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Short communication

HPPMS deposition from composite targets: Effect of two orders of magnitude target power density changes on the composition of sputtered Cr-Al-C thin films

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ABSTRACT

The effect of target power density, substrate bias potential and substrate temperature on the thin film composition was studied. A Cr-Al-C composite target was sputtered utilizing direct current (DCMS: 2.3 W/cm^2) and high power pulsed magnetron sputtering (HPPMS: 373 W/cm^2) generators. At floating potential, all Cr-Al-C thin films showed similar compositions, independently of the applied target power density. However, as substrate bias potential was increased to −400 V, aluminum deficiencies by a factor of up to 1.6 for DCMS and 4.1 for HPPMS were obtained. Based on the measured ion currents at the substrate, preferential re-sputtering of Al is suggested to cause the dramatic Al depletion. As the substrate temperature was increased to 560 °C, the Al concentration was reduced by a factor of up to 1.9 compared to the room temperature deposition. This additional reduction may be rationalized by thermally induced desorption being active in addition to re-sputtering.

Magnetron sputtering is widely used to synthesize a large number of compound coatings either by co-sputtering from a number of different elemental targets or by sputtering from a compound or powder metallurgically fabricated composite target consisting of the desired thin film composition. The latter two approaches are attractive from an industrial application point of view due to process simplicity, improved repeatability [1] and a more homogeneous coating composition [2]. However, thin films deposited from multi-element targets often exhibit a considerable compositional deviation to the desired target composition. These compositional deviations stem from differences in emission angles and energy distributions [3–5], gas phase scattering behavior [6–8], sticking probabilities [5,9–13], preferential re-sputtering [5,9–13] and selective evaporation behavior [1,14–16] of the individual target constituents. In particular, targets containing constituents with significant mass differences, such as TiW [5,9–13], TiB [3], Ti_3SiC_2 [8,15,17], Ti_2AlC [18] and Cr_2AlC [4] are prone to drastic deviations between the target and film composition, which e.g. may prevent the desired phase formation, as observed for Ti_3SiC_2 [15,17]. It was shown for direct current magnetron sputtering (DCMS), that the magnitude of compositional deviation between target and thin film depends on the pressure-to-distance product [3,4,8], the substrate bias potential [3,5,12,13] and the deposition temperature [1,14–16]. Additionally to these parameters, high power pulse magnetron sputtering (HPPMS), a technique employing peak target power densities on the order of kW/cm^2 [19], is used to tailor the thin film microstructure and phase formation [20–22]. It is a well-known fact that the high peak power density in HPPMS leads to a significantly higher fraction of ionized sputtered material [23] compared to DCMS.

However, the effect of HPPMS on compositional deviations between compound or composite targets and deposited thin films has yet not been systematically studied. Synthesis reports of Ti_3SiC_2 [17] and V_2AlC [24] from compound/composite targets by HPPMS suggest compositional deviations with respect to the target composition. Therefore, it is meaningful to determine the

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magnitude of the film – target – composition deviation and to identify the underlying physical mechanisms.

In the present study, we utilize a Cr-Al-C powder metallurgically fabricated composite target for thin film growth by DCMS and HPPMS, as it possesses constituents with significantly different masses and binding energies. The effect of target power density, substrate bias potential and substrate temperature on the magnitude of the film – target – composition deviation is investigated systematically.

The Cr-Al-C thin films were synthesized by magnetron sputtering in an industrial scale physical vapor deposition (PVD) system (CemeCon CC 800/9). A powder metallurgically fabricated Cr-Al-C composite target (Plansee Composite Materials GmbH) having a composition of 49.8 at.% Cr, 26.9 at.% Al and 23.3 at.% C was used. The deposition parameters are presented in Table 1. The peak target power density was varied from 2.3 W/cm^2 (~4.6 W/cm^2 with respect to race track area) for DCMS to 373 W/cm^2 (~746 W/cm^2 with respect to race track area) for HPPMS. A substrate bias potential ranging from floating to −400 V was either applied constantly for DCMS or in synchronized pulses of 200 μs length during HPPMS. The longer pulse length of the substrate bias compared to the target on-time was chosen in order to ensure that the bias is still applied during the afterglow. Si (100) substrates with a 1 μm thick TiN diffusion barrier were either heated to 560 °C prior to deposition or were neither heated nor cooled (RT).

Plasma chemistry and energetics were investigated in a lab-scale magnetron sputtering system operating at an Ar partial pressure of 6.5×10^{-3} mbar. The base pressure was below 4×10^{-8} mbar. A 2 inch powder metallurgically fabricated Cr-Al-C composite target (Plansee Composite Materials GmbH) was installed approximately 7 cm away from the mass-energy analyzer (PPM 422, Pfeiffer Vacuum). The pulse period was increased to 4500 μs while the pulse on-times was kept at 50 μs, in order to obtain target power densities of 3.3 W/cm^2 for DCMS and 361 W/cm^2 for HPPMS. The target power densities are thus comparable to the depositions carried out in the industrial chamber.

Chemical composition data was obtained by Time-of-Flight elastic recoil detection analysis (ToF-ERDA) using ^{127}I ions with an acceleration voltage of 36 MeV. Four samples (DCMS at −400 V bias and 560 °C, HPPMS at −100 V and RT, HPPMS at −400 V and RT, HPPMS at −400 V and 560 °C) were analyzed using a JEOL JSM-6480 scanning electron microscope (SEM) with an EDAX Genesis 2000 energy dispersive X-ray spectroscopy (EDX) device, utilizing an acceleration voltage of 12 kV and a Cr-Al-C thin film sample quantified by ToF-ERDA as a standard. The target composition was measured in a Bruker S8 TIGER Series 2 wavelength dispersive X-ray fluorescence spectrometer.

Impurity incorporation from residual gas [25] in the analyzed films resulted in 2 at.% for oxygen, 0.3 at.% for hydrogen and 0.3 at.% for nitrogen. The chemical composition data is shown in Fig. 1 for DCMS (2.3 W/cm^2) and HPPMS (373 W/cm^2) as a function of applied substrate bias potential for RT and 560 °C substrate temperature.

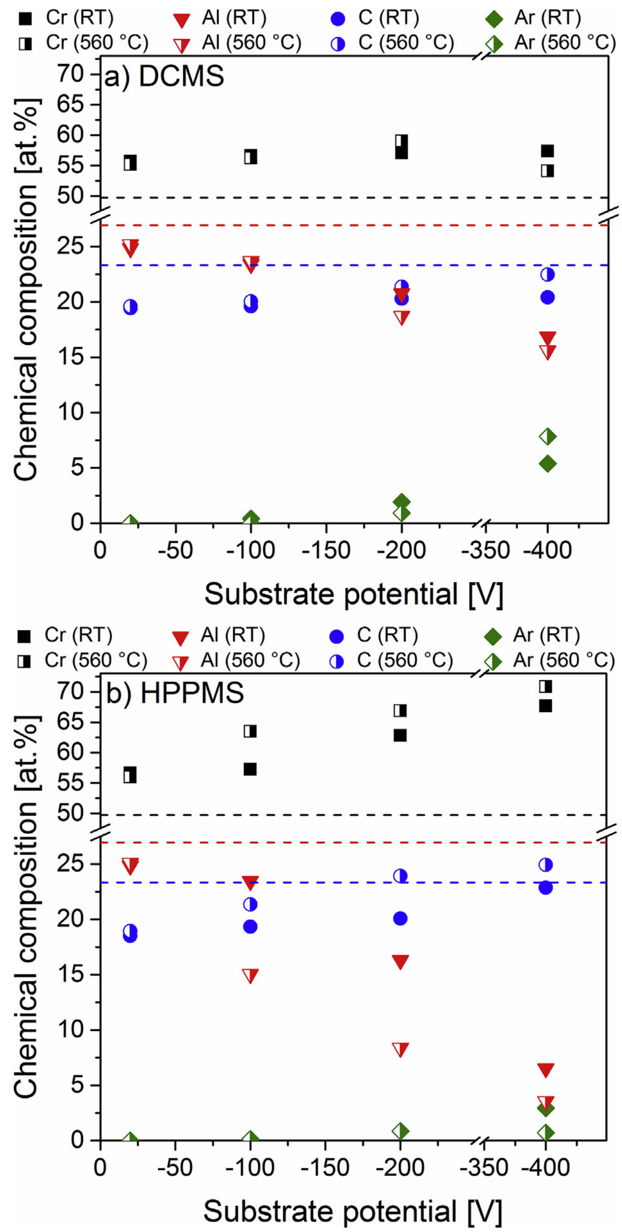

Fig. 1. Chemical composition of the Cr-Al-C films as a function of substrate bias potential and temperature for (a) DCMS (2.3 W/cm^2) and (b) HPPMS (373 W/cm^2). The dashed lines indicate the target composition of 49.8 at.% Cr, 26.9 at.% Al and 23.3 at.% C.

Table 1
Deposition parameters utilized in the industrial CemeCon deposition system.

Deposition parameter	Value
Base pressure	$< 6 \times 10^{-7}$ mbar
Ar pressure	$3.6 \times 10^{-3} - 3.9 \times 10^{-3}$ mbar
Substrate	Si (100) with a 1 μm thick TiN diffusion barrier
Target – substrate distance	7.5 cm
Substrate temperature	Room temperature or 560 °C
Substrate bias potential	Floating, −100 V, −200 V or −400 V
Power supply:	Melec SIPP2000USB-10-500-S
Time-averaged power density	2.3 W/cm^2
Peak power density	373 W/cm^2 and 2.3 W/cm^2
Pulse on-time	50 μs (HPPMS) or 4000 μs (DCMS)
Pulse period	4000 μs