Electrochemical analysis of strain-induced crack formation of bilayer barrier plasma polymer films on metal and polymer substrates

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ABSTRACT

Barrier performance and crack formation of amorphous silicon a-Si(O, H)/diamond-like carbon (a-C:H) bilayer thin films were studied under uniaxial stretch forming. The plasma polymer films were prepared on bare and PET film coated stainless steel substrates to enable the investigation of the influence of different substrate mechanics on the crack formation. In-situ electrochemical impedance spectroscopy (EIS) results indicated that film thickness reduction and onset of crack formation depend on the substrate mechanics. The reduced residual compressive internal stresses on the PET coated metal substrate caused film failure as early as at 3% strain. On the contrary, for the bare metal substrate, first cracks were observed at 8% strain, typically at defect sites. Moreover, it was demonstrated that for such a bilayer film system, individual layers can fail independently, indicating the importance of local stress fields.

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1. Introduction

Plasma deposited silicon oxide (SiO_x) thin films are widely investigated as diffusion barriers for polymeric materials in pharmaceutical or food packaging industry or as corrosion protective layers for metallic substrates [1–5]. High barrier performance against oxygen and water vapor, low cost and applicability to complex surfaces make the plasma-deposited SiO_x coatings excellent alternatives to conventional metallic coatings. One of the major drawbacks of such films is their limited flexibility. Strain induced crack formation leads to a loss of barrier properties already at about 2–3% strain [6]. Titz and Grundmeier studied the flexibility and crack formation of SiO_x plasma polymer films on zinc coated steel substrates by means of in-situ electrochemical analysis. They observed a strong decrease in the barrier properties at about 2.5% strain along with grain orientation dependent crack formation [7,8].

Failure of brittle films on ductile substrates has been experimentally and theoretically studied [9,10]. Typically, coating failure such as cracking or delamination of the coating is driven by the residual film stresses forming during the film deposition where the sign and the magnitude of the residual film stresses play a critical role on the mechanical response of the coating [11]. In addition to the intrinsic stresses, external forces (thermal or applied tensile stress) usually lead to sequential crack formation where the crack density as a function of external strain can be explained by shear lag models [10].

Plasma-deposited thin films based on aliphatic precursors, such as hydrogenated amorphous carbon (a-C:H) or so-called diamond-like carbon (DLC) films are promising alternatives as they combine chemical inertness with a variable state of crosslinking [12–14]. Moreover, a combination of excellent properties, such as high hardness, wear resistance, lack of magnetic response, and chemical inertness against a wide range of pH, increases the interest in DLC coatings [15]. One of the challenges for the applicability of DLC layers is the poor adhesion to metallic substrates. Gradient layers or bilayers of amorphous silicon/DLC are proposed to optimize adhesion, mechanical stability, and barrier performance. A silicon oxide interlayer acts as an adhesion promoting layer making silicide bonds between the metal surface and the amorphous carbon layer [16,17].

Typically, the mechanical characterization of DLC films includes hardness measurements, fracture toughness, elastic modulus, and scratch testing. Such tests give insight to the structure–property relationship of DLC films, such as change of hardness and elastic modulus with sp^3/sp^2 bonding ratio. However, the above mentioned characterization tools fail to disclose the barrier performance as a function of external mechanical load, particularly when the picture becomes complicated, as in the case of bilayer or multilayer systems.

In this study, mechanical and barrier performance of a-Si(O, H)/a-C:H bilayers were investigated on stainless steel and PET coated stainless steel substrates. A combination of in-situ electrochemical impedance spectroscopy (EIS) and FE-SEM imaging was performed to monitor the barrier performance as a function of strain. Presented results indicate the decisive role of the substrate for achieving optimized barrier performance under mechanical load.

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2. Experimental

0.5 mm thick stainless steel sheets (type 1.4301, 18% Cr, 8% Ni) were mirror polished and cleaned in acetone in an ultrasonic bath to remove surface contaminations from polishing. To improve the adhesion of PET films on stainless steel substrates, an adhesion promoting layer of (3-Aminopropyl)triethoxysilane (99%, Sigma-Aldrich) was prepared by immersion of the substrate in a 1 mM aqueous solution followed by extensive rinsing with pure water and heat treatment at 105 °C.

Spin coating of PET was performed with the following procedure: 0.25 wt.% PET was dissolved in hexafluororisopropanol (HFIP) (99%, Sigma-Aldrich) using a reflux condenser to prevent solvent evaporation. The solution was heated up to 80 °C under constant stirring. Typically, 100 μl of solution was used for each sample for the spin coating procedure. Optimized coating parameters are as follows: rotation speed = 3000 rpm, ramp = 1000 rpm/s, spinning duration = 60 s. After coating, samples are kept under the fume-hood to allow the residual HFIP to evaporate. Thickness and coverage of spin-coated PET film was characterized with AFM imaging and nanoshaving. High-load was applied to the surface in contact mode in order to remove the material from the surface. Thickness of the scratched area was checked with tapping-mode AFM.

Due to the nature of the spin-coating process, it is expected that there is a thickness gradient on the prepared films, where the center of the substrate is predictably thicker than the edges. For this reason, the local electrochemical measurements were performed in the middle of the samples in order to ensure comparable PET thickness.

Barrier coatings were deposited by means of a capacitively coupled plasma. Its design is based on a GEC reference cell [18], and is described in detail elsewhere [19]. Briefly, the reactor consists of two parallel electrodes of 100 mm diameter, which are 30 mm apart. The lower electrode, which holds the samples, is powered at 13.56 MHz. The upper electrode is connected to the chamber walls and grounded. Therefore, it has a much larger surface, inducing a self-bias potential at the powered electrode.

The barrier coatings consist of two layers, deposited in two consecutive steps: first, a 10 nm a-Si(O, H) layer was deposited from SiH$_4$:crystal Mixture: Silan, Ultra high purity 10% + Argon N50 (90%) (Air Liquide GmbH, Düsseldorf, Germany) at a flow of 50 sccm, a pressure of 3 Pa and a self-bias voltage of −165 V. Second, a 20 nm a-C:H layer was deposited from acetylene (UN 1001, Messer Griesheim GmbH, Krefeld, Germany) at a flow of 20 sccm, a pressure of 1 Pa and a self-bias voltage of −275 V. The deposition rates for a-C:H and Si(O, H) films were determined using a Veeco Dektak 6 M Stylus profilometer, by measuring a large (<500 nm) step between the coated and an uncoated area on a silicon wafer. Those deposition rates where validated for smaller film thicknesses (10–100 nm) using a J.A. Woollam Vase ellipsometer. A Tauc–Lorentz model and a parametric semiconductor-layer model was used for the for a-Si(O, H) and a-C:H films, respectively. The deposition time was then set accordingly to achieve the desired film thickness. More details of the plasma deposited bilayer can be found in Ref. [19]. Overview of the studied barrier films is given in Table 1.

To assess the induced intrinsic stress, often the curvature of a silicon wafer before and after the deposition has been measured and inserted in the so called Stoney formula [20]. In order to investigate the influence of different substrate materials, we deposited an a-C:H layer on a silicon wafer and a PET strip (Hostaphan 500 μm thick, co-extruded, biaxially oriented PET from Mitsubishi Polyester Films Wiesbaden, Germany) with different bias voltages. The bias is often regarded as the key for the control of the stress in a-C:H layers, because it directly influences the energy of ions impinging on the substrate surface [21]. The radius of curvature was measured using a Dektak 6 M Stylus Profiler (Veeco Germany, Mannheim).

Electrochemical impedance measurements were performed with a Reference 600 potentiostat (Gamry Instruments, USA). In the capillary cell (Fig. 1), a three-electrode setup was used where the sample (working electrode) was exposed to an area of 0.20 cm^2. A gold counter electrode and a Ag/AgCl reference electrode with a potential of +198 mV against a standard hydrogen electrode (SHE) was used. All electrochemical experiments were carried out in borate buffer solution, prepared with 0.2 mol/L H$_3$BO$_3$ (≥99.8%, Sigma-Aldrich), 0.05 mol/L Na$_2$SO$_4$ (99.5% VWR), 0.05 mol/L Na$_2$B$_7$ ∗ 10 H$_2$O (≥99.5%, Sigma-Aldrich). Electrochemical impedance spectra were obtained at the open circuit potential with an AC amplitude of 20 mV in the frequency range of 0.1 Hz up to 100 kHz before and after stretch forming. Rectangular specimens with a size of 50 × 10 × 0.5 mm were placed in a linear tensile testing device from Kammrath & Weiß GmbH (Dortmund, Germany). Strain was applied along the long axis with increments of 0.5–1% elongation. Electrochemical Impedance measurements were performed after each forming step. A flexible silicon ring was used to seal the buffer solution and was kept in contact with the substrate surface during forming, where the measurement position was not changed during forming. A force gauge was used to monitor the applied contact pressure by the glass capillary. Fig. 1 shows the experimental setup for EIS measurements.

Film chemistry was investigated with Raman spectroscopy (In-Via, Renishaw, Gloucestershire, UK). The Raman spectra were excited by a frequency doubled Nd:YAG-Laser at 532 nm with a power of 50 mW and a 50× objective was used. The spectrum was fitted with Gaussian function to obtain D and G band ratio. FTIR measurements were performed with VERTEX 80v (Bruker) spectrometer at a resolution of 4 cm^{-1} and 256 single scans were collected for each measurement. Film morphology and forming-induced cracking of bilayer films was investigated by means of a NEON 40 FE-SEM (Carl Zeiss SMT AG, Oberkochen, Germany) using a field emission gun.

Table 1
Overview of the studied barrier films.

Substrate	Interlayer	Barrier coating
Stainless steel	PET (200 nm)	–
Stainless steel	PET (200 nm)	a-Si(O, H) (10 nm)/a-C:H (20 nm)
Stainless steel	–	a-Si(O, H) (10 nm)/a-C:H (20 nm)
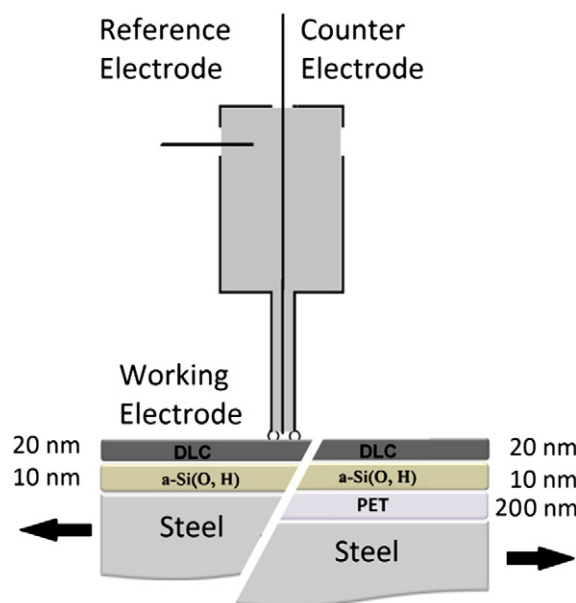
Fig. 1. Schematic illustration of the electrochemical analysis of multilayer barrier films on metal and polymer substrates composed of a-Si(O, H) and a-C:H layers.