Controlled vanadium doping of MoS\(_2\) thin films through co-sputtering and thermal sulfurization

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**Abstract**

Recently, transition metal dichalcogenides (TMDs) have gained great attention owing to their remarkable properties. The electronic structure of TMDs can be modified by substitutional doping, which could give rise to novel and exciting properties. In this study, a strategy is presented for controlled vanadium (V) doping of MoS\(_2\), in which V doped MoS\(_2\) films with good uniformity are prepared by thermal sulfurization of V-Mo alloy films deposited using co-sputtering. The V incorporation in MoS\(_2\) induces p type doping, which enhances the electrical conductivity of MoS\(_2\) by a factor of 35-40. Such doping strategy and consequent conductivity improvement may be useful in many applications such as catalysis, nanoelectronics and optoelectronics.

**Keywords:** MoS\(_2\), doping, vanadium, transition metal dichalcogenides, thin film

1. Introduction

Since the discovery of graphene, there has been a growing interest in 2D materials [1–4]. Analogous to graphene, TMDs exhibit a layered structure, where each layer has a composition of MX\(_2\) (M: transition metal, X: S, Se or Te) [5]. The transition metal and chalcogenide atoms are linked by strong covalent bonds whereas individual layers are stacked together by weak van der Waals interactions [5]. TMDs have been extensively studied for their electronic, optoelectronic, sensing, catalytic and tribological properties [6–10]. One of the most widely investigated TMD material is MoS\(_2\). Bulk MoS\(_2\) is an indirect bandgap semiconductor with a gap value of 1.2 eV while single layer MoS\(_2\) has a direct bandgap of 1.8 eV [11]. Field effect transistors fabricated using single layer MoS\(_2\) show high on/off current ratios with decent carrier mobility, which makes it promising for low power and flexible electronics [12,13]. Ultrasonic photodetectors have been fabricated using MoS\(_2\) [14,15]. Low friction MoS\(_2\) lubricant coatings have been demonstrated [16,17]. MoS\(_2\) has also been shown to be a promising catalyst for hydrogen evolution reaction (HER) [18–22].

Doping has been used in semiconductor industry for many decades to improve device performance. Similarly, doping can be utilized to alter the electronic structure of MoS\(_2\) opening new venues in electronics, optoelectronics and catalysis. For example, Se doped MoS\(_2\) nanosheets with tunable optical properties have been synthesized by simultaneous sulfurization and seleniumization of MoO\(_3\) powder, in which Se doping causes a shift in the bandgap value of MoS\(_2\) [23]. Nipane et al. demonstrated p-type doping of MoS\(_2\) by low energy phosphorus implantation [24]. Lateral p-n junction devices fabricated by selective regional phosphorus doping of MoS\(_2\) exhibited nearly ideal and air stable diode behavior. Furthermore, chlorine doping was shown to reduce the contact resistance of MoS\(_2\) by 2-3 orders of magnitude, resulting in enhanced mobility [25]. Moreover, Pulickel et al. [26], Xie et al. [27] and Li et al. [28] investigated the electronic transport properties of W\(_x\)Mo\(_{1-x}\)S\(_2\), MoS\(_2\)Se\(_{2(1-x)}\) and Co,Mo\(_{1-x}\)S\(_2\) alloys.

The catalytic activity of MoS\(_2\) is hindered by low conductivity and lack of active sites on its basal plane [21]. Theoretical studies suggest that substitutional doping of MoS\(_2\) can increase the conductivity as well as alter the binding energy of adsorbed hydrogen on sulfur favorably, inducing additional active sites, which would in turn enhance HER activity [29,30]. In the light of these potential benefits, many doping strategies for MoS\(_2\) have been developed. Solution processing methods have been used to synthesize Zn, Ni, Co, Fe, Cu doped MoS\(_2\) nanosheets [31–33]. P, Se

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and V doped MoS₂ prepared by high temperature solid state reaction techniques have been reported [34–36]. In addition, Cr doped MoS₂ films and MoS₂–Se nanobelts have been produced by CVD method [37,38]. In this study, a method is reported for controllable V doping of MoS₂. V doped MoS₂ thin films with different V/Mo ratios were prepared through co-sputtering of V-Mo alloy films and subsequent thermal sulfurization step. Simultaneous deposition of V and Mo atoms by co-sputtering enables to synthesize homogeneously doped MoS₂ films with good control of dopant concentration and thickness. The structural properties of the V doped MoS₂ films were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements. Four-point probe measurements were conducted to reveal the effect of V doping on the sheet resistance of MoS₂ film.

2. Materials and Methods

A multi-target magnetron sputtering system (Vaksis Angora) was used for the deposition of the V-Mo alloys. 20 nm thick V-Mo alloy films were deposited on n-type (100) Si substrates by co-sputtering of V and Mo targets (99.9% purity, Kurt Lesker) in RF and DC mode, respectively. The chamber was evacuated to 5x10⁻⁶ Torr before deposition. The Ar pressure was kept at 10 mTorr during the sputtering. Targets were cleaned at each run by pre-sputtering for 5 minutes while shutters were closed. The substrate holder was rotated at 5 rpm during the deposition to ensure uniformity. The desired alloy content was obtained by varying the sputter rate of each target, which was controlled by sputter power. Four different samples of VₓMo₁₋ₓS₂ were prepared with increasing amounts of x.

The sulfurization was carried out in a tube furnace (MTI OTF-1200X-S-NT-LD) with 50.8 mm diameter quartz tube. The deposited alloys films were placed at the center and 0.5 g sulfur powder (Merck) at the upstream side of the furnace. The tube was flashed with high purity nitrogen to remove oxygen for 1h prior to sulfurization and nitrogen flow with a rate of 100 sccm was continued during the sulfurization. The center of the furnace was gradually heated up to 800 °C in 80 min and kept at 800 °C for 1h before cooled down to room temperature naturally. The sulfur powder was at 150 °C (above its melting temperature) during the reaction.

X-ray diffraction measurements were carried out by Rigaku D-Max with Cu Ka source. The morphology and chemical composition of the films were investigated with Zeiss Supra 40VP scanning electron microscope. Raman spectroscopy measurements were performed on Kaiser Raman Rxn with a laser wavelength of 514 nm. The sheet resistance of the films was determined by four-point probe measurements.

3. Results and Discussions

XRD measurements were performed in order to examine the crystal structure of the V doped MoS₂ films (Figure 1). The XRD patterns of all samples are in good agreement with hexagonal MoS₂ phase (PDF#01-075-1539). The fact that no VS₂ phase was detected and all samples exhibit hexagonal MoS₂ phase indicate that V substitutionally doped MoS₂ and the crystal structure of MoS₂ has been preserved. The undoped MoS₂ film exhibits two pronounced peaks originated from (100) and (101) planes due to the preferential growth of the film in vertical direction [39]. With the increasing V content, the (002) peak becomes prominent whereas the intensity of (100) and (101) peaks decreases. The intensity ratio of the (002) peak to the (100) peak is calculated to be 0.19, 2.24, 2.59, 5.44 and 25.4 for the MoS₂, V₀.₀₉Mo₀.₉₁S₂, V₀.₂₃Mo₀.₇₇S₂, V₀.₃₅Mo₀.₆₇S₂ and V₀.₅Mo₀.₅S₂ films, respectively. The increasing ratio of (002) to (100) with higher V concentration indicates that V doping promotes the horizontal stacking. Furthermore, the interplanar spacing of the doped MoS₂ films is close to that of the undoped MoS₂ film, further suggesting that V doping did not alter the crystal structure of the MoS₂ film significantly.

![Fig. 1. XRD plots of the undoped MoS₂ and V doped MoS₂ films.](image-url)
The Raman spectra of the undoped MoS$_2$ and V doped MoS$_2$ films are shown in Figure 2. All the samples exhibit the characteristic peaks of MoS$_2$: E$_{2g}^1$ originated from the in-plane vibrations of Mo-S atoms and A$_{1g}$ resulted from the out-of-plane vibrations of Mo-S atoms [40]. Note that both peaks are significantly broadened compared to atomically thin MoS$_2$ films reported in literature [41, 42], which may be resulted from the polycrystalline nature of the films. No peaks corresponding to VS$_2$ has been detected, confirming the substitutional doping of V in MoS$_2$. The undoped MoS$_2$ film shows an ambiguous E$_{2g}^1$ peak and a strong A$_{1g}$ peak pointing out the vertically grown MoS$_2$ layers [43]. However, as the V concentration is increased, the intensity ratio of E$_{2g}^1$ to A$_{1g}$ grows dramatically, which implies a transition from vertical to horizontal growth with increasing V/Mo ratio. These results are also consistent with the XRD outcome.

Figure 3 shows the SEM images of 20 nm thick V-Mo alloys sulfurized at 800 °C for 1 h, in which V$_{0.05}$Mo$_{0.95}$S$_2$, V$_{0.23}$Mo$_{0.77}$S$_2$ and V$_{0.33}$Mo$_{0.67}$S$_2$ have a granular morphology (50 nm average grain size) while V$_{0.5}$Mo$_{0.5}$S$_2$ exhibits more like a layered structure. Additionally, nanoribbon-like structures with widths down to 20 nm and lengths up to 6 µm were detected in V$_{0.05}$Mo$_{0.95}$S$_2$ and V$_{0.23}$Mo$_{0.77}$S$_2$ films (Figure 3a, c and d). The EDX mapping results confirm the presence of S, V and Mo elements and indicate that their distribution is homogeneous throughout the films (Figure 4).

Figure 4. EDX mapping results of the V doped MoS$_2$ films.

Four-point probe measurements were conducted in order to reveal the effect of V doping on the electrical characteristics of MoS$_2$. Figure 5 shows the sheet resistance values of the undoped and doped films, in which the doped films exhibit 35-40 times lower sheet resistance compared to undoped MoS$_2$. The lowest sheet resistance value of 1.96 kohm/sq has been achieved at 33 at. % V doping. As $R_s = \rho \cdot t$ and $\sigma = 1/\rho$ (R$_s$ sheet resistance, $\rho$ resistivity, $t$ thickness and $\sigma$ conductivity), it can be concluded that V doping has increased the conductivity of the MoS$_2$ film by a factor of 35-40. The conductivity of a semiconductor is given by $\sigma = q(n\mu_e + p\mu_h)$, where $q$ is the elemental charge, $n$ and $p$ are the electron and hole carrier concentration, $\mu_e$ and $\mu_h$ are the electron and hole mobility. Thus, the conductivity enhancement in the V doped MoS$_2$ films can be attributed to the increase of carrier concentration. Since V has one less valence electron than Mo, the incorporation of V atoms in the MoS$_2$ crystal causes an electron deficiency in the bonding orbitals; hence p-type doping is induced in MoS$_2$. 

Fig. 2. Raman spectra of the undoped MoS$_2$ and V doped MoS$_2$ films.

Fig. 3. Scanning electron microscopy images of (a, b) V$_{0.05}$Mo$_{0.95}$S$_2$, (c, d) V$_{0.23}$Mo$_{0.77}$S$_2$, (e, f) V$_{0.33}$Mo$_{0.67}$S$_2$ and (g, h) V$_{0.5}$Mo$_{0.5}$S$_2$ films.
4. Conclusions

In summary, V doped MoS$_2$ films with varying V/Mo ratios have been successfully prepared by sulfurization of sputter deposited V-Mo alloys. The doping concentration is adjusted by changing the relative deposition rates of V and Mo. The structural characterization results show that MoS$_2$ hexagonal structure is maintained upon V doping, V doping is uniform throughout the films and horizontal layer stacking becomes preferred with increasing V content. The V doped MoS$_2$ films exhibit greatly enhanced conductivity, which could be useful for catalysis applications such as hydrogen evolution or oxygen reduction reactions. Moreover, this method can be extended to synthesize various ternary TMD alloys, where controlled doping, thickness and morphology may be beneficial to study fundamental properties of such alloyed materials.

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