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Optical emission of two-dimensional arsenic sulfide prepared by plasma

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ABSTRACT

For the first time optical emission of prepared in plasma two-dimensional arsenic sulphide materials “beyond graphene” has been demonstrated. A strong structural photoluminescence exited by continuous wave operation lasers with a laser excitation wavelength of 473 nm and 632.8 nm has been observed. The influence of excitation parameters, chemical composition, structure, and annealing conditions on the intensity of photoluminescence of the chalcogenide materials has been established. Mass-spectrometry and Raman spectroscopy were coupled with quantum-chemical calculations to reveal the fragments which are the building blocks of the 2D As-S materials. A plausible mechanism of formation and modification of the arsenic sulfide luminiscenting structural units has been proposed. The properties of the 2D pole-structured and layered arsenic sulphide could be a key to advancing the 2D photosensitive devices.

1. Introduction

Since the discovery of graphene in 2004 [1], study of 2D materials “beyond graphene” brings about a growing interest of scientists. Among the family of chalcogenide materials, 2D-layered transition-metal dichalcogenides demonstrate excellent electronic and optical properties, outstanding mechanical flexibility, and exceptional catalytic performance. For that reasons, MoS_2, WS_2, WSe_2, etc., are promising candidates to be used in many potential applications, especially in energy-related fields, particularly, in energy storage and conversion systems [2]. Unlike graphene, the two-dimensional layered dichalcogenides possess a forbidden band of 1.2–1.4 eV transforming from indirect-gap bulk semiconductors into direct-band gap ones [3] at thicknesses of 5–7 monolayers. It has been also established that the specific honeycomb structural fragments forming the 2D layered structures of dichalcogenides are responsible for the structural luminescence phenomena [4].

In the same time, chalcogenides like As_2S_3, As_2Se_3, etc., have never been considered as materials capable of forming similar structures. It could be due to the limitations of the methods used for those materials preparation. In the present paper, we

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would like to show, how the honeycomb structural fragments are possible to be formed in plasma on the example of the well-known arsenic sulfide chalcogenide system.

Historically speaking, the types and parameters of As—S bonds in the realgar and orpiment structures were studied in detail and reported as early as 1950s [5]. It was shown that realgar and orpiment are built from the same basic (As_2S_2) structural units, giving rise to similar bond distances and angles in both cases. In the case of the orpiment an additional sulfur atom is added to each As_2S_2 unit to account for the required stoichiometry, and the realgar consists of discrete As_4S_4 units, while orpiment is a layered structure. In addition, in 1972 in Ref. [6] it was found that realgar As_4S_4 shows certain striking structural similarities to orpiment As_2S_3, although these are not apparent from a cursory inspection of the two structures. Despite of the scientific premises, the synthesis of As-S with a polymer structure, consisting of As_2S_2 monomers seemed impossible for a long while.

Recently, we demonstrated that the 2D $(As_2S_2)_n$ polymeric structure is possible to be obtained when plasma is used as the way of initiation of chemical interaction between As and S precursors [7,8]. Moreover, the chalcogenide materials treated by plasma at low pressures possess a substantial degree of purity that enables gaining insight into their intrinsic properties [9—11]. In the current work we are aiming to demonstrate the conditions of appearance and enhancing of structural luminescence in monochalcogenide $(As_2S_2)_n$ polymeric structure.

2. Experimental

2.1. Deposition

As-S samples were prepared by the plasma discharge-based deposition equipment described in Refs. [12,13]. The initial substances - elemental arsenic and sulfur - were loaded into quartz reservoirs with external heaters. The temperatures into the reservoirs were 200 °C and 380 °C for sulfur and arsenic, respectively. High pure argon was used as a plasma feed gas and as a carrier gas. It was blown at a constant total rate of 30 ml/min through the reservoirs to supply the precursors into the plasma discharge. The plasma chemical rector is a quartz flask with an external inductor. The bottom of the reactor is a stainless steel vacuum flange with a substrate holder cooled by water. The substrate temperature was constantly maintained at 22 °C. High-pure quartz glass and sodium chloride were chosen as the substrate materials in terms of different measurements. The samples were the films with the thickness about a few microns. The pressure during the process of deposition was constantly kept 0.1 Torr and the reactor walls temperature was about 150 °C. The plasma discharge was excited by an RF generator with a frequency of 40 MHz and power of 50 W.

2.2. Characterization

The study of the samples composition was carried out 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. Raman spectra were studied by means of 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. 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 in the range 1 mW—1 μW. The Raman spectra of the samples were studied in reflection configuration at room temperature in the range of 50—900 cm^{-1}. Photoluminescence study was performed at room temperature employing continuous wave operation lasers with a laser excitation wavelength of 473 nm and 632.8 nm. The arsenic sulfide materials were analyzed by mass-spectrometer DSQII to reveal their main structural fragments.

2.3. Theoretical modeling

Quantum-chemical calculations have been performed to gain insight into the plasma synthesized As-S chalcogenide structures. The structural fragments have been proved using the RB3LYP/6-31 + G(d) method and Gaussian 03 software package [19].

3. Results and discussion

3.1. Scanning electron microscopy study of the arsenic sulfide

Scanning Electron Microscopy (SEM) images typical of the arsenic sulfide with a composition $As_{40}S_{60}$ are illustrated in Fig. 1 (a) and (b). The striking difference in the surface morphology and structure is due to the very different conditions of the plasma deposition.

Both pictures (1a and 1b) illustrate arsenic sulfide structures consisting of $(As_2S_2)_n$-units (see below) formed in plasma by spherical structural fragments with a diameter of about 100 nm [7]. Fig. 1a shows a pole-structured material and Fig. 1b depicts a 2D layered structure, the theoretical possibility of existence of which has been described in Refs. [5,6]. We have reported quantum-chemical estimations of these structures [8] together with experimental results on the unusually broad