Surface & Coatings Technology 290 (2016) 77–81

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Direct metallization of PMMA with aluminum films using HIPIMS

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ARTICLE INFO

Article history:
Received 29 June 2015
Revised 26 October 2015
Accepted in revised form 29 October 2015
Available online 30 October 2015

Keywords:
High power impulse magnetron sputtering
HIPIMS
HPPMS
Plexiglas
PMMA
Metallization
Direct metallization
Adhesion
No pretreatment
Ionization
Tape test
Cross cut test
Aluminum

ABSTRACT

Ionized sputtering like high power impulse magnetron sputtering HIPIMS opens new horizons for cost effective, environmental friendly plastic metallization with excellent adhesion. First reports on HIPIMS deposited films on polymer foils, textiles, and different untreated plastics showed significant adhesion improvement of the metallic or oxide coatings applied. Plexiglas (PMMA) is a very attractive substrate material due to its properties for several commercial applications. Since PMMA is very sensitive to the UV radiation of technical plasmas, direct metallization of the surface by sputtering is conventionally not possible. Using ionized sputtering it is shown that the adhesion can be enhanced to excellent level, passing a combined cross cut and tape test without any failure. The study of the interface correlated to the different peak current densities of the HIPIMS processes shows some trends for the significant adhesion improvement. With increasing peak current in the HIPIMS discharge, i.e. increasing degree of ionized species forming the film, the adhesion is significantly improved. The failure mechanism changes from adhesive failure and poor adhesion to a cohesive failure and excellent adhesion. Furthermore, the surface of the polymer was modified as a result of the increasing ionization. The PMMA surface reorganizes and roughens due to ions forming the film and additionally electrons providing local thermal annealing by recombination.

1. Introduction

Environmental friendly metallization of plastic parts today mainly uses evaporation or magnetron sputtering. The benefits of evaporation are a high deposition rate and low thermal loading of the substrates. Its main drawback is that, sometimes, it results in weak adhesion. Regardless of the process used, pretreatments, lacquers or interface coatings usually have to be applied prior to metallization [1–5]. Therefore, the main challenge is a reliable and improved film adhesion. The ideal case would be a PVD process that could directly deposit excellent adhering coatings, without any pretreatment.

High Power Impulse Magnetron Sputtering (HIPIMS) is a powerful PVD technique based on the common Magnetron Sputtering process [6–8]. The difference to commercial sputtering is that the HIPIMS discharge generates plasmas with very high ionization degree of the film forming sputtered species, which can reach up to 90%, depending on the material. Since ions can be guided by electric or magnetic fields, it is now possible to coat pieces with complex geometry more conformal. Furthermore, the ionized particles of the sputtered material can reach the substrate with more energy than neutral particles. This provides a higher mobility of the film forming species and can lead to denser films with higher quality microstructure. The bombardment of the substrate with energetic ions can also lead to ion implantation and modifications of surface morphology. This can improve the film's adhesion. The HIPIMS discharge produces also hot electrons at the beginning of the pulse, which can cause further surface modifications, once they are absorbed by the substrate.

In spite of all these advantages, only very few work on HIPIMS deposition on polymer substrates is published. Nevertheless, all publications point out that the adhesion can be improved. For instance, high quality and adherent brass and silver coatings on polyethylene terephthalate substrates were reported with HIPIMS [9–10]. Also, aluminum oxide was deposited onto a polymer substrate by DC magnetron sputtering and HIPIMS. A comparison between both processes showed improved adhesion for HIPIMS [11]. Furthermore, a reactive plasma pre-treatment using HIPIMS was proposed to improve adhesion of films to polymer substrates [12]. At the Fraunhofer Institute IST, simple preliminary investigations were carried out using titanium as metal on different untreated plastics (PPSU, PEI, PEEK, PESU, PSU). The results showed significant adhesion improvement of the HIPIMS films, using a simple tape test for evaluation, compared to mid-frequency sputtering [13].

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http://dx.doi.org/10.1016/j.surfcoat.2015.10.070

This work focusses on the deposition of aluminum on Plexiglas (PMMA). Since PMMA is very sensitive to the UV radiation of technical plasmas, direct metallization of its surface by sputtering is not possible [14–15]. In contrast to DC sputtering, by HIPIMS it was possible to enhance the adhesion of aluminum on PMMA to an excellent level, passing a combined cross cut and tape test without failure. The very adherent films were produced with a single step. No pretreatment or interlayer was necessary. AFM and FTIR investigations of the coated substrates were carried out to explain the adhesion improvement.

2. Material and methods

For the deposition an Inline Coater™ IC 300 from Impact Coatings AB was used. The machine has one load lock and three very compact sputtering chambers (300 × 180 × 50 mm). The evacuation of the load lock takes less than a minute time. Then the samples will be moved to the process chamber. For the investigations one chamber was equipped with a planar aluminum target, with purity of 99,95%. The nominal target area was approximately 210 cm^2. For the HIPIMS investigations a HPP 2000/1000 pulsing unit from Magpuls GmbH, powered by a Pinnacle 12 K 400 DC power supply by Advanced Energy was used. The processes were operated in voltage control. The charging voltage was modified to reach a certain peak current. Then the off-time was modified to adjust a fixed average power.

DC depositions were performed at a working pressure of 1 Pa and an average power of 3 kW. The PMMA samples were just softly wiped with a cleanroom cloth and isopropanol. The deposition time was between 30 s and 2.5 min. HIPIMS depositions were performed at 1 Pa and 1.5 Pa. An average power of 3 kW and a pulse on-time of 250 μs were kept constant. The peak current was varied along with the charging voltage. For films deposited at 1 Pa, peak currents were 50 A, 100 A, and 160 A (0.24, 0.48, and 0.76 A/cm^2). For films deposited at 1.5 Pa, peak currents were 100 A, 200 A, and 300 A (0.48, 0.95, and 1.43 A/cm^2).

After deposition, the surface and interface of the coatings were characterized by atomic force microcopy (AFM). First, the morphology and roughness of the coating surface was analyzed. Then, the aluminum coating was removed with NaOH and the same analyses were performed at the remaining polymer surface. In addition, the aluminum coating was mechanically peeled off. Therefore a two component epoxy was applied on top of the Al-coating. After hardening of the epoxy a crack was initiated at the interface using a sharp knife. Then the epoxy with the aluminum was peeled off from the PMMA substrate. Both, the remaining polymer and the aluminum interfaces were then analyzed. Furthermore, the interface towards the substrate of the removed aluminum was characterized with grazing incidence microscopic FTIR spectroscopy (Bruker Vertex 70, Hyperion 1000), in order to detect the possible presence of residual organic material. The adhesion of the aluminum film was investigating by performing a tape test on cross cuts, according to the DIN EN ISO 2409 standard.

3. Results and discussion

Due to the high degree of ionization in HIPIMS a better surface mobility, subplantation, surface heating or modification is expected. These effects shall lead to improved coating adhesion. First tests were carried out using titanium on different plastic substrates [13]. As reference process mid-frequency sputtering was used. Titanium was selected since it is one of the most studied material using HIPIMS deposition [16–18]. It turned out that without any pretreatment direct metallization was possible by HIPIMS. Furthermore, the film adhesion was overall improved for any used substrate. Following this results Plexiglas (PMMA) was used for direct metallization with aluminum. In general, UV radiation, as provided from the plasma will modify and weaken the PMMA and result in very poor adhesion. Therefore, state of the art for coating Plexiglas is either using a lacquer, or evaporating thermally an interface layer like SiOx prior to plasma coating. Following the successful preliminary investigations and reports on different plastics, investigations on direct metallization of PMMA with aluminum were carried out.

3.1. Influence of the peak current density on the adhesion

Following the first evaluations, it seemed that the increased ionization allows for direct metallization, without prior etching or activation. Furthermore, PMMA would suffer from a plasma pretreatment more than benefit. Therefore, the peak current, which is correlated to the ionization [19] was varied. The coated PMMA samples were tested with respect to adhesion using a cross cut test following DIN EN ISO 2409 combined with tape test.

Fig. 1 shows the aluminum coated PMMA samples. At the left side of the sample a tape test and on the right hand side a combined cross cut and tape test were performed. Starting with a DC reference very poor adhesion, as expected is observed (Fig. 1a). With increasing peak current density, i.e. increasing ionization the adhesion is steady improved (50 and 100 A, Fig. 1b, and c, respectively) and 150 A peak current results in good adhesion (Fig. 1d). Further increase in peak current leads, as discussed in the following showed excellent adhesion (300 A).

3.2. Topographic investigation of the coating-substrate interface

Following the results of the cross cut and tape tests (Fig. 1), the surface and interface of the samples were investigated to gain insight in the measured adhesion improvement. All samples were prepared at a pressure of 1.5 Pa and an average power of 3 kW using a HIPIMS pulse with 250 microsecond pulse length. The off-time was modified to match the average power. The peak current was set to 100, 200, and 300 A by varying the charging voltage of the power supply. The adhesion improved from poor adhesion (100 A) over good (200 A) to excellent adhesion (300 A). All deposited aluminum films were opaque. The coating thickness according to reference samples was approximately 50 nm.

For the investigation, the coated PMMA samples were first mapped using atomic force microscopy. After that, the aluminum was removed chemically using NaOH and the remaining surface was mapped again. Since PMMA shows a high resistance against NaOH, no effect on the surface topography by the aluminum removal is expected. Additionally the aluminum coating was mechanically peeled off using a two component epoxy, as described earlier. Both, the resulting polymer and the aluminum interfaces were analyzed. Finally, FTIR microscopy under grazing incidence spectroscopy was performed for the spectroscopic analysis of the removed aluminum interface.

First the surfaces of Al coated PMMA samples for peak currents of 100 A, 200 A, and 300 A were investigated. Fig. 2a shows the bare PMMA substrate surface. The sample with the lowest peak current of 100 A shows a very smooth surface with a RMS of 7 nm (Fig. 2b). The resulting film adhesion according to the cross cut and tape test was poor. Increasing the peak current in the coating process leads to an increase of the coating adhesion for 200 A peak current (Fig. 2c). From the AFM measurements this is accompanied with an increase in roughness (RMS: 26 nm). Excellent adhesion is observed for peak current of 300 A. The resulting RMS roughness was 35 nm (Fig. 2d).

With the increasing peak current, also a higher fraction of the film forming species is ionized. Furthermore, a higher number of ions with high energy is generated. This leads to higher energetic bombardment of the growing film. Therefore, an increased surface temperature is expected. This higher surface temperature will result in a modified topography. Several papers report on a wrinkle-like formation of polymer surfaces, induced either by plasma treatment and consequent heating to glass transition temperature, or by deposition of metal and consequent heating to glass transition temperature [15,20–22]. Since no additional heating was applied, the thermal energy was most likely delivered by the arriving ions. Additionally the electrons, created at the beginning of each pulse also arrive on the substrate surface. For