

Surface modification of amorphous substrates by disulfide derivatives: A photo-assisted route to direct functionalization of chalcogenide glasses

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ABSTRACT

A novel route for chalcogenide glass surface modification is disclosed. The formation of an organic monolayer from disulfide derivatives is studied on two different glasses of formula $\text{Ge}_x\text{As}_y\text{Se}_z$ by water contact angle measurement, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR). The potential anchoring group is the disulfide functionality. Since thioctic acid derivatives absorb around 335 nm, an irradiation step is included, in order to favor S–S disruption. Three types of disulfide compounds are grafted onto small glass breaks for contact angle and XPS analyses. The results show effective changes of surface state. According to contact angle measurement, the deposited organic layer functionalized by a small polyethylene glycol chain leads to a more hydrophilic surface, long alkyl chain or a perfluorinated carbon chain leads to a more hydrophobic surface. XPS shows the presence at the surface of an organic layer with sulfur and ethylene oxide chains, or augmentation of organic carbons or fluorine and C–F bonds. The photo-assisted grafting of the disulfides onto an ATR prism made of chalcogenide glass shows that this surface modification process does not affect infrared transparency, despite UV treatment, and accurate structural analysis can be performed.

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1. Introduction

Chalcogenide glasses form a large class of glassy inorganic materials [1] which have a poor transparency in the visible wavelength range. Their name comes from the presence in their molecular bulk composition of at least one of the chalcogen elements except O, *i.e.* S, Se or Te. The chalcogen element is associated with more electropositive elements such as As and Ge. Both heteropolar and homopolar bonds can be formed, so an excess of Se is commonly found in the glass formulation. A high percentage of Se or Te gives a better transparency in the infrared range because of low energy vibrations in the glassy network [2]. They are band gap semiconductors and infrared transmitting materials, and can be prepared as bulk glasses, fibers or thin films [1,3]. Because of their vitreous nature, the preparation of optical devices is possible by molding [4,5]. Chalcogenide glasses are known to have an excellent transmission in the near and mid infrared [1,3,5]. They found applications from many years in infrared optics for energy management, thermal default detection, temperature monitoring or night vision [1]. More recently, chalcogenide glass fibers were used as waveguides for laser power transmission [1,4] and were also considered for applications in telecommunications [6]. In the 2000s, because of their intrinsic advantages *versus* crystalline germanium, chalcogenide glasses gained a great interest for infrared thermal imaging devices [4] but also for chemical sensors and biosensors using chalcogenide fibers, thin films or

optical waveguides [7–9]. A good compromise – when aiming low-cost optics applications – is the germanium–arsenic–selenium system (GAS) for several reasons like good transparency in the infrared range, high resistance towards devitrification (crystalline structures are undesired) and an easy control of the molding process [4]. Since the 1990s, the use of chalcogenide glasses for chemical sensors led to several publications [10]. In this context, one research group tried to set a method for direct surface modification of chalcogenide fibers [11] on the analogy of Si surface modifications. The molecules used for grafting were (3-aminopropyl)-triethoxysilane, followed by glutaraldehyde, and (γ -glycidoxy)-triethoxysilane, in order to further immobilize the enzyme glucose oxidase onto the surface [12]. These authors left this method, because of the restricted enzyme density, for a thick-film coating approach [10]. Thus, except those few papers from the same research group, no study of direct modification of chalcogenide glasses can be found so far in the scientific literature. Organosulfur compounds, including disulfides, are well-known to adsorb and coordinate strongly to metallic surfaces such as gold and silver [13], but they are also able to form monolayers on gallium arsenide [14–16]. In addition, thioctic acid, also named lipoic acid, is a recognized ligand for arsenic, therefore used as antidote [17].

In the present work, disulfide compounds prepared from thioctic acid are considered as good candidates to bind directly onto the chalcogenide glass surface. Syntheses are easily carried out by amide coupling of thioctic acid with the desired chain comprising one primary amine functionality. To our knowledge, the compounds used here are new and their syntheses unpublished (see supplementary material for details). The disulfide functionality is coupled to a heptaethylene glycol

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chain in order to form hydrophilic surfaces (PEG7 compound) or is coupled to a long alkyl chain (C18 compound) and a fluorinated alkyl chain (F15 compound) to assess the formation of hydrophobic surfaces. The three prepared disulfides are depicted on Fig. 1. These compounds may have ability to combine their sulfur atoms with As from the glass and/or with Se. In addition the presence of the amide group should generate H-bonds between the neighboring chains that favor molecular self-assembly at the surface [18,19]. Besides the novelty of a direct grafting on such surfaces, the originality of our method lies on an irradiation step under UV light after deposition of the molecules (see materials and methods) which gives a photo-assisted grafting process instead of a simple coating protocol. As a matter of fact, dihydrolipoic acid, which is the reduced form of thioctic acid, is used as a ligand that binds with semiconductor nanocrystals (Quantum Dots) or metallic nanoparticles [20–23]. Thioctic acid has an absorption band around 335 nm and photoirradiation decomposes the 1,2-dithiolane ring to give dihydrolipoic acid, after recombination of the dithiyl radical with H atoms coming from intra or intermolecular abstraction [24,25]. The three thioctic acid derivatives used in this work feature the same absorption around 335 nm (see supplementary material). The present irradiation protocol permits to avoid one synthetic step by using directly the disulfide form and preparing *in situ* the reactive dithiyl radical or the dihydro form. A disulfide precursor is also more convenient for handling than a dithiol which is more prone to oxidation. As said before, the only example of direct grafting on chalcogenide surface was made with the triethoxysilane anchoring group, which is already known to form a monolayer on crystalline germanium surface [26]; thus the use of disulfide here is more original than a silane compound. Two different glasses were investigated as substrates: IG2 containing 55% of Se, 33% of Ge and 12% of As; IG4 containing 50% of Se, 40% of As and 10% of Ge. The balance of the Ge/As ratio between two different chalcogenide glasses could change the reactivity of the anchoring group towards the surface since disulfide is supposed to bind stronger with arsenic. The grafting of disulfide may be helped by eventual sulfur–selenium bonding.

2. Material and methods

2.1. Chalcogenide glasses

Two types of chalcogenide glasses (IG2 and IG4) were purchased from Vitron Spezialwertstoffe GmbH (Jena-Maua, Germany). According to the manufacturer, the bulk composition of the glass is $\text{Ge}_{10}\text{As}_{40}\text{Se}_{50}$ for IG4 and $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ for IG2. The lenses received from the manufacturer have a 50.8 mm diameter and are 2.0 mm thick, and ATR prisms have 50.0 × 20.0 mm dimensions and are 2.0 mm thick. For the experiments, a lens is cut into several 10 × 10 mm squares. The

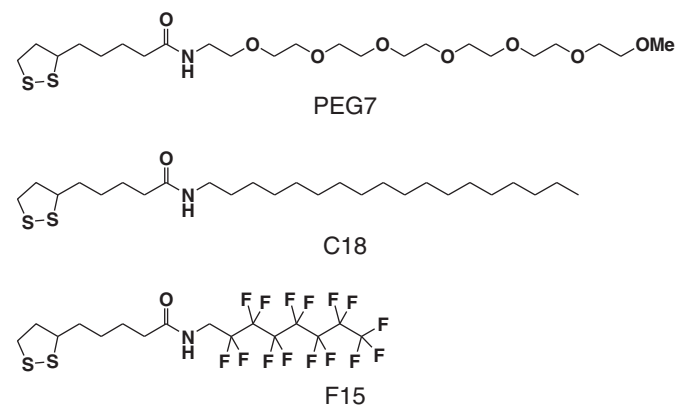


Fig. 1. Disulfide compounds synthesized from thioctic acid and used for surface modification of chalcogenide glasses.

samples named “native” are used as received from the manufacturer. ATR prisms are used for infrared measurements.

2.2. Surface modification

2.2.1. Preliminary studies

Different potential anchoring groups (disulfide, bis-phosphonate, bis-phosphonic acid and catechol) were probed in a preliminary study that designated the disulfide motif, as the most valuable functionality, for the linkage of an organic layer to a chalcogenide glass surface.

Several procedures (immersion, deposition or evaporation; nature of solvent and concentration of disulfide molecules; methods and cycles of deposition) were compared by contact angle measurement and XPS in order to optimize the surface modification. The processes used to prepare the samples for this work, are those which gave the most promising results, for one given glass with one given disulfide molecule.

The details of the preliminary studies are reported in the supplementary material (Section VI).

2.2.2. Blank samples

Blank samples are native glass breaks (10 × 10 mm) treated like modified samples without the disulfide molecule. They are prepared following the same process described in supplementary material (Section III.1.a), without the PEG7 compound.

2.2.3. Chalcogenide glasses pre-treatment

Before the use of the chalcogenide glasses substrates, well-known cleaning processes like ultrasonication or UV/O₃ treatment are not applied, because such treatments would lead to important alterations (oxidation, devitrification) of the glassy network, and most probably affect the infrared transparency of the material. Instead of these, a Soxhlet treatment in refluxing chloroform is applied for grease contamination removing. A detergent pre-cleaning process is also probed (see supplementary material, Section III.1.).

2.2.4. Irradiation and rinsing steps

Each procedure comprises a deposition step, which is followed by an irradiation step and a rinsing step. Those two last steps are performed as follows: the surface is irradiated during 120 min under UV light at 360 nm wavelength (3 × 8 W BLB lamps, placed above samples at a distance of 10 cm). Non grafted molecules are removed by washing the sample two times during 3 min in ethanol and one time during 3 min in chloroform on a stirring plate (200 rpm). After each washing, the sample surface is dried under argon flow.

2.2.5. Surface modification of IG4 or IG2 by PEG7, C18 or F15 disulfide derivatives

Two main protocols are performed:

- A direct deposition process, in which 25 to 100 μL of disulfide solution, 10^{−3} M in the appropriate solvent, is deposited on the upper surface of a glass break of 10 × 10 mm. After evaporation of the solvent at room temperature and pressure, the surface is irradiated and rinsed as described above (Section 2.2.4).
- An evaporation process, in which the sample is immersed in 5 mL of disulfide solution, 10^{−3} M in the appropriate solvent, which is allowed to slowly evaporate during 24 h at room temperature. The surface is then irradiated and rinsed as described above (see Section 2.2.4).

All the samples are prepared either by the “direct deposition” process only, or by a two-step process including both “direct” and “evaporation” processes. The type of process applied depends on the glass (IG4 or IG2) and the disulfide derivative (PEG7, C18 or F15). These procedures are detailed for each sample in the supplementary material (Section III).

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