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Atomic Resolution Characterization of Cr Thin Films Produced from Cr^{3+} Electrolytes

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Due to environmental and health risks caused by Cr(VI) compounds, the most recent developments indicate that future application of Cr electrodeposition will involve exclusively coatings produced from Cr^{3+} solutions. Review of the literature data suggests that successful electrodeposition from Cr^{3+} containing solutions can be achieved from electrolytes which have a strong complexing agents such as formats, thiocyanates, and hypophosphite complemented with different additives including glycolic acid, citrates and sulfamates [1]. The current understanding of crack formation in Cr films identifies the high stability of Cr^{3+} in water as a root cause. The Cr^{3+} forms a strong complex with water molecules. This causes its solubility at the interface to be strongly dependent on interfacial pH (pHi) having a great tendency to form an insoluble hydroxide. The amorphous oxide phase is found to precipitates mainly at the grain boundaries of Cr. This affects Cr thin film fracture toughness which renders a Cr films with high propensity for crack formation. In addition to that, Cr-hydride phase formed during electrodeposition yields a large post deposition tensile stress relaxation and liberation of free hydrogen leading to hydrogen embrittlement problems and additional cracking. Here we present successfully grown Cr films from Cr^{3+} electrolytes using standard DC and Pulse Deposition current approach. The structural analysis is performed using high resolution TEM which identifies structural difference between these films and points to the right approach towards electrodeposition of Cr films with minimum density of cracks and optimum mechanical integrity.

In the following work we present a combination of methods to demonstrate the potential for characterization using techniques such as Focus Ion Beam (FIB), and atomic resolution TEM. In Figure 1 we present the FIB imaging along with its respective SEM images. Here one can identify the presence of a relatively large number of constituents on the sample. The lifted out sample along with its respective backscattering images are given in Figure 1b-c. In Figure 1c can be observed the presence of several layers in backscattering electrons. Those layers are associated with the different constituents of the thin film. In Figure 2 we can observe the chemical analysis for the specific areas using EDS. What it is interesting is the EELS analysis (inset in Figure 2, for Cr) showing that all the chromium deposited in the sample has Cr^{3+} chemical state, i.e. it is present as oxide. Therefore, here we demonstrate that it is possible to synthesize sound Cr thin films using by means of electrodeposition. Furthermore, the films are generated in the absence of visible cracks or other major defects that can compromise its integrity. The HAADF image is crucial in this study as it clearly depicts similar characteristics as those observed in the SEM-Backscattering image. One can conclude from there that both techniques are in agreement. What is further more interesting is the presence of the following elemental layers: C, O, Si, Ti, Cr, and Cu. The C is present in the sample by two reasons, the first one it is part of our deposits, but the most important source of carbon is the FIB as this element is used as protective layer as well as soldering. Yet, the outstanding result here is to demonstrate that our technology is capable of generating purely Cr

layers and this result is possible by means of the combination of techniques presented herein.

References:
[1] AK Golder, AN Samanta and S Ray, Journal of Hazardous Materials **141** (2007), p. 653.

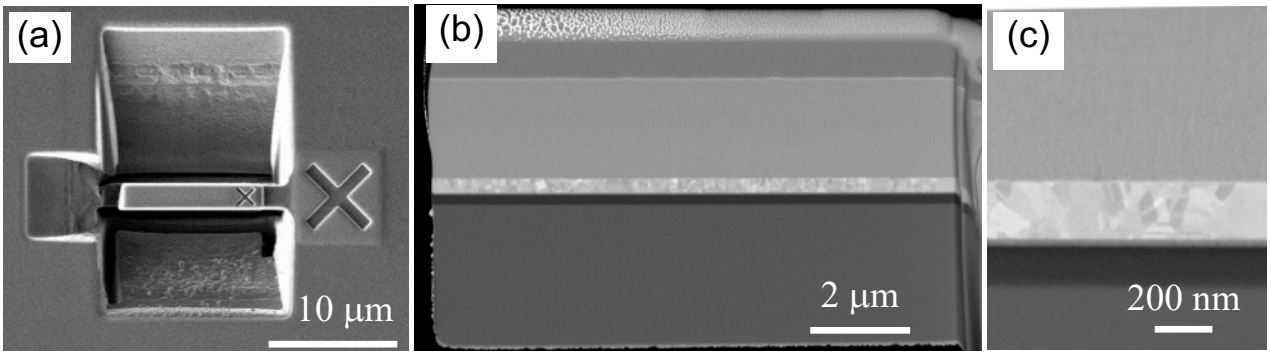

Figure 1. Focus Ion Beam procedure showing the sample preparation process (a) sample before the lift out, (b) lifted out sample, and (c) SEM image in backscaterring electrons.

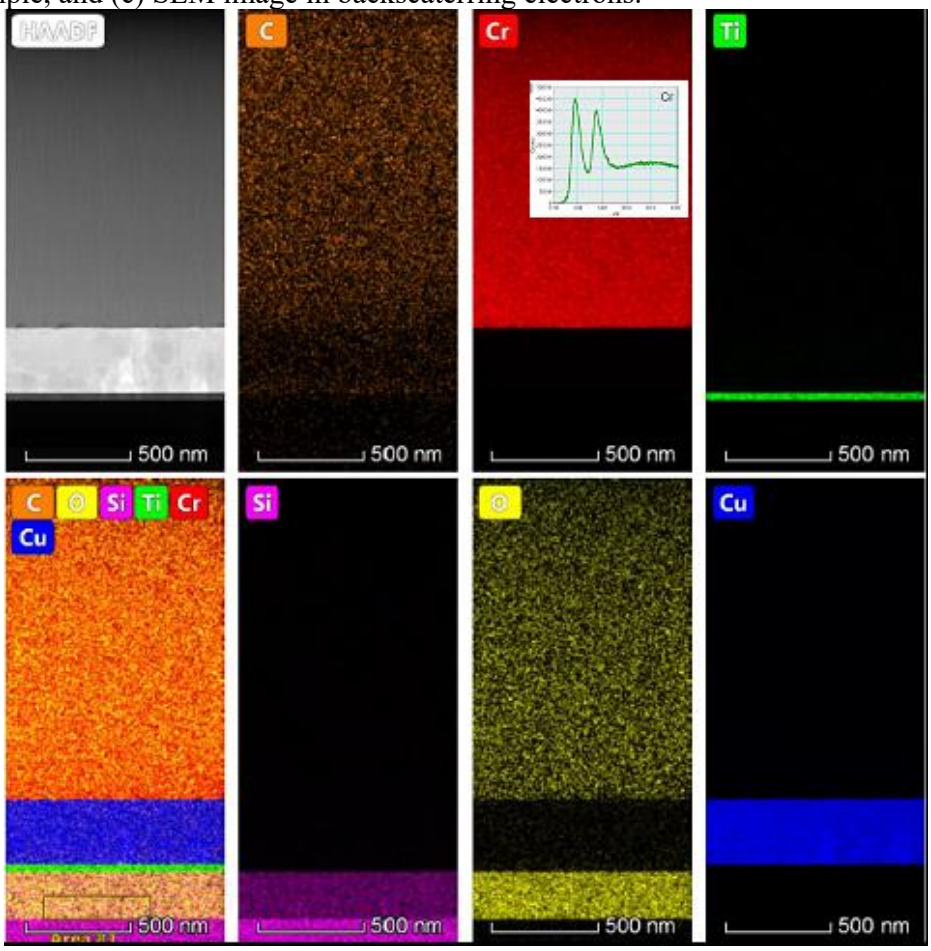

Figure 2. EDS and EELS mapping of the thin films showing the tandem composition of the sample. The HAADF image elucidates a microstructure similar to that observed with backscattering electrons. Furthermore, the inset in the Cr^{3+} map clearly shows the presence of a layer composed purely of Cr^{3+}.