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Self-organized pattern formation on silicon, stainless steel and zinc coated steel substrates

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ARTICLE INFO

ABSTRACT

In this research, a self-organized pattern formation employing polystyrene/aluminum bilayer coatings on three different substrates was studied. Two new substrate materials, stainless steel and zinc coated steel for self-organization application were introduced. Influence of polystyrene molar mass on pattern formation was studied with five different polystyrene samples having molar masses between 27 and 247×10^3 g/mol. Polystyrene/toluene solutions were applied onto the substrates using the spin coating technique and aluminum layer was created by chemical vapor deposition (CVD). Self-organized pattern formation was induced thermally, by heating the layered substrate/polystyrene/aluminum structures above the glass transition temperature of polystyrene. Sub-micron–micron sized wrinkles or island-like surface patterns were achieved on all substrates. The molar mass of polystyrene was found to have effect on the dimensions of the formed structures. It was also observed that the characteristic surface structure of substrates influences self-organization and thereby directs the structure formation.

1. Introduction

Spontaneous pattern formation of layered structures is a phenomenon probably best known from human skin, as wrinkling [1]. In many cases, especially in the field of materials engineering, the spontaneous and uncontrolled wrinkling has been previously considered as an undesired phenomenon. In novel materials science the structure formation by self-organization is also seen as a versatile tool that can replace the conventional lithography processes [2–6].

During past few decades self-organized pattern formation in systems having different kinds of layered structures has been widely studied. Factors and mechanisms affecting the pattern formation have been investigated using both experimental and theoretical [7,8] approaches. Concerning a substrate/polymer/metal trilayer system, the thermal wrinkling of a thin and stiff superstrate layer occurs when the sandwich structure is heated above the glass-transition temperature (T_g) of polymer [3,9]. At the used temperature polymer changes to a rubbery state and loses its mechanical stiffness. A high increase in the thermal expansion property of the polymer produces thermal stress to the system. The wrinkling of the polymer/metal bilayer starts when the compressive stress of the system exceeds the critical stress value of

the wrinkling [9–15]. Several factors are reported to have influence on forming structures, like thickness of the polymer layer and the physical and mechanical properties of the materials used to form the trilayer. Differences in thermal expansion coefficients and Young's moduli of the used materials are considered as the most dominating factor in wrinkling. A sufficiently large difference in thermal expansions of superstrate and substrate ensures a compressive stress to be formed in the substrate/polymer/superstrate interfaces [13,16–18].

In previously reported studies on self-organization of polymers, silicon has been widely used as a hard substrate [2–4]. From a scientist point of view silicon is good substrate material because it is easily available as ready-to-use wafers, quite cheap, inert and can be thought as a standard substrate, which makes the results comparable with each other. On the other hand silicon is very fragile which makes use of material, especially on a larger scale, unfeasible. In this research, silicon has been considered as a reference substrate.

In this study, two new substrate materials are introduced. Stainless steel (SST) and zinc coated steel (ZST) have not been used before as hard substrates in the study of self-organized pattern formation in PS/Al coatings. Moreover, the influence of the characteristic surface patterns of the substrate material and molar mass of PS on the self-organized pattern formation and dimensions of the formed patterns is studied.

2. Experimental

Single side polished silicon wafers (Ø 100 mm, <1 0 0>, Compart Technology Ltd.), SST wafers (Ruukki Metals, 304, Ø 100 mm,

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Table 1
GPC and DSC analysis results of PS samples.

M_W (g/mol)[a]	M_W (g/mol)$_{experimental}$	Dispersity	T_g (°C)
PS35000	27,000	103	63
PS97400	62,000	1.8	103
PS192000	163,000	3.9	103
PS280000	247,000	5.1	102
PS350000	229,000	3.9	101

[a] Molar mass from the supplier.

thickness 0.5 mm) and ZST wafers (Ruukki Metals, 355, Ø 100 mm, thickness 0.5 mm) were cleaned in trichloroethylene and methanol, 5 min each, using ultrasonic treatment and dried under nitrogen. The native oxide layer of silicon wafer was retained.

Polystyrene/toluene solutions with concentration of 10% (weight/volume) were made from five PS materials having M_W molar masses of 35,000, 97,400, 192,000, 280,000 and 350,000 g/mol (Sigma–Aldrich Co.). Solutions were spin-coated (8 s 1000 rpm, 60 s 3000 rpm) onto silicon, SST and ZST wafers. After spin-coating the wafers were kept at 60 °C for 12 h to remove the residual solvent and stress formed in coating [19]. The thickness of the PS layer on the wafers was determined by a stylus pro-filometer (Veeco Dektak 150; rate 500 μm/20 s, tip 12.5 μm). Pure aluminum (99.999%) was evaporated (1.5×10^{-5} mbar; 1–8 Å/s) (Leybold-Heraeus Univex 300) on top of the wafers in thickness of 50 ± 4 nm to construct the capping layer. Coated wafers were kept at 130 °C for 12 h for wrinkle formation.

An atomic force microscope (AFM, Thermo Microscopes Explorer) was used to determine the structures and the dimensions of wrinkled bilayer coatings on silicon, SST and ZST substrates. The non-contact mode of AFM (Antimony doped Si tip, f_0: 200–410 kHz, k: 20–80 N/m) and the line analysis and the peak/valley measure-ment tools of SPMlab 5.01 software were employed to analyze the dimensions of the patterns. The minimum peak height was set to 5 nm.

The values of the experimental molar masses and dispersities of PS having different M_W were determined by gel permeation chromatography (GPC, Waters GPCV2000, 45 °C, THF 1 ml/min) employing the Styragel HT5, HT4 and HT3 columns and PS stan-dards 4000–4,000,000 g/mol. To determine the T_g values of the PS samples, differential scanning calorimetry (DSC, Mettler Toledo 823^e) with aluminum standard crucibles with a pin, was used. The determination method consisted of two cycles and each cycle com-prised of heating and cooling the sample at the rate of 10 °C/min. The first cycle was performed to remove the thermal history of polystyrene. The glass transition temperature was obtained from the second heating [20].

3. Results and discussion

The GPC was employed in determination of the actual values of the molar masses and dispersities of the polystyrenes. The glass transition temperatures were obtained by DSC.

The GPC results listed in Table 1 reveal large deviations of 30,000 g/mol between the given and experimental molar masses of PS. In case of molar mass 229,000 g/mol the difference between determined and given value of the M_W is over 100,000 g/mol, which is significant.

For most of the polystyrenes dispersities determined by GPC varied from 1.8 to 5.1. The M_W/M_n value of PS35000 with the molar mass of 27,000 g/mol was 103, which is considerably high and much higher than the corresponding values of the other polystyrenes, which varied between 1.8 and 5.1. The high dispersity value is explained by a bimodal molar mass distribution. For the other

polystyrene samples employed, the molar mass distributions were unimodal.

The results of the DSC measurements show that T_g values of the polystyrenes PS97400, PS192000, PS280000 and PS350000 were between 101 and 103 °C, which are normal T_g values for PS. In the literature the T_g of polystyrene is reported to be approximately 100 °C [16]. For PS having the molar mass of 27,000 g/mol, the T_g value is 63 °C which is an atypical value. The measurement was repeated several times to confirm the result. The high dispersity and abnormal T_g value of PS35000 are likely to be related. The smaller molar mass PS fraction can act as a plasticizer in the material and thereby lowers the T_g value [21–23].

The uncoated substrates (silicon, SST and ZST wafers) were characterized with AFM (Fig. 1). Silicon wafer is a homogeneous substrate and does not contain any visible surface structure. According to AFM the silicon substrate contains surface structures with the average height of 5 nm. The roughness on the surface may be due to dust particles from the air or the non-contact AFM mode. The average heights of surface structures of uncoated SST and ZST wafers were 300–500 nm, determined by AFM. The surface of SST wafer is considered heterogeneous due to the surface structure. Closer observation on SST wafer reveals the two-level character of the surface. The uncoated surface comprises plate-like struc-tures. The lateral size variation of the individual plate structures is notable. This microscopic surface structure is repeated similarly over the wafer, and therefore the surface is quite homogeneous. The surface structure of the ZST wafer, with the uppermost layer con-sisting of zinc, is heterogeneous and dimensions of the plate-like surface structures vary considerably over the wafer [24].

The thickness of the PS layer on silicon wafer was determined to be about 1 μm. On SST and ZST wafers the average thickness of PS layer was about 400–500 nm. The difference in PS layer thicknesses between the silicon wafer and the SST and ZST wafers is due to the high roughness of the uncoated SST and ZST surfaces. Some of the PS/toluene solution is used to level out the rough surface and fill the pits. To confirm the repeatability of the results at least three parallel samples were prepared. The self-organized surface patterns were characterized with AFM and the dimensions were determined from several points of each sample wafer.

Due to the different structural roughness of SST and ZST sur-faces it was expected that the characteristic surface structure of the uncoated substrate will direct self-organized pattern formation. Wrinkles or wrinkle-type structures were formed on all substrates and the shape and dimensions of the wrinkles varied on the basis of substrate and molar mass of PS (Fig. 2). No fractures were observed on the top of the patterned wafers indicating that adhesion between the layers was sufficient for the structure formation.

On the silicon substrate the wrinkle patterns are wave-like, labyrinthine-type and randomly orientated regardless of the molar mass of PS employed. The changes in the dimensions of wrinkles due to change of M_W of PS can be clearly observed in the AFM images a1–a2 (Fig. 2). For polystyrene with the molar mass of 27,000 g/mol the size scale of the formed structures is considerably larger com-pared to PSs with the other molar masses.

On the SST substrate the shape of the self-organized patterns changes from wave-like to bumpy structures due to increase in the molar mass of PS. The structures possessing shape of wrin-kles are achieved employing PS samples having molar masses of 27,000 and 62,000 g/mol. Employing PS192000, PS280000 and PS350000 a gradual change to more bumpy structures is observed. Structures with the largest heights are achieved by using the PS having the smallest molar mass and hence the shortest chain length.

Even with the same polystyrene samples employed, the shape of the self-organized structures on silicon and SST wafers differ sig-nificantly from each other. The pattern formation is influenced and