Metal-polymer interfaces play a key role for many important applications such as solar cells and energy storage devices. Analysis of the formation of metal layers on polymer surfaces is crucial for the understanding of these interfaces [1-4]. In the present report, the deposition, formation and growth of metal nanoparticles on thin polymer films is observed in real-time utilizing in situ grazing incidence small angle X-ray scattering (GISAXS). Temperature and metal source are varied to investigate their influence on growth rate and growth mechanism.

Figure 1: Selected 2D GISAXS data taken during in situ sputter deposition of gold on P(S-b-B) DBC at sputtering times of (a) 10, (b) 50, (c) 100, (d) 200, (e) 400 and (f) 600 s, respectively. With increasing sputtering time, while an increasing load of Au is deposited on the polymer surface, the intensity of the scattering pattern increases. A side peak can be observed that moves with increasing metal load towards the qy = 0 position.

Thin films (60 nm) of the diblock copolymer (DBC) poly(styrene-block-butadiene), with a number average molar mass of Mn =88 kg/mol and a polydispersity of Mw/Mn =1.19, were prepared by spin coating. The molar fraction of the polystyrene block f(PS) =31.8% suggests the formation of a cylindrical morphology with a periodic distance of approximately 50 nm (calculated according to GISAXS data). In situ GISAXS utilizing the DC sputtering technique [1-2] allowed the investigation of the formation and growth of metal nanoparticles on thin polymer films at different temperatures. The measurements were performed at beamline P03 of the PETRA III storage ring at DESY (Hamburg) and were carried out for Au and Ag, each at room temperature and at approximately 70 °C. It has to be stated that the temperature in the sputtering chamber could be kept constant only to a low extent and fluctuated in the range of ± 5 °C. The sputter deposition occurred in argon atmosphere at a pressure of 1.5 × 10^{-2} mbar for a total time period of 600 s and 1000 s for Au and Ag, respectively. For data acquisition, each 0.095 s a full 2D GISAXS image was collected in real-time, using a noise-free Pilatus 1M detector (see Fig. 1). In these data, a side peak is observed, that appears and grows in intensity with increasing sputter time. The qy position of this side peak is a measure for the inter-particle distance. Therefore its migration with increasing metal load provides information on the characteristics of metal particle growth and layer formation.
To determine the impact of temperature on the metal deposition, the position of the primary side peak has been determined by fitting Lorentzian functions to the peaks in the out-of-plane cuts (along qy direction). The evolution of the peak position with sputter time is shown in Fig. 2. The initial slope of the decay with time is steeper for higher temperatures, which indicates faster metal particle migration and film growth. This observation is backed-up by fitting of the curves using an exponential decay function of second order. Large decay constants for the high temperature deposition process are observed, 18% and 22% larger compared to the room temperature deposition process for Au and Ag, respectively. After approximately 200 seconds, the metal growth becomes significantly slower and reaches saturation in a similar way for room temperature as well as for higher temperatures. At this time, a uniform metal layer has already been formed.

The observed behavior is qualitatively the same for both silver and gold, while the peak position decay slope is generally much steeper for silver deposition compared to gold. These results show that increased temperature leads to enhanced kinetics of metal particle assemblies and faster metal film growth on polymer surfaces. This can be explained by faster migration of metal atoms on the surface due to their higher internal energy. However, the basic growth mechanism of nucleation and layer formation seems to be largely unaffected, as the general behavior and shape of the out-of-plane cuts and the resulting peak position over time graphs are very similar for all regarded temperatures. As a conclusion, the growth of metal films on polymer surfaces can be affected by increased temperature in terms of faster kinetics. The effect of temperature during the sputter deposition step on the film properties is yet to be investigated.

References