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J. Dejeu, R. Salut, M. Spajer, F. Membrey, A. Foissy, et al.. Self assembled film thickness determination by focused ion beam. Applied Surface Science, 2008, 254 (17), pp.5506-5510. 10.1016/j.apsusc.2008.02.114 . hal-00266004

HAL Id: hal-00266004

<https://hal.science/hal-00266004>

Submitted on 21 Apr 2021

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Self-assembled film thickness determination by focused ion beam

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The thickness evolution of multilayer film is investigated by focused ion beam (FIB) in the domain of polymer multilayers. This method, currently used in the modification and the characterization of integrated circuits, proves it is possible to determine the polymer film thickness. Sample cutting and its observation of the cross-section are performed in the FIB without leaving the vacuum chamber. Two main conclusions can be drawn: (1) the roughness of the film increases with the number of layer deposit, (2) the film growth changes from nonlinear (called exponential) to linear beyond 300 nm (70 layers).

The self-assembled polyelectrolytes films are obtained by successive and alternate adsorption of two polyelectrolytes of opposite charge. This procedure was previously described by Decher in the early 90s [1]. Recent reviews on the subject show that many theoretical and practical aspects of the interaction between the two polymers along with the film growth remain ambiguous and debated [2]. The multilayer film formed layer by layer is an efficient method for controlling the shell permeability [3] or the release of the active matter in electronics [4], electrocatalysis [5] and many other areas [6]. Controlled release was performed with an appropriate choice of the thickness and porosity of the shell, the polyelectrolytes properties (hydrophobic, hydrophilic) and the incorporation of counterions [7]. Two types of multilayer growth process were reported: films with thickness that increases linearly with the number of deposition steps [1] and other systems whose thickness growth is nonlinear and usually called exponential [8]. Linear growth is due to the fact that during the build-up process the

polyelectrolyte from the solution interact only with a polyelectrolyte of opposite charge forming the outer layer of the film [1]. For the “exponential” growth, on the other hand, it was stated that it results from the diffusion “in” and “out” of the whole film of at least one of the polyelectrolytes which constitute the multilayer [9]. However, this view appears oversimplified since the recent observation that the exponential growth regime only holds in fact over a limited number of deposition steps, before the crossover to a linear growth regime [10]. The thickness increment is usually much smaller in the linear regime than in the exponential one (typically a few nanometers versus hundreds of nanometers). For the couple of polymers studied here, the two types of growth process are found: linear [1] or exponential [11], depending on the pH of construction condition.

The thickness of the multilayer film is usually measured by ellipsometry [12], AFM [13], confocal spectroscopy [14], X-ray [15], laser reflectometry [16], and optical waveguide lightmode spectroscopy (OWLS) [17]. All these techniques can be used with any auto-assembled films but have specific advantages: the two first methods require a sample with a small roughness, the confocal a transparent sample and the last one a thickness film inferior to near 200 nm [18]. In this study, the deposition of multilayers is

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realized on silica substrate. The roughness obtained for a great number of layers forbids the traditional techniques. They are replaced by FIB milling [19]. The focused ion beam (FIB) is an important tool in failure analysis, defect characterization, design modification, and process control in a variety of industries. In this work, it is used to cut the film and measure its thickness. Scanning ion microscopy (SIM) offers a spatial resolution of 5 nm, with different contrast mechanisms than those of electron microscopy. With this technique, we have determined the thickness of different thick auto-assembled films (up to 320 layers) and then deduced the type of growth.

2. Experimental procedures

2.1. Materials and chemicals

The sodium salt of Poly(4-styrenesulfonate) (PSS) with an average molecular weight 70 kDa was purchased from Alfa Aesar. PSS is a strong polyacid that is totally ionized in the whole range of pH used in this study. The Poly(allylamine hydrochloride) (PAH) from Sigma-Aldrich had a similar average molecular weight. The silicon/silica wafers substrates used for the preparation of films were purchased from ACM (Villiers St. Frederic 78640, France). They were 150 mm in diameter, with a silicon (orientation 100) thickness $625 \pm 15 \mu\text{m}$ and thermo-oxide layer of approximately 100 nm or 300 nm. They were cut in 1 cm bands to be adapted to the reflectometer.

2.2. Layer by layer deposit on the silica wafer

The wafers were cleaned by immersion in a Piranha solution (2 parts of sulphuric acid 98% to 1 part of hydrogen peroxide 33%), rinsed and finally stored in Milli Q water. The deposit on the wafers was done by circulating the solutions (100 mg/L, NaCl 10^{-3} M, pH 9) in an impinging jet cell similar to that used for reflectometric measurements [20]. No water washing was performed between the deposit steps. The deposit time, 5 min for each layer, was sufficient to obtain the plateau of adsorption (no variation in the reflectometric signal after 2 min). In this cell, the flow was perpendicular to the silica wafer. The FIB analyses were done at the stagnation point at which molecules were transported onto the surface by diffusion only.

3. Characterization of polymer films

The polymer film deposit on the wafer was covered with a chromium layer by cathodic sputtering. The aim of this layer is to increase the picture contrast and to avoid charge accumulation on the deposit which would reduce the stability of the ion beam. The cathodic sputtering was done on a Plassys apparatus with a pressure of 7×10^{-3} mbar, a continuous current of 1 A, deposition rate of 120 nm/min during 1 min and 15 s.

The 30 keV focused Ga^+ ions (FIB Orsay Physics Canon 31) was used to etch polymer films of various thickness and their Si/SiO_2 substrate. After FIB irradiation, scanning ion microscopy (SIM) was used to observe the surface. The wafer was tilted and viewed at an incidence angle of 40° or 35° : the same ion beam, with a current limited to 30 pA, was used as a scanning probe to image the cross-section of the film.

Different layers of materials can be clearly identified due to good material contrast in the ion-induced secondary electron image. The thickness of SiO_2 and polymer film can be measured directly from the cross-section view by compensating the tilt angle, the apparent width of the layers being divided by $\sin$ of the tilt angle.

4. Results and discussion

4.1. Wafer with no adsorbed polymer film

A silicon wafer recovered by 300 nm of silica by thermo-oxidation was etched on a rectangle of $2 \mu\text{m} \times 5 \mu\text{m}$. On the image of the wafer (Fig. 1), the different layers, silica and chromium, are clearly differentiated.

The thickness of the layers deduced after angular correction from the scale on Fig. 1 is, respectively, of 150 and 330 nm for chromium and silica. The discrepancy with the measurements given by ellipsometry remains within the uncertainty. This reference experiment gives the thickness of the chromium layer deposited on the multilayer films.

4.2. Wafer with adsorbed polymer film

Different numbers of polyelectrolyte layer (from 5 to 160 bilayers) are deposited on the wafers. A cross-section is realised on each deposit and their images are obtained by SIM (Fig. 2).

Fig. 2 shows an important change of the morphology of the deposits with the increase of the number of bilayers. For a low number of bilayers, the upper surface of the deposit has a smooth structure with some bumps. When the number of layers increases, the surface becomes more and more granular to reach a typical "cauliflower" structure. Above 80 layers, the observed deposit presents holes and cracks inside the adsorbed polymer layer. We are entitled to wonder if these defects do not result from sample drying and/or from the vacuum of the FIB chamber. A previous study has shown that the drying step do not change the morphology of the deposit beyond 5 bilayers [11]. However, this structure can be obtained by the conformation of the polymer during the adsorption. Indeed, in a previous paper [11], we have shown that the polyelectrolytes form PAH/PSS aggregates on the silica surface and that PAH can adsorb on the top of the aggregates and so coalesce to aggregates by the summits. In this process, cavities form between two aggregates and can be observed by FIB.

4.3. Polymer film thickness

In Fig. 2, it is impossible to differentiate the chromium layer from the polymers. This chromium layer is however present and must be subtracted from the total thickness. For 30 layers of polyelectrolytes, the thickness of total film (chromium + polymers)

Fig. 1. SIM image of the silica wafer covered of chromium with a tilt of 40° to study the cross-section. All the scales must be divided by $\sin(40^\circ)$ to give the real thickness.

Fig. 2. SIM images of film multilayer deposit on silica wafer and covered by chromium layer with a tilt of 40° (images b–f) or 30° (image a and g) to study the cross-section. (a) 5 bilayers, (b) 10 bilayers, (c) 15 bilayers, (d) 20 bilayers, (e) 40 bilayers, (f) 80 bilayers, (g) 160 bilayers. All the scales must be divided by $\sin 40^\circ$ (image b–f) or $\sin 35^\circ$ (image a and g) to give the real thickness.

Fig. 3. Thickness variation vs. the number of layers obtained by FIB (grey) and laser reflectometry (black).

on the silica substrate is 270 ± 50 nm. As the measured chromium layer deposited on polymer film was 150 nm, the polymer film is $270 - 150 = 120 \pm 50$ nm. The same calculation can be done for the other films. For the thin polymer film, the thickness can be determined by laser reflectometry [11], and the Fig. 3 compares the thickness found by the two methods. The uncertainty of the measurements comes from the granular texture and the surface roughness which are visible on the cross-section.

In a previous work, we have shown that the thickness exhibits a peculiar trend. It increases strongly during the first layers (near 60 nm after 4 layers) and increases slowly after. This quasi plateau is attributed to the polymer film concentration. After the formation of coacervates between PSS and PAH on the substrate in the first layer, there are densification of the aggregates by diffusion of the PSS into the aggregates [11]. Similar results were found by Buron et al. [21] for MAQUAT/PAA.

A good concordance is found between the two methods. So the focused ion beam can be used to determine the thickness of the polymer film when it is impossible by the other methods, because of the laser diffusion at the polymer film surface. The diffusion of the laser depends on the polymer couple and on the adsorption condition (pH, ionic strength, etc.). In our case, it is observed beyond 30 layers. The thickness of the polymer film are summarized in Fig. 4.

A change of the multilayer growth is observed the Fig. 3. In a first approximation, nonlinear to linear transition takes place near

Fig. 4. Thickness variation vs. the number of layers.

300 nm (70 layers). This value is close to that found with the other couples of polymers [22] where the transition is in the range of 150–250 nm. This transition is still not fully understood. Exponential growth results from the diffusion of at least one of the two polyelectrolytes in the multilayer film formed by aggregates [23].

It has been proposed that the linear growth after an exponential growth results from a gradual restructuration of the multilayer consecutive to the diffusion process, which progressively hinders the diffusion of polyelectrolytes into the restructured zone, which becomes inaccessible by diffusion. This forbidden zone then grows with the number of deposition steps and the outer zone of the film, which is still concerned by diffusion keeps a constant thickness and moves upward as the total film thickness increases. This process was proposed by Hubsch et al. [24] and more recently by Salomaki et al. [10] for, respectively (PGA_x-PSS_{1-x}/PAH) and (PDADMAC/PSS).

With a total thickness of the polymer film about 2.1 μm and an assumed refractive index of the adsorbed layer of 1.47, the total polyelectrolyte adsorbed amount is evaluated, by the De Feijter relationship [25], at 1.7 ± 0.35 g m⁻².

5. Conclusion

The thickness of multilayer film can be evaluated by focused ion beam when the other methods are affected by roughness, mainly for thick polymer film. FIB milling creates a cross-section in the polymer film. The thickness of the film is observed with the same device in scanning microscopy mode after tilting the sample. The thickness determined for a thin film (30 layers) is in agreement with the value found by laser reflectometry. Beyond a thickness of 300 nm, the growth multilayer changes from exponential to linear. The roughness of the multilayer film increases with the number of deposited layers.

The study of the thick polyelectrolyte auto-assembled film allows to better understand the mechanism of the multilayers growth. A further paper will demonstrate how the present characterization method allows (1) to develop the reflectometry model in order to convert the reflectometry signal to adsorbed amount of polymer, and (2) to analyse the film composition.

Acknowledgments

This work was supported by the EU under contract NMP4-CT-2003-001428: Nano-capsules for Targeted Controlled Delivery of Chemicals and by a CNRS grant.

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