Nanocomposite materials: Templated metal nanostructures

Creating tailored thin metal electrodes is crucial in the field of thin film applications e.g. organic photovoltaics (OPV) and organic electronics (OE). Thus, the investigations about the growth of thin metal layers or metal nanostructures evolved tremendously in the recent years. In order to investigate the growth of nanoparticles or clusters on the surface grazing incidence small- and wide-angle X-ray scattering (GISAXS/GIWAXS) as well established approach are used in this science field.[1] First combinatorial experiments in our group investigated the metal layer morphology of noble metal on a polymer layer, where a gradient in the metal layer was installed using penumbra deposition. This approach allowed for correlating the height differences of the deposited nanoparticles with their positions in the gradient.[2] In a next step a comparison between evaporation and sputter deposition – both heavily used in creating tailored thin metal electrodes – was performed and allowed to investigate the isolated nanoparticle to coalescent layer transition.[3] First combined in situ sputter deposition and GISAXS studies were directly performed on the gold electrode formation on a conductive polymer, typically used in OPV.[4] This experiment was followed by investigating the growth of aluminum on conductive polymer P3HT.[5] In further studies GISAXS was used exploiting a coherent nano-sized beam to reveal information about gold contacts on a photoactive polymer film or changes of gold cluster morphology deposition across on fiber-type structures.[6,7] With the geometrical model of Schwartzkopf et al. it was possible to extract characteristic parameters e.g. radii and height of the clusters during high-speed sputter depositions.[8] This novel approach enabled to investigate industrial rate sputter deposition of gold on a thin polystyrene film for the first time in situ. The rate-dependent, differently evolving growth morphologies for the nanoparticles and the rate-dependent specific percolation thresholds are depicted in Figure 1.[9] This is especially interesting for applications in sensor technology or catalysis.

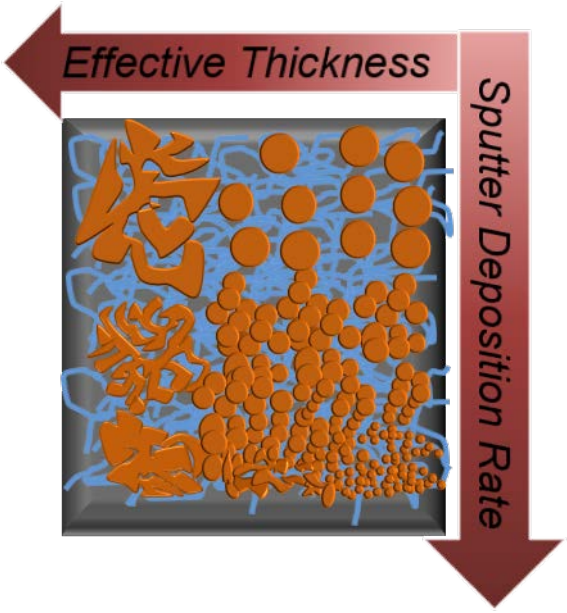

Figure 1: Schematic representation of different sputter rates and the resulting morphology with different layer thicknesses. For more details see reference [9].

In addition to gold, several electrode and polymer/small molecule combinations have been investigated in situ. For example, the silver growth on silicon or Alq3 [10,11] for elucidating the nanoscale origin of the surface-enhanced Raman scattering (SERS) effect or the establishment of diffusion layers in OE has been successfully investigated. Directional hierarchical metal-polymer nanostructures were installed exploiting glancing angle deposition (GLAD) and selective wetting of the metal on a diblock copolymer. [12] Metal decoration on block copolymer or colloidal polymer templates was further investigated for iron and cobalt, being a step towards high-density flexible data storage media.[13-15] A next step was to investigate the gold growth on advanced systems as e.g. triblock systems or quantum dots.[16,17]

Especially the correlation of the directional nanostructure with the directional optical response was established. The nanostructure-optical function relationship was further investigated in situ, allowing to hint at the origin of plasmon enhancement in OPV. [18] These investigations allow us to establish four different growth regimes: the nucleation/island growth (I), the partial coalescence (II), the domain coarsening (III) and the percolation/layer growth (IV). During sputter deposition, non-equilibrium conditions prevail. Owing to the high energy of the atoms impinging on the surface of the polymer film, nanostructures are not only created on the surface, but metal is also embedded in the polymer film in the upper polymer layer as shown in Figure 2. The density profile in Figure 2b shows the different Au layers on the polymer film established during sputter deposition. They include an embedding layer, a fully percolated gold layer with a porous layer on top. This shows the complexity of nanoscale contacts.

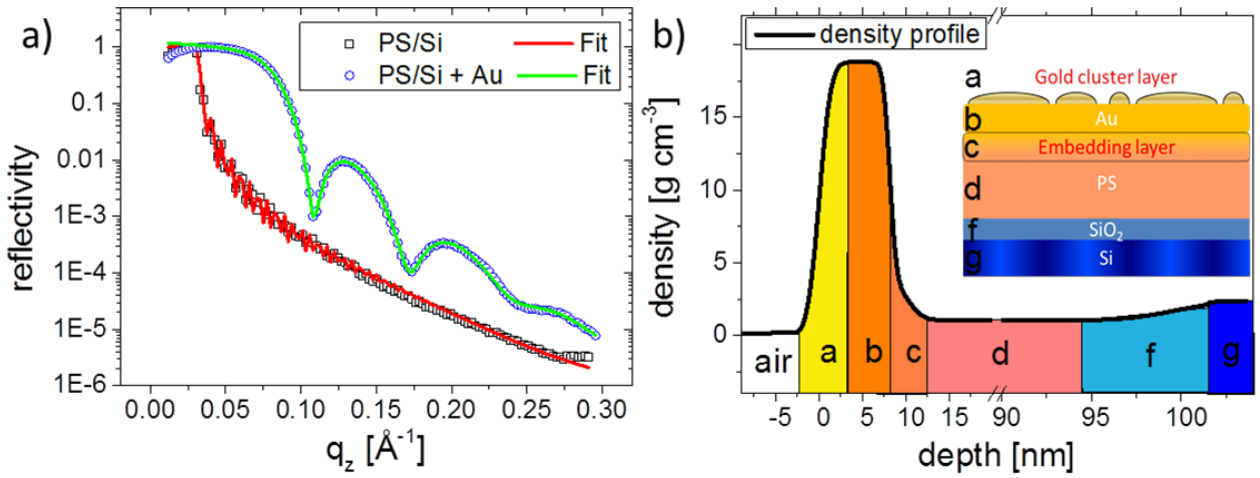

Figure 2: a) Reflectivity curves with fits of a PS thin film on silicon and with an Au layer on top. b) Density profile extracted from the reflectivity analysis. The gold layer consists of different layers, which are marked with a, b and an embedding layer with c. d is the PS layer following a SiO_2 layer and a final Si layer. Figures by Schwartzkopf is licensed under CC BY [18].

In a very recent step, the full opto-electronic properties of a metal-polymer composite have been investigated in situ. We focused on silver growth as an example to replace gold as a contact or in sensor applications. The growth of silver on copolymer systems was investigated by Gensch et al. [19] Silver in comparison to gold seems to chemically interact much stronger with polymer film. Due to differences in the mobility of the silver clusters on the polymer domains, they selectively decorate the block copolymer domains. The electrical properties and the morphological evolution

of the cluster were correlated and show excellent agreement between the nanostructure derived from GISAXS and the macroscopically measured electrical properties.

A recent publication by Löhrer et al. investigated the growth of gold on advanced low-band gap polymer films which can be used for organic solar cells or organic transistors. [20] The evolution of the crystallinity of gold clusters was measured at the same time with GIWAXS, allowing to follow the crystalline orientation and direction of the gold clusters on the polymer template. The metal growth on conjugated polymer systems was continued by two contributions from Gensch et al. [21,22] The influence of the chemical bonds was shown by these publications for Ag and Al on the same diblock copolymer template PMMA-*b*-P3HT. A further study on PS-*b*-PEO diblock copolymer for polymer lithium-ion batteries (LIBs) reveals the growth of the copper electrode for these composites materials. [23]

Featured publications:

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