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Infrared and Raman spectroscopy study of As—S chalcogenide films prepared by plasma-enhanced chemical vapor deposition

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ABSTRACT

As—S chalcogenide films, where As content is 60–40 at.%, have been prepared via a RF non-equilibrium low-temperature argon plasma discharge, using volatile As and S as the precursors. Optical properties of the films were studied in UV–visible-NIR region in the range from 0.2 to 2.5 μm. Infrared and Raman spectroscopy have been employed for the elucidation of the molecular structure of the newly developed material. It was established that PECVD films possess a higher degree of transparency (up to 80%) and a wider transparency window (>20 μm) in comparison with the "usual" As—S thin films, prepared by different thermal methods, which is highly advantageous for certain applications.

1. Introduction

As—S chalcogenide glasses cause a strong interest due to they possess high refractive index values, high IR transparency, high optical non-linearity, stability to crystallization, possibility to be modified by a femtosecond laser irradiation and inertness to environment [1]. These also make them suitable candidates for fabrication of miniature optical photonic circuits, integrating on a single substrate a vast array of functional components such as: laser diode light source, switches, modulators, interconnecting waveguides and photonic detectors. Through such integration, a more compact, stable, and functional photonics systems can be produced [2].

Physical and chemical properties of chalcogenide thin films strongly dependent on deposition technique, due to the manufacturing method determines the thin films stoichiometry and structure, surface quality and impurities content. Nowadays a lot of methods are used for preparation of As—S films [3–12].They may be classified by means of initiation of chemical interaction - plasma and thermal methods, and on the kind of the initial substances used - bulk samples or volatile derivatives of constituents (hydrides, halides of elements, or metal-organic compounds). The existing methods have common disadvantages such as lack of chemical and structural uniformity, high roughness of the thin films surface (e.g. due to disproportion of As_2S_3 in gas phase) and the substantial contamination of the materials deposited because of incomplete conversion of the precursors.

That is why we have developed recently a novel method of preparation of chalcogenide glasses in general [13–15], and chalcogenide thin films, in particular [16–19], in which the thermal heating has been substituted by plasma initiation of the chemical interaction between precursors. During the Plasma-Enhanced Chemical Vapor Deposition (PECVD) process, the precursor's vapors are excited through electron collisions at a low overall process temperature, which means that low substrate temperatures can be achieved during the deposition. This enables deposition of amorphous materials on thermally sensitive substrates and the use of precursors with low reactivity. An additional advantage of the PECVD beyond the conventional PVD methods of films preparation includes a very precise control of the processes parameters and hence of the chalcogenide glasses structure parameters by means of controlling the electron temperature and concentration in the plasma discharge. Besides, the elemental As and S have been chosen as the initial substances to minimize the contamination of the final materials.

The main goal of this work is to correlate the structural and optical properties of As—S films prepared by the novel PECVD method, with the specific glass-net structure.

2. Experimental

2.1. Deposition

As—S chalcogenide films have been prepared using a setup described in detail in [16]. The initial chemical reagents - elemental arsenic and

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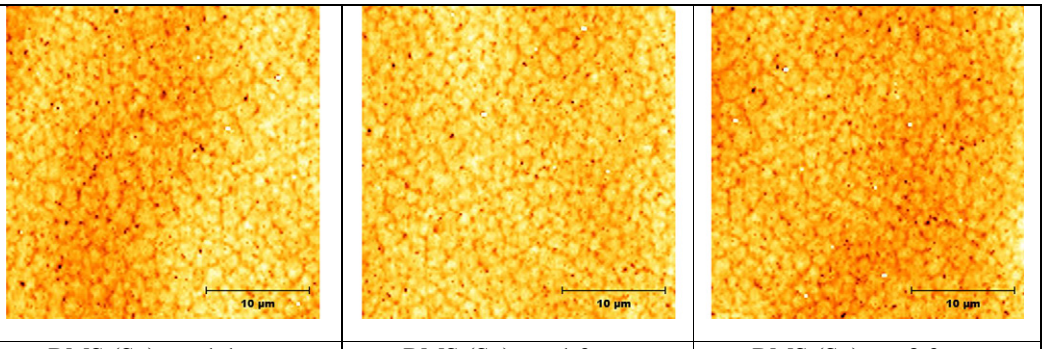

RMS (Sq): 1.1 nm	RMS (Sq): 1.3 nm	RMS (Sq): 2.3 nm
$As_{55}S_{45}$	$As_{50}S_{50}$	$As_{45}S_{55}$

Fig. 1. Surface morphology of PECVD As—S films of different stoichiometry.

sulfur - were loaded into quartz reservoirs with external heaters. The temperatures of the reservoirs were kept in the range 180–200 °C for sulfur and 340–380 °C for arsenic. High pure argon was used as a plasma feed gas and as a carrier gas. It was blown at a constant total rate 30 ml/min through the reservoirs to supply the precursors into the plasma discharge. The plasma discharge was excited by an RF generator with frequency 40 MHz and power 50 W. The substrate temperature was constantly maintained at 22 °C. High-pure quartz glass and NaCl (200) with lateral sizes 10 × 10 mm and thickness of 1 mm was chosen as the substrate materials to fit the different measurements requirements. The base pressure during the process of deposition was constantly kept 0.1 Torr and the reactor walls temperature was about 160 °C.

2.2. Characterization

The samples chemical composition was determined by X-ray microanalysis using a scanning electron microscope JSM IT-300LV (JEOL) with an energy-dispersion detector for elemental analysis X-MaxN 20 (Oxford Instruments) under high vacuum and at accelerating voltage of 20 kV. Transmission spectra in the range 0.2–3.3 μm were measured by spectrometer Agilent Carry 5000 UV–vis-NIR using a two-beam scheme with a step of 1 nm and accumulation time of 0.1 s. Transmission spectra of the samples in the IR range (2.5–25 μm) were measured with a spectral resolution of <1 cm^{-1} by Perkin Elmer BX II FTIR spectrometer at room temperature. The Raman spectra were studied by means of an NTEGRA Spectra system for Raman spectroscopy, produced by the NT-MDT Company (Zelenograd), using a He-Ne laser with a wavelength of 632.8 nm for excitation. The beam was focused by a 100× objective lens with a numerical aperture of 0.95. The unfocused laser power measured by a silicon photodetector 11PD100-Si (Standa Ltd) was about 1.5 μW. The Raman spectra of the samples were studied in a reflection configuration at room temperature in the range 50–900 cm^{-1} with an exposition time of 600 s.

3. Results and Discussion

3.1. Surface Morphology Investigation of As—S Films by Atomic Force Microscopy

The typical surface morphology of representative PECVD As—S samples with different chemical compositions and an average thickness of 5 μm, studied by Scanning Probe Microscope (SPM) is illustrated in Fig. 1. The chemical composition of the samples was given by the ratio of the initial substances in gas phase through the equations of dependence of vapor pressures of precursors on temperature and controlled in the deposited solid phase by EDX analysis with accuracy 1 at.%.

The surface morphology reveals structural units of 20 nm in size. The roughness values of the PECVD films vary from 1.1 nm for the sample with stoichiometry $As_{55}S_{45}$ to 2.3 nm for the sample with content $As_{45}S_{55}$. Obviously, the roughness means increase with increasing of sulfur content in chemical composition of the films.

It should be mentioned that these RMS values seem to be among the best ever reported in scientific literature for the films of As—S chalcogenide system. E.g. A. Moldovan et al. [20] have reported roughness of 10 nm for As_2S_3 thin films prepared by the vacuum evaporation technique. Thus, the represented data manifests a high potential of further quality improvement of the chalcogenide materials, e.g., in photolithography applications.

The perfect quality of the surface was supplied by regulation of conditions of plasma-chemical deposition process. In comparison with the traditional thermal evaporation, there are two additional parameters to affect the process – temperature and concentration of electrons in

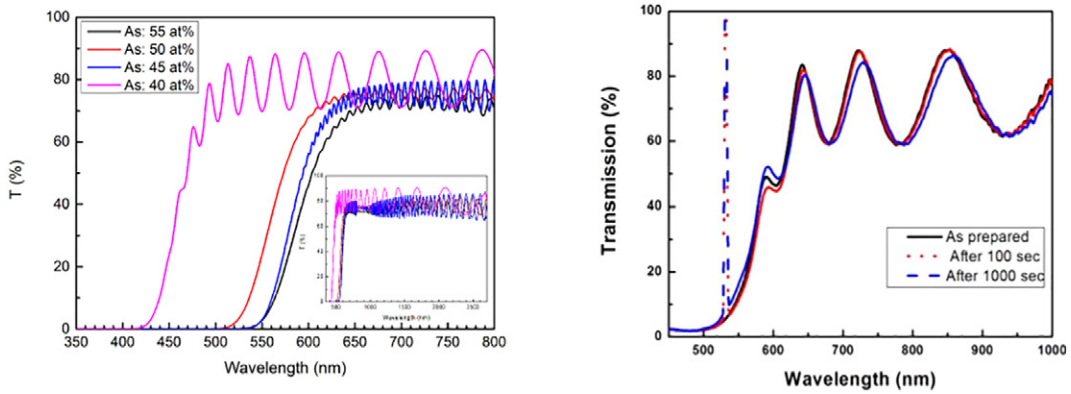

Fig. 2. (a) - Transmission spectra of PECVD As—S films with different stoichiometry in the UV–vis-NIR region of spectrum; (b) – data from [21] for comparison.