Research Paper

Electrical and Optoelectrical Properties of 1T'-phase MoTe₂ Atomic Layer Film

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ABSTRACT

Transition metal dichalcogenides with two-dimensional ultrathin film-type structures are suitable for applications in semiconductor devices owing to the presence of a direct band gap. Among these materials, tungsten ditelluride (WTe₂) and molybdenum ditelluride (MoTe₂) have potential applications in optical and electrical devices as they easily control the phase and exhibit unique electrical transport characteristics. In this study, 1T'-phase few-layers MoTe₂ thin films were grown on a silicon dioxide/silicon substrate using a metal organic chemical vapor deposition system; the phase of the grown MoTe₂ thin film was analyzed using Raman spectroscopy and few-layers MoTe₂ were observed using atomic force microscopy. A high-performance photodetector and field effect transistor were fabricated and used to analyze the photocurrent density and electrical characteristics of the thin films. On comparing the current of the laser with and without illumination for a photodetector based on the 1T' phase, the results indicated a significant increase in the photocurrent under illumination. This indicates the strong dependence of the few-layers MoTe₂ thin film on laser power. Thus, the 1T'-phase few-layers MoTe₂ thin film with a high photocurrent density and excellent electrical transport characteristics is considered a promising material for high-performance photodetectors.

Keywords: 1T'-phase, Photodetector, MoTe₂, Metal organic chemical vapor deposition, Field effect transistor

I. Introduction

A typical two-dimensional (2D) graphene structure is known to have excellent electrical, mechanical, and optical properties compared to three-dimensional graphite structures, as reported in previous studies [1]. Further, other 2D materials have been studied, because graphene has no band gap energy [2]. Transition metal dichalcogenide (TMD) is particularly attractive in materials research in the fields of transparent electronics and photonics, because it can be synthesized in 2D forms with a direct band gap. Furthermore, 2D TMDs have an ultrathin structure. Thus, they have the potential for yielding excellent properties such as high photoresponsivity when applied to photodetectors [3-5]. Moreover, 2D TMDs have a great advantage as room temperature photodetectors owing to their bandgap of 1.1 to 2.1 eV, covering a wide range (i.e., visible to short-wavelength infrared range) [6]. Molybdenum ditelluride (MoTe₂) is also known to have a direct band gap of 1.07 eV, which is relatively narrow among that of TMD materials, and it is attributed to the quantum confinement of MoTe₂ in the monolayer [7,8]. Thus, the MoTe₂ material can also cover a wide range from visible to short-wavelength infrared range. Recently, many studies have been conducted on the electrical characteristics and photo detection of field effect transistors (FETs), based on 2H-phase MoTe₂ flakes [9-12]. However, the electrical properties and photo-detection of the 1T'-phase few-layers MoTe₂ thin film grown using metal organic chemical vapor deposition (MOCVD) have not been researched sufficiently. In this study, few-layers MoTe₂ thin films are

synthesized in large areas on silicon dioxide/silicon (SiO₂/Si) substrates using MOCVD to obtain MoTe₂ thin films with excellent thickness uniformity and polycrystalline structure. For the evaluation of optoelectrical and electrical properties, photodetectors are fabricated by forming metal electrodes, using a shadow mask on the obtained few-layers MoTe₂ thin film. In addition, top-gate FET devices are fabricated through photolithography and e-beam lithography.

II. Experimental details

1T'-phase few-layers MoTe₂ thin films were grown on a p-type Si substrate with a 300-nm thick SiO₂ layer by using MOCVD with a reactor pressure of 10 Torr and a growth temperature of 400 °C. The substrate was treated with acetone, isopropyl alcohol, and deionized water before loading the chamber. Molybdenum hexacarbonyl (Mo(CO)₆) and di-tert-butyl telluride ((C₄H₉)₂Te) were used as sources of molybdenum (Mo) and tellurium (Te), respectively. The molar flow of (Mo(CO)₆) and (C₄H₉)₂Te were precisely controlled using a mass flow controller. Gas phase molar flow ratios for 1T'-phase MoTe₂ thin films were established: H₂/Te = 3.5 and Te/Mo = 166.6. The morphology of the fully covered MoTe₂ films was investigated via scanning electron microscopy (SEM, S-4800, Hitachi). An energy dispersive X-ray spectroscopy (EDS) study was performed using a JEOL JEM-2100F equipped with a spherical aberration (Cs) corrector (JEOL Inc.). A dispersive Raman microscope (Renishaw, inVia) was used to record the Raman spectra of the samples; excitation was induced with a 633-nm laser

diode having a spot size of 0.7 μm and laser power of 8 mW. X-ray photoemission spectroscopy (XPS, SES-100, VG-Scienta) techniques were employed to measure the binding energies of Mo and Te in the multilayer MoTe_2 films; XPS was carried out with a non-monochromatic magnesium $\text{K}\alpha$ source under ultra-high vacuum conditions ($<10^{-8}$ Torr).

The top-gate FET devices were fabricated using the conventional photolithography process. A photoresist (SU-8 2002) was spin-coated at 5,000 rpm on the few-layer MoTe_2 film side and then exposed using a mask aligner (MJB4). It was developed with an SU-8 developer to form mesa and under-cut structures [13]. Mesa etching was carried out using a reactive ion etcher (Exelan HPT, LAM Research) under the following process conditions: chamber pressure of 300 mTorr; RF power of 50 W; and O_2 and CF_4 flow rates of 10 and 50 sccm, respectively. Pd (50 nm) electrodes were deposited using an e-beam evaporator. The photoresist was eliminated using a PG remover (Microchem). Following the metal liftoff, atomic layer deposition was used to deposit a 40-nm thick layer of aluminum oxide as a top-gate dielectric. The top-gate electrode was defined using an e-beam lithography step. The top-gate metal contact was deposited as a 5/50-nm stack of Ti over Au. Finally, a metal liftoff in acetone was used to complete the device fabrication process. The electrical measurement of the device was performed at room temperature using an in-house four-probe station with a semiconductor parameter analyzer (4156A, Hewlett-Packard). To fabricate the photodetector, the metal electrode (Pd: 300 nm) was deposited atop the few-layers MoTe_2 film using an e-beam evaporator, except for an active area of $0.6 \times 0.5 \text{ cm}^2$. Photoelectric measurements at visible regions (white lamp with a power density of 16.4 mW/cm^2) were performed on a four-point probe station equipped with a semiconductor analyzer (4156B, Agilent, Inc.).

III. Results and discussion

Figure 1 shows the SEM image of the surface of 1T'-phase few-layers MoTe_2 thin film synthesized using MOCVD. The silicon substrate on which an oxide film is deposited is uniformly and completely covered by the grown few-layers MoTe_2 thin film. MoTe_2 specimens are prepared and characterized by peeling off a bulk MoTe_2 material using tape such as in the graphene exfoliated method [14,15]; this method has the advantage of easily obtaining an excellent crystalline structure. However, its limitation is that it is difficult to obtain a thin film with a uniform thickness over a large area as the thickness and size of the flake are randomly formed. To overcome this

Figure 1. Top view scanning electron microscope (SEM) image of few-layers MoTe_2 film grown on SiO_2/Si substrate.

limitation, few-layers MoTe_2 thin film specimens are prepared by a large-area growth method using MOCVD. Thus, the thickness of the thin film is controlled evenly at the atomic level, and it is uniformly grown over the whole wafer over time [16]. Thus, the 1T'-phase few-layers MoTe_2 thin film is obtained by adjusting the growth conditions such as growth time, temperature, and pressure gas flow. Typically, the structure of the MoTe_2 material appears in two forms: hexagonal (2H) and octahedral (1T or 1T'). Depending on the phase structure, the 2H-phase material has semiconductor properties, whereas the 1T'-phase material has semi-metal properties. Figure 2 shows the Raman spectrum images of few-layers MoTe_2 thin films deposited by MOCVD. The phase of few-layers MoTe_2 thin films can be confirmed from the Raman spectra, and the positions of the observed 11 cm^{-1} Au , 16 cm^{-1} B_g , and 272 cm^{-1} A_g Raman peaks were compared to the previously reported positions to prove that they are 1T'-phase few-layers MoTe_2 thin films [17,18]. The 1T'-phase few-layers MoTe_2 thin films used in this study are expected to have semi-metal properties. XPS measurements are used for the component analysis of few-layers MoTe_2 thin films, and the results confirm the presence of Mo and Te. The 571.2- and 581.6-eV peaks observed in the $\text{Te}3d$ scan of Fig. 3(a) correspond to $\text{Te}3d_{5/2}$ and $\text{Te}3d_{3/2}$, respectively, which are characteristic of MoTe_2 . The two peaks observed at 574.8 and 585.5 eV are generated by TeO_2 produced by the native oxide on the surface of the sample exposed to the atmosphere. In the $\text{Mo}3d$ scan of Fig. 3(b), the $\text{Mo}3d_{3/2}$ and $\text{Mo}3d_{5/2}$ peaks appear at 226.5 and 229.8 eV, respectively, which is consistent with the previously reported binding energy positions of MoTe_2 [19–22]. The XPS peak at 234.2 eV is caused by the native oxide produced on the surface of the sample exposed to the atmosphere [21,22]. The atomic force microscopy

Figure 2. (Color online) Raman spectra result of MOCVD-grown 1T'-phase few-layers MoTe_2 thin film.

Figure 3. (Color online) (a) $\text{Te}3d$ -scan XPS and (b) $\text{Mo}3d$ -scan XPS obtained with a grown 1T'- MoTe_2 specimen.

Figure 4. (Color online) AFM image of a grown MoTe₂ sample. The right side was etched for thickness measurement.

Figure 5. (Color online) (a) Optical image of top-gate MOSFET device, and (b) I-V characteristic of top-gate MOSFET with 1T'-phase few-layers MoTe₂ thin film.

(AFM) image in Fig. 4 confirms that the surface is homogeneous, and the local etching through nitric acid shows that the thickness of the grown few-layers MoTe₂ thin film is ~3.5 nm.

To evaluate the electrical properties of the 1T'-phase MoTe₂ thin film, a top-gate FET device is fabricated, as shown in the optical microscope image of Fig. 5(a). The bar pattern of a few-layer MoTe₂ thin film is fabricated via photolithography and a reactive-ion etching process; the width and length are 50 and 500 μm, respectively. A top gate with a width and length of 16 and 580 μm, respectively, is also fabricated through e-beam lithography. The applied drain voltages are 0.1, 0.55, and 1 V, and the gate voltage is swept from -25 to 5 V; then, the drain current is examined. As shown in the graph of Fig. 5(b), the electrical properties of the 1T'-phase MoTe₂ thin films show the characteristics of p-type metal-oxide semiconductor field-effect transistors (MOSFETs); however, the I_{on}/I_{off} current ratio is very low (~2.4). The current conductivity is high and the gate controllability is poor, which indicates that the thin film has semi-metallic characteristics.

Figure 6(a) is a schematic of a photodetector based on a 1T'-phase MoTe₂ thin film. The area of the irradiated photodetector is 0.3 cm². The opto-electric properties of the 1T' phase few-layers MoTe₂ thin film-based photodetector are investigated by irradiation using a white lamp. The photocurrent can be determined by comparing the currents when light is irradiated and when it is dark. Figures 6(b) and 6(c) show the current measured at room temperature (300 K) and low temperature (80 K), respectively. Both graphs show the current density (J) and voltage (V) characteristics measured by photodetectors for the current (I_D) when it was dark and the current (I_L) under white lamp

Figure 6. (Color online) (a) Schematic image of photodetector with 1T'-phase few-layers MoTe₂ thin film, (b) room temperature (300 K) J-V characteristics in the dark (I_D) and under white lamp illumination (I_L), and the photodetector photocurrent ($I_P = I_L - I_D$), (c) low temperature (80 K) J-V characteristics, and the photodetector photocurrent.

irradiation. When the bipolar bias is applied, the photocurrent ($I_P = I_L - I_D$) calculated from the J-V curve increases, and it saturates at about 70-V bias voltage [23]. The saturated photocurrent (1.4×10^{-2} A/cm²) at low temperature (80 K) is approximately twice as large as the measured value (8.0×10^{-3} A/cm²) at room temperature (300 K). This result suggests that the 1T'-phase few-layers MoTe₂ thin film has a relatively low band gap.

IV. Conclusions

Few-layers MoTe₂ thin films were fabricated uniformly over a large area on a SiO₂/Si substrate by using MOCVD. The Raman spectroscopy and electrical transport properties confirmed that the 1T'-phase was the dominant phase of the few-layers MoTe₂ thin film; the on/off ratio was verified using field-effect transistors fabricated on the few-layers MoTe₂ thin film. Furthermore, photodetectors were fabricated and used to measure the photocurrent and current density under white lamp irradiation and in the dark. Under illumination, the photodetector showed a significant increase in photocurrent indicating strong dependence on laser power, which is considered a stable photo-response. 1T'-phase few-layers MoTe₂ films with a high photocurrent and current density are thus promising materials for high-performance photodetectors.

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