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Vapor deposition coating of fused silica tubes with amorphous selenium☆

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ABSTRACT

A set of optimized deposition conditions for the inner wall coating of fused silica tubes with amorphous selenium was elaborated. The method is based on the vapor transport deposition of pure elemental selenium on a cooled substrate held at liquid nitrogen temperatures. Morphological and structural examination of the deposited layer was performed by optical microscopy and X-ray diffraction studies. Neutron activated selenium was used to monitor the deposition pattern and its stability under high gas flows. Monte Carlo simulations allowed the estimation of the different Se species composing the amorphous phase, at the given experimental deposition conditions. The versatility of the coating method presented in this work allows for the coating of tubes of different lengths and diameters, opening the way for several applications of amorphous selenium films in various fields.

1. Introduction

At room temperature and atmospheric pressure, the major allotropic forms in which selenium exists are crystalline (trigonal, α-, β-, γ-monoclinic), amorphous (red, brown and black Se), and vitreous selenium [1]. The most thermodynamically stable form is trigonal selenium, also known as gray, hexagonal, or metallic selenium. Trigonal Se consists of polymeric Sen helical chains, in which contiguous atoms form single covalent bonds [2], and it is less chemically active than the other allotropes [3]. The structure of the amorphous phase has been long discussed and various models have been proposed [4–8]. It is generally accepted that the amorphous allotrope consists of a mixture of selenium ring-like molecules of different sizes and branched chains of diverse length, interconnected to each other by Van der Waals forces [9,10]. At slow heating of the red amorphous selenium at temperatures higher than 37 °C, this allotrope undergoes a phase change, transforming gradually to the black amorphous one [11,12].

During the last decades, amorphous selenium (a-Se) acquired high importance in the field of technology [13,14,15,16], in the biomedical area [17,18], as well in the environmental and safety sectors [19,20]. For the production of a-Se as thin films or nano-powders different techniques were applied, such as chemical vapor deposition [21], chemical bath deposition [22] and vacuum evaporation [23]. However, all of these techniques were conducted on flat substrates, limiting the uses of this chalcogen.

In the present work, a vapor transport and fast quenching deposition method is used for the coating of inner walls of fused silica tubes with amorphous selenium – in particular, with the red amorphous allotrope – since the quenching of selenium vapors at low temperatures leads to the production of amorphous (red) selenium [12,24,25].

The here presented technique does not require sophisticate instrumentation; unlike solution growth techniques, electrodeposition or chemical bath deposition, this system can be easily kept free from impurities like water, organic substances and oxygen in order to avoid their incorporation into the deposited selenium layers, which typically influences their physical and chemical properties [26,27]. Using this method, a-Se coatings of the desired thicknesses can be prepared, just by varying the selenium amount used as starting material. Furthermore, the proposed method is safe, since it avoids the use or production of poisonous compounds like H_2Se and SeO_2, it is reproducible and inexpensive.

Since a-Se is a metastable state which undergoes a phase change to the most thermodynamically stable trigonal selenium, a set optimized vapor transport deposition conditions was elaborated in order to limit the spontaneous a-Se crystallization process.

☆ Abbreviations: In the present work amorphous selenium is referred to as "a-Se".

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Recently, the coating technique discussed here was applied for the coverage of the inner walls of quartz columns with amorphous selenium for radiochemical studies [28].

2. Experimental details

2.1. Pretreatment of the fused silica tubes

Fused silica tubes (i.ø = 4 mm; length = 1 m) were rinsed with MeOH (anhydrous, ≥99.8%, Sigma-Aldrich), AcOH (VWR) and EtOEt (anhydrous, ≥99.0%, Sigma-Aldrich) in the mentioned order, and dried under a pure N_2 gas flow.

2.2. Selenium deposition

A fused silica tube (3) is placed in the vapor transport system as shown in Fig. 1. A high purity stream of He carrier gas is passed through a tantalum getter-oven (2) kept at 1273 K in order to remove H_2O and O_2 traces. The content of ($H_2O + O_2$) in the gas, measured with a trace oxygen sensor (Ionic Systems TOS 3.0), is 0.5 ppm after 2 h of running the carrier gas. The He gas flow rate of 300 mL/min, established during the experiments, is controlled by a mass flow controller (1) (Series 5850E, Brooks Instruments) and measured with a Buck calibrator (A.P. Buck, Inc.). High purity (>99.999%) elemental gray Se (Fluka Chemicals) is volatilize inside the fused silica column in the sublimation oven (4) kept at 653 K (internal temperature: 620 K), and transported by the carrier gas to the liquid nitrogen cooled fused silica column, where the deposition of the a-Se takes place. A third oven (5), kept at 653 K (column internal temperature: 620 K), is placed adjacent to the liquid nitrogen cooling tank (6), and is used as a thermal buffer. The temperature gradient established along the fused silica tube is shown in Fig. 2. All the resistive ovens are connected to VARIAC autotransformers type W20HMT3, and the temperatures are measured with a Voltcraft K202 digital thermometer connected to K-type thermocouples placed inside the tubular ovens. After the total selenium evaporation, ovens (4) and (5) are switched off and the system is allowed to reach room temperature under the dry He gas flow. The non-deposited selenium vapor is captured in a charcoal trap placed at the end of the fused silica tube (7).

2.3. Characterization

2.3.1. Optical microscopy

The morphology and the homogeneity of the deposited a-Se were examined by optical microscopy using a Bresser microscope (magnification: 4–100×). Photomicrographs were taken using a DinoEye® digital ocular camera.

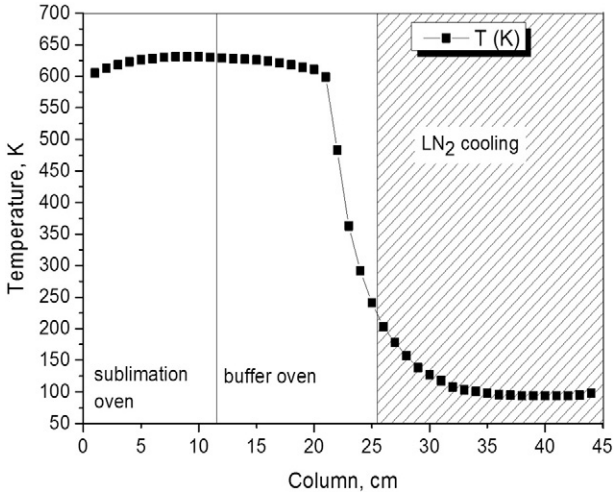

Fig. 2. The temperature gradient established inside the fused silica tube.

2.3.2. ^{75}Se deposition

In order to characterize quantitatively the deposition pattern of the amorphous selenium and its stability on the substrates under high gas flows, radioactive ^{75}Se containing samples ($t_{1/2}$ = 119.78 days; main γ-lines = 136 keV (59.2%), 265 keV (59.8%)) were used as tracer. ^{75}Se samples were produced by irradiation of the initial elemental gray Se (purity >99.999%, Fluka Chemicals) with thermal neutrons at the neutron activation rabbit system installed at the spallation neutron source SINQ at the Paul Scherrer Institute. The method of deposition was the same as for the non-irradiated selenium. The deposition of the radioactive ^{75}Se isotope along the fused silica column was determined via measuring the specific γ-activity with a high-purity germanium γ-ray detector collimated by a lead shield with a 1 cm × 0.5 cm window. Thus, the data acquisition and analysis system Canberra Genie2k® in conjunction with standard spectroscopy electronics enabled the quantification of the ^{75}Se activity in each centimeter of the column.

2.3.3. X-ray diffraction

Selected sections of the fused silica tube coated with selenium were weighed and ground to a fine powder using an agate mortar. The

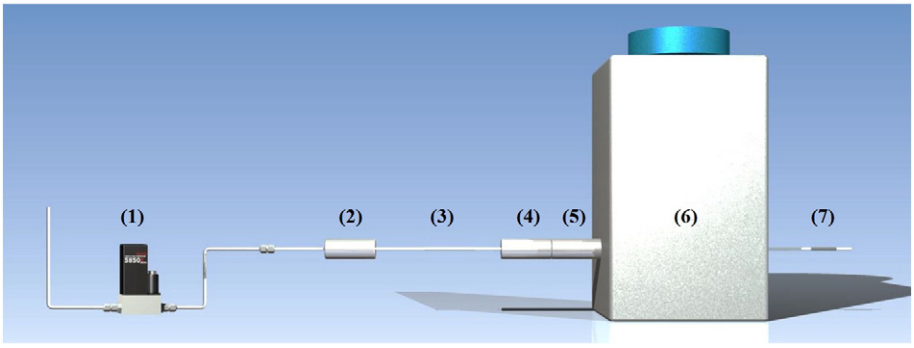

Fig. 1. Sketch of the setup used for volatilization and deposition of selenium: The He gas flow regulated by a mass flow controller (1) passes through a tantalum getter oven (2) kept at 1273 K. There are no connections between the tantalum getter oven and the fused silica tube (3) in order to minimize the oxygen and water intake. A high purity pellet of elemental selenium (~0.08 g) is placed inside the fused silica tube, where the sublimation oven (4) is positioned. After 2 h of flushing the setup by dried He gas, the oven (5) is switched on and the liquid nitrogen tank (6) is filled. After 1.5 h the temperature gradient is established and the sublimation oven (4) can be switched on. The evaporation of ~0.08 g of selenium takes about 8 h. The selenium which is not deposited in the fused silica column is captured in the charcoal trap (7).