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Growth and optical studies of tungsten disulphide single crystals doped with gold

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ABSTRACT

Tungsten disulphide single crystals doped with gold (WS_2:Au) have been grown by the chemical vapor transport method using iodine as a transporting agent. The structure of the materials was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and Raman measurements. The doping effects of the materials are characterized by surface photovoltage (SPV) and piezoreflectance (PzR) measurements. The SPV spectrum reveals an impurity level located below the A exciton. The direct band-edge excitonic transition energies for WS_2:Au show redshifts and the broadening parameters of the excitonic transition features increase due to impurity scattering.

1. Introduction

Tungsten disulphide (WS_2) belongs to group VIA transition metal dichalcogenides MX_2 that exhibit many interesting physical properties with a pronounced two dimensional character [1]. The peculiar properties of these materials result from their layered structure, consisting of almost covalently bonded X-M-X sheets linked by weak van der Waals forces. WS_2, an indirect-gap semiconductor, has the subject of great interest, because its band gap is well matched to the solar spectrum. Taking into account prevention of photocorrosion, WS_2 can act as an efficient photoconductive layer in photovoltaic devices and photoelectrochemical solar cells [2]. Up-to date, only a few works concerning the doping effect on the properties of WS_2 was reported [3,4].

In this work, we report a detailed characterization, including scanning electron microscope (SEM), X-ray diffraction (XRD), Raman, surface photovoltage (SPV) and piezoreflectance (PzR) measurements of Au-doped WS_2 single crystals. The effects of dopant (Au) on the optical properties of WS_2 were analyzed and discussed.

2. Experiment

Single crystals of the system Au-doped WS_2 were grown using the chemical vapor transport (CVT) method with Br_2 as a transport agent. The total charge used in each growth experiment was about 10 g. The stoichiometrically determined weight of doping material was added in the hope that it will be transported at a rate similar to that of Mo. Before the crystal growth, the powdered compounds were prepared from the elements by reaction at 1000 °C for 10 days in an evacuated quartz ampoule. Prior to the crystal growth, a quartz ampoule (22 mm OD, 17 mm ID, 20 cm length) containing Br_2 (~5 mg/cm^3) and the elements (W, 99.99% pure; Au, 99.99%; S, 99.999%) was evacuated to 10^{-6} Torr and sealed. It was shaken well for uniform mixing of the powder. The ampoule was placed in a three-zone furnace and the charge prereacted for 24 h at 800 °C with the growth zone at 950 °C, preventing the transport of the product. The temperature of the furnace was increased slowly. The slow heating was necessary to avoid any possibility of explosion due to the exothermic reaction between the elements. The furnace was then equilibrated to give a constant temperature across the reaction tube, and was programmed over 24 h to produce the temperature gradient at which single crystal growth took place. Optimal results were obtained with temperature gradient of approximately 960 °C → 930 °C. After 240 h, the furnace was allowed to cool down slowly (40 °C/h) to about 200 °C. The ampoule was then removed and wet tissues applied rapidly to the end away from the crystals to condense the Br_2 vapor. When the ampoule reached room temperature, it was opened and the crystals removed. The crystals were then rinsed with acetone and deionized water. Single crystalline platelets up to 10 mm × 10 mm surface area and 2 mm in thickness were obtained.

The morphology of the WS_2:Au was recorded using a JEOL-JSM6500F field-emission scanning electron microscope (FESEM).

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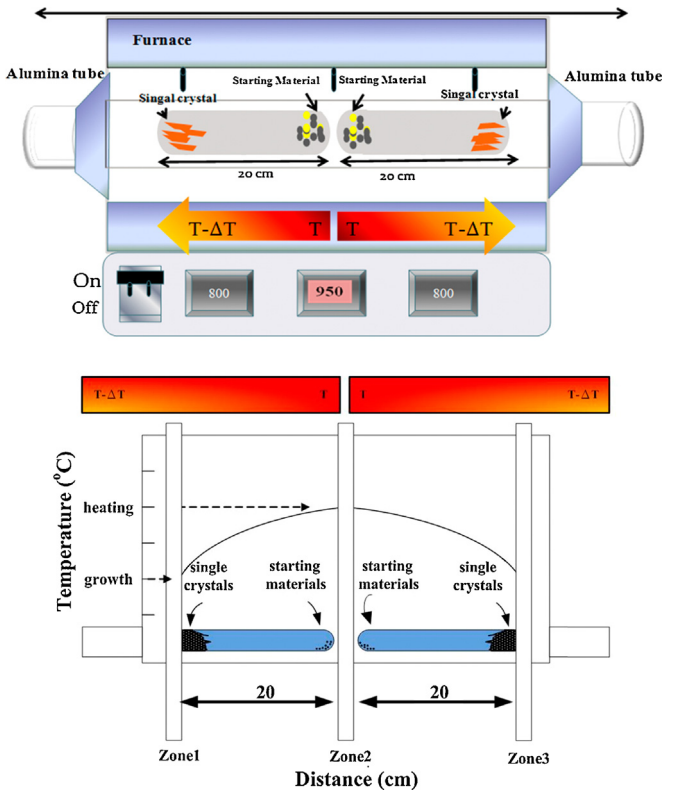

Fig. 1. The schematic diagram of the CVT setup and temperature profile for the growth of Au-doped WS_2 single crystals.

For X-ray studies, several small crystals from each grown batch of WS_2:Au were finely ground into powders. The powder X-ray patterns were taken and recorded by means of a slow moving radiation detector. The copper K_α radiation ($\lambda = 1.542$ Å) was employed in the X-ray diffraction measurements and a silicon standard used for experimental calibration.

The SPV measurements, which used normalized incident light intensity, were performed at normal incidence using a fixed grid and probe light chopped at 200 Hz [5]. The method of PzR has been described in the literature [6]. The measurements were achieved by gluing the thin single-crystal specimens on a 0.15 cm thick lead zirconate titanate piezoelectric transducer driven by a 200 V_{rms} sinusoidal wave at 200 Hz. An RMC model 22 closed-circle cryogenic refrigerator equipped with a model 4075 digital thermometer controller was used for low-temperature measurements. The measurements were made between 15 and 300 K with a temperature stability of 0.5 K or better (Fig. 1).

3. Results and discussion

The photo of the pristine WS_2:Au single crystals with centimeter sizes grown by CVT is shown in Fig. 2(a). The FESEM image of the WS_2:Au single crystals after preliminary mechanical exfoliation is depicted in Fig. 2(b) and most of the flakes have a random shape. The structure of WS_2:Au single crystals was further examined by the XRD measurement. Fig. 3 illustrates the XRD patterns. Four major diffraction peaks centered at 29.0°, 44.0°, 59.9°, and 77.2° were detected, which belong to a single orientation group of ⟨0 0 1⟩ (*c*-axial) (JCPDS #381367) for the mixed of rhombohedral and hexagonal structure of WS_2. Fig. 4 depicts the Raman scattering measurements for the WS_2:Au single crystals, the intensity of Raman lines in unpolarized and polarized ($Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$) configurations differ appreciably showing the first order Raman active modes. Two major Raman modes, respectively, at around 353 and

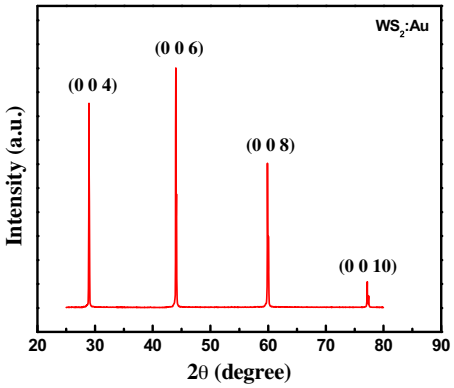

Fig. 3. The XRD pattern of WS_2:Au single crystals.

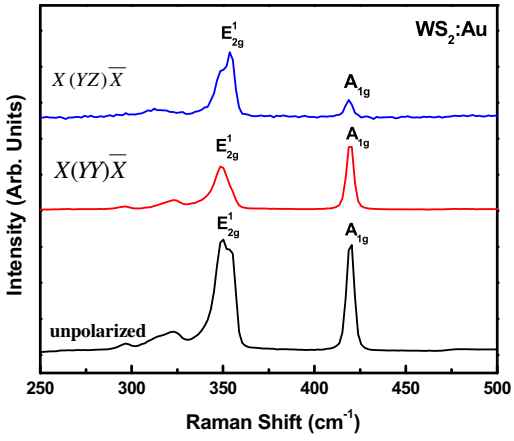

Fig. 4. The Raman spectra of WS_2:Au single crystals.

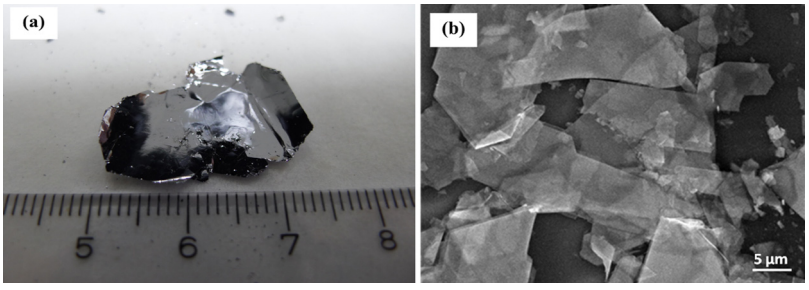

Fig. 2. (a) Photograph and (b) SEM image of WS_2:Au single crystals grown by CVT.