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Full Length Article

Photoswitching of fulgimides in different environments on silicon surfaces

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ABSTRACT

Reversible light-modulation of fulgimide based monolayers on Si(1 1 1) and Si(1 0 0) was investigated using ATR-FTIR spectroscopy. Fulgimide monolayers were prepared from neat COOH-terminated SAMs on Si(1 1 1) obtained from methyl undec-10-enoate, (1:1)-diluted COOH-terminated monolayers on Si(1 1 1), and GPTMS monolayers on Si(1 0 0). The epoxy-terminated monolayer on oxidized Si(1 0 0) was characterized with ellipsometry, XPS, as well as contact angle measurements, and ATR-FTIR spectroscopy revealed a strong influence of toluene water content on reproducible high-quality monolayer formation. The results of this study show that environmental polarity has a strong influence on fulgimide imide IR band locations and read-out options for the two photostationary states PSS(365 nm), containing *E/Z*- and *C*-isomers, and PSS(545 nm), with solely the *E/Z*-isomers. Neat COOH-terminated monolayers on flat Si(1 1 1) have the advantage of high functional group concentration, orientation and stability, and an upright arrangement of fulgimide head groups.

1. Introduction

Modifying and adjusting monolayers on semiconductor surfaces by external stimuli is attractive for controlling chemical and physical properties of surface components, and already a broad sphere of action in molecular electronics, device development and photovoltaics [1–4]. In the past, photo-responsive well defined structural states on surfaces were realized with P-type and T-type photochromic compounds [3,5]. Such surfaces have great potential for all kind of nanotechnological applications due to reversible changes of physical and chemical properties upon light irradiation or thermal relaxation, e.g. wettability, conductance, and nonlinear optical response [3,5–7]. Properties of photoswitches on surfaces strongly depend upon immediate environmental influences, e.g. monolayer structure and rigidity and head group localization. Precise strategies are rare because of the low number of comprehensive studies focusing on short- and long-term high-quality read-out of reversible structural state formation upon e.g. external light-stimulation. Fulgimides, as a class of photoswitch of choice in our work toward effective two-dimensional confined non-linear optical (NLO) switching materials [7–9] show excellent switching reversibility and resistance to fatigue in solution. Immobilized on the solid substrate, they allow photochemical studies, due to changes of vibrational modes upon light-induced ring-opening and -closing reactions [8,9]. Additionally, large changes in the first-order molecular hyperpolarizability between different forms were observed upon photoisomerization [7]. Herein we provide a comparison of fulgimide-terminated monolayers prepared under wet chemical conditions from atomically flat H-terminated Si(1 1 1) with monolayers on Si(1 0 0) having a rough but also flat underlying silicon surface (Fig. 1). For fulgimide monolayer preparation on Si(1 1 1) we chose the neat, but also a (1:1)-diluted COOH-terminated monolayer [8,10]. Neat COOH-terminated monolayers guarantee a high degree of functional group arrangement and organization in well-defined rows on the molecular scale, because 50% of neighboring head groups of COOH-terminated self-assembled monolayers (SAMs) are aligned by single hydrogen bonds [11,12]. An even tighter surface packing and an increase in hydrophobic environment seems to be possible by dilution of headgroups [1,10], thereby allowing additional stabilization of monolayers due to the hydrophobic environment, and protection against solvent molecules, water and oxygen. However, lower concentrations of fulgimide head groups will allow a broader variability in head group orientation, and the associated variations in properties and read-out options have to be clarified for Si(1 1 1) but also for Si(1 0 0). Thermal reactions of the oxidized surface on Si(1 0 0) with alkylsilanes lead to formation of monolayers with a stable covalent Si-O-Si network. Methods strongly depend on oxide preparation, oxide monolayer thickness, solvents, presence of water (on surface and in solvents), silane concentration, and temperature [1,13–16], and side reactions are silane polymerization in solution phase, multilayer formation and generation of unordered (mono)layer structures [17]. Functionalized monolayers on Si(1 0 0) are well

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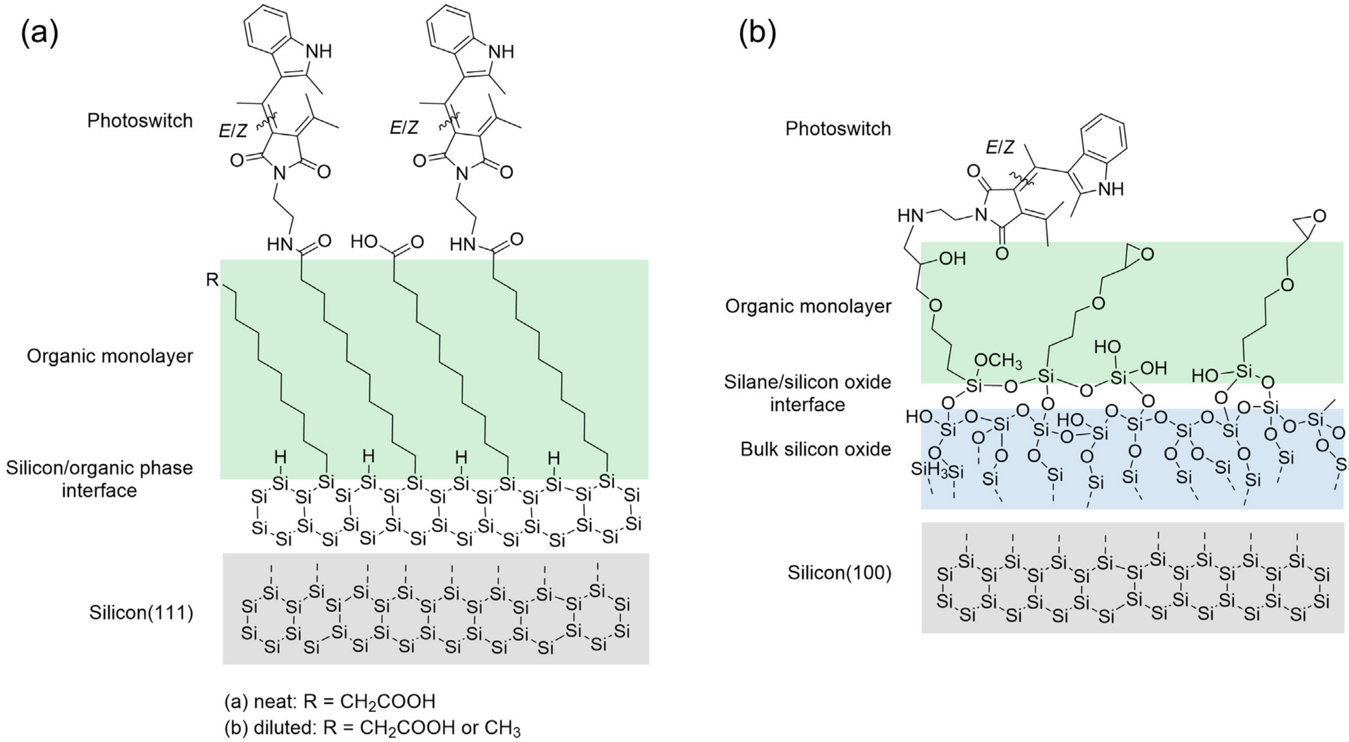

Fig. 1. Overview of fulgimide-terminated monolayers investigated in this study: (a) neat and (1:1)-diluted SAMs on Si(1 1 1) and (b) SAMs on oxidized Si(1 0 0).

established, because of their liquid-type soft environment when choosing shorter linker molecules [13]. For siloxane-anchored COOH-functionalized SAMs interactions amongst head groups and with water molecules by hydrogen bonding were found to be problematic [11,12], but epoxy-terminated monolayers are an attractive and valuable alternative [18], and reactions of epoxide head groups with appropriately, e.g. amine-functionalized peptides, oligonucleotides, or polymers, were used in nanoscale device technology [19–24].

We report herein the formation of monolayers on the oxide of Si (1 0 0) starting from (3-glycidyloxypropyl)trimethoxysilane (GPTMS, **1**) containing a short linker with an additional oxygen linkage, and subsequent functionalization with amine-functionalized fulgimide-linker-conjugate **2**. For comparison neat and (1:1)-diluted fulgimide monolayers on Si(1 1 1) were prepared (Fig. 1). Monolayers on Si(1 0 0) were characterized by ellipsometry measurements, water contact angle measurements, and X-ray photoelectron spectroscopy (XPS). To the best of our knowledge an in-depth infrared study of epoxy-terminated monolayer formation under the influence of the water content in the silanization process was not reported before. Attenuated total reflection Fourier-transformation infrared spectroscopy (ATR-FTIR) provided key structural information on all monolayers formed on Si(1 1 1) and Si (1 0 0), and the photochromism of the fulgimide head groups.

2. Experimental section

2.1. General remarks

Samples for ATR-FTIR were cut in rectangle shape, dimensions 1.1 × 2.5 cm, from silicon wafers (Sil'tronix, double side polished Si (1 0 0) ± 0.5°, FZ, non-doped, R = 1000–1600 Ωcm, d = 500–550 μm) and grinded and polished on the shorter side at 45° angle. Samples for XPS were broken into two (1.1 cm × 1.2 cm) pieces before the last synthesis step, in order to evaluate the last coupling reaction. For procedures on monolayer preparation and functionalization, see SI.

2.2. ATR-FTIR measurements

Spectra were recorded on a Bruker Vertex70v ATR-FTIR spectrometer containing a liquid nitrogen-cooled mercury – cadmium – telluride (MCT) detector, while the sample compartment was kept under nitrogen. The spectral range between 370 and 4000 cm^{-1} was investigated, with 4 cm^{-1} resolution. Freshly prepared oxidized samples were used as references. The switching experiments were done in the dark, under inert gas atmosphere (nitrogen), and were allowed for 30 min per irradiation time period. IR data were analyzed using the software OPUS 6.5 (Bruker).

2.3. Ellipsometry measurements

Layer thickness measurements were carried out with a Sentech SE 850 ellipsometer. The angle of incidence of light was 70°, the measurements were performed in the wavelength range 300–800 nm. For the analysis of the measurements the software SpectraRay3 was used. Initially, the thickness of the SiO_2 layer was determined from reference samples. The thickness of the epoxy-terminated monolayer was calculated using a two layer SiO_2/epoxysilane monolayer model. The refractive indices of the epoxysilane monolayer and the silicon oxide are assumed to be constant and equal to the bulk values of 1.429 and 1.461, respectively.

2.4. Water contact angle measurements

Static water contact angle measurements were performed on an Easydrop instrument (Krüss, Germany) using the sessile drop method. All measurements were carried out at ambient temperature and humidity. Each sample was prepared in triplicate at least. Usually five or more drops of MilliQ water with a volume of ~1 μL were placed on each sample and measured. The typical average error was ± 3° at maximum, obtained as the fitting error of each measurement. Measurements of the irradiated silicon samples were conducted in the dark, the light source of the goniometer was covered with a red plastic