Applied Surface Science 404 (2017) 276–281

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Anisotropic Raman scattering and mobility in monolayer $1T_d$-ReS_2 controlled by strain engineering

Z.H. Zhou, B.C. Wei, C.Y. He, Y.M. Min, C.H. Chen, L.Z. Liu*, X.L. Wu*

Key Laboratory of Modern Acoustics, MOE, Institute of Acoustics and Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 7 September 2016
Received in revised form 16 January 2017
Accepted 30 January 2017
Available online 1 February 2017

PACS:
73.20.At
73.30.+y
74.78.Fk

Keywords:
Anisotropy
ReS_2
Raman scattering
Mobility
Strain engineering

ABSTRACT

Regulation of electronic structure and mobility cut-on rate in two-dimensional transition metal dichalcogenides (TMDs) has attracted much attention because of its potential in electronic device design. The anisotropic Raman scattering and mobility cut-on rate of monolayer unique distorted-1T ($1T_d$) ReS_2 with external strain are determined theoretically based on the density function theory. The angle-dependent Raman spectrum of A_g-like, E_g-like and C_p models are used to discriminate and analysis structural anisotropy; the strain is exploited to adjust the structural symmetry and electronic structure of ReS_2 so as to enhance mobility cut-on rate to almost 6 times of the original value. Our results suggest the use of the strain engineering in high-quality semiconductor switch device.

1. Introduction

Recently, the transition metal dichalcogenides (TMDs) has attracted much attention because its tunable electronic and vibrational properties in promising applications [1]. They are expected to exhibit a wide range of electronic structures and exotic transport properties arising from the various electron configurations of transition metals, such assuperconductivity [2], half-metallic magnetism [3] and charge density waves. Furthermore, as two-dimensional (2D) materials, they are the potential candidates to overcome the bottleneck: severe short-channel effects which conventional metal-oxide-semiconductor encountered [4–10].

In this letter, we will be focused on a semiconductor material in TMDs family: rhenium disulfide (ReS_2). The distorted-1T ($1T_d$ ReS_2 takes on novel properties in optics, transport and vibration. Unlike hexagonal TMD materials, ReS_2 crystallizes in a distorted 1T diamond-chain structure with the triclinic symmetry, as a result of charge decoupling from an extra valence electron of Re atoms. This structural distortion leads to a much weaker interlayer coupling. Consequently, the band renormalization is absent and bulk ReS_2 behaves as electronically and vibrationally decoupled monolayer [11]. Therefore, in this work, we will focus on the monolayer $1T_d$ ReS_2 behavior. A detailed analysis to previous researches discloses that the properties are closely related to anisotropy of the structure. Hong-Xia Zhong's group studied the anisotropic optical response and anisotropic excition of ReS_2 from PDOS analysis [11]. Erfu Liu's group measured the carrier mobility of the $ReS_2$and revealed the transported property is different on various angles [12]. Daniel's group conducted experiments to obtain the angle-dependent Raman intensity distribution the modes ranging from 110 cm^{-1} to 158 cm^{-1} and noted that the relative intensities of the Raman modes are highly sensitive to the orientation of the in-plane crystallographic axes for few-layer samples [13].

However, our understanding to essence the anisotropy of ReS_2 is so limited and hitherto no study has been done to adjust the anisotropy. In this report, we will introduce angle-dependent Raman, an accurate tool, to discriminate the anisotropic structure of ReS_2. And as an innovative job, we apply the strain engineering to adjust the anisotropic carrier mobility and verify theoretically the anisotropy of carrier mobility can be enhanced remarkably. External strain can be easily implemented by introducing a specific substrate in the fabrication of T_d ReS_2 nanostructure [14].

* Corresponding authors.
E-mail addresses: lzliu@nju.edu.cn (L.Z. Liu), hkxlwu@nju.edu.cn (X.L. Wu).

http://dx.doi.org/10.1016/j.apsusc.2017.01.305
0169-4332/

This is an effective way to regulate the structural anisotropy and carrier mobility, and by which electronic device's performance in fact can be manipulated. For examples, the strain engineering can be employed to optimized the properties of GaN/AlN and help reduce the quantum-confined Stark effect, which increases light output power and suppresses efficiency droop in vertical-structure in InGaN/GaN MQW LEDs without modifying their epitaxial layers [15–17]. So, in this letter, we will employ angle-resolved Raman spectrum to discriminate the anisotropy of the monolayer T_d ReS_2 and apply external strain which is unavoidable especially in the frication of nanostructures to modify the carrier mobility anisotropy.

2. Theoretical methods

The theoretical method is based on the density functional theory in Perdew-Burke-Ernzerhof (PBE) generalized approximation (GGA), using the CASTEP package code with projector augmented wave pseudopotenials [18–20]. The plane-wave energy cutoff of 750 eV is used to expand the Kohn-Sham wave functions and relaxation is carried out until convergence tolerances of 1.0×10^{-5} eV for energy and 0.001 Å for maximum displacement are reached. The Monkhorst-Pack *k*-point meshes (in two-dimensional Brillion zone) are$3 \times 3 \times 1$ for the 2-D structure, which has been tested to converge.

3. Results and discussion

Firstly, the structural symmetry is firstly displayed in Fig. 1. The 1×1 primitive cell of $1T_d$ ReS_2 is shown in Fig. 1(a). The crystal lattice parameters we acquired from the calculation are listed as follow: OA = 6.57 Å, OB = 6.40 Å, ∠AOB = 60.16°, which are similar with the result of other groups [1,12], the slight difference can be originated from the different pseudo potentials adopted and the k-point set. The lattice parameters show that the $1T_d$ ReS_2 structure has asymmetric crystal structure, and its structural anisotropy is benefit to regulation of mobility cut-on rate. The Fig. 1(b) present the top view of the 3×3 supercell, the disparity between along a-axis and along b-axis (zigzag) is evident. The anisotropy can also be conveyed form the side view [see Fig. 1(c) and (d)]. Among the TMDs that have been reported to be stable individual layers of MoS_2, $MoSe_2$, WS_2, and WSe_2 have 1hexagonal (1H) structure in their ground state and dichalcogens of Ti, V, and Ta are in the 1H phase [1]. However, the atomic structure of ReS_2 single layer is $1T_d$ structure. One remarkable disparity between 1H, 1T and $1T_d$ structure is that the symmetry and isomorphism around the principal axis. Hence the $1T_d$ structure of monolayer ReS_2 outstands the unique anisotropy atomic structure among TMDs family.

In order to discuss the anisotropic electron structure of $1T_d$ ReS_2, we make sections of the electron density distribution [see Fig. 2(a) slice 1 and slice 2]. The electron clouds of the S atoms located at almost the same height (S_a, S_b, S_c, S_d) are examined. The *p*-orbitals of S_a and S_b share little with each other [see slice 1], nevertheless, as it shown on slice 2. The S_c and S_d share electron so as to form an interaction parallel the OAB plane. Details of the S atoms around Re1 and the interactions exerted on Re1 are shown on Fig. 2(b), (c) and (d), respectively. The maximum deviation rate ρ are defined as below to measure the anisotropy quantitatively:

$$\rho_f = \frac{f_{max} - f_{min}}{f_{min}} \quad (1)$$

where, *f* represents Mulliken Charge of atoms (M), population of bonds(P),or length of bonds (L), respectively. $\rho_M = 850\%$, $\rho_P = 42\%$, $\rho_L = 8\%$. The anisotropy among the Mulliken Charge (effective charge) is most notable, which can also be inferred from the analysis to the slice 1 and slice 2. The anisotropy among the bond population is considerable either, which indicates that the iconicity and covalence of the bonds are various. The S6-Re1 bond is most covalent and S5-Re1 is most iconic. The variation among the length of the bonds partly explains the dissymmetry in lattice parameters.

Table 1
Our calculation result (GGA-PBE method), Feng Group's calculation result[18] and experiment result (GGA-PW91 method)[18] of 18 A_g modes.

Symmetry	Ourresult (cm^{-1})	Calculation[18](cm^{-1})	Expt[18] (cm^{-1})
A_g-like	134.7	129.3	139.2
A_g-like	138.2	137.2	145.3
E_g-like	151.5	148.3	153.6
E_g-like	161.5	158.4	163.6
E_g-like	213.4	208.9	217.7
E_g-like	220	228.7	237.7
C_p	258.2	261.9	278.3
C_p	261.3	268.8	284.7
E_g-like	299.5	295.9	307.8
E_g-like	301.7	298.2	311.0
C_p	306.4	303.5	320.6
C_p	312.1	311.1	324.9
C_p	336.5	332.7	348.8
C_p	359.0	354.7	369.5
C_p	368.1	363.3	377.4
C_p	398.7	393.5	408.3
A_g-like	411.0	406.8	419.3
A_g-like	427.6	424.7	437.5

Zhou et al. Table 1.

Raman scattering is a useful tool to identify 2D material structural anisotropy, so the polarized-dependent Raman behavior are discussed subsequently. As an accurate test method to specify material, Raman spectrum have played important role in condensed matter physics, molecular biology and chemistry. Recent studies discovered that anti-Stokes Raman processes can be exploited to remove phonons and achieve laser cooling [21,22]. In following discussion, we will apply angle-dependent Raman scattering to discriminate the anisotropic of $1T_d$ ReS_2. ReS_2 is isomorphic to the point group C_i [13], the irreducible representations of the 36 Γ-point phonon modes (for primitive cell contains 12 atoms) can be written as

$$\Gamma = 18(A_g \oplus A_u). \quad (2)$$

The 18 A_g modes are Raman active and almost all of them can be detected in previous experiments [13,23]. Among the 18 A_u modes, 15 are infrared active modes, and 3 are zero-frequency modes. As it is shown in Table 1, the frequency of 18 A_g modes we obtained from GGA calculations are agree well with the theoretical and experiment results of other groups [23]. The consistency between the Raman peaks in our calculation and other groups' studies demonstrate that our optimized structure of 1Td ReS_2 should be appropriate. According to the classical Placzek approximation the anisotropic Raman intensity under the parallel configuration is [24,25]

$$I = \left| \left(\cos\theta,\ \sin\theta,\ 0\right) \tilde{R} \left(\cos\theta,\ \sin\theta,\ 0\right)^T \right|^2 \quad (3)$$

where θ is the angle between the laser polarization (linear polarized) and zigzag direction [24]; $\tilde{R}$ is the Raman tensor. We depict the angle-resolved Raman intensity distribution of several typical A_g-like, E_g-like and C_p modes in Table 2, with the vibration animation attached. In the C_p mode at 368.1 cm^{-1}, the S atoms move horizontally; while in the A_g-like mode at 427.4 $cm^{-1}$the S atoms vibrate vertically. So the vibration modes also outstand strong anisotropy. We also discover that the motion of the S atoms and Re atoms can be decoupled, for the C_p mode at 270.3 cm^{-1} shows that the S atoms shift while the Re atoms stay still. Scrutinizing the four angle-dependent intensity distributions (Table 2), it is found that the direction where the intensity of the C_p mode