



Deposition and characterization of magnetron sputtered amorphous Cr–C films

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ABSTRACT

Thin films in the Cr–C system with carbon content of 25–85 at.% have been deposited using non-reactive DC magnetron sputtering from elemental targets. Analyses with X-ray diffraction and transmission electron microscopy confirm that the films are completely amorphous. Also, annealing experiment show that the films had not crystallized at 500 °C. Furthermore, X-ray spectroscopy and Raman spectroscopy show that the films consist of two phases, an amorphous CrC_x phase and an amorphous carbon (a-C) phase. The presence of two amorphous phases is also supported by the electrochemical analysis, which shows that oxidation of both chromium and carbon contributes to the total current in the passive region. The relative amounts of these amorphous phases influence the film properties. Typically, lower carbon content with less a-C phase leads to harder films with higher Young's modulus and lower resistivity. The results also show that both films have lower currents in the passive region compared to the uncoated 316L steel substrate. Finally, our results were compared with literature data from both reactively and non-reactively sputtered chromium carbide films. The comparison reveals that non-reactive sputtering tend to favour the formation of amorphous films and also influence *e.g.* the sp²/sp³ ratio of the a-C phase.

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1. Introduction

Transition-metal carbides are known to have material properties such as high hardness and wear resistance and thin films of these carbides are therefore well suited for use in different applications. Metal carbide thin films are easily deposited with magnetron sputtering. They are usually polycrystalline or exhibit a nanocomposite structure with nanocrystalline carbide grains distributed in an amorphous matrix such as amorphous carbon (a-C). The properties of nanocomposite films depend strongly on relative amounts of carbide and matrix and can usually be controlled by tuning the experimental parameters (see *e.g.* ref. [1] for an overview).

Magnetron sputtered metal carbide films can also be amorphous. Such films are likely to exhibit completely different chemical and physical properties compared to polycrystalline or nanocomposite films and are therefore interesting to study in more detail. It is, however, important to note that films can be considered to be amorphous by different methods, *e.g.*: (i) X-ray amorphous films with crystalline carbide grains too small to yield X-ray diffraction (XRD) peaks or (ii) completely amorphous films, preferably studied by transmission electron spectroscopy (TEM) and with a structure similar to metallic glasses. It is likely that many

films described in the literature as “amorphous” in reality are nanocomposites with nano-sized grains. On the other hand, there are experimental observations including high-resolution TEM, which confirm that sputtered metal carbides indeed can form completely glassy structures without nanocrystalline grains (see *e.g.* ref. [2,3]).

The Cr–C system is an interesting binary carbide system with potential applications not only as wear resistant materials but also for corrosion protection [4,5]. The Cr–C system contains several crystalline phases with complex structures such as Cr₃C₂, Cr₇C₃ and Cr₂₃C₆. In addition, several authors have reported [6–9] that sputtered Cr–C films can be amorphous. In most cases, however, the proposed amorphous structure is based on X-ray diffraction results only. A survey of previous studies on Cr–C sputtering shows major differences in observed film structure depending on the type of sputter process. As can be seen in Table 1, both reactive and non-reactive sputtering processes have been investigated. It seems that reactive sputtering using a hydrocarbon gas tends to give nanocrystalline or nanocomposite films with nanocrystalline carbide grains in an amorphous matrix [6,10–15]. For example, Gassner *et al.* [6,11–13] have in several papers studied the structural evolution of Cr–C films using CH₄ and C₂H₄ as a carbon source using a broad range of analytical techniques. They observe an amorphous structure for more chromium-rich films but a nanocomposite structure of metastable cubic CrC nanoparticles in an amorphous a-C:H matrix for more carbon-rich films. In contrast, it can be seen in Table 1 that non-reactive processes with either

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Table 1

Summary of previously reported studies on magnetron sputtered Cr–C thin films. N/a means that a clear conclusion about the structure could not be deduced from the referenced paper.

Author	Deposition technique	Structure	Structure analysis
Gassner et al. [6,11–13]	Reactive magnetron sputtering	Nanocomposite ^a	TEM, XRD, XPS, Raman
Panjan et al. [14]	Reactive magnetron sputtering	Nanocomposite	TEM, XPS, Raman
Agarwal et al. [10]	Reactive magnetron sputtering	Nanocrystalline/nanocomposite	XRD, XPS
Sharma et al. [15]	Reactive magnetron sputtering	Nanocrystalline/nanocomposite ^b	TEM
Groudeva-Zotova et al. [16]	Non-reactive magnetron sputtering (Cr and C targets)	Crystalline/nanocomposite (Amorphous) ^c	XRD, XPS
Ziebert et al. [9]	Non-reactive magnetron sputtering (Cr ₃ C ₂ target)	Amorphous ^d	XRD
Jellad et al. [7,28]	Non-reactive magnetron sputtering (Cr ₃ C ₂ target)	Amorphous ^e	XRD
Maréchal et al. [8]	Non-reactive magnetron sputtering (Cr ₃ C ₂ target)	Amorphous	XRD
Dai et al. [24]	Reactive magnetron sputtering	N/a ^f	XPS, SEM, Raman
Bertóti et al. [20]	Non-reactive magnetron sputtering (Cr and C targets)	N/a	XPS
Wilson et al. [27]	Non-reactive magnetron sputtering (Cr and C targets)	N/a	XPS

^a Amorphous at high Cr content.

^b Only 5–20 at.% C in films.

^c See discussion in section 3.

^d Amorphous at lower argon ion energies.

^e Amorphous for film deposited at RT.

^f Low Cr content of 3–20 at.% in films.

elemental targets or a chromium carbide target tend to give amorphous films. The explanation of this difference between reactive and non-reactive processes is presently unclear but can be due to the presence of hydrogen in the reactive process or other factors such as differences in growth rate. Furthermore, more detailed studies of the structure, bonding and physical properties using several analytical techniques have been limited to a few studies on reactively sputtered Cr–C films (see e.g. [6,11]). No such systematic studies have yet been reported for non-reactively sputtered films. This is partly due to the fact that the use of chromium carbide compound targets limits the composition range of the deposited films. However, Groudeva-Zotova et al. [16] have studied magnetron sputtering in a wide composition range using elemental targets of Cr and graphite. They report the formation of both nanocrystalline and X-ray amorphous films but the structures are not supported by TEM and the phase analysis is based on one, possibly two broad and unclear peaks. Furthermore, although some X-ray photoelectron spectroscopy (XPS) results are presented, no systematic study of the correlation between chemical bonding and the physical properties of the films is presented [16].

The aim of this study is to systematically investigate the structure and chemical bonding in non-reactively sputtered Cr–C films with different carbon contents using TEM, XRD, XPS and Raman spectroscopy. The difference in structure and bonding will be correlated to mechanical, electrical and electrochemical properties (i.e. corrosion resistance) of the films. Finally, our results will be compared with those of previously studied films with a special emphasis on the differences in reactive and non-reactive sputtering.

2. Experimental

Chromium carbide thin films were deposited using unbalanced, non-reactive DC magnetron sputtering in an UHV chamber with a base pressure of 1×10^{-7} Pa. During depositions, Ar gas was used at a pressure of 0.4 Pa. Separate 2 inch elemental targets (obtained from Kurt J. Lesker Ltd.) were used with a purity of 99.999% for carbon and 99.95% for Cr. Different compositions were obtained by tuning the Cr magnetron current while keeping the carbon magnetron current constant. In total, films with five different compositions were deposited, with 25–85 at.% carbon at a deposition rate of 12–45 Å/min (depending on composition) to yield approximately 0.5 µm thick films. The substrates were placed on a rotating substrate holder with a distance of about 14 cm between the substrate and targets. The films were deposited at 300 °C

substrate temperature and a bias of –50 V was applied to the substrate. Silicon substrates were used for the scanning electron microscopy (SEM), XPS, Raman spectroscopy and XRD analyses, while amorphous SiO₂ substrates were used for resistivity measurements. Al₂O₃ (0001) substrates were used for both the nanoindentation and annealing experiments. Stainless 316L steel substrates were used as substrates for the films used in electrochemical (i.e. corrosion) experiments, while NaCl substrates were used for top-view TEM analysis. Prior to deposition, all substrates, except NaCl, were cleaned pre-deposition using iso-propanol and ethanol in an ultrasound bath for 5 min each and then dried using nitrogen gas. To study the thermal stability, films with three different compositions were annealed and further analysed. The films were annealed in an UHV furnace with a pressure of about 1.0×10^{-7} Pa for 60 min. Heating and cooling was performed rapidly by moving the furnace over and away from the silica tube of the vacuum system. Three samples with carbon content of 25 at.% C, 43 at.% C and 67 at.% C were annealed at 500 °C and another sample with 25 at.% C was annealed at 800 °C. For all annealing experiments Al₂O₃ substrates were used to minimize interaction between film and substrate.

The films were analysed using a Physical Systems Quantum 2000 X-ray photoelectron spectrometer with monochromatic Al K α radiation. Depth profiles were acquired to analyse the bulk composition of the samples. To obtain the compositions of the films, sensitivity factors determined from elastic recoil detection analysis (ERDA) of reference samples were used to calibrate the intensities obtained from XPS measurements. High-resolution XPS spectra were acquired after 40 min of sputtering with 200 eV Ar⁺ ions on an area of 1×1 mm², yielding a sputter rate of about 0.06 Å/s. The high-resolution spectra were used to identify bond types, peak shifts etc. for the samples. To attain even more information about the chemical bonding, peak fittings were carried out for the high-resolution C1s spectra, in which simultaneous fittings of several spectra with connected peak parameters were performed using the XPS-Peak software. Voigt-functions were used to fit different spectral contributions over a Shirley-type background. To obtain more information about the carbon bonding conditions, the films were also analysed using a Renishaw Micro Raman 2000 spectrometer using an Ar ion laser at 514 nm, an intensity of 10 mW and a spot size of 5 µm.

The crystal structure of the deposited films was studied using a Philips MRD X'Pert diffractometer with parallel beam geometry while annealed samples were studied using a Siemens D5000 X-ray diffractometer. Both diffractometers were operated in grazing

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