Thin Solid Films 581 (2015) 99–106

Contents lists available at ScienceDirect

Thin Solid Films

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

Identification of the growth defects responsible for pitting corrosion on sputter-coated steel samples by Large Area High Resolution mapping

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ARTICLE INFO

Available online 11 December 2014

Keywords:
Physical Vapour Deposition
Magnetron sputtering
Corrosion
Salt spray test
Defect mapping
Growth defects
Pinholes
Titanium nitride

ABSTRACT

Coatings deposited by Physical Vapour Deposition techniques have been characterised for decades for their corrosion protection capabilities. The coating microstructure has often been stated to be the key factor. Improvements, mostly based on electrochemical corrosion measurements, often did not prove true when verified by neutral salt spray test. The pitting corrosion then observed has usually been explained by the presence of growth defects.

With the Large Area High Resolution mapping a method has recently been developed which allows localizing and characterising the growth defects responsible for pitting corrosion attacks. It is based on scanning the topography of the entire surface (several cm^2) of lab sized coated samples with a lateral resolution in sub-μm range by confocal microscopy. Using this method on the same sample before and after a corrosion test enables to trace back the corrosion pits to their responsible growth defects. Furthermore reliable defect statistics, defect maps and Cartesian coordinates for each individual defect are available.

The method is introduced in detail including issues that had to be solved like dust particles being present on the sample surfaces during the scan. Finally results for TiN coatings deposited by dc magnetron sputtering are presented. These results indicate that large as well as very small growth defects are the only reason for pitting corrosion attacks on the investigated samples. A corrosion relevance of different defect sizes is determined and correlations between the defect concentration and the appearance of the samples after the neutral salt spray test are presented.

1. Introduction

Today hard coatings are deposited on a multitude of different kinds of parts by different Physical Vapour Deposition (PVD) methods, mainly for wear protection and decorative applications. In most applications a contact of the coated parts with surrounding media is unpreventable. Even if most of the coating materials themselves are inert to corrosion, these media can get into contact with the substrate material in case that any kind of open path through the coating does exist, inducing local corrosive attacks driven by the different electrochemical potentials of the substrate and the coating. Since the area of the cathode (coating) is much larger than that of the anode (substrate) pitting corrosion is the predominant corrosion type.

Thin films deposited by various PVD techniques have been investigated for decades for their capabilities to protect metallic substrate materials from corrosive attack [1]. A poor microstructure with voids even not visible in a scanning electron microscope (SEM) has often been stated to be the key factor for the corrosion protection capabilities of a thin film [2–4]. Improvements were published, based on different electrochemical corrosion measurements like potentiodynamic polarization measurements [2,3,5]. However, these improvements often did not prove true when being verified by exposing the coated samples to neutral salt spray (NSS) test [6,7]. The pitting corrosion observed was explained by the presence of microscopically visible growth defects [6–8]. Other research groups directly related corrosion effects found in electrochemical corrosion measurements to the presence of growth defects [9,10], especially for the droplet rich arc bond sputtered coatings [11,12] or cathodic arc evaporation (CAE) deposited ones [13]. Often the abovementioned growth defects have been referred to as “macroscopic defects” in order to differentiate them from far smaller intercolumnar or intergranular defects (often named pores or pinholes) in the undisturbed growing coating. Different types of growth defects have been extensively characterised by Panjan et al. [14–17] by cutting these defects with the focused ion beam technique.

Growth defects mainly originate from any kinds of elevations present on the substrate before and/or during the coating deposition. These elevations (also called “seeds”) get overgrown by the coating and due to shadowing effects the growth on the elevation is far more coarse columnar than in the undisturbed flat regions of the substrate. These hillock shaped defects are referred to as nodules [2,8,18], hillocks [10], peaks [14], cones [14] or cauliflower defects. The elevations can be any kinds of foreign particles like coating flakes spalled off the vacuum chamber walls [15], environmental dust from the deposition laboratories or

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http://dx.doi.org/10.1016/j.tsf.2014.12.014
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production facilities, or residuals from the wet cleaning caused by insufficient purging or drying procedures. Another kind of elevations are micro- or macro-droplets emitted from the deposition source, the latter especially occurring in CAE, where they represent the majority of defects. Since foreign particles can have a poor adhesion to the substrate, large overgrown ones sometimes spall off during or after the deposition due to intrinsic film stress, leaving holes which are also named craters [14], pits [15], cavities [17] or dish-like defects [18]. Depending on the moment of the spall-off (during or after the deposition) areas of naked substrate may or may not be found on the bottom of these holes. Fig. 1 shows several forms of growth defects: hillocks, holes and partly broken out hillocks on an rf sputtered (Ti,Cr)BN coating. Panjan et al. gave a good overview of the different defect types and suitable terms [15]. To keep things simple in the following only the terms “holes” and “hillocks” will be used.

Small foreign particles stick to the surface mainly by electrostatic forces [16] as also known from semiconductor industry. So especially small ones cannot get blown off the substrates before insertion into the vacuum chamber and they also do not just drop off by gravitational force. Coatings without any types of growth defects can thus only be produced under cleanroom conditions and with special care paid to the wet cleaning procedures as well as defined clean conditions inside the vacuum chamber.

Given that growth defects have a major impact on the corrosion behaviour of coated steel substrates, the concentration of such defects on a certain substrate is of major interest. Up to now little effort has been made in that field. Panjan et al. [16,17] published defect density data measured by a 3D stylus profilometer for sputtered thin films. A detailed height distribution of the hillock defects is given, but only for a measured area of 1 mm^2 and the defect density values were commented as having a large scattering even for samples from the same deposition batch. Warren et al. [19] used Electrogenerated Chemiluminescence to find corrosion permitting pinholes i.e. to acquire exposed naked steel substrate by light emission detection in pH11 solution. He combined this technique with corrosion testing by Scanning Vibrating Electrode Technique. This has been done on a surface area of 1 cm^2, but with no indication of the lateral resolution of the method. It has basically been applied on coated steel sheets after forming procedures, hence especially looking for cracks and breaks in the coating. Growth defects have not been the target and no defect characteristics are available.

Since in CAE droplets from the target are the main source of macroscopic defects and the droplet concentration is very high, earlier effort has been made to gain concentration data. A lot of defect concentration values have been published by Creasey et al. [20] for arc bond sputtered coatings. In this hybrid process the interface is produced by CAE, followed by a magnetron sputtered coating. It is known that the majority of growth defects are caused by droplet emission from the arc source during the production of the interface [18]. The defect concentration data were gained by image analysis of SEM images for very small areas in the range of 0.03 mm^2. Since the published values show clear dependencies from the parameters and materials used during CAE, these small scan areas are presumably suitable to produce significant results for CAE processes.

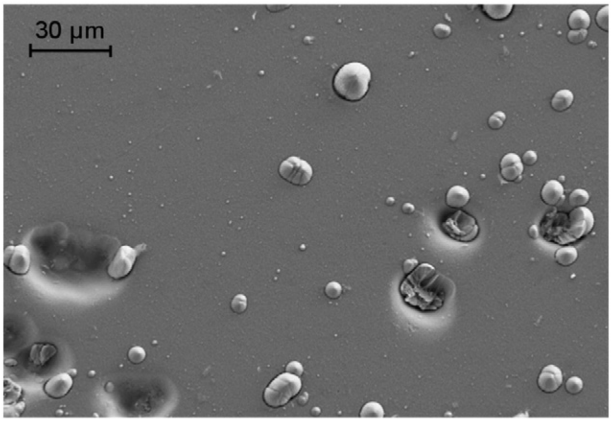

Fig. 1. Different forms of growth defects in an rf magnetron sputtered (Ti,Cr)BN coating.

However, especially for magnetron sputtered coatings with their overall low defect density the knowledge of the true number and concentration of growth defects on a certain sample is a crucial factor for corrosion studies as has been previously stated [6]. A method for determining these data could cause a major progress in evaluating the true corrosion protection capabilities of thin films.

2. Large area high resolution mapping

2.1. Technical details

In order to gain detailed data of the growth defects and their dimensions, the topography of complete samples has been three-dimensionally scanned by a confocal microscope Nanofocus µsurf custom. Confocal microscopes today are able to automatically execute a lot of scans in one run and combine these to one large single measurement (“stitching”). However, also with this method it is not possible to scan surface areas of several cm^2 due to memory limitations of today's computers. The Large Area High Resolution (LAHR) mapping is thus realised by performing the scanning as well as the subsequent evaluation of the data in batch mode, i.e. to handle each scan separately. In this way the number of scans and thus the size of the entire possible scan area in principle become infinite and are only limited by time consumption. The areas scanned for corrosion investigation of thin films on polished steel samples herein described ranged from 1.9 to 4.5 cm^2, all with an optical as well as digital lateral resolution of less than 1 µm. Even very small defects are thus detectable, of course for the price of generating huge amounts of data.

All scans for LAHR-mapping were carried out using a special 20-fold magnification objective lens (Olympus MPlan Apo) with high aperture (0.6) and a square shaped image section of 0.64 mm^2. This gave a digital resolution of 0.66 µm^2/pixel by using a one megapixel camera (984 × 984 pixels) and thus a detailed reproduction of defects as shown in Fig. 2. The batch mode combined with an autofocus ensured a continuous scan of large surfaces consisting of several hundreds of single scans. In order to clarify the terms herein used, the term “single scan” denotes one single 3D-scan, covering an area of (0.8×0.8) mm $= 0.64$ mm^2. The term “batch scan” stands for a continuous scan of a large fraction of a coated surface (between 1.9 and 4.5 cm^2) consisting of several hundreds of adjacent single scans (between 300 and 675).

The evaluation of the data including the detection, classification and counting of the defects is carried out by the software “Mountains Map®” (Digital Surf) using self-built templates. Beside a depiction of the surface (Fig. 3) this complex template executes a low frequency filtering to eliminate curvature, and subsequently a binarisation of the measured 3D-profile at certain threshold height or depth levels. For this binarisation the 3D-profile is virtually cut at each chosen level above (or beneath) the level of the undisturbed coating surface. Each place where a cut occurs is counted as a defect, i.e. each binarisation turns the 3D profile into binary data: “defect” and “no defect”. Furthermore the size of each individual cutting area (=defect size at a certain height/depth) is measured and three lateral size ranges are defined (see Fig. 4 for details). By using different height and depth levels all defects can get ranked into a tight classification pattern (details see Section 2.2).

The result of this evaluation process is a) several hundreds of evaluated single scans, each one showing a fraction of the surface as 3D-image as well as b) the numerical data containing the number of defects for each defined defect class for each single scan in an ASCII-file. This file again has to undergo several further evaluation steps. In order to