Applied Surface Science 254 (2008) 6611–6618

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Ion sputtering rates of W-, Ti- and Cr-carbides studied at different Ar^+ ion incidence angles

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ARTICLE INFO

Article history:
Received 28 September 2007
Received in revised form 10 April 2008
Accepted 10 April 2008
Available online 20 April 2008

PACS:
81.65 Cf
68.55.Nq

Keywords:
Ion sputtering rates
Sputtering yields
Carbides
W
Ti
Cr
C
Depth profiling

ABSTRACT

To study the ion sputtering rates of W-, Ti- and Cr-carbides, trilayer structures comprising C-graphite (59 nm)/WC (50 nm)/W (38 nm), C-graphite (56 nm)/TiC (40 nm)/Ti (34 nm) and C-graphite (46 nm)/C_3C_2 (60 nm)/Cr (69 nm) with a tolerance ±2% were sputter deposited onto smooth silicon substrates. Their precise structural and compositional characterization by transmission electron microscopy (TEM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) revealed that the WC and Cr_3C_2 layers were amorphous, while the TiC layer had a polycrystalline structure. The ion sputtering rates of all three carbides, amorphous carbon and polycrystalline Cr, Ti and W layers were determined by means of Auger electron spectroscopy depth profiling as a function of the angle of incidence of two symmetrically inclined 1 keV Ar^+ ion beams in the range between 22° and 82°. The sputtering rates were calculated from the known thicknesses of the layers and the sputtering times necessary to remove the individual layers. It was found that the sputtering rates of carbides, C-graphite and metals were strongly angle dependent. For the carbides in the range between 36° and 62° the highest ion sputtering rate was found for Cr_3C_2 and the lowest for TiC, while the values of the sputtering rates for WC were intermediate. The normalized sputtering yields calculated from the experimentally obtained data for all three carbides followed the trend of theoretical results obtained by calculation of the transport of ions in solids by the SRIM code. The sputtering yields are also presented in terms of atoms/ion. Our experimental data for two ion incidence angles of 22° and 49° and reported values of other authors for C-graphite and metals are mainly inside the estimated error of about ±20%. The influence of the ion-induced surface topography on the measured sputtering yields was estimated from the atomic force microscope (AFM) measurements at the intermediate points of the corresponding layers on the crater walls formed during depth profiling.

1. Introduction

Different carbides such as tungsten-, titanium- and chromium-carbides are increasingly used for various technological applications due to their outstanding mechanical and physicochemical properties [1,2]. The most widely used application is as protective hard coatings [3–5] and component parts of steels and composite materials [6–8]. The properties of coatings are influenced by their microstructure and composition which are dependent on the deposition technique used [9,10]. Factors that add to the complexity of carbide systems are that tungsten carbide and chromium carbide exist in different phases [11,12] and titanium carbide can be highly substoichiometric [13]. Further, in tungsten carbide layers produced by different techniques a mixture of WC and W_2C was found [11,14].

To ensure well-defined coatings with the desired properties, their characterization on a microscopic scale is of outstanding importance. Particularly depth profiling with one of the surface analytical techniques like Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) or SIMS in combination with ion sputtering of the sample, has proved most useful for detailed chemical composition studies of thin films and metallurgical coatings [15,16]. However, the ion sputtering of carbides can dramatically alter their composition and produce ion yields which do not correlate with the bulk stoichiometry [17]. It is worth noting that the experimentally determined ion sputtering yields of metal carbides are not generally known over a large range of ion incidence angles. Therefore the characterization of carbide coatings is not trivial.

In this work, we studied the influence of ion incidence angle on the ion sputtering rates and ion sputtering yields of amorphous C-

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doi:10.1016/j.apsusc.2008.04.049

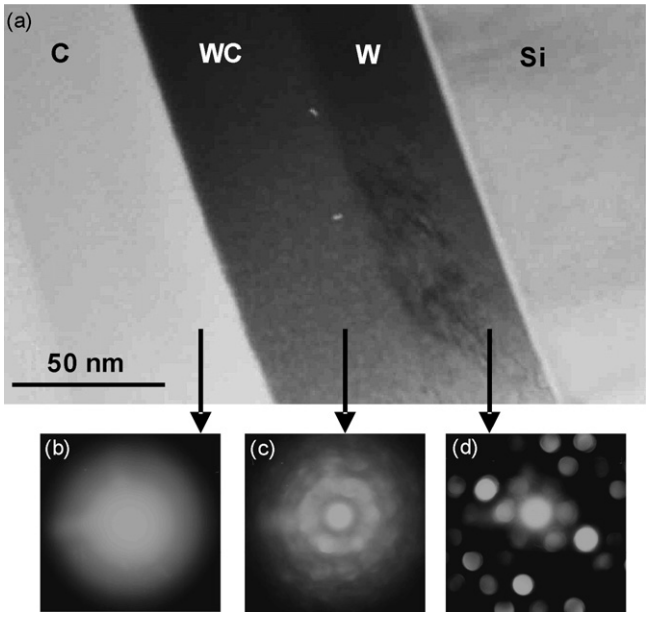

Fig. 1. (a–d) TEM micrograph of a cross-sectioned C-graphite (59 nm)/W_xC_y (50 nm)/W (38 nm) trilayer structure on a smooth silicon substrate (a), and convergent beam diffraction patterns (CBDP) of the C-graphite layer (b), W_xC_y layer (c) and W layer (d).

graphite, nanocrystalline tungsten carbide and polycrystalline W in the C-graphite/W_xC_y/W trilayer and amorphous C-graphite, polycrystalline Ti_xC_y and polycrystalline Ti in the C-graphite/Ti_xC_y/Ti trilayer. In our previous work [18] with the same sputtering parameters we studied the ion sputtering rates and ion sputtering yields of amorphous C-graphite, amorphous chromium carbide and polycrystalline Cr in the C-graphite/Cr_3C_2/Cr trilayer and the results are compared with those obtained in this work. The composition and the crystalline structure of the trilayers were investigated using AES, XPS and transmission electron microscopy (TEM). The experimental sputtering rates were determined from the AES depth profiles of the trilayer samples ion sputtered at different ion incidence angles. The normalized experimental sputtering yields were compared to theoretical results obtained by applying the SRIM 2003 code [19,20]. The sputtering yields in terms of atoms/ion were calculated taking into account the corresponding measured sputtering parameters and the materials' characteristics. Our experimental sputtering yields for C, W, Ti and Cr at two ion incidence angles of 0° and 49° were compared with previously published data by Seah [21,22] and Eckstein [23]. To estimate the influence of the surface topography on the measured sputtering yields, the roughness induced by ion bombardment was measured with an atomic force microscope (AFM) at the corresponding layers on the crater walls after depth profiling.

2. Experimental

The C-graphite/W_xC_y/W, C-graphite/Ti_xC_y/Ti and C-graphite/C_3C_2/Cr trilayers were sputter deposited onto smooth silicon (1 1 1) substrates in a Balzers Sputron plasma chamber. The sputtering parameters used for sputter deposition of all three samples have been given already in Ref. [18] in which we described the preparation of the C-graphite/C_3C_2/Cr sample. Here are given only the data relevant for other two samples. Targets of W (99.98%), Ti (99.96%) and pyrolitic graphite with a diameter of 60 mm were interchangeable in situ. The base pressure was about 5×10^{-5} Pa and at the working argon atmosphere for C, W, Ti and Cr deposition about 0.2 Pa. For W_xC_y, Ti_xC_y and C_3C_2 deposition the partial pressure of C_2H_2 in the argon atmosphere was about 8.5×10^{-2}, 6.0×10^{-2} and 9.0×10^{-2} Pa, respectively. The deposition rates of C, W, Ti and Cr were 2.1, 8.8, 10.0 and 10.0, respectively and of the carbides W_xC_y, Ti_xC_y and C_3C_2 were 11.5, 10.0 and 10.0 nm/min. The thicknesses of the individual layers were measured using a quartz crystal microbalance during sputter deposition. After the deposition, the thickness of the individual layers and the total thickness were determined by cross-sectional transmission electron microscopy using a JEOL 2010F microscope. The crystallinity of the individual layers was investigated using electron diffraction (Figs. 1a–d and 2a and b and in Ref. [18], Fig. 1a–c). The C-graphite/W_xC_y/W trilayer consisted of amorphous C-graphite, nanocrystalline tungsten carbide and crystalline W layers with thicknesses of 59 nm, 50 nm and 38 nm (±2%), respectively, the C-graphite/Ti_xC_y/Ti trilayer consisted of amorphous C-graphite, crystalline Ti_xC_y and crystalline Ti layers with thicknesses of 56, 40 and 34 nm (±2%), respectively and the C-graphite/C_3C_2/Cr trilayer consisted of amorphous C-graphite, amorphous chromium carbide and crystalline Cr layers with thicknesses of 46, 60 and 69 nm (±2%), respectively.

The density of the selected individual sputtered layers of W, Ti, WC, TiC and Cr_3C_2 was determined by the weight-gain method in combination with profilometry. A precise microbalance (Mettler, UM3) was used to determine the weight of the samples before and after deposition on the smooth silicon substrates, while a Taylor–Hobson profilometer was used for thickness measurement. The film density was determined from the weight gain and the film's dimensions.

All the trilayers were analysed with a PHI 545 A scanning Auger microprobe at a base pressure in the vacuum chamber of $<2 \times 10^{-7}$ Pa and the argon pressure during depth profiling was about 7.3×10^{-3} Pa. A static primary electron beam of 3 keV, 1 μA, with a diameter of ~40 μm, was used. The angle between the ion beam direction and the direction of the primary electron beam was in all cases about 76°.

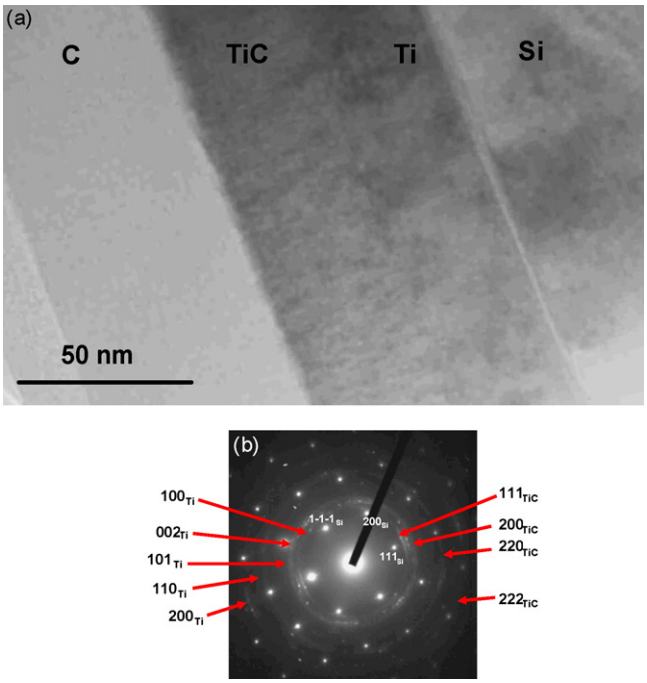

Fig. 2. (a and b) TEM micrograph of a cross-sectioned C-graphite (56 nm)/Ti_xC_y (40 nm)/Ti (34 nm) trilayer structure on a smooth silicon substrate (a), and a selected area electron diffraction pattern (SAED) of the whole region of the C-graphite/Ti_xC_y/Ti trilayer on the Si substrate (b).