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Amorphous carbon nanocomposite films doped by titanium: Surface and sub-surface composition and bonding

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ABSTRACT

Hydrogen free Ti-doped amorphous carbon layers were prepared by dual beam pulsed laser deposition using two excimer lasers. The air-exposed surfaces were analyzed by high-energy resolved and angular-resolved core-level photoelectron spectroscopy, and were then step-by-step sputtered with an argon gas cluster ion beam (ArGCIB), which is known to be a very gentle technique with respect to changes in surface chemistry. The results show that the top surface of the sample and its sub-surface region differ in composition and in bonding. The top surface is enriched by oxygen-bearing species. Carbon-bearing species located on the surface are mostly in sp^3 hybridization. Titanium carbide clusters, TiC, are not directly exposed at the surface. They are embedded in a carbon network with dominating C sp^2 hybridization. Their interface is formed by a distinct carbon-rich titanium carbide with stoichiometry close to TiC_3. The surface damage induced by ArGCIB was found to be minimal, verifiably affecting carbon atoms in the carbon network.

1. Introduction

Metal doped carbon nanocomposite films are currently under extensive study for applications in medicine [1–4]. These films are characterized by better adhesion and by lower internal stress than undoped amorphous carbon (a-C) films. Metals such as Ti, Cr and W react with carbon atoms to form metal carbide phases which induce the transformation of carbon atom hybridization from sp^3 to sp^2 in a-C films and in this way change the properties of the film, particularly the strain [5–7]. a-C films doped by Ti (a-C:Ti), prepared by various technologies, have already been analyzed by X-ray induced photoelectron spectroscopy (XPS) [1,3,5,7–9], and also by angular-resolved XPS (ARXPS) [10–12]. However, most studies have presented the spectra in low-energy resolution, and in addition there is only limited bonding information from the surface and sub-surface regions. Regarding stoichiometry, the phase diagram shows that TiC has a thermodynamically stable composition from about $TiC_{0.4}$ to $TiC_{0.97}$ [13].

Ion beams are currently used in surface science and in engineering for cleaning solid surfaces and for concentration depth profiling. The interaction between conventional (monoatomic) ion beams and solid surfaces is a complex process [14,15]. It includes the formation of an altered surface layer with a modified composition and modified bonding, structural damage, and high gradients of mechanical stresses, which often all result in sputter-induced artefacts. Much effort has been devoted to suppressing the formation of altered surface layers. The most promising method seems to be the application of multi-atomic or molecular ion beams consisting of large aggregates of atoms or molecules, known as clusters [16–18].

Argon is frequently used as a working gas for generating cluster ion beams, because it does not react with atoms on solid surfaces and practically no Ar atoms are left on the surface [17–21]. Argon gas cluster ion beam (ArGCIB) bombardment is characterized with respect to conventional Ar ion beams by a high sputtering yield per cluster ion, by enhanced lateral sputtering effects, by lowered surface roughness, and by substantially suppressed damage to the surface structure [20–25].

The following topics are currently under investigation by scientists and are addressed in this paper:

(i) Hybridization of carbon atoms and modifications to them in the presence of embedded TiC clusters. This issue, which is important for applications, has in the past not been investigated in great detail. In addition, binding energy positions of C sp^2 and C sp^3 contributions has been questioned.
(ii) The appearance of an extra C—Ti bonding state resolved in the C 1s photoelectron spectra, labelled as C—Ti*. This bonding state has not been observed in C 1s photoelectron spectra recorded from bulk single phase titanium carbide [26], and has been attributed to

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disorder, and/or to the TiC-carbon network interface in a-C:Ti nanocomposite films [7]. It was found that the C—Ti* peak intensity increased extensively for sputter-cleaned a-C:Ti layers when a monoatomic ion beam was used [10], indicating the depth distribution of the C—Ti* bonding states. In addition, the C—Ti* peak intensity correlates with the mean inverse size [7] and, therefore, with the surface area of the TiC clusters.

(iii) Detection and the evolution of possible surface structural damage induced by ArGCIB sputtering, which is a novel method.

In this study, we investigate a-C:Ti films with the use of high-energy resolved and angular-resolved XPS before and after ArGCIB sputtering. First, ARXPS spectra were recorded from the virgin surface of the sample to obtain qualitative information on surface and sub-surface composition and bonding by a non-destructive method. Then, the sample was sputtered step-by step by ArGCIB and was analyzed. The results of an ARXPS analysis of the virgin surface of the sample are compared with the results of a sputter depth profile analysis. We then continue with a systematic investigation of a-C:Ti films with different Ti contents [1,4], in order to achieve a deeper understanding of their surfaces and near-surface properties with a view to medical applications.

2. Materials and methods

a-C:Ti films were prepared by dual beam pulsed laser deposition using two KrF excimer lasers ($\lambda = 248$ nm, $\tau = 20$ ns). The flows of these target materials are directed at a rotating Si(100) substrate. The first laser beam (Coherent, Complex Pro) was focused onto a high purity graphite target with energy density of 8 J·cm^{-2}, and the repetition rate was set to 18 Hz. The second laser beam (Lumonics PM-800) was focused onto a Ti target with energy density of 5 J·cm^{-2}, and the repetition rate was set to 23 Hz. More detailed information on the preparation conditions is presented elsewhere [1]. The layers are considered as a two-phase material, amorphous carbon network with embedded TiC clusters [27]. The mean size of the TiC clusters was estimated from the XRD spectra to be 3 nm. The mean bulk Ti atomic percentage, estimated by wavelength dispersive X-ray spectroscopy (WDS), was 27.0 ± 1 at.%. Thickness of the films was 100 nm. Although the undoped a-C films were smooth, the a-C:Ti layers exhibit a number of droplets at the surface, typically around 10 μm in diameter and several micrometers in height [1].

The high-energy resolved ARXPS spectra were recorded from as-received surfaces with an AXIS-Supra photoelectron spectrometer (Kratos Analytical Ltd., UK), using monochromatized Al Kα radiation (1486.6 eV, 300 W, analyzed area — 0.7 × 0.3 mm^2), and with an Ar cluster ion source. The samples did not undergo any surface cleaning treatment before they were introduced into the spectrometer chamber, and also when they were in the chamber. Only the peaks of Ti, O, and C were observed in the XPS survey spectra (not shown here). The high-energy resolved spectra of Ti 2p, O 1s and C1s were collected with pass energy of 10 eV and with a step of 0.05 eV, resulting in overall energy resolution of 0.45 eV, measured on the Ag 3d$_{5/2}$ line width (FWHM). Binding energy calibration was performed with respect to the C sp^2 contribution, which peaked at 284.3 eV. The angular-resolved spectra were recorded from the virgin surface of the sample by tilting the sample at photoelectron emission angles of 90°, 80°, 70°, 60°, 50°, and 40° with respect to the surface plane. Quantification was performed using integrated area of C 1s, O 1s and Ti 2p core level spectra after standard Shirley's electron inelastic background subtraction and the atomic sensitivity factors given in the ESCApe software (Kratos Analytical Ltd.). The C 1s and Ti 2p spectra were analyzed by peak fitting using Voigt peak shapes.

The virgin (air-exposed) sample surface was sputtered step-by-step by ArGCIB, and was analyzed by high-energy resolved XPS at a normal electron emission angle. The ion beam impact area was 2 × 2 mm^2 at an incident angle of 50° from the surface normal. The following sputtering conditions were adjusted and were used in work: 5 keV ion beam energy, 7 nA ion beam current, and the average number of Ar atoms in the clusters was set to 2000. The average energy per Ar atom was as-low-as 2.5 eV. It is expected that sputtering under the conditions described above has a very gentle impact on the treated surface. However, the sputtering yield is rather low and the crater depth is shallow. Using AFM technique we measured the crater depth and evaluated the erosion rate — 0.14 nm/min. In this work we designate the "bulk" titanium carbide in clusters as TiC and the interface titanium carbide as TiC$_x$.

Table 1
Apparent composition calculated from the C 1s, O 1s and Ti 2p peak areas and the photoelectron sampling depth values (= 3λsinα, λ is the inelastic mean free path of photoelectrons, α is the emission angle), calculated for C 1s photoelectrons with energy of 1200 eV moving in graphite [28].

Emission angle α [°]	C [at.%]	Ti [at.%]	O [at.%]	Sampling depth [nm]
90	74.5	13.8	11.6	6.3
80	74.2	14.2	11.6	6.2
70	73.8	14.1	12.0	5.9
60	73.4	14.2	12.4	5.5
50	73.1	13.4	13.5	4.8
40	73.4	12.0	14.6	4.1

3. Results

3.1. An investigation of the virgin surface of the sample by ARXPS

The apparent composition of carbon, oxygen and titanium for all measured emission angles is presented in Table 1, together with the photoelectron sampling depth values. The method used here is more surface sensitive when there is a smaller emission angle. We observed a slight decrease in carbon and titanium with a smaller emission angle, while there was an increase in oxygen. This means that there is a concentration gradient with higher oxygen concentration close to the surface covering carbon and titanium.

The C 1s photoelectron spectra recorded from the virgin surface of the sample at the normal emission angle (90°) and, by tilting the sample, at several different emission angles are displayed in Fig. 1(a).

Three well-resolved peaks are clearly seen in the spectral line envelopes for all emission angles that were used, and more markedly for the normal emission angle. The C 1s spectra were peak-fitted into six different bonding states, as shown in the bottom spectrum for illustration. Individual lines are ascribed to the following bonding states: the spectral intensity, ascribed to C—Ti at 281.9 eV; ascribed to C—Ti* (interface and/or disorder effects [7]) at 283.0 eV; ascribed to C sp^2 at 284.3 eV; ascribed to C sp^3 at 285.2 eV; ascribed to C—O at 286.2 eV; and ascribed to C=O at 288.7 eV. The C sp^2 and particularly C sp^3 peak positions will be further discussed in Section 4. Note that we leaved out aliphatic carbons from our peak fitting because the top surface of the sample appears to be enriched by oxygen-bearing species (see Table 1). Hydrocarbons from atmosphere covering the surface typically have a binding energy in the 284.5–285.0 eV range [29]. However, we cannot rule out that our samples have some CH$_x$ species at the top surface of the sample, but we expect from the angular-dependent carbon content and particularly from the angular-dependent C sp^2 + C sp^3 contributions shown below in Fig. 2 that such an effect is relatively small. The C 1s peak fitting results are summarized in Table 2. In Fig. 1(b), we present the C 1 s photoelectron spectra recorded from the virgin surface of the sample at two different emission angles (i.e. at two different sampling depths, see Table 1) and their difference spectrum. From the difference spectrum, we reveal clearly and directly the influence of the surface on the spectra. Specifically, the rise in spectral intensity ascribed to C—Ti*, C—Ti, and C sp^2 indicates that they are located mostly in the sub-surface region, and the drop in spectral intensity ascribed to