properties by offsetting the onset of thermally-induced phase transitions.

Polycrystalline TiN, ZrN, and HfN thin films are grown on Si(001) substrates biased at –60 V by reactive dc magnetron sputtering (DCMS) in typical HV magnetron sputtering system using rectangular 8.8×50 cm² targets (>99.9 at% pure, excluding Zr in the case of Hf target) and Ar/N₂ gas mixture with N₂ partial pressure $p_{N_2} = 5.8 \times 10^{-4}$ Torr (76 mPa). The total pressure during deposition is 3 mTorr (0.4 Pa), while the system base pressure p_b

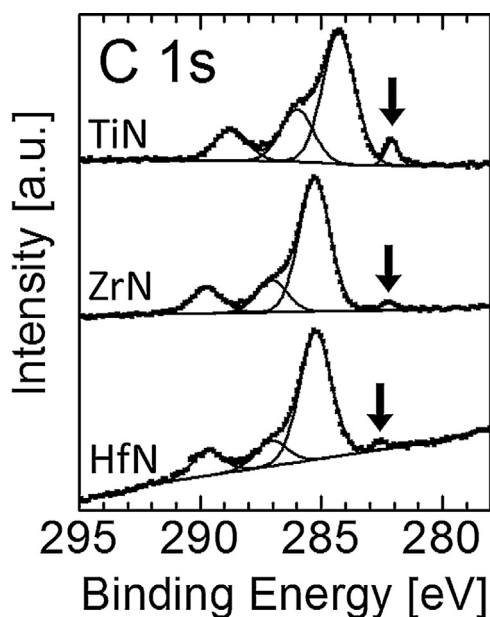


Fig. 1. C 1s XPS spectra obtained from as-received air-exposed (~ 2 min) polycrystalline TiN, ZrN, and HfN thin films grown on Si(001) substrates by reactive DCMS in typical high-vacuum magnetron sputtering system at 430°C . Arrows indicate the carbide component.

before and after the film growth is 2.3×10^{-6} Torr (0.3 mPa) and 1.5×10^{-7} Torr (0.02 mPa), respectively. The average target power during 25-min-long deposition is 4 kW resulting in film thickness of $1.2 \mu\text{m}$. The substrate temperature is 430°C and the venting temperature is 270°C .

XPS spectra are acquired from TiN, ZrN, and HfN films in a Kratos Analytical instrument, with a base pressure of 1.1×10^{-9} Torr (1.5×10^{-7} Pa), using monochromatic Al K α radiation ($h\nu = 1486.6$ eV). All samples exhibit pronounced cut-off in the density of states near the Fermi level – the Fermi Edge (FE), which occurs within ± 0.03 eV within that of the sputter-cleaned Ag sample used for calibration. Thus, core-level spectra are referenced to the FE that defines “zero” on the BE scale. Deconvolution and quantification are performed using the CasaXPS software with elemental sensitivity factors supplied by Kratos Analytical Ltd [22].

Fig. 1 shows C 1s core level spectra acquired from TiN, ZrN, and HfN surfaces exposed to the ambient atmosphere for ~ 2 min necessary to transfer samples to the XPS instrument. All spectra possess clear signature of four contributions corresponding to four chemical states of C atoms in the probed surface region.

The three strongest peaks are due to adventitious carbon contamination: C–C/C–H (284.3–285.3 eV), C–O (286.0–287.1 eV), and O–C=O (288.7–289.7 eV). While the relative BE shifts between these three components are the same in all cases, the absolute values vary between the samples (e.g. C–C/C–H component is present at 284.3 eV for TiN and at 285.3 eV for ZrN film), which is the consequence of the fact that BE is not only set by the chemical environment but also the type of the underlying surface matters (in this case surface oxides with different conductivity). In addition to adventitious carbon there is also a clear contribution at significantly lower BE visible in all three cases, which is assigned to carbide formation. The position of this peak varies slightly from 282.1 eV for TiN to 282.2 and 282.4 eV for ZrN and HfN respectively [23–25]. The magnitude of BE shift in the case of carbide peak (0.3 eV) is thus significantly smaller than that observed for adventitious carbon (1.0 eV) which indicates that carbide species are buried below the surface native oxide layer, formed after the film growth, hence their BE is not affected by oxide conductivity. The concentration of carbon assigned to carbide species varies from 0.28 at% for ZrN sample, to 0.25 and 0.11 at% for TiN and HfN, respectively.

The angle-dependent XPS studies are used to reveal details of carbon chemical state evolution during film growth. Fig. 2(a) shows normalized C 1s spectra of TiN sample acquired at the photoelectron take-off angle ϕ of 90° and 10° . In the latter case the probing depth is reduced by a factor of $1/\sin(\phi) = 5.7$, which has a pronounced effect on the relative peak intensities. The C–O and O–C=O components are drastically reduced with respect to C–C/C–H contribution, indicating that former species are located closer to the native oxide surface. The most striking difference, however, is the lack of carbide peak in the surface-sensitive spectrum. This reveals that Ti–C species are buried under the oxide layer, in agreement with the previous assessment of carbide formation during film growth, which is followed by C–O/O–C=O and C–C/C–H buildup upon air exposure. The following stages of C chemical state evolution are mapped out in Fig. 2(b), where the C 1s spectra recorded from TiN films as a function of air exposure time, from 2 to 10^4 minutes (~ 1 week), are shown. The main effect is the accumulation of C–C/C–H-type carbon that eventually dominates the signal and leads to severe attenuation of the carbide signature which is barely detectable after one week. Thus, the here reported observation of carbide species was enabled by minimizing the air exposure time.

In order to exclude possibility that TiC forms upon contact with air rather than during film growth, an additional TiN layer is deposited and Al-capped *in-situ* in the deposition system prior to air-exposure. Recent studies showed that 15-Å-thick Al capping layer provides effective barrier to TiN sample oxidation [21]. Here,

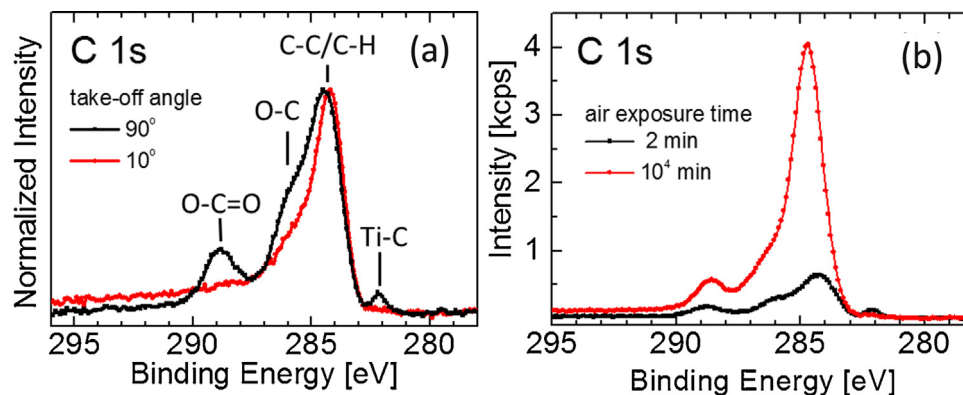


Fig. 2. (a) C 1s XPS spectra obtained from as-received air-exposed (~ 2 min) polycrystalline TiN/Si(001) sample at the electron take-off angle of 90° (black curve) and 10° (red curve); (b) C 1s XPS spectra obtained from polycrystalline TiN/Si(001) sample at the electron take-off angle of 90° as a function of air-exposure time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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