CHIN. PHYS. LETT. Vol. 33, No. 4 (2016) 046201

Raman Scattering Modification in Monolayer ReS_2 Controlled by Strain Engineering *

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(Received 6 January 2016)

Regulation of optical properties and electronic structure of two-dimensional layered ReS_2 materials has attracted much attention due to their potential in electronic devices. However, the identification of structure transformation of monolayer ReS_2 induced by strain is greatly lacking. In this work, the Raman spectra of monolayer ReS_2 with external strain are determined theoretically based on the density function theory. Due to the lower structural symmetry, deformation induced by external strain can only regulate the Raman mode intensity but cannot lead to Raman mode shifts. Our calculations suggest that structural deformation induced by external strain can be identified by Raman scattering.

PACS: 62.23.Eg, 67.80.dm, 68.55.−a DOI: 10.1088/0256-307X/33/4/046201

Two-dimensional (2D) layered materials have attracted a large amount of research interest due to their rich physics and tremendous application potentials.[1−3] Lattice structure and symmetry are vital in determining materials' fundamental properties. Most studied 2D transition metal dichalcogenides (TMDs) exhibit isotropic behavior due to high lattice symmetries.[4] However, lowering the symmetry in TMDs could induce interesting anisotropic properties of both scientific and technologic importance. As the last stable element discovered in nature, the transition metal rhenium (Re) exhibits a wide range of oxidation states and crucial applications, such as superalloys and catalytic reforming.[5−7] Its sulfide, rhenium disulfide (ReS_2), is a semiconducting TMD that was recently discovered to have weak interlayer coupling and a unique distorted 1 T structure.[8] As shown by the top view of the monolayer ReS_2 crystal structure in Fig. 1, it consists of two hexagonal planes of S atoms (yellow) and an intercalated hexagonal plane of Re atoms (blue), there are two principle axes, i.e., the x and y axes, which correspond to the shortest and second-shorted axes in the basal plane. The angle is 61.03° and 118.97°, thus ReS_2 is an ideal material candidate for studying semiconducting 2D TMDs with low symmetry.

While lattice symmetries play a crucial role in determining their fundamental properties, most experimentally investigated 2D layered materials have high lattice symmetry, such as graphene and MoS_2.[9,10] For these materials, usually there are low-frequency rigid-layer Raman active modes 100 cm^{-1} in the few-layer and bulk samples due to the stacking structures. These modes have very weak intensities, which presents a huge challenge for traditional Raman spectroscopy to experimentally identify all the symmetry allowing Raman active peaks given the strong Rayleigh scattering and special probing approaches needed.[11−13] ReS_2 was recently found to have very weak interlayer coupling and a quite low symmetry. Using x-ray diffraction, Wildervanck *et al.* proposed that bulk ReS_2 crystallizes in a triclinic structure with the space group $P\bar{1} - C_i^1$ (No. 2).[14] This structure, with one unit cell containing one sandwich, has been confirmed by several groups.[15−17] With only one single layer in its unit cell, ReS_2 may exhibit novel and intriguing vibrational properties in Raman spectra.

In experiments, different nanostructures can be obtained, which exhibit obvious different physical characteristics. Comprehensive experimental and theoretical analysis discloses that its excellent physical characteristics are strongly related to intrinsic microstructures' transformations. Thus the identification to the monolayer ReS_2 structure by Raman scattering becomes an important physical problem, which is sensitive to slight variation in lattice symmetry. The morphology transformation and intrinsic defect will result in a local deformation, which is equated with an applied strain. This physical mechanism may be related to its novel phonon behavior. For this purpose, one needs to understand the responses of monolayer ReS_2 structural deformation to different strain fields. However, the understanding of strain-dependent Raman scattering in monolayer ReS_2 is quite limited so far.

External strain is unavoidable especially in the fabrication of the nanostructures and thin films. The re-

*Supported by the National Natural Science Foundation of China under Grant Nos 61264008, 61574080 and 61505085.
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sponses of a nanostructure to the external strain are determined by its mechanical properties, which are strongly influenced by introducing a specific substrate in the fabrication of monolayer ReS_2 structure. For instance, it has recently been proposed that strain induced by absorption of atoms on grapheme nanoribbons can be so strong that it may fold the nanoribbons forming single-walled nanotubes.[18] We have known that structural deformation can affect the monolayer ReS_2 structure phonon behavior; if strain is applied on this system, many new physical phenomena will be presented. This may lead to more complicated behavior in their Raman spectra of strain-related monolayer ReS_2 nanostructures. However, our understanding of strain-dependent Raman scattering properties of monolayer ReS_2 is very limited so far.

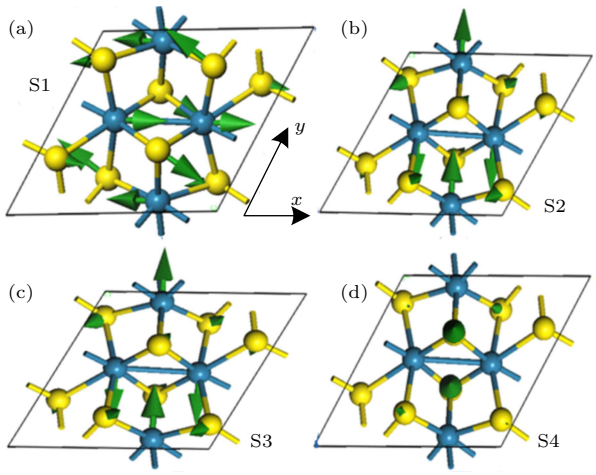

Fig. 1. (Color online) Schematic Raman modes of monolayer ReS_2 structure. Yellow and blue spheres stand for S and Re atoms, respectively.

In this Letter, monolayer ReS_2 is chosen as a model system to study the relationship between external strain and Raman scattering. The theoretical derivation discloses that asymmetric deformation induced by uniaxial strain can only regulate the Raman mode intensity but cannot lead to Raman mode shifts. Some weak vibration modes are enhanced to display in their Raman spectra, and their behaviors are also strongly dependent on the applied strain, which can be used as a fingerprint to identify the deformed monolayer ReS_2 microstructure.

Our calculations are performed under the framework of density functional theory as implemented in the CASTEP package. Electron–ion interactions are described by the projector augmented plane wave method, and the wave function is expanded in a plane wave basis set with an energy cutoff of 500 eV. The k points in the Brillouin zone are sampled on a $5\times5\times1$ mesh. The norm-conserving pseudo-potential method is chosen together with the gradient correction and the Perdew–Burke–Ernzerhof potential function.[19,20] The calculated lattice constants of monolayer ReS_2 are $x = 6.421$ Å, $y = 6.524$ Å. Finally, the optimized geometrical structure is employed to construct and diagonalize the Hessian matrix

$$D^{k,k'}_{\alpha,\alpha'} = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{\alpha} \psi^{k,k'}_{\alpha,\alpha'} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_\alpha}, \tag{1}$$

where $\psi^{k,k'}_{\alpha,\alpha'}$ are the matrix force constants related to the bond length and the bond angle. The vibrational frequencies are obtained as the square roots of the phonon wavevector $\boldsymbol{q} = 0$. The ratio of atom mass and bond length of Re and S atoms are $m_{\rm Re}/m_{\rm S} = 5.806$, respectively. The optimized cell eigenfrequency can be simply written as[21]

$$\omega_0^2 = \frac{1}{m_{\rm Re(S)}} \sum_{i=1}^{n} k_{\rm Re(S)}, \tag{2}$$

where $m_{\rm Re(S)}$ is the Re (S) atom mass and $k_{\rm Re(S)}$ is the corresponding parameters determined by the Re–S bond length and force constants. Those formulas indicate that its Raman mode behavior strongly depends on the symmetrical structure change. The deformed monolayer ReS_2 structure is characterized by two different types along the x- or y-direction, as shown in Fig. 1(d).

The lattice constant of optimized primitive (1×1) monolayer ReS_2 is $x = 6.421$ Å, $y = 6.524$ Å, and the angle between x and y axes is 121.2°, as shown in Fig. 1. For most 2D materials, the lattice constants of x and y axes are equal, and the angle is 120°, which provides good symmetries. However, the symmetry of monolayer ReS_2 is obviously different, the optimized structure leads to 18 Raman modes, four typical Raman modes marked by S1 (A_g mode), S2 (A_g mode), S3 (E_g mode) and S4 (E_g mode) are shown in Figs. 1(a)–1(d), respectively. We can infer that those Raman modes with different vibration directions can exhibit different Raman features, which also strongly depend on the structural deformation.

To more clearly display the Raman feature, the Raman spectra of ReS_2 with asymmetric deformation along the x-direction are calculated, as shown in Fig. 2. Without external strain in Fig. 2(c), five typical Raman modes are located at 135.7 cm^{-1} (S0 mode), 151.4 cm^{-1} (S1 mode), 273.4 cm^{-1} (S2 mode), 273.4 cm^{-1} (S2 mode), 335.8 cm^{-1} (S3 mode), and 418.4 cm^{-1} (S4 mode), which are in agreement with the previous reports of 139.2 cm^{-1} (A_g-like), 153.6 cm^{-1} (E_g-like), 278.3 cm^{-1} (Cp mode), 332.7 cm^{-1} (Cp mode), 419.2 cm^{-1} (A_g-like). When uniaxial strain along the x-direction is applied, the degenerate Raman mode intensity (S0 and S1) is obviously changed while positions are not shifted effectively. As compressed deformation induced by uniaxial strain along the x-direction decreases ($x = -2\%$) in Fig. 2(b), the S0 peak intensity is enhanced even in

excess of S1 peak. Another important feature is that S2 and S3 modes are also enhanced, while S4 mode is suppressed. This changed feature is similar to that of tensile deformation ($x = 2\%$) in Fig. 2(d), and this can be ascribed to the original structure being lower symmetry. The Re atom mass is much larger than the S atom, the asymmetric deformation can only affect the mode intensities but cannot affect the Raman mode position. When further compressing the x-direction deformation to $x = -4\%$ in Fig. 1(a), the intensities of S0 and S1 modes are almost equal, other Raman modes are decreased obviously, especially S3 mode at $x = -2\%$ deformation is depressed. A different feature in tensile deformation at $x = 4\%$ is that S1 mode is much larger than that of S0 mode in Fig. 2(e), and the other modes can be more obviously depressed. This is due to the fact that the vibration directions of S0 and S1 are restricted in the 2D plane (as shown in Fig. 1(a)), thus those intensities are responsible for the deformation. On the contrary, the other modes (as shown in Figs. 1(b)–1(d)) are not completely restricted in the 2D plane, therefore those mode changes are more complex. We can see that the symmetrical destruction makes newly Raman mode intensities change, which can be used to identify the monolayer ReS_2 microstructure transformation.

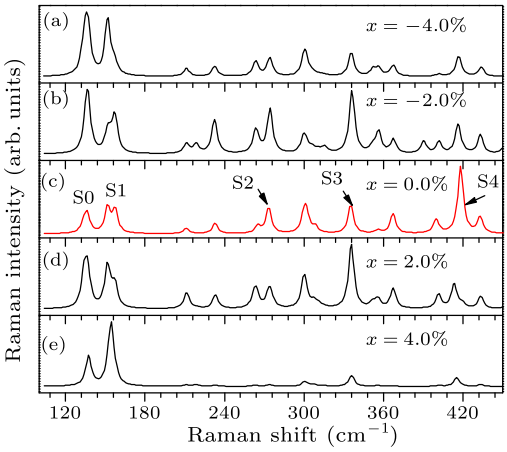

Fig. 2. (Color online) Calculated Raman spectra of monolayer ReS_2 structure with asymmetric deformation induced by strain along the x-direction.

To further disclose the asymmetric deformation effect, the Raman spectra of monolayer ReS_2 with asymmetric deformation along the y-direction are also calculated, as shown in Fig. 3. The Raman spectrum feature of S0 and S1 modes in ReS_2 with asymmetric deformation along the y-direction is similar to that of asymmetric deformation along the x-direction, while the deformations at $y = -2\%$ and $y = 4\%$ make newly Raman modes S5 and S6 exhibit in Raman spectra as shown in Figs. 3(b) and 3(e), which can be used to identify the deformation direction in the ReS_2 microstructure transformation. When the y-direction lattice is compressed to $y = -2\%$ in Fig. 3(b), the S1 mode intensity is larger than that of S0 mode, meanwhile S5 mode is activated and becomes the strongest peak. However, this special S5 mode disappears at $y = -4\%$ in Fig. 3(a). These results further imply that the original ReS_2 structure is unsymmetrical, and suitable compressed deformation can improve its symmetry, and newly strongest Raman modes appear in the Raman spectra. In addition, the tensile deformation at $y = 2\%$ in Fig. 3(d) not only changes the relative intensity of S0 and S1 modes, but also leads to the increase of S3 mode. Further increasing tensile deformation to $y = 4\%$ in Fig. 3(e), all Raman modes are enhanced accordingly, which is different from the x deformation. All those results disclose that the external strain can effectively change the Raman mode intensity, while cannot affect the Raman mode positions, which has a more complicated Raman scattering behavior.

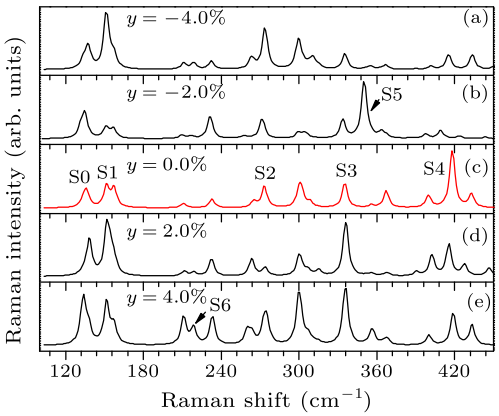

Fig. 3. (Color online) Calculated Raman spectra of the monolayer ReS_2 structure with asymmetric deformation induced by strain along the y-direction.

To compare intensity changes, the relative intensities of S0 and S1 as a function of the external strain (deformations along x and y) are calculated, as shown in Fig. 4. We can see that the relative intensity of S0/S1 is not changed linearly, the values reach the maxima at -2% external strain, and become a minima at 1% external strain, which are strongly related with the lower symmetric structure. In addition, the values of the x-direction are larger than that of y-direction, due to the fact that the lattice constants of $x = 6.421$ Å are smaller that $y = 6.524$ Å, and the deformation along the x-direction will lead the ReS_2 structure to more asymmetric states. Therefore, the deformation induced by the external strain in these special ReS_2 materials makes complex Raman spectra change. Those results indicate that their Raman behavior is strongly dependent on deformation induced by the external strain, and the strain can effectively affect their Raman spectrum feature, as a main factor should be considered in experimental results analysis.

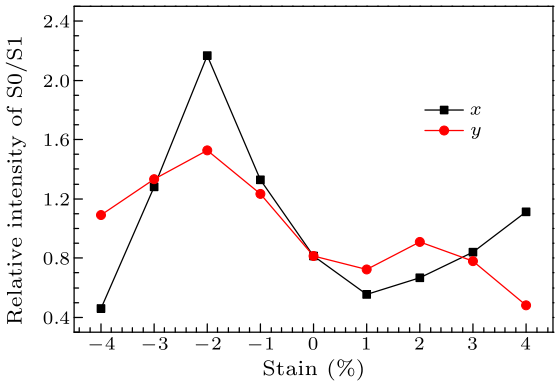

Fig. 4. (Color online) Calculated relative intensities of S0 and S1 modes of the monolayer ReS_2 structure as a function of the external strain.

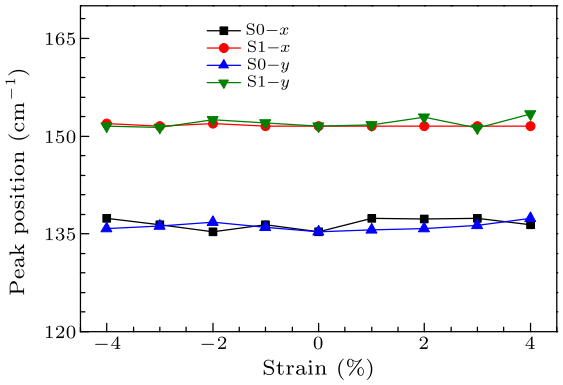

Fig. 5. (Color online) The calculated S1 and S0 mode peak positions of the monolayer ReS_2 structure with different deformations (x and y) as a function of the applied strain value.

Another important Raman feature is that the peak positions are hardly changed with the external strain, as shown in Fig. 5. The peak positions of S0 and S1 are displayed typically, and we find that S0 and S1 modes fluctuate at 135 cm^{-1} and 151 cm^{-1}, respectively. This is completely different from other 2D materials.[5,9,10] This special behavior is ascribed to larger relative masses of Re and S atoms ($m_{\rm Re}/m_{\rm S} = 5.806$). This special Raman scattering behavior makes the ReS_2 phonon vibrational physical mechanism more mysterious, and more in depth research should be carried out.

In summary, the deformation induced by the external strain can further enhance the crystal asymmetry, and deformation induced by the external strain can only regulate the Raman mode intensity but cannot lead to Raman mode shifts. Their Raman peak relative intensity decreases and increases caused by strain changes can be used as a fingerprint to identify the inner lattice and symmetric changes. The Raman spectrum feature of monolayer ReS_2 with symmetric deformation becomes more complex, and their changes cannot be described by a simple linear relation. The complex microstructural changes induced by the asymmetric deformation can be clearly displayed by the Raman spectra.

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