Surface & Coatings Technology 204 (2010) 1722–1728

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Approaches to influence the microstructure and the properties of Al–Cr–O layers synthesized by cathodic arc evaporation

Leandro de Abreu Vieira [a], Max Döbeli [b], Alex Dommann [a], Eva Kalchbrenner [c], Antonia Neels [a], Jürgen Ramm [c,*], Helmut Rudigier [c], Jürgen Thomas [d], Beno Widrig [c]

[a] Centre Suisse d'Electronique et de Microtechnique CSEM SA, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland
[b] Ion Beam Physics, Paul Scherrer Institute and ETH Zurich, Schafmattstrasse 20, CH-8093 Zürich, Switzerland
[c] OC Oerlikon Balzers AG, Iramali 18, LI-9496 Balzers, Liechtenstein
[d] IFW Dresden, Leibniz-Institut für Festkörper-und Werkstoffforschung, Helmholtzstrasse 20, D-01069 Dresden, Germany

ARTICLE INFO

Article history:
Received 23 August 2009
Accepted in revised form 30 October 2009
Available online 10 November 2009

Keywords:
Arc evaporation
Ternary oxide
Multi-layer
Ion current
Pulsed arc discharge

ABSTRACT

Al–Cr–O layers were synthesized by reactive cathodic arc evaporation utilizing DC as well as pulsed operation of the arc sources. The observed increase of the substrate ion current in the pulsed mode is attributed to the increased ionization of the oxygen reactive gas. The influence of the substrate ion current and the oxygen flow on the microstructure of the layers has been investigated. A strong influence of the oxygen gas flow on morphology and crystal structure has been observed. The increased substrate ion current in the pulsed mode has seemingly no influence on layer morphology at low bias voltages, but influences the nucleation behavior of the layer. The appearance of a multi-layer structure in the synthesized layers utilizing a single composite target has been ascribed to partial ion splitting of the target constituents in the curvilinear arc discharge.

1. Introduction

Cathodic arc evaporation is the dominant PVD technology to produce wear resistant coatings for cutting tools. Reasons for this are the robustness and the low running costs of this technology in comparison with sputtering and hollow cathode evaporation. Another reason is the simplicity to produce not only pure metallic layers, but also binary and ternary nitrides and carbo-nitrides in reactive processes which does not require a sophisticated control of the reactive gas flow as it is the case for sputtering and evaporation. This process feature is especially important for batch-type processing in production environment with its varying loadings and the limited control over degassing of the different substrate types due to the fabrication steps before the PVD arc deposition.

Recently, the arc technology has been extended to the formation of oxides in the pulse enhanced electron emission (P3e™⁾) production approach [1]. One interesting feature of the technology is the low deposition temperature of only 500 °C, while still forming high temperature crystalline corundum-type structures under this condition [2]. The advantage is two-fold. On the one hand, substrate materials can be coated which cannot resist the high process temperatures in CVD oxide processing, e.g. high speed steel. On the other hand, the extrinsic stress due to the thermal mismatch between oxide layer and substrate is reduced. The reliability of reactive arc evaporation has been already proven in the production of wear resistant coatings. However, the wide process window of this technology needs additional investigations if the coatings should be optimized for dedicated applications in this field. The search for process parameters influencing the microstructure, morphology and crystal structure of the layers is therefore essential to adapt the layer properties to the multifaceted applications in tool coating.

A distinctive feature of the arc evaporation in pure oxygen atmosphere is the reduced substrate ion current not only in comparison with the evaporation of metals in argon gas, but also in comparison with the operation of the arc sources in nitrogen atmosphere. For example, the substrate ion current obtained for the same target with the same arc current and the same gas flow of 400 sccm is reduced by a factor of 2.5 if pure oxygen instead of pure nitrogen is used. For nitride deposition it is well established that the substrate ion current in combination with the substrate bias influences the layer morphology. This plays a substantial role in the formation of the layer stress which in turn may affect the hardness and toughness of the coating. It is also known that pulsing of the arc sources during the evaporation of metals and in the synthesis of metal nitrides results in an increase of the ion current. This is valid for discontinuous (interrupted) [3,4] and continuous [5] pulsed arc currents. According to literature [6], the addition of gas to the pulsed arc discharge is expected to reduce the number of multiple charged ions but increases the gas ionization. Therefore, the P3e™ approach has been investigated for its potential

---

* Corresponding author. Tel.: +423 388 4994.
E-mail address: juergen.ramm@oerlikon.com (J. Ramm).

0257-8972/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2009.10.055

to compensate for the loss of the substrate ion current for the deposition of oxides.

For the oxide synthesis in this work, Al–Cr composite targets were utilized for evaporation. The as obtained oxide layers show surprisingly clear multi-layer structures with bilayer thickness in the nanometer range for the DC as well as for the pulsed operation of the arc sources. The use of such multi-layers is of interest for applications in the field of tool coatings, especially if they can be produced in production systems. It is expected that the bilayer thickness of the multi-layer influences the size and the phase of the synthesized oxides. In addition, the multi-layer formation allows altering the intrinsic layer stress and may have consequences on the hardness and toughness of the synthesized oxides — basic requirements to optimize the oxide coatings for specific applications. Therefore, it was of interest to explain the origin of the multi-layer formation.

2. Experimental

The experiments were performed in an INNOVA production system of OC Oerlikon Balzers AG. The substrates (polished cemented carbide inserts and pieces of silicon wafers) were wet-chemical cleaned before deposition. After evacuation of the process chamber below 10^{-5} mbar, standard heating and etching steps were performed to ensure a good layer adhesion to the substrate. For the deposition of the samples in the experiments, only three arc sources were utilized. Two of them were equipped with a Cr target for the deposition of the interface. One powder-metallurgical Al–Cr composite target with a nominal composition of 70 at.% Al and 30 at.% Cr was used in the third source to synthesize the Al–Cr–O functional layer. Only one substrate-tree (4) (Fig. 7) was left at the substrate table (2). The substrates were mounted on this single substrate-tree at the height of the Al–Cr target. They experienced two-fold rotation: the slower rotation of the substrate table and the rotation of the substrate-tree placed at the periphery of the substrate table with a higher frequency. This “open loading” is quite artificial and different from production loadings, but it was chosen to gain more detailed understanding of the layer formation from a composite target.

An adhesion layer of about 150 nm Cr was deposited first. The arc sources were operated in pure argon gas during this process step. In the next step the evaporation of the Al–Cr composite target was initiated and oxygen controlled by a gas flow meter was added to the chamber. Simultaneously, the argon flow was ramped down and the two Cr sources were switched off after a few minutes. The deposition of the substrates with the Al–Cr–O functional layer was performed in pure oxygen atmosphere and with constant oxygen flow. The arc sources were operated either with DC current (sample A and C) or with pulsed current (sample B and D). An arc current of 200 A was chosen for the DC mode. In the pulsed mode, a continuous base current of 50 A was superposed with current pulses. This pulse operation has been described in literature before [7,8]. In our experiments, a single commercially available power supply was used which could be operated in the DC as well as in the pulsed mode. For the pulsed operation the pulse parameters (pulse width 0.5 ms, pulse height 420 A, frequency 666 Hz) were chosen so that the time average of the pulsed arc current was 200 A as well. For all depositions, a substrate temperature of 550 °C and a substrate bias of −60 V were selected. The low bias voltage was intentionally chosen to allow for a better tracing of the influence of substrate ion current and oxygen flow on oxide layer properties. The symmetric bipolar bias voltage had a frequency of 25 kHz with a negative pulse length of 36 µs and 4 µs positive pulse length. The low bias voltage results in an ion bombardment during the whole pulse of the arc current, however at energies which make sputtering of the substrate surface in pure oxygen atmosphere very unlikely. The deposition parameters are summarized in Table 1. Because the depositions were performed in pure oxygen reactive gas the total pressure given in Table 1 is about the oxygen partial pressure. Differing deposition parameters of additional experiments are mentioned in the description. A more detailed description of the deposition process and the P3e™ approach is given elsewhere [1].

Table 1
Process parameters for samples A, B, C and D.

	Sample A	Sample B	Sample C	Sample D
Target	AlCr (70:30)	AlCr (70:30)	AlCr (70:30)	AlCr (70:30)
Substrate bias [V]	−60	−60	−60	−60
Substrate temperature [°C]	550	550	550	550
Oxygen flow [sccm]	400	400	600	600
Total pressure [Pa]	1.0	1.0	1.7	1.7
Average arc current [A]	200	200	200	200
Arc current parameter	DC	Base: 50 A Pulse: 420 A Steepness: 10^6 A/s	DC	Base: 50 A Pulse: 420 A Steepness: 10^6 A/s

The substrate ion current was measured with an oscilloscope for the complete substrate holding assembly, i.e. the rotating substrate table and the rotating substrate-tree. It is the time average of the current during the negative bias pulse.

A LEO 1530 scanning electron microscope was employed to examine the morphology of the fracture cross-sections (X-SEM) of the oxide layers deposited on the cemented carbide inserts.

The layer composition was analyzed by Rutherford Backscattering Spectrometry (RBS) [9]. The measurements were performed using a 2 MeV, ^{4}He beam and a silicon surface barrier detector under 165°. The collected data were evaluated using the RUMP program [10]. Under these conditions, this method allows an analysis of the top layer down to a depth of about 500 nm.

The crystal structure of the layers was studied by X-ray diffraction analysis. The measurements were performed on a PANalytical X'Pert MRD PRO instrument using Cu Kα-radiation in the $\omega/2\theta$ mode. The ICDD-data base [11] was used to identify the crystallographic phases being present in the coatings. In the $\omega/2\theta$ scans, the peaks from the substrate (WC) are dominating with respect to the layer peaks. In order to obtain more information on the deposited functional layer and interface, the XRD measurements were additionally performed at a grazing incident angle of 1°. High resolution XRD was also used to determine the stress of selected layers deposited on silicon substrates. The curvature of the Si(001) substrate was determined by the “traveling peak” technique which consists in the measurement of Rocking Curves of the Si(004) reflection at different positions on the sample. The observed relative peak shift is used to calculate the curvature radius and the stress based on the Stoney [12] equation. The as obtained value of the stress combines therefore extrinsic and intrinsic stress.

The microstructure of the layer cross-sections was investigated by transmission electron microscopy (bright and dark field imaging). The cross-sections were prepared by the focused ion beam technique (FIB) using a Zeiss 1540XB cross beam instrument equipped with an ion and an electron column which allows to cut a thin TEM lamella and to weld it onto a TEM support grid under scanning electron microscopic observation. A TEM/STEM FEI Tecnai F30 microscope working at an accelerating voltage of 300 kV with a field emission gun was used. The microscope was equipped with a Si(Li) EDX spectrometer which allows high spatial resolution energy dispersive X-ray spectroscopy (EDXS) compositional analysis in combination with scanning transmission electron microscopy (STEM). The crystal structure of the coatings was studied by selected area electron diffraction (SAED).

3. Results and discussion

The substrate current as a function of time is shown in Fig. 1a for DC operation of the arc source and the process parameters of sample