SIMS DEPTH PROFILING OF THIN NITRIDE- AND CARBIDE-BASED FILMS FOR HARD COATING

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Abstract. Secondary ion mass spectrometry (SIMS) with argon ion beam has been used to determine the depth profile of thin (Ti,Cr) nitride- and carbide-based multilayered hard coatings deposited on stainless or carbon steel substrates. The aim of the study is to show advantage of the SIMS method for elemental depth profiling and characterization of impurities in such thin systems. We discuss the matrix effects in SIMS analysis, particularly oxygen influence on the main elements detection in the films, and ion mass interference observed for positive and negative analysis of the Cr(N,C) multilayers. The use of a low energy beam sputtering in conjunction with detection of molecular ions is proposed for monitoring of the multilayered CrN/CrC films. The profile of $(^{28}Si^{12}C_2)^-$ accomplished by a ultra-low energy of the beam provides accurate distribution of Si dopant in the TiC material indicating the SiC film creation on the top of the coating with the thickness of about 500 nm. The depth profiles of the (Ti,Cr)N coatings show higher oxygen contamination in the case of TiN layers than in the CrN, while higher nitrogen concentration was recorded in the chromium nitride matrix. Furthermore, Auger study of the investigated structures provides additional information on quantitative distribution of main components in the coating films.

1. INTRODUCTION

Many new tribological materials have been developed for hard coating films. They include covalently bonded materials (SiC, B_4C), ionically bonded metal oxides (Al_2O_3, TiO_2), diamond, diamond-like-carbon, BN, and carbide or nitride alloys [1,2]. These different coatings can be deposited as single layer film, or they can be created as multilayer or superlattice structure. Due to good chemical inertness and enhanced hardness, such layers provide corrosion-protection and increase operational life of tools.

Recent publications suggest that mechanical properties of protective layers depend on both atomic concentration and depth distribution of elements incorporated into the coating [3,4]. Thus quantitative depth profiling of these films with the required sub-nm accuracy is an analytical challenge [4,5].

Secondary ion mass spectrometry (SIMS) is an essential technique for investigation of such thin coating films and offers high in-depth precision only, if ultra-low impact energy is used for sputtering [6]. However, the quantitative depth profiling of such materials is not straightforward in the presence of

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a surface contaminations, mass interferences and matrix effects [7].

In this work we present a detailed SIMS study of several systems, like: TiN/CrN, CrN/TiN, TiC:Si, TiCrN alloys and multilayered CrN/CrC and CrN/TiN thin coatings created on carbon steel or stainless steel substrates using various deposition methods. The aim of this work is to analyze distribution of elements and contaminations in the films and interface regions as well as to obtain chemical characterization allowing description of nitridation and carbonization mechanisms in coating production. In order to achieve a more precise quantification, we have been monitored the multilayered films using ultra-low energy of primary ion beam (880 eV). Part of the structures have been investigated by Auger electron spectroscopy (AES) to provide additional information on quantitative distribution of main components. SIMS depth profiles of these films show higher oxygen contamination in the case of TiN layers than in the CrN, while higher nitrogen concentration was recorded in chromium nitride films.

2. EXPERIMENTAL

2.1. Sample preparation

Binary TiN, CrN and multilayered ($2 \times$ TiN/CrN)/TiCrN coatings on carbon steel St.3 (< 0.18 weight %C) (for SIMS study) or silicon (<100> oriented) substrates (for AES study) were formed by condensation from a plasma phase in a vacuum with the alternating ion bombardment of the samples surface combining the titanium and chromium plasma flows of variable density in a residual nitrogen atmosphere [8,9]. Arc currents of Ti and Cr cathodes (kept constant) were 100 A during deposition process and the deposition time of one layer was 1.5 min. Prior to the deposition, the substrate surface was cleaned and heated to 450°C by chromium ion bombardment for 1 min. with the substrate bias being -1 kV in 10^{-3} Pa condition. The coatings deposition was initiated by N_2 gas injection (pressure 10^{-1} Pa) into the vacuum chamber with the substrate bias equal to -120 V.

The multilayered CrN/CrC and TiC films on stainless steel (SS) substrates were produced using reactive magnetron sputtering and reactive arc deposition, respectively. Additionally, in order to form the top silicon carbide film coating, the TiC film was Si implanted.

The thickness of the formed coatings was evaluated by the resulting SIMS crater using a Tencor α-step 100 profilometer.
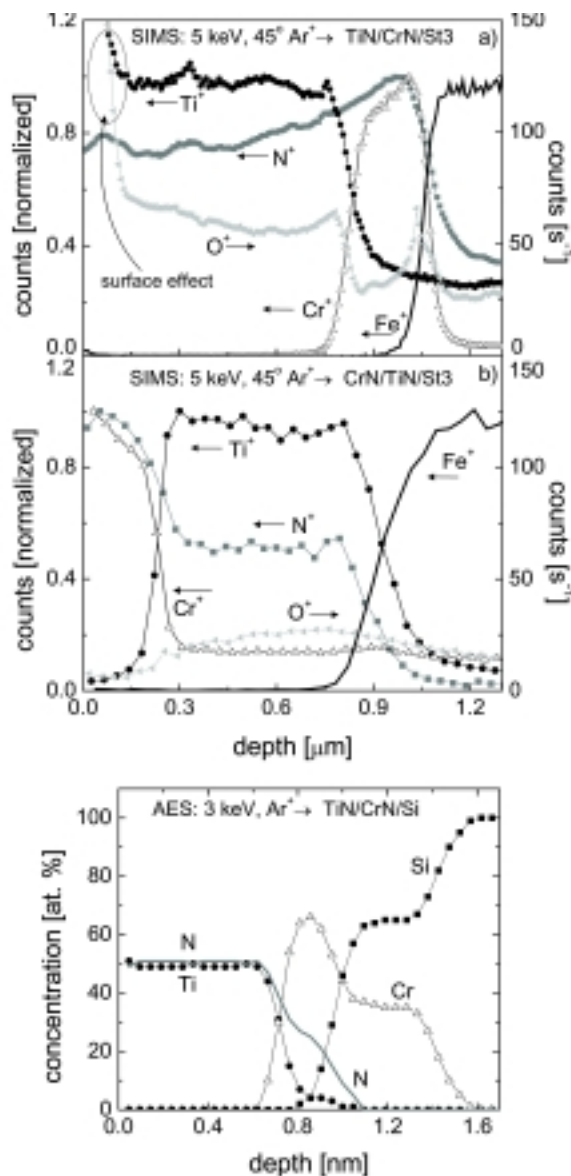

Fig. 1. Positive SIMS depth profiles of: (a) TiN/CrN/St.3; (b) CrN/TiN/St.3 structures obtained with 5 keV Ar⁺ ion beam sputtering; (c) AES depth profiles of TiN/CrN/Si structures taken with with 3 keV Ar⁺ beam.

2.2. Depth profile analysis

The SIMS measurements have been performed using SAJW-05 instrument with a low (5 keV) and ultra-low (880 eV) energy of Ar⁺ beam. The apparatus is equipped with a 16 mm Balzers quadrupole mass spectrometer and a Physical Electronics argon ion gun. The ion beam, of about 100 μm in diameter, has been employed with incidence
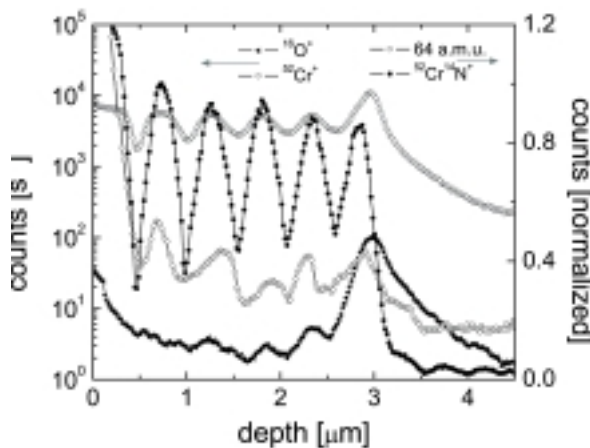
Fig. 2. SIMS depth profile of 6 × (CrN/CrC) multi-layered coating prepared on stainless steel substrate taken with 5 keV Ar⁺ beam.

angle 45° to the surface normal. Spirally scanned primary ion beam across 1000×1500 μm² and 500×750 μm² areas was used for depth profiling of the investigated samples. The smaller area of the crater was used for coating erosion with the use of ultra-low energy ion beam.

Prior to the depth profile analysis, we have been performed the mass spectrum of the sample surface, which is an intensity vs. mass-to-charge ratio plot and gives helpful data about species and mass interferences needed to make decision as to which ions provide the real or the best detection limit. We have selected the following negative and positive secondary ions for TiN/CrN, CrN/CrC and TiC:Si coatings respectively: $^{52}Cr^+$, $^{48}Ti^+$, $^{14}N^\pm$, $^{12}C^\pm$, $^{16}O^\pm$, $^{52}Cr^{14}N^\pm$, $^{52}Cr^{12}C^-$, $^{53}Cr^{12}C^\pm$, $^{48}Ti^{12}C_2^-$, $^{28}Si^{12}C_2^-$.

Quantitative analysis has been obtained by AES with step by step sputtering of the coating surface created on silicon with argon ion beam of 3 keV and 1 keV energy.

The monitoring of $^{56}Fe^+$ as well as $^{12}C^\pm$ secondary ion intensities is proposed for SIMS substrate monitoring, while Si for AES.

3. RESULTS AND DISCUSSION

3.1. Depth profiling of binary films

Here, we focus on the investigation of nitride based coatings deposited on the St.3 substrates to find differences in elemental depth concentration of the protective films taking the nitrogen and oxygen distribution into consideration. We will compare depth

profiles of two coatings consisted of two binary films: TiN/CrN (850 nm/150 nm thick) and CrN/TiN (250 nm/700 nm thick respectively). The SIMS examples of depth profiles taken with 5 keV Ar⁺ primary beam of the coatings are illustrated in Figs. 1a and 1b, where positive ion intensity of O⁺ and normalized signals of main components represented by Ti, Cr, N, and Fe ions are plotted against depth. In comparison to SIMS depth profile the AES data of the TiN/CrN coating are shown in Fig. 1c. The SIMS results show that TiN and CrN films as well as coating/substrate interface regions are oxidized and the highest oxygen intensities are measured in the titanium nitride films. Titanium is much more reactive in comparison to Cr and thus oxygen (or other impurities) from the ambience can be easily incorporated into the Ti-based layer and can affect the nitridation process. This unfavorable result can increase the secondary ion yields of Ti⁺ as well as Cr⁺ during SIMS sputtering and overestimate elemental atomic concentration. Monitoring of N in the coatings shows its non-uniformity in depth distribution. The highest concentration of nitrogen is detected in the CrN films. However, AES data represent the opposite results (about 50% atomic concentration of N was measured in the TiN films and approximately 30% in the CrN material) (see Fig. 1c). For this ambiguity might be responsible SIMS matrix effects, in which the secondary ion yield of N can be much higher in chromium surroundings than in the case of titanium nitride matrix. However, more efficient incorporation of nitrogen into chromium based films is not excluded. Previous work of gradient variable composition of ternary TiCrN alloys [9] shows rather homogeneous distribution of nitrogen in the coatings from both SIMS and AES analyses. Also higher Cr concentration is observed in AES profile in the interface region (coating/substrate), which is connected with formation of transition Cr-layer. The layer is created by pretreatment of substrate as it is described in Experimental section.

Assuming the realistic concentration from AES data and basing on recent investigations by Vishnyakova *et al.* [10], we can suppose that hardness of our chromium nitride films (30% at. conc. of N) is lower than titanium based coatings, however decreasing of mechanical properties of Ti-based coating films can be observed due to higher oxygen content.

Also noteworthy is that depth profiles of the coatings are complicated by surface contamination and initial measurements of all elements in the top sur-
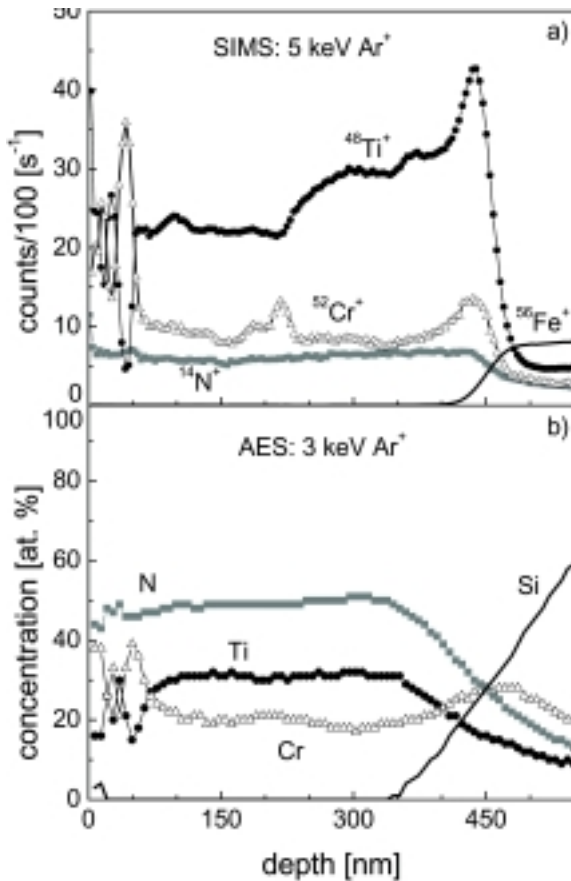
Fig. 3. Depth profiles of 2 × (CrN/TiN)TiCrN structure done using: (a) SIMS with 5 keV Ar⁺ ion beam sputtering; (b) AES with 3 keV Ar⁺ beam.

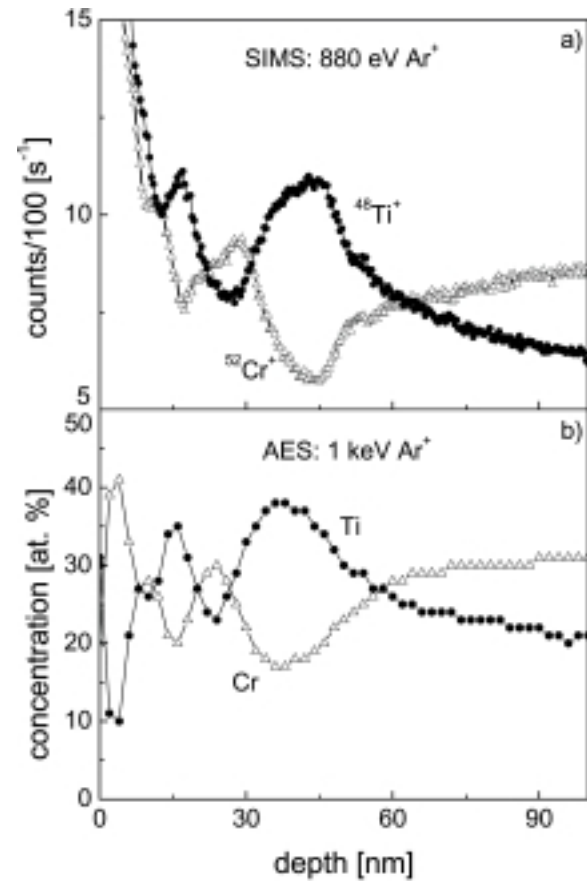**Fig. 4.** Ultra-low energy depth profiles of multilaered CrN/TiN top coating system done using: (a) SIMS; (b) AES.

3.2. Depth profiling of multilayered coatings

The choice of secondary ion species depends on the elements to be monitored and should be adequately selected to provide the best profile monitoring. The molecular ions can sometimes give better detection limits, real elemental depth distribution and lesser matrix effect than atomic species. Here we present SIMS investigation of the multilayered films for hard coatings and we show, how ion mass interferences (including isotopes) complicate the interpretation of SIMS data.

Fig. 2 illustrates the depth profiles of a 6- bilayer CrN/CrC (with thickness of approximately 300 and 200 nm each film respectively) multilayered system on SS substrate. Some of the secondary ion currents have been normalized and presented

face layers are not very meaningful (the surface effects).

in the right axis of the graph in linear scale, these are: (64 a.m.u.)⁺ and $^{52}Cr^{14}N^+$. We observe that C⁺, C⁻ (not shown) as well as CrC⁺ (positive or negative) secondary ions have insufficient yield to monitor chromium carbide films. Moreover, as one can see, the profile of $^{52}Cr^{12}C^+$ (64 a.m.u. – atomic mass units) is probably influenced by $^{50}Cr^{14}N^+$ (64 a.m.u.) secondary emission. The last ion has relatively higher yield than $^{52}Cr^{12}C^+$ indicating that the profile of the ion mass equal 64 a.m.u. is represented by $^{52}Cr^{12}C^+$ just in the minima (CrC films), while $^{50}Cr^{14}N^+$ is recorded in the maxima (CrN films). The only secondary ion for chromium carbide films detection, which cannot be affected by N containing species is $^{53}Cr^{12}C^±$ (65 a.m.u.; the ^{51}Cr isotope does not exist). However, the ion intensity of 65 a.m.u. exhibits insufficient value of sputtering yield to characterize chromium carbide films with argon ion beam. Thus in order to increase the secondary emission, one can choose an O_2^+ species as primary beam. The effect of incidence angle on the
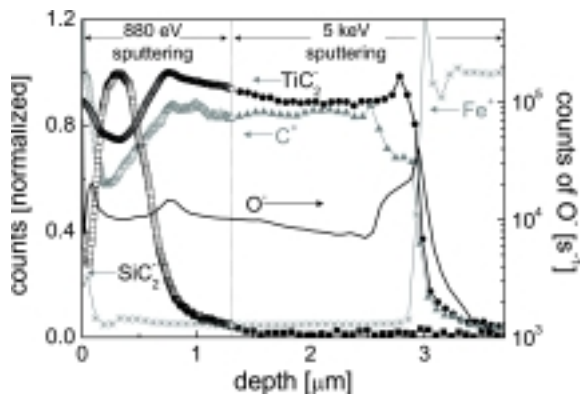
Fig. 5. SIMS analysis of TiC – Si implanted film profiled with low (5 keV – full symbols) and ultra-low (880 eV – open symbols) energy Ar⁺ primary beam.

secondary emission is also of crucial importance, and in sputtering process, the yield rises to a maximum at an angle of about 70° to the normal of the sample surface [11]. But, even if we increase the angle from 45° up to about 70° in SAJW-05 apparatus, and accomplish the depth profiling, than the sputtering yield can at most double but can not increase an order of magnitude for successful detection of $^{53}Cr^{12}C^{\pm}$ in chromium carbide material.

Additionally, non-homogeneous distribution of chromium in the coating has been noticed. Higher emission of $^{52}Cr^+$ was recorded in the CrN films than in CrC. This can be interpreted either as due to a slightly higher oxygen content in the chromium nitride films, what increases the emission of $^{52}Cr^+$, or because the yield of $^{52}Cr^+$ becomes more efficient during sputtering away the CrN than the one of CrC material. Also about 1.5 higher sputtering yield of CrN with respect to CrC matrix have been obtained by us using TRIM simulations [12]. Thus such relation reinforces our view that concentration of chromium might be homogenously distributed in the investigated coating despite of non-homogenous SIMS profile of $^{52}Cr^+$.

The SIMS and AES depth profiles taken with 5 keV and 3 keV energy of primary beam respectively of other multilayer coating consisted of (2 × TiN/CrN)/TiCrN/St.3 is presented in Fig. 3. The results show constant secondary ion signal of nitrogen recorded across the coating. The presented signals correspond to AES atomic concentration:

about 45-50% of nitrogen, 30% and 20-25% of titanium and chromium respectively. The ultra-low energy of primary ion beam in the SIMS and AES analyses of top multilayer films (Fig. 4) of the coating allows us to perform depth distribution of Cr and Ti with higher depth resolution. The results show separated two bilayers of about 15 nm thick each film, followed by TiCrN ternary layer (towards the substrate).

In SIMS, the quantification is difficult of accomplishment because of matrix effects presence during sputtering. In Fig. 3a we observe a very non-homogeneous distribution of Ti⁺ and Cr⁺ and increase of titanium emission towards the substrate. This indicates that SIMS technique has the advantage that it is very sensitive to matrix changes. Thus the case of SIMS data has to be explained as a real feature because constant signal of oxygen (not shown) was measured in the coating excluding the interface region (410-460 nm) where the increase of both titanium and chromium signals have been registered due to higher oxygen content. The AES data presented in Fig. 3b illustrate rather homogeneous distribution of Ti and Cr concentration in the TiCrN film, however a little higher Cr content has been noticed in the middle part of the profile (at the depth of about 220 nm) - the same feature reveals SIMS analysis.

3.3. SIMS depth profiling of TiC:Si/ stainless steel structure

Here we present SIMS study of titanium carbide film deposited on stainless steel substrate. The deposition was followed by silicon implantation into the TiC material. The results of depth profile analysis are illustrated in Fig. 5, where top part of the coating (up to the depth of about 1.3 mm) has been profiled with the use of ultra-low energy primary beam. The rest of the structure was analyzed using low energy 5 keV Ar⁺ bombarding. The profiles of Fe⁺ and O⁻ of the whole film coating have been measured using 5 keV Ar⁺ sputtering. The SiC_2^- and TiC_2^- negative ion intensities have been selected for silicon and titanium monitoring across the coating respectively. Secondary ion current of oxygen is presented in the right axis of the graph while other species have been normalized (for more clear depiction) to the maximum values of the intensities respectively. We observe relation between maximum content of Si (SiC_2^-) and the minimum values of TiC_2^- and C⁺ at the depth of about 300 nm. The Si implantation has the effect on the SiC film creation (with the thickness of about 500 nm)

slightly under the surface of the coating. This results in TiC/SiC/TiC protective coating fabrication on SS substrate. The TiC/SiC and SiC/TiC as well as TiC/SS 'interfaces' are oxidized what is revealed by the increased signals of O^- recorded in these regions. We have observed a characteristic feature: the shapes of TiC_2^- and O^- are similar. Higher concentration of oxygen is recorded together with higher titanium content (higher TiC_2^- intensity). Thus we come to a conclusion that the ability of Ti to oxidize can be the origin of the buried oxygen at the SiC/TiC and TiC/SiC interfaces richer in titanium. However the Si-implantation process would have also an effect on the oxygen distribution in the coating. The silicon could moved the oxygen from surface (rich in oxides) deep into the TiC during penetration. In the case of coating/substrate interface, about 300 nm thick oxide layer is observed. This additional presence of oxygen results in lower content of carbon in the region and higher yields of TiC_2^- and Fe^+ secondary ions emission.

4. CONCLUSIONS

We have discussed the SIMS depth profiling using Ar^+ ion beam bombarding of thin (Ti,Cr) carbide and nitride films and multilayered coatings deposited on stainless or carbon steel substrates. The TiN-based coatings show higher oxygen contamination than CrN films, indicating the ability of Ti-based films to oxidize, however higher emission of nitrogen has been measured in chromium nitride films. We have also presented the influence of matrix effects and mass interferences in depth profiling of CrN/CrC multilayered structure. The choice of secondary ions is of crucial interest in SIMS depth profiling of multilayered system. We propose the detection of $^{52}Cr^{12}C^+$ and $^{52}Cr^{14}N^+$ molecular ions for depth profiling of CrN/CrC multilayers because they reduce matrix effects with respect to atomic species. However relatively higher yield of $^{50}Cr^{14}N^+$ (64 a.m.u.) secondary emission leads to ion mass interference and affects the detection of $^{52}Cr^{12}C^+$ (64 a.m.u.) in Cr-carbide films.

Si-implantation into TiC coating results in creation of 500 nm thick silicon carbide film on the top of the coating. Oxygen distribution in the system indicates that SiC/TiC and TiC/SiC interfaces are richer in Ti.

AES study of binary coating gives a realistic concentration of nitrogen distributed in the investigated coatings and shows, in contrary to SIMS data, higher nitrogen concentration in Ti-based layer.

Secondary ion mass spectrometry has proven to be an essential tool for characterization of dopants and impurities in coating films and offers high in-depth precision in ultra-low energy ion beam analysis. However the ultra-low energy bombardment decreases the sputtering rate as well as sensitivity due to lower primary beam current.

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