Effect of relative humidity on the microstructure of electrospray deposited polymer thin films

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Polymer nano-structured thin films have great potential in applications in semiconductor industries [1], as an active component in opto-electronic devices [2], in biotechnology [3], and for coatings that modify surface properties, like stimuli-responsive polymer nanocoatings [3]. With a proper combination of the composition and morphology of the thin film a wide range of film properties and functionalities can be achieved. Microstructure of thin films is highly important for film properties such as super-hydrophobicity [3].

In this study we use electrospray (ES) deposition to create polymer thin films of different microstructures. Unlike to the most popular method for making polymer thin films, spin coating, ES allows to deposit thin films onto complex surfaces, however, it has one significant drawback – low throughput. ES produces highly charged mono-disperse droplets that dry out to become nano- or micro-particles which are attracted to the substrate forming a thin film. Changing the particle size and morphology one can create thin films with different microstructures. It is well-known which parameters control particles size, but to our knowledge the parameters that affect morphology of particles in ES deposition have not been studied. We have found that one important parameter that has a strong effect on the shape and morphology of a polymer particle is the relative humidity of the ambient gas during electrospray deposition.

In this work thin films have been generated from electrosprays of dilute polymer solutions (0.1-1.0 wt%) of ethylcellulose (EC), polystyrene (PS), and poly(methyl methacrylate) (PMMA) in organic solvents with electrolyte added, at various values of RH. Under dry conditions films consisting of compact individual sphere- or disk-like particles were obtained for all polymer solutions (figure 1a-d, left column). The solutions for which an addition of small amount of water causes polymer to precipitate due to an anti-solvent effect of water, e.g. EC in dichloromethane and PS in 2-butanone, produced films made of porous particles at high RH (figure 1a-b, right column). We believe that the following mechanism explains particle porosity. Solvent evaporation from the droplet causes concentration of the polymer at the surface of the droplet as well as cooling and consequent water condensation onto the droplet. The condensed water diffuses into the droplet and causes precipitation of the polymer. Similar mechanism has been proposed to explain the effect of RH on film morphology during spin coating (Breath Figure Formation [4]). For other solutions where large relative amount of water was needed to cause precipitation (EC in butanone and EC in Isopropanol-Acetone), as was determined experimentally, non-porous wrinkled particles were formed for high polymer concentration (1.0 wt%) (figure 1c) while for lower concentration (0.1 wt% EC or PMMA in Isopropanol-Acetone) continuous uniform thin films were formed under high RH (figure 1d).

References

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Figures

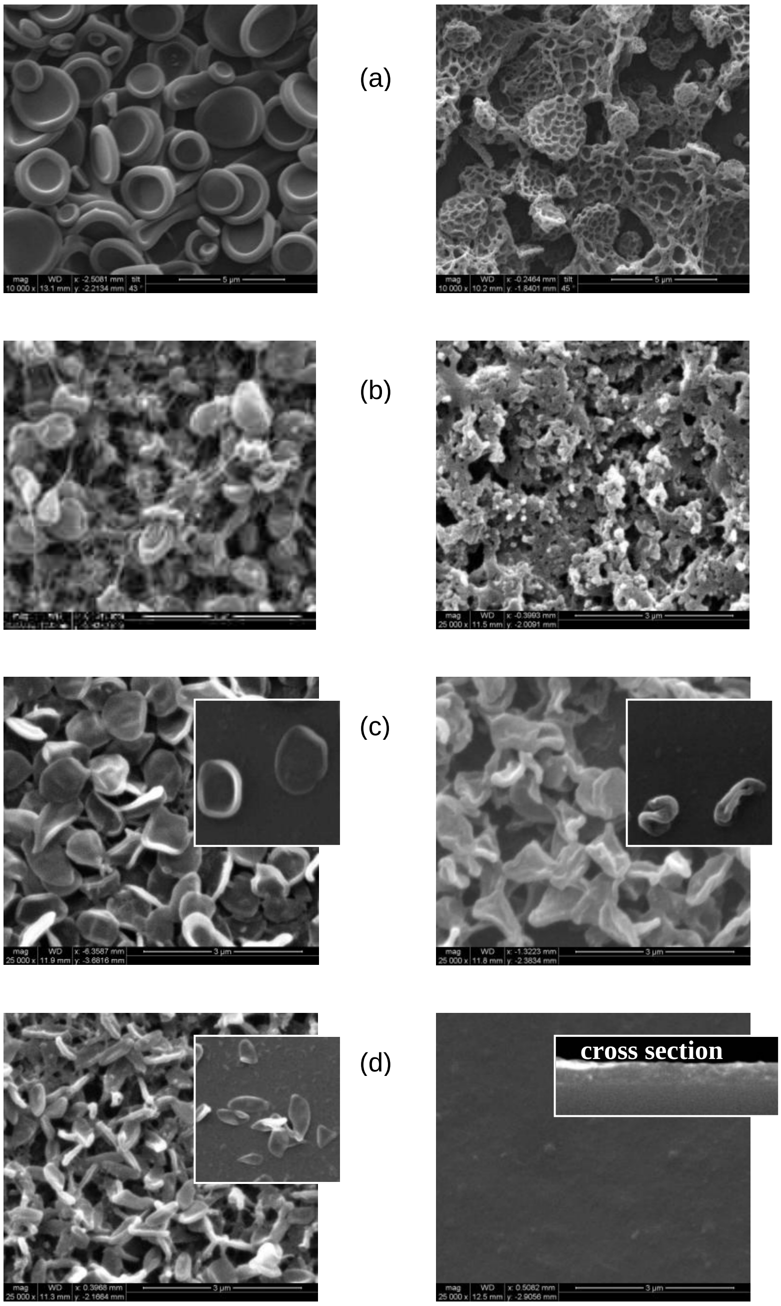

***Figure 1**. SEM images of polymer thin films deposited by electrospray on silicon wafer under different relative humidity (left column – 10 % RH, right column – 60 % RH); (a) 1.0 wt% EC in DCM; (b), 0.1 wt% PS in 2-butanone; (c) 1.0 wt% EC in IPA-Acetone (50-50 v%); (d) 0.1 wt% EC in IPA-Acetone (50-50 v%)*