The synthesis of ReS$_2$ flakes and its application in photodetectors

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Abstract. ReS$_2$ is attracting much attention because of its stable trion state. This kind of stable trion state arises on account of weak interlayer coupling as well as anisotropic crystal structure. In this research, we have synthesized ReS$_2$ flakes successfully by using chemical vapor deposition (CVD) method. Stable ionic states in hexagonal wafers are observed by photoluminescence spectroscopy (PL). This substance is stable at room temperature. The HRTEM image from the single ReS$_2$ hexagon reveals that the individual hexagon is single crystal. EDS spectroscopy indicates the purity of the synthesized product. We find that the Re and S atoms ratio in pure ReS$_2$ is 1:2. Then we fabricate a photo detector on individual ReS$_2$ flakes and test its performance. We compare the photocurrent in dark current and under a 500 nm incident light for two media (air and 100 ppm H$_2$). Emission current increases from 1.15 μA to 1.67 μA (forward) and from 7.9 μA to 13.8 μA (reverse). Therefore, the ReS$_2$ hexagonal wafer is an ideal choice for stable and reliable room temperature optical gas sensor. And the material can also be used for fast switch.

1. Introduction

ReS$_2$ is a key member of graphene layered materials with excellent electro-optical properties. ReS$_2$ has a direct band gap and anisotropic crystal structure, which makes it a good choice for high efficiency optoelectronic devices$^{[1]}$. It has reported that ReS$_2$ has great potential in the fields of anisotropic electronics and optical detectors$^{[2]}$. However, research on gas sensing using ReS$_2$ layered structure is still lack. We find that ReS$_2$ is a good choice for gas sensor due to the presence of stable ions and stable physical and chemical properties. In this experiment, hydrogen-assisted CVD is used to grow high quality hexagonal scales. The ratio of hydrogen to nitrogen is the most important part for the growth of high quality, uniform surface structure of ReS$_2$[3]. Raman spectroscopy is used to identify the quality of the growth samples. Excitons and trions with two distinct characteristics are observed in PL spectroscopy at room temperature. The adsorption behaviour of gas molecules on the surface of ReS$_2$ is observed by light detector measurement in different gas environments. It indicates that ReS$_2$ has a good application prospect in photoelectric devices.

2. Experimental part

2.1. Synthesis of the samples

In this experiment, ReO$_3$ (10 mg) powder and S (3 g) sulfur powder are used as precursor materials. Under the atmosphere of high purity (N$_2$ and H$_2$) with constant current, it is heated to 625°C within
15min and the holding time is 10min. ReS$_2$ is synthesized by CVD process in a horizontal tube furnace, and the growing samples are cooled to room temperature in the furnace. What’s more, we test the performance of the sample on an optoelectronic device. The photoelectric devices are fabricated on ReS$_2$ wafers by lithography with electrode thickness of 10/50 nm Ti/Au respectively. The samples are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The optoelectronic device is illuminated by a 500 nm light source.

3. Result and Discussion
Large-size homogeneous growth of ReS$_2$ wafers on SiO$_2$/Si substrates is investigated. Firstly, we use a mixture of N$_2$: H$_2$ = 1:1 as a gas environment under normal pressure. We observe that the ReS$_2$ showed 3D flowery growth rather than uniform 2D growth. Figure 1 shows the low and high magnification scanning electron microscopy (SEM) image of the 3D flower-like structure of ReS$_2$. It can be seen from the image that the three-dimensional flower-like flakes are uniformly distributed on the SiO$_2$/Si substrate, and the average particle size is about 5 μm. In addition, in order to obtain uniform surface structure, we change the ratio of N$_2$ to H$_2$ in the gas from 1:1.5 to 1:2.

![Figure 1. It shows the low and high magnification scanning electron microscopy (SEM) images of the 3D flower-like structure of ReS$_2$.](image)

The higher hydrogen concentration in the carrier gas creates stress in the growing ReS$_2$. Due to the strain generated by these stresses and weak interlayer coupling, the influence of strains can be very high in ReS$_2$, for example, interlayer coupling of ReS$_2$ (18 meV) as compare to MoS$_2$ (460 meV) [4]. Therefore, with the increase of the proportion of N$_2$ and H$_2$ in the gas, the influence of strains gradually decreases. It thus obtains uniform ReS$_2$ hexagonal in the experiment. Figure 2(a) and Figure 2 (b) show HRTEM image and energy dispersive spectroscopy (EDS) of individual ReS$_2$ hexagons, respectively. The HRTEM image from the single ReS$_2$ hexagon reveals that the individual hexagon is single crystal. EDS spectroscopy indicates the purity of the synthesized product [5]. It is shown that the Re and S atoms ratio in pure ReS$_2$ is 1:2.
Figure 2. HRTEM image (a) and energy dispersive spectroscopy (EDS) (b) of individual ReS$_2$ hexagons.

Raman spectroscopy is used to further investigate the quality and purity of the samples. Raman spectra in Figure 3 confirms that the synthesized hexagonal slices are pure ReS$_2$, and the positions of in-plane E$_{2g}$ modes (151 cm$^{-1}$, 161 cm$^{-1}$, 211 cm$^{-1}$) and out-plane A$_{1g}$ modes (139 cm$^{-1}$) are consistent with those described in the literature. The sharpness of the peak of the sample reflects the quality of the synthesized ReS$_2$ crystal$^{[6]}$. It can be seen from the figure that, compared with other samples, when the ratio of N$_2$ to H$_2$ gas is 1:2, the peak of Raman spectrum of the sample is sharper, which indicates that the sample ReS$_2$ obtains crystals of high quality and purity at this ratio$^{[7]}$. This result is consistent with the conclusion obtained in Figure 2.

Figure 3. Raman spectroscopy of as-synthesized hexagonal ReS$_2$ flakes with different ratio of gases. (N$_2$: H$_2$ = 1:1/ 1:1.5/ 1:2)

In order to study the photoelectric properties of a single ReS$_2$ wafer, photodetectors are prepared on uniform ReS$_2$ wafer samples by standard lithography. The device schematic diagram is shown in Figure 4, in which the photodetector device consists of two Au electrodes with a thickness of 10 nm Ti or 50 nm Au, and the separation is about ~8 μm.
To investigate the gas sensitive properties of individual ReS$_2$ sheets, photodetectors are measured in gaseous atmosphere with air and gaseous mixtures (N$_2$ and 100 ppm H$_2$) respectively. Figure 5 shows the photocurrent comparison of two media (air and 100 ppm H$_2$) under dark current with 500 nm incident light. In dark condition, when the device is exposed to 100ppm H$_2$ gas, the forward bias (41 nA) and the reverse bias (111 nA) are significantly enhanced, which is very important for two-dimensional materials as gas sensors. When the gas molecules are adsorbed on the surface of ReS$_2$, electron exchange occurs between the gas molecules and the two-dimensional layer$^8$. This electron exchange may cause a change in the band structure$^9$.

To investigate this change in band structure, we further measure the device under 500 nm light in two different media (air and H$_2$). In light condition, the forward bias (0.51 $\mu$A) and negative bias (5.85 $\mu$A) are significantly increased when exposed to air and 100ppm H$_2$ gas. When we change the sensing conditions (air and H$_2$) from dark to illumination, the enhancement is around 12 times in the forward bias and about 52 times in the reverse bias, as shown in Figure 5. These results clearly indicates that the gas molecules adsorbed on the surface of ReS$_2$ and electron exchange occurs after adsorption. The dark current increases from 12 nA to 53 nA(forward) and from 21 nA to 132 nA(reverse). After electron exchange, the band structure changes and the emission current increases from 1.15 $\mu$A to 1.67 $\mu$A (forward) and from 7.9 $\mu$A to 13.8 $\mu$A (reverse).

Figure 5. The comparison of photocurrent in dark current and under a 500 nm incident light for two media (air and 100 ppm H$_2$).
4. Conclusions
In conclusion, the CVD technique uniformly synthesizes the uniform ReS$_2$ hexagons successfully. The results show that the concentration of hydrogen (N$_2$: H$_2$) in the carrier gas is the key factor for the final morphology and the growth of high-quality crystal. High concentration of hydrogen will lead to the growth of out-plane weakly coupled lamellar structures and form three-dimensional flower-like structures. We find that the Re and S atoms ratio is 1:2 in pure ReS$_2$. We compare the photocurrent in dark current and under a 500 nm incident light for two media (air and 100 ppm H$_2$). Emission current increases from 1.15 μA to 1.67 μA (forward) and from 7.9 μA to 13.8 μA (reverse). Therefore, ReS$_2$ hexagonal flakes can be a good choice for fast switch, reliable room temperature gas sensor.

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