Optical study of interphases and diffusion of an amorphous fluoropolymer at a gold interface

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Amorphous fluoropolymers offer a new and interesting application as an optical material. Surface plasmon resonance and leaky waveguide mode spectroscopy were used to investigate the optical properties of a transparent fluoropolymer film at a gold interface and in bulk at the same time. An anisotropic interphase near the gold-polymer interface with a higher density than in bulk was found.

1 Introduction

Polymers at interfaces are important in many applications such as coatings and sensor devices. In fluorinated polymers the hydrogen atoms are substituted by fluorine atoms. These polymers (e.g. Teflon) are usually semicrystalline however the development of amorphous fluoropolymers offers new applications as a transparent optical material with a remarkable low refractive index. Since fluoropolymers are inert, functional end groups are necessary to bind an interface thereby changing the properties of the polymer near the interface compared to the bulk. Because these polymers are frequently applied as thin protective coatings, it is important to characterize the influence of an interface to the polymer.

Fluoropolymers are inert against solvents but they have a high gas permeability due to a high free volume. Therefore they are used as a diffusion barrier to separate gas from a solvent. The diffusion coefficient of a gas diffusing in a polymer mainly depends on the polymer density. This can be used to analyze the mass density in the interphase and in the bulk.

Polymers are known to behave differently at an interface than in bulk. The affinity of the polymer chains to the interface proves to be a crucial parameter. A depletion layer, as well as an adsorption layer may develop. [1] These layers are called interphases.

In this work the optical properties of an amorphous fluoropolymer (Cytop, Asahi Glass) coated on a gold film are investigated. Since Cytop has functional end groups to form a bond at inorganic interfaces, the properties in the interphase are compared to those in the bulk.

Combining surface plasmon resonance and leaky waveguide mode spectroscopy, the optical properties of a polymer film in the interphase and in the bulk can be analyzed simultaneously. [3]

2 Amorphous Fluoropolymer Cytop

The polymer Cytop CTL 809M is a fluoropolymer. The C-F bond is very polar which results in a low refractive index of n = 1.3395 (λ = 632.8 nm). Because of the cyclic structure of the monomer the polymer is amorphous and thus transparent. It can be used in optical fibers and as an anti-reflective coating. As Cytop is very inert, further applications are: electrical insulator, water and oil repellant and protective coating.

In this work polymer films were spun-coat from a 9 wt. % solution with a speed of 1000 rpm. The resulting film thickness was approximately 1.3 µm.

3 Sensor Concept: Kretschmann Configuration

Figure 1 shows the Kretschmann Configuration which is used to characterize the optical interhpase and the bulk properties in one measurement. The fundamentals and the experimental setup are explained in [2] and [3].

Due to their field distributions ranging across the whole polymer film waveguide modes are able to scan the bulk while surface plasmons (SP) will see the interphase area only, see Figure 1.

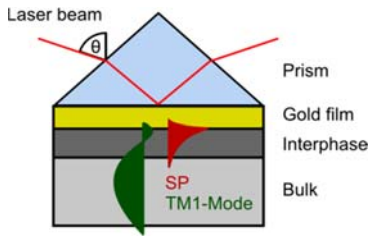

Figure 1: The combination of a waveguide mode and a SP is particularly suited to characterize a polymer film in the interphase and in bulk simultaneously

4 Two-layer model of the polymer film

Figure 2 shows both the measured and the simulated reflectivity as a function of the angle of inci-

dence for the sensor shown in Figure 1. The simulated spectrum has been calculated by using Fresnel's Equations and the Transfer-Matrix Algorithm. First, a one-layer model of the polymer was used. The measured angular position of the TM1-TM3 modes fit the simulation (red line) well but the SP shows a clear deviation. To fit the SP-branch, an additional interphase layer according to Figure 1 was introduced. The thickness of the interphase was set equal to the penetration depth of the SP which was 220 nm. The refractive index of the interface n_{IP} was then varied until the simulation coincided to the experimental scan resulting in an interphase layer with a lower refractive index than in the bulk.

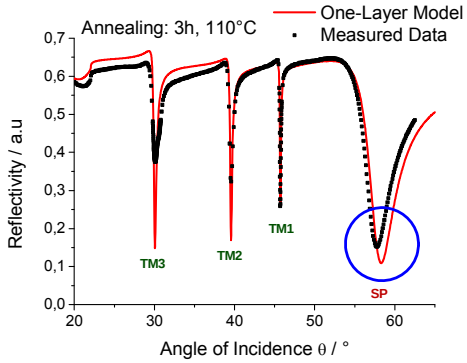

Figure 2: The one-layer model of the polymer film shows a good agreement to the angular position of the waveguide modes but a clear difference to the SP

Heating the same sample for additional 22h at 200°C and 1mbar, a reduced thickness of the polymer film was observed. This indicates that solvent diffused out of the film. Interestingly, though the refractive index of the bulk did not change, n_{IP} of the interphase layer changed from a refractive index lower than in bulk to a refractive index higher than in bulk. The higher refractive index is indicative of a possible anisotropy or a higher mass density in the interphase.

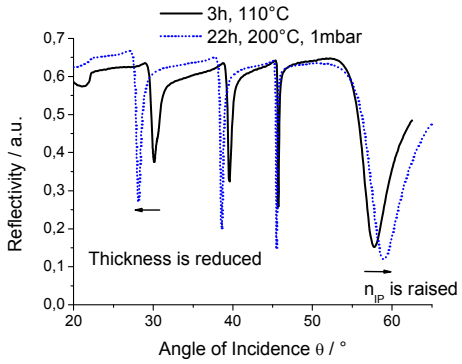

Figure 3: Additional heat treatment leads to a reduced film thickness and a raised interphase n_{IP}

A potential optical anisotropy of the interphase layer was investigated using TM- and TE-polarized light. An anisotropic refractive index n_x, n_y, n_z corresponding the x and y, which are in a plane parallel to the gold film, and z direction which is perpendicular to it. n_x and n_y were equal to the refractive index in bulk whereas n_z was lager, indicating an anisotropy perpendicular to the gold interface.

The mean of the refractive index of the interphase layer $\bar{n}_{IP}$ proves to be higher than the refractive index in the bulk which means that the interphase layer is oriented and has a higher mass density.

These findings suggest that after spin-coating the low-refractive-index solvent accumulates in the interphase. The additional heat treatment above the glass transition temperature removes the solvent and leads to a reorientation of the polymer chains in the interphase. The functional end groups can bind to the gold interface and form an oriented interphase with a higher density.

5 Diffusion of toluene in the polymer film

Molecules diffusing in the polymer film lead to an increase of the refractive index. In this work the time dependent shift of the resonance minima during the diffusion process of 0.3% toluene vapor in 99.7% nitrogen was analyzed. The shift of the minimum of both the TM1 mode and the SP relative to the maximum shift in saturation as a function of time is depicted in Figure 3. The TM1 mode and the SP show a different behavior. While the TM1 mode shifts immediately when the diffusion starts the SP starts when the vapor molecules reach the interphase through the bulk. The TM1 mode reaches the saturation earlier than the SP which implies a higher mass density in the interphase.

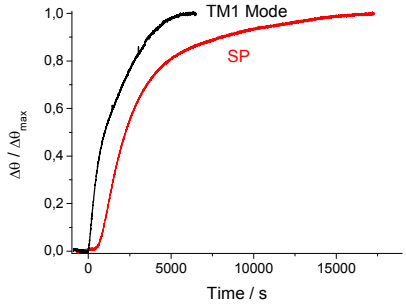

Figure 4: Diffusion of 0.3% toluene in the polymer film shows a different behavior for the TM1 mode and the SP

References

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[3] E.T. Hoppe et al, "Optical Properties of Pulybutadiene in the bulk and near a gold interface" in *Colloid Polym.Sci.*