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Abstract. Two-dimensional (2D) materials have been intensively studied due to their outstanding chemical, physical, electronic and optical properties potentially offering a breakthrough in the search of a direct integration of these materials with the silicon (Si) technology. Among them, platinum diselenide ($PtSe_2$) is of significant interest for applications in electronics, spintronics, sensors, catalysis, etc. In this paper, we report a large-scale synthesis of $PtSe_2$-layers by thermally-assisted selenization of pre-deposited platinum films in a horizontal quartz-tube chemical vapor deposition (CVD) reactor. The overall structural information and quality of the $PtSe_2$-films is analyzed by Raman spectroscopy and Raman active modes identification. The electrical characterization via V-I characteristics reveals sheet resistance values in the range of $\sim 10^3$ Ω.

1. Introduction

Novel materials in a 2D structural configuration have been intensively explored due to their diverse chemical, physical, electronic and optical properties that may lead to a breakthrough in botn fundamental and applied science [1]. One of the widely investigated materials, platinum diselenide $PtSe_2$ [2], the parent compound in the noble transition metal dichalcogenides (TMDs) family, provides promising prospects for applications in opto-electronics, spintronics, sensorics and catalysis.

$PtSe_2$ and noble TMDs exhibit various physical properties: sophisticated electronic structure with a notable indirect band gap controlled by the layer thickness [3], defects [4], applied strain [5]. In a monoatomic layer form, the system reveals a semiconducting nature with a band gap in the range 1.2 – 1.8 eV [2]. The bandgap decreases with the number of layers thus transforming the 2D material into a semimetal type. Importantly, $PtSe_2$ shows the highest electron mobility among the 2D materials, reaching values of 3000 $cm^2\ V^{-1}\ s^{-1}$ [2]. This allows effective tuning of the semiconducting/semimetal properties evolution.

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One of the advantages of $PtSe_2$ is its relatively high environmental stability (a main weakness of almost all TMDs in a 2D form) and especially its conformity with the requirements of various synthesis approaches: thermally-assisted conversion (TAC, selenization of a pre-deposited Pt layer on a substrate) [2], chemical vapor deposition [6,7], molecular beam epitaxy [8], among others. In addition, the synthesis/growth conditions (at relatively low temperatures) are also compatible with the already established industrial technologies.

The present paper systematizes the first steps in a TAC synthesis of a $PtSe_2$ monolayer and an initial structural study via Raman spectroscopy and basic electrical characterization.

2. Synthesis and experimental details

The $PtSe_2$ films were synthesized by a TAC process [2] using a direct selenization of Pt precursor layers pre-deposited by magnetron sputtering. Thin Pt films of varying thicknesses (designated by the sputtering time, in seconds) were deposited onto a dry thermal silicon oxide (SiO_2) layer on a fused quartz substrate. The films were prepared in a dual-zone gradient tube furnace, which was heated to a growth temperature of 550 °C under a 5% H_2/ 95% Ar gas mixture flow (high temperature zone). Selenium (Se) vapor was produced by heating Se powder to ~ 220 °C in an independently controlled, upstream heating zone of the furnace (low temperature zone), and carried downstream to the Pt films for 2 h, after which the furnace was naturally cooled to room temperature. A schematic of the CVD reactor is shown in figure 1.

The $PtSe_2$ layers were obtained by a direct selenization from the Se vapor, as well as by a reaction with hydrogen selenide (H_2Se) formed at high temperature by Ar/H_2 gas mixture reacting with Se:

$$2H_2 + Se_2 \Leftrightarrow 2H_2Se, \quad (1)$$

$$Pt + 2H_2Se \Leftrightarrow PtSe_2 + 2H_2. \quad (2)$$

It is important to note that Pt, as a noble metal, has a relatively high resistance to oxidation.

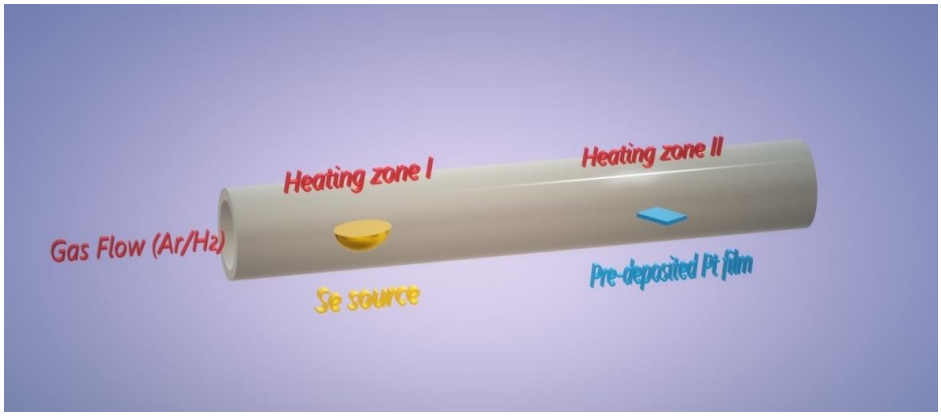

Figure 1. Schematic of a CVD system with a quartz tube reactor for synthesis of $PtSe_2$ 2D transition-metal dichalcogenide (TMD) material.

The $PtSe_2$ films were characterized by Raman spectroscopy carried out on an 80-cm Dilor XY-800 apparatus with a triple monochromator allowing for multi-channel liquid-nitrogen-cooled CCD detection or single-channel PM detection. The electrical characterization was performed using an Ossila four-point probe station for sheet resistance, resistivity, and conductivity measurements (probe spacing of 1.27 mm).

3. Results and discussion

The most prominent characteristics of all 2D materials, and PtSe in particular, are a direct consequence of the layered lattice structure with a strong anisotropy and electronic topological nature.

The resulting complex vibrational energy spectrum of the crystal lattice and important parameters, as the layer thickness, band structures, carrier, strain, chemical doping and phonon interactions, can be analyzed in detail using the versatile Raman spectroscopy. We analyzed the as-synthesized $PtSe_2$ thin film (12-s Pt deposition) on a SiO_2/fused silica substrate.

In figure 2, the Raman data in the spectral interval 100 – 600 cm^{-1} are shown for vertical (A) and horizontal (B) polarization modes.

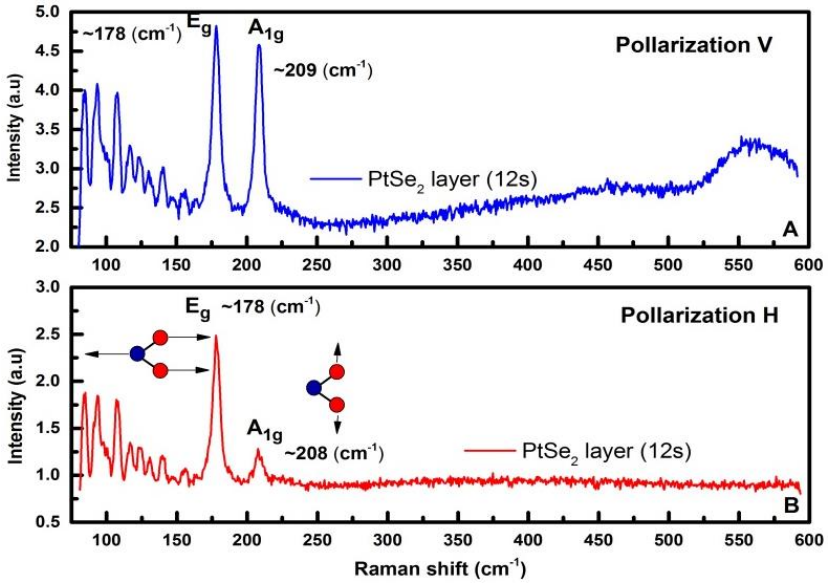

Figure 2. Raman spectra for $PtSe_2$ in polarization-dependent vertical (A) horizontal (B) configurations. The main vibrational modes are identified.

Two major vibrational modes are visible (typical feature for all 2D TMDs) corresponding to the in-plane and out-of-plane motions of atoms in the lattice. The peaks are identified using the phonon frequency predictions (O'Brien et al. [9]) for perfect crystals and assigned as E_g (~178 cm^{-1}) and A_{1g} (~209 cm^{-1}). The polarization-dependent (horizontal *vs* vertical) measurement reveals a decrease in the A_{1g} mode relative intensity, confirming the out-of-plane nature of the chalcogen atoms motion. We also identified the characteristic SiO_2 substrate peak observed at ~550 cm^{-1} (vertical polarization). The acquired Raman data are comparable with those of high-quality samples [10,11] in the literature, which proves the successful preparation and realization of $PtSe_2$ in a 2D form.

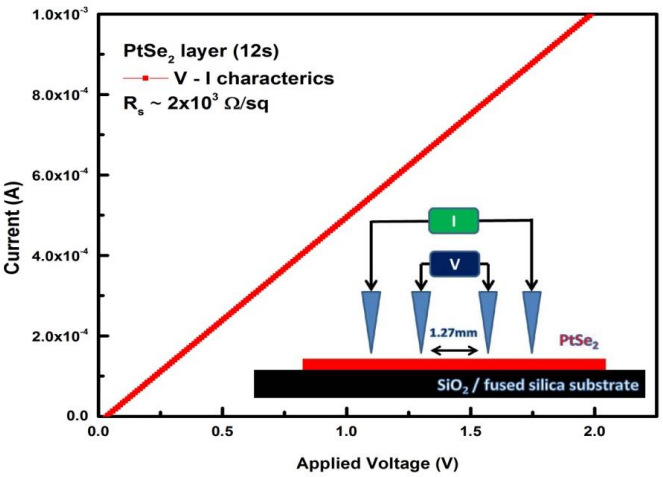

Figure 3. V-I characteristics and sheet resistance of $PtSe_2$. Sheet resistance measurement schematics (inset).

We emphasized above the sophisticated electronic behavior of $PtSe_2$. We therefore performed initial tests of the electro-transport properties of $PtSe_2$ films by means of V-I characteristics. The experimental data are presented on figure 3, showing a distinct linear type. We found resistivity values (measured at the sample center) in the range of ~10^3 Ω/sq.

The results agree well with those presented in the literature for identical $PtSe_2$ samples [12]. In addition, we observed some variations in the resistivity (about one order of magnitude) in the different sectors of the thin film, which could be related to geometric effects, namely, a distorted electric-field profile close to the edges, but also could be the result of a thickness inhomogeneity [3,10]. As we noted in the previous paragraph, the semiconducting/semimetal evolution of $PtSe_2$ is dependent on the layer number (thickness); consequently, this affects the resistive properties of the nanostructure.

4. Conclusions

We presented initial steps in the preparation (via TAC) and initial characterization of $PtSe_2$ films using Raman spectroscopy and electro-transport measurements. The successful realization of the compound in a 2D form is verified by the Raman data and the presence of characteristic in-plane and out-plane vibrational modes (E_g ~178 cm^{-1}) and (A_{1g} ~209 cm^{-1}). The films are also analyzed by electro-transport measurements, identifying resistivity values in the order of ~10^3 Ω/sq.

Acknowledgments

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