Magnetron sputtered WS\(_2\); optical and structural analysis

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Abstract. Remarkable properties of graphene have renewed interest in inorganic, Transition Metal Dichalcogenits (TMDC) due to unique electronic and optical properties. TMDCs such as MoS\(_2\), MoSe\(_2\), WS\(_2\) and WSe\(_2\) have sizable bandgaps that change from indirect to direct in single layers, allowing applications such as solar cells, transistors, photodetectors and electroluminescent devices in which the graphene is not actively used. So, fabrication and analysis of these films are important for new generation devices. In this work, polycrystalline WS\(_2\) films were grown by radio frequency magnetron sputtering (RFMS) on different substrates like n-Si(100), n-Si(111), p-Si(100), glass and fused silica. Structural, morphological, optical and electrical properties were investigated as a function of film thickness and RF power. From XRD analysis, signals from planes of (002), (100), (101), (110), (008) belong to the hetzagonal WS\(_2\) were obtained. Raman spectra of the WS\(_2\) show that there are two dominant peaks at \(\sim 351\) cm\(^{-1}\) (in-plane phonon mode) and \(\sim 417\) cm\(^{-1}\) (out-of-plane phonon mode). XPS analysis of the films has shown that binding energy and the intensity of tungsten 4f shells shifts by depending on the depth of the films which might be due to the well-known preferential sputtering.

1. Introduction

Unique optical and electrical properties of 2D materials permit many important device applications. One of the most well-known 2D material graphene attracts attention for semiconductor device applications due to its strong interaction with photons in a wide energy range and its high carrier mobility, in a broad wavelength range [1-3]. However, field effect transistors produced from graphene cannot be effectively switched off and have low on/off switch ratios due to lack of bandgap [4]. This brings up the importance of other 2D materials. Many other 2D materials are known such as TMDCs (transition metal dicalcogenides), MX\(_2\), M; transition metal (Mo, W, i.e) and X; chalcogenide (S, Se, i.e) [4, 5]. TMDC materials such as MoS\(_2\) and WS\(_2\) are covalently bonded to six chalcogenide neighbors within the same plane, but weakly linked to sheets above and below by van der Waals force. The layers are stacked along the c-axis. If the thin films grown with the c-axis parallel to substrate, i.e. the X-M-X layers are perpendicular to the substrate, they will referred to as “ \(\perp\) c “. The “\(\perp\) c” orientation has the advantage of photovoltaic materials, with c axis perpendicular and layers parallel to the substrate [6].

Important properties of 2D materials are [2]: 1) their surfaces are naturally self-passivated without any dangling bonds, making the integration of 2D materials with photonic structures easy, for example such as waveguides and cavities. 2) It is possible to raise vertical hetero-structures using different 2D materials without the conventional lattice mismatch, due to sheets with different lattice constants in hetero-structures are only weakly bonded by van der Waals force as in layered materials. 3) Even if the thin films exist atomically thin, many 2D materials interact with light strongly. For example a single layer tungsten disulfide (WS\(_2\)) absorbs roughly %10 at exitonic resonances (615nm) [7]. 4) 2D materials can cover a very wide electromagnetic spectrum, since their diverse electronic properties [2].
In this paper, WS\textsubscript{2} thin films grown by sputtering are investigated depending on the film thickness and substrate. The structural analysis has been performed by using X-ray diffraction (XRD). Raman spectroscopy used to the phonon modes that can provide a fingerprint for WS\textsubscript{2} thin films. X-ray photoelectron spectroscopy (XPS) was used in order to investigate the elemental analysis together with the depth profile analysis.

\section{Experimental Produce}
WS\textsubscript{2} thin films were deposited by Radio Frequency Magnetron Sputtering (RFMS), using \%99.99 WS\textsubscript{2} target. Substrates were chemically cleaned prior to the insertion in the vacuum chamber. Base pressure of 2\times10^{-7} Torr was reached in the sputtering chamber before the growth process. Growth pressure was 8.6 mTorr. Five different substrates were put in the chamber in order to investigate the substrate effect on the WS\textsubscript{2} films. The substrates temperature was 350 °C during the deposition. Details of the deposition parameters are summarized in table 1.

| Table 1. Parameters of sputtering system |
|-----------------------------------------|
| Target (purity) | WS\textsubscript{2} (99.99\%) |
| Target diameter | 2 inc |
| Target to substrate distance | 80 mm |
| Base pressure | 2\times10^{-7} torr |
| Sputtering pressure | 8.6 mTorr |
| Substrate temperature | 350 °C |
| Substrates | Si(100), Si(111), fused silica, quartz, glass |

Structure of the thin films was studied by x-ray diffraction (XRD) with Empyrean, PANalytical with Cu K\textsubscript{α} radiation. The measurements were performed at grazing incidence angle of 0.5° degree. Further evidence for composition of the grown thin films was obtained using XPS which was performed with a Thermo Scientific K-Alpha–Monochromated high-performance XPS spectrometer. Raman measurements were conducted with Ar+ laser wavelength of 514.5 nm with a CCD camera attached to the 1 m long monochromator.

\section{Results and discussion}
A comparison of the XRD profiles of WS\textsubscript{2} thin films grown in different RF power is illustrated in Fig. 1. Polycrystalline nature of thin films is observed in multiple peaks in the XRD spectra. Three distinct peaks clearly observed in the figure. The first one appeared around 13.24° degree which is belong to the (002) plane. Second peak observed in the XRD spectra of the thin films attributed to the combined (10l) (l is 0,1,2..), third peak which is (103) observed only in the thin film grown at 6 WRF power 38.08 degree and forth peak is observed at 60.9 degree which is (11l). Dominant crystal orientation in the grown thin films has changed by changing the RF power from (002) to (10l) as shown in Fig. 1. The degree of preferred orientation, which can be inferred from the peak heigh of the (002) peak is dramatically decreased by increasing RF power in the growth process. FWHM (full width half maximum) of the all peaks observed in the XRD spectra given aboveshowrs that FWHM increases while increasing of RF power (i.e. FWHMs of (002) and (112) peaks are increasing from 3.30 to 6.31 and from 2.35 to 2.84 respectively but FWHMs of (100)+(101) peak are decreasing from 2.24 to 1.68, while RF power increased).
This might be due to the observation of some extra peaks, namely (103), plane as observed in the thin film grown at 60W. Also, (002), (112) and combined (100)+(101) peaks are slightly has shifted smaller angles as a function of RF power. If diffraction occurs off of the horizontal planes (tensile strain), and the Bragg peak shifts to higher angle as the interplanar spacing decreases [8, 9]. Then it can be confirm that the (002), combine (101) + (101) and (112) plane exposure to compresive strain.

Raman Spectroscopy was used to characterize the samples’ structural quality and vibrational properties. Since it is non-devastating technique and it is widely used to characterize the structural and electronic properties of monolayer materials such as graphene, WS$_2$ and MoS$_2$ [10-12]. To reason out this observation we fitted the Raman peaks using a Voigh function and positions and modes depending on the type of the substrate. The clear observation of the raman modes indicates good quality of the material. The Raman spectra for the various substrate (p-Si(100), n-Si(111) and fused silica) in 310nm WS$_2$ thin films are shown in Fig. 2. It is confirmed that the WS$_2$ exhibit first order modes at wavenumber of 348 cm$^{-1}$ and 418 cm$^{-1}$ separated by about 70 cm$^{-1}$, corresponding to the $E_{2g}^1$ and $A_{1g}$ modes from in plane and out-of plane vibrations, respectively.

**Fig. 1.** XRD-patterns in different RF power of WS$_2$ films on n-Si(111) substrate.

**Fig. 2.** Room-temperature Raman spectra from a monolayer WS$_2$ region; 310nm thickness of WS$_2$ thin films on various substrate (45W RF Power).
The peak of $E_{2g}^{1}$ mode is broad due to consisting of another mode so called 2LA(M) (second-order longitudinal acoustic mode) [11, 13, 14]. In generally, 2LA(M) peak which matches in energy with the density of states absorption peak, is prevalent as a small left portion of the $E_{2g}^{1}$ peak [14]. small changes observed depending on the substrate type in Raman modes. This might be due to the different strain in which the grown WS$_2$ thin films are subjected to. In addition Raman peak shifts are showing a trend to decrease in frequency of the optical $E_{2g}^{1}$ phonon mode and an increase in frequency of $A_{1g}$ phonon mode with increasing thickness of the thin films (Fig. 2.). These variations in the Raman frequency of the $A_{1g}$ and $E_{2g}^{1}$ modes depending on the different substrate can be explained by weak interlayer substrate can be explained by weak interactions and the reduced long-range Coulomb interaction between the effective charges caused by an increase in the dielectric screening, respectively [13, 15, 16]. No raman signal corresponding to the WO$_3$ has been observed.

XPS measurements performed in order to find out the concentration of the elements. As shown in Fig. 3, XPS survey spectrum of WS$_2$ shows that only C, O, W and S is observed all of the films in. To identify the chemical composition of WS$_2$ thin films, XPS was used to measure the binding energy of W and S as well as carbon and oxygen.

**Fig. 3.** XPS survey spectrum of WS$_2$ thin film after 100s etched.

Depth resolved XPS measurements were used to understand the elemental profile of W and S. Ar gun was used to achieve etching processXPS data was acquired 120s of sputter between every measurement. The characteristic W4f and S2p XPS spectrum of WS$_2$ thin film is shown in figure 4. The binding energy profile for W4f$_{7/2}$ and W4f$_{5/2}$ is represented by two peak at 31.5eV and 33.8eV, respectively, corresponding to W in WS$_2$ [17-19], after the film is etched for the first 120s. the W 4f spectrum has consisted of 4 peaks for the last three XPS measurements (see fig. 4.a). The appeared peaks shows a shift to higher binding energy values i.e. 35.7eV and 37.6 which might be corresponding to tungsten in WO$_3$ (W$^{6+}$) [17, 20] While W4f$_{7/2}$ peak intensity of WS$_2$ decreases with the depth profile, possible observed peaks belong to the WO$_3$ starts to increase, as shown in Fig. 4. a. As shown in figure 4.d, the S2p spectrum is deconvoluted to a dublet consisting of S2p$_{3/2}$ and S2p$_{1/2}$ Peaks centered at binding energy values of 161.88eV and 163.18eV which correspond to S$^{2-}$ in WS$_2$.

In order to find the peak energy position of the W 4f belonging to WS$_2$. Lorentz function were used to fit observed data (see fig.4.c). Binding energy shifts has observed in 4f features as shown in the inset of figure 4c.
Fig. 4. XPS analysis of WS$_2$ thin film, a) W4f$_{7/2-5/2}$ b) Schematic illustration of grid zone in an XPS depth profile c) the Lorentz fit data graph of WS$_2$ thin film at fig 4.a and also shown is the binding shifts while the etch time is increasing (inset) d) S2p binding energy.

Figure 5 shows the UV visible absorption spectrum of WS$_2$ thin film.

Fig. 5. Optical absorption of WS$_2$ thin film in a wavelength range of 350-1100 nm with an computed optical bandgap $\sim$1.17 eV from the calculated at the lineer fit of optical absorbance plot data, as shown in the inset.
The figure inset shows the bandgap energy obtained from plotting the \((\alpha h\nu)^{1/2}\sim(h\nu-E_g)\) graph, where \(\alpha\) is the absorption coefficient of the WS\(_2\), \(h\nu\) is the incident photon energy, and \(E_g\) is the optical bandgap. Bandgap energy of the WS\(_2\) was obtained from the linear fit as shown in the inset of the figure 5 as 1.17 eV which is very close to the bulk indirect bandgap of the WS\(_2\).

4. References

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Acknowledgments

We appreciate Hasan Feyzi Budak for the XRD measurements. This project was supported by Atatürk University Scientific Research Project Unit under contract No: 2015/343. We would like to thank to Enver Kahveci for the XPS measurements. We are thankful to Prof. Dr. Atilla Aydınlı for discussion on the Raman measurements.