Low-dimensional nanomaterials for the optical sensing of organic molecules on liquid and gas interfaces

Final report for the project K-131515 (01.12.2019-30.11.2023)

The aim of the project was to develop structures and concepts for the investigation of solid-liquid interfaces, to identify suitable configurations, best optical arrangements and materials, finally, to demonstrate the applicability of different concepts demonstrated in a broader sense. The major results according to the above objectives are listed below.

We constructed new optical cells, performed test measurements and improved the cells. We prepared a membrane-based mid infrared cell (Fig. 1) and measured polymer nanospheres to demonstrate the capabilities of the setup [1]. We created an internal reflection flow-cell for optical measurements with a multi-layer structure for the detection of protein adsorption [2]. The structure has a resonance at the wavelength of 270 nm, at which the proteins can be detected with a higher sensitivity. We also investigated other layers and materials for optical and sensor applications [3–9]. We have shown that the immobilization of flagellar filaments for electrochemical Ni-sensing applications can be followed by in-situ ellipsometry [8]. We proposed a method for the improved characterization that combines ellipsometry with Auger spectroscopy [10]. We have created low-dimensional nanostructure-based layers [8,11–13] to use these structures for sensor applications. We demonstrated the sensing capabilities on flagellar nanotubes immobilized on gold surfaces and used it in optical and electrochemical configurations [8,14]. We have prepared a cell for gas sensing with a heatable plate and multiple angle of incidence capabilities [15].

We have simulated layer structures for the enhanced measurements, tested different concepts using Bragg layers and other material systems in order to push the resonant wavelength from the usual gold plasmonic region to the absorption region of proteins [2]. We have prepared separate systems for both the visible and mid infrared spectral ranges in Kretschmann- and membrane-based geometries [1,2]. We have investigated the modeling of 2D layers, measuring the change of dielectric function as a result of corrugation caused by heat treatment of single-layer graphene [16]. We have created genetically engineered protein nanotubes from bacterial filaments. Special binding sites have been created for the binding of heavy metals from water. We have immobilized the nanotubes on gold electrodes for the electrochemical detection from water. Reference characterizations have been made using spectroscopic ellipsometry, atomic force microscopy, and calorimetry [14]. We have created surfaces with nanoparticles, oxides and nitrides [11,17–19] to investigate the modeling and optical properties for in-situ optical characterizations. We have checked the surfaces by atomic force microscopy and electron microscopy, and used in-situ ellipsometry to investigate phase changes [18]. Porous layers have also been investigated in combination with plasmonic structures [20,21].

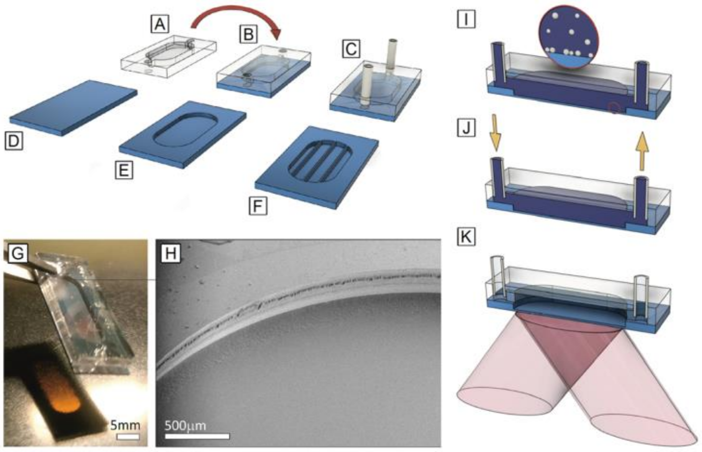

Figure 1: Membrane-based liquid cell for mid-infrared ellipsometry measurements. [A−F] Fabrication of a sealed chamber based on the membrane structure and the assembled flow cell with the thin (semi-transparent) silicon membrane. [G] and [H] show the cell and the edge of the membrane. [I−K] Design of the membrane-based IRSE cell. (From Ref. [1].)

In the final phase of the project the objectives were the monitoring of surface reactions and tracking the sensing process, investigation of spatial and temporal processes in the optical model developed for the layer system. Adsorption and diffusion models have been investigated on gold surfaces [21] also combined with silica nanoparticles [20], as well as in Zr during oxidation at high temperatures [15]. In the latter case the optical models have been extended by an analytical diffusion model that describes the process in the initial stage in a limited range of temperatures described in the article. The adsorption and surface binding of polymer structures have already been investigated in Ref. [1], whereas plasmonic nanoparticles embedded in polymer matrix have also been studied [17]. 3D nanostructures have been modeled for sensor application using finite element methods to specify the best parameters that are also in line with the sample preparation capabilities using electron beam lithography and sputtering [22].

We have developed quantitative models to describe a novel plasmonic structure and determined reference dielectric functions of AgAl layers in the whole range of compositions, which are used in the Kretschmann-Raether flow-cell configuration. The layer structure includes a silicon nitride waveguide capping layer [23]. We have measured the dynamics of surface adsorption of hydrocarbon molecules on van der Waals materials revealing different processes taking place until saturation of the surface [24]. We have demonstrated measurement configurations for both in-situ [1,23,25–27] and ex-situ [16,28–31] characterization of nanomaterials in the ultraviolet-near infrared wavelength range. The extension to the mid infrared has also been demonstrated [1]. We have developed optical models to describe low-dimensional materials used in plasmonics [16,25] and on highly ordered surfaces [24]. We have shown that ellipsometry is a powerful tool to determine spectroscopic material properties in nanomaterials even during processing. Effective medium and dispersion models have been developed to determine the formation of nanomaterials at interfaces during processing [23,25–27].

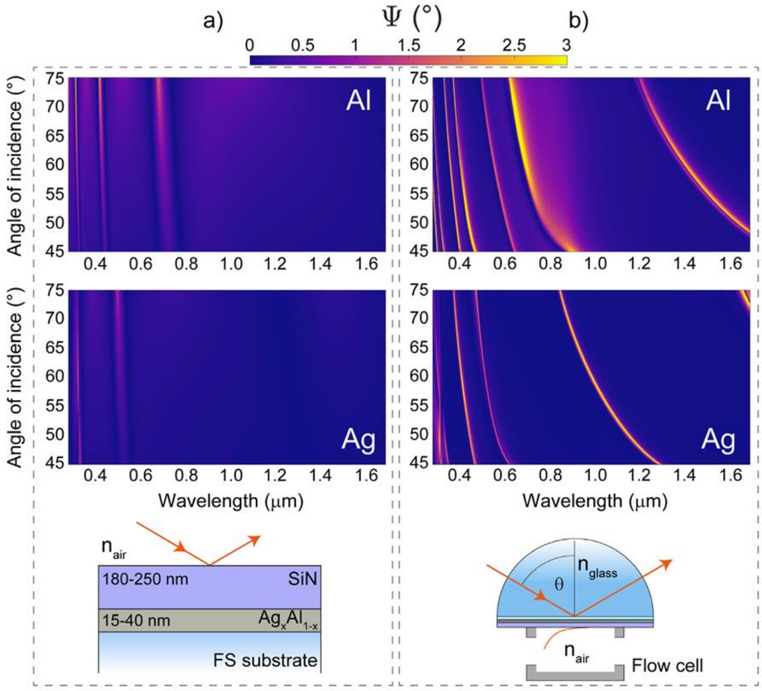

Figure 2: The simulated effect of a 1-nm thickness change in Ag$_x$Al$_{1-x}$ layer at x=0 and 1 using reflection configurations measuring from (a) the ambient and (b) from the substrate (Kretschmann-Raether configuration). (From Ref. [23].)

We identified the best configuration for plasmonic sensing using ellipometry in an AgAl nanolayer-based Kretschmann-Raether flow cell that revealed sensitivities in the range of 10^{-6} for the refractive index with a simultaneous spectroscopic capability in the wavelength range of 190-1700 nm (photon energy of 0.7-6.5 eV) and a temporal resolution down to one second for the whole wavelength range. In this configuration, the sensitivity can be adjusted also by the angle of incidence. By measuring the surface of a gold nanolayer during plasmonic excitation in a Kretschmann configuration, and by measuring the high-temperature reference dielectric function of gold, we have revealed the few-nanometer thick hot-electron layer that has a different dispersion than the thermal electrons of the bulk gold generated during laser excitation [25]. Sensitivity down to the nanometer level was also needed to show the dynamics of hydrocarbon molecule adsorption on highly oriented pyrolytic graphite surface with a saturation time of two weeks [24] and corrugated graphene layers [16]. Due to their plasmonic applications the investigation of different metal and semiconductor structures were of primary importance both in-situ and ex-situ. The studies using our own in-situ hardware developments include Refs. [25], [1] and [26] utilizing a self-made heat cell, and by [27] using an in-situ chamber to investigate the damage created in germanium during ion implantation. Amorphous semiconductors [30,32] as well as different magnetic [33] and oxide [29,31,34–36] materials have also been investigated mainly as developments for potential sensor applications. At the end of the project we have written several review papers on the applied metrologies [37–39].

Publications in frame of the project

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