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Critical review

Sputter deposition of transition-metal carbide films — A critical review from a chemical perspective

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ABSTRACT

Thin films based on transition-metal carbides exhibit many interesting physical and chemical properties making them attractive for a variety of applications. The most widely used method to produce metal carbide films with specific properties at reduced deposition temperatures is sputter deposition. A large number of papers in this field have been published during the last decades, showing that large variations in structure and properties can be obtained. This review will summarise the literature on sputter-deposited carbide films based on chemical aspects of the various elements in the films. By considering the chemical affinities (primarily towards carbon) and structural preferences of different elements, it is possible to understand trends in structure of binary transition-metal carbides and the ternary materials based on these carbides. These trends in chemical affinity and structure will also directly affect the growth process during sputter deposition. A fundamental chemical perspective of the transition-metal carbides and their alloying elements is essential to obtain control of the material structure (from the atomic level), and thereby its properties and performance. This review covers a wide range of materials: binary transition-metal carbides and their nanocomposites with amorphous carbon; the effect of alloying carbide-based materials with a third element (mainly elements from groups 3 through 14); as well as the amorphous binary and ternary materials from these elements deposited under specific conditions or at certain compositional ranges. Furthermore, the review will also emphasise important aspects regarding materials characterisation which may affect the interpretation of data such as beam-induced crystallisation and sputter-damage during surface analysis.

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1. Introduction

Transition-metal carbides have for decades been the focus of extensive research, both as bulk and thin film materials. Many researchers have studied the growth of metal carbide films using a range of different deposition techniques including solution-based techniques, chemical vapour deposition (CVD), and different types of physical vapour deposition (PVD) processes. As thin film materials, transition-metal carbides are used in many applications to increase wear-resistance, reduce friction and improve corrosion properties (see, e.g., reference [1] and references therein). Examples of other applications are catalysis [2], electronics including electrical contacts [3] and fuel cell electrodes [4], optical components [5,6] and biomedical components [7].

Carbide-based systems are very different from their corresponding nitride counterparts. A primary reason for this is the possibility to form free carbon as, for example, an amorphous phase, a-C(:H)[1] surrounding nanocrystalline carbide grains. This will lead to films with lower hardness at higher carbon contents compared to corresponding transition-metal nitride films and limit their use on, for example, cutting tools. However, it also opens up the possibility to produce, for example, low-friction coatings using the beneficial properties of carbon to form graphitic structures in tribological contacts.

One of the most widely used techniques to grow transition-metal carbide films is sputter deposition. During the last decades, a huge number of papers on sputter-deposited carbide films have been published using elemental, compound, or composite targets as well as various reactive processes with hydrocarbons as the carbon source. Sputtering can be used to form a wide range of metal carbide materials with different properties, and also to produce films with different microstructures including nanocomposites as well as amorphous films. One of the challenges in these studies has been to design the physical and chemical properties of carbide films by a careful tuning of the phase composition and microstructure. Some control is obtained through careful choice of process parameters such as deposition temperature, target power, deposition pressure, magnetron configuration, and substrate bias. An alternative approach, however, is to use trends in the chemistry of transition-metal carbides. Properties such as thermal stability, hardness, corrosion and oxidation resistance, etc. can be varied depending on choice of the transition metal. Many of these properties can be described based on general trends in metal–carbon bond strength. In addition, the carbide film properties can be dramatically changed by the addition of a third element, either in the form of another transition-metal or a non-metal such as boron or silicon.

This review will focus on the chemical effect of the addition of other elements to binary transition-metal carbides synthesised by magnetron sputtering, and will be limited to carbide based materials, i.e. binary and ternary materials where carbon is the most electronegative element. Furthermore, this review will be limited to coatings obtained at low to moderate temperatures. Thus, some more complex structures only obtained at higher deposition temperatures will only be mentioned briefly. The extensive literature on transition-metal carbonitrides and oxycarbide thin films is not included in the review. Multilayer structures as well as metal-doped diamond-like carbon films are also beyond the scope of this paper.

We begin in Section 2 with a general overview of the structural chemistry at thermodynamic equilibrium of (primarily) binary transition-metal carbides and how they are affected by solid solution with other metals or non-metals. In Section 3, we will describe some general trends in sputter deposition of binary transition-metal carbide films. This is a very large research field with thousands of published articles and we will summarise important results obtained during the last decades. The most important part of this review is Section 4 where we discuss the effect of adding a third element during sputter deposition. For the alloying with a second metal, the discussion will be based on the separation into early transition-metals which are strong carbide-formers (Section 4.1) and later transition metals which have a low affinity for carbon (Section 4.2). We will discuss how the use of weak carbide-forming metals can affect, for example, grain size and relative phase distribution in nanocomposites and how this also changes the physical and chemical properties of the material. For the non-metals (Section 4.3), we will focus on boron and silicon, which have a strong effect of film structure. Finally, in Section 5, we will review how amorphous films can be obtained by addition of a third element to a binary transition-metal carbide.

2. Crystal structure of transition-metal carbides

The transition-metal carbides can crystallise in many different crystal structures with various degrees of complexity. A detailed description of the crystal chemistry of metal carbides is outside the scope of this review, but a short summary is required for the discussion of sputter deposited films. The binary carbides typically form compounds with a structure depending on the difference in electronegativity between carbon and the second element. This leads to a wide range of compounds with quite different physical and chemical properties as described in Section 2.1. Further complexity can be obtained if a third element, such as a p-element or another transition metal, is dissolved into the binary carbide. As will be discussed below, such solid solutions are frequently obtained as metastable phases during magnetron sputter deposition. At thermodynamical equilibrium, a large number of ternary carbides crystal structures are known. These include perovskites such as Ti_3AlC and Ni_3MgC. Another well-known group of ternary carbides is the MAX-phases, with the composition $M_{n+1}AC_n$ (n = 1,2,3) where M is an early transition-metal and A typically an element from groups 13 to 14 [8]. They can be described as natural nanolaminates and have recently been widely studied as thin film material for various applications including corrosion resistant coatings and electrical contacts [9]. Other examples of ternary carbide compounds are the κ-carbides (for example $W_9Co_3C_4$) and η-carbides with a general formula M_3Me_3C or Me_4M_2C, where M and Me are an early and late transition metal, respectively.[2] These rather complex carbides generally require high temperature to be synthesised, and can be formed in steels or in cemented carbide cutting tools and are therefore technologically important. As will be discussed in Sections 4 and 5, these complex ternary carbides are difficult to form in most sputtering processes, a fact leading to

[1] Here, and throughout the review "(:H)" denotes possible hydrogenation of the amorphous carbon phase, which is expected if hydrocarbon gas has been used as a carbon source in a reactive process, but not from a non-reactive process.

[2] This notation with M for an early (and strong carbide forming) transition metal, and Me for a late transition-metal or a weak/non-carbide forming metal will be used throughout this review.