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Textured MoS_2 thin films obtained on tungsten: Electrical properties of the W/MoS_2 contact

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Textured films of molybdenum disulfide have been obtained by solid state reaction between the constituents in thin films form when a (200) oriented tungsten sheet is used as substrate. The crystallites have their *c* axis perpendicular to the plane of the substrate. The annealing conditions are $T=1073$ K and $t=30$ min. The films are stoichoimetric and *p* type. Such highly textured films are achieved without foreign atom addition (Ni, Co...). It appears, as shown by x-ray photoelectron spectroscopy, that a thin WS_2 layer is present at the interface W/MoS_2. The crystallization process is discussed by a van der Waals texturation (pseudoepitaxy) onto dangling bond sulfur terminated surfaces, these surfaces being ordered. After characterization of the W/MoS_2 structure by x-ray diffraction and x-ray photoelectron spectroscopy, an upper electrode of tungsten was deposited by sputtering. The electrical properties of these W/MoS_2/W structures have been investigated by analyzing the behavior of the current–voltage characteristics as a function of the measuring temperature. It is shown that an ohmic contact is obtained with a contact resistance smaller than the resistance of the MoS_2 film. © *2000 American Institute of Physics.* [S0021-8979(00)08103-2]

I. INTRODUCTION

Considerable interest has currently been shown in layered metal dichalcogenide compounds such as WSe_2, WS_2, and MoS_2,[1] which can serve as the absorber in solar cells.[2] Conversion efficiencies in excess of 17% may be obtained with WSe_2 single crystals, for example,[3] and for economic reasons these materials have been prepared as thin films[4] but they exhibited disappointing performances. However it has been reported that WS_2 films, having their basal (002) planes parallel to the substrate, can be obtained after annealing at high temperature ($\geqslant$1073 K) when the substrate is covered with a thin Ni layer. Such films have been obtained by annealing either WO_3 films under an H_2S atmosphere[5] or amorphous WS_{3+x} films in flowing argon[6] or in flowing argon[7] with 5% H_2S, multilayered Mo/S/Mo...Mo/S structures in flowing argon.[8–10] However it has been shown by x-ray photoelectron spectroscopy depth profiles that, in such films, Ni diffuses through the thickness of the films and that 1% of Ni is visible at the surface of the films.[9] As a consequence, different Ni phases have been in evidence such as Ni_3S_2 (Ref. 8) and NiW.[7] The presence of such more or less conductive heterogeneities in the films probably will induce strong damage to the sandwich structure of future solar cells by the occurrence of short circuit effect of the MoS_2 absorbing layer. Moreover, if the presence of the thin Ni layer allows the achievement of textured films, it induces also the growth of broad crystallites randomly distributed in the films.[8] Therefore the use of another process to achieve photoconductive films appeared necessary. This article reports results on textured photoactive MoS_2 films obtained by a simple conventional evaporation process without any additive atoms such as nickel, which has a negative effect for photovoltaic applications.

In Sec. II we describe the preparation conditions of the films and the characterization techniques used. Section III is related to experimental results. In Sec. IV the results are discussed on the conception of ''van der Waals texturation.''

II. EXPERIMENT

A. Film preparation

The depositions were done in a vacuum of 10^{-4} Pa. The Mo and S layers were sequentially deposited by sputtering and evaporation, respectively. Mo and S had a purity of 99.99% and 99.999%, respectively. The deposition rates were 3 nm/s for Mo and 10 nm/s for S, and the film thicknesses were measured *in situ* by two specific quartz monitors. The thickness of each layer was calculated to achieve the atomic ratio Mo/S=1/3 and varied from 8 to 150 nm. The number of layers Mo/S/Mo.../Mo/S varied from five to nine for each component. A last sulphur layer (200 nm) was evaporated to protect the metal film from oxidation during transfer from the deposition apparatus to the oven for the annealing treatment. The sulphur excess was eliminated during annealing. The MoS_2 films were synthesized by the solid state reaction, induced by annealing, between the constituents in thin film form. The multilayer structures were introduced into a silica tube, placed in an oven with the samples. Before annealing, the silica tube was evacuated and the oven was heated at 373 K for 1/2 h. Then, argon was flowed trough the silica tube (40 ℓ/h) and the samples heated. The heating temperature was 1073 K and the annealing time was 1/2 h.

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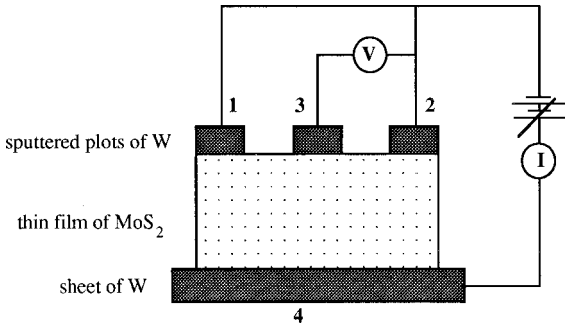

FIG. 1. Scheme of the three-point measurement of contact resistivity.

B. Thin film characterization

The structure of the films was examined using an x-ray goniometer. The preferential orientation of the crystallites was deduced from the x-ray diffraction patterns. The grain size was estimated from the full width at half maximum of the diffraction peaks and given directly by the graphics program EVA used by the diffractometer.[11] The preferential orientation of the crystallites $F(00\ell)$ was calculated from the x-ray diffraction patterns. The degree of preferred (00ℓ) type orientation, i.e., the crystallites with the c axis perpendicular to the plane of the substrate was calculated from:

$$F(00\ell)=\sum_{hk\ell}\frac{I(00\ell)}{I_0(00\ell)}\Bigg/\sum_{hk\ell}\frac{I(hk\ell)}{I_0(hk\ell)}, \tag{1}$$

where $I(hk\ell)$ is the intensity of the $(hk\ell)$ peak of MoS_2 thin films and $I_0(hk\ell)$ is the intensity of the $(hk\ell)$ line of a randomly oriented powder sample according to JCPDS data. The quantitative x-ray photoelectron spectroscopy (XPS) studies were based on the determination of the Mo $3d$ and S $2p$ peak areas with sensivity factors of 2.5 and 0.125, respectively, as given by the manufacturer, Leybold. The MoS_2 depth profiling was determined by recording successive XPS spectra obtained after ion etching for short periods. Using an ion gun, etching was accomplished at pressures of less than 5×10^{-4} Pa with a 10 mA emission current and 5 kV beam energy. The Ar^+ ion beam was rastered over the entire sample surface. At the surface of the films there is a carbon–carbon bond corresponding to surface contamination. In the apparatus used, this C–C bond has a well defined position at 284.6 eV and the carbon peak was used as a reference.

For the electrical characterization upper electrodes of tungsten were deposited by sputtering onto the MoS_2 films. The tungsten deposits were 300 nm thick for an area of about 5 mm^2 and spaced 1 mm. Contact resistance was measured by the three-point technique[12] shown in Fig. 1. Contact 3, connected to a high impedance (>300 TΩ) voltmeter, draws negligible current and thus the voltage drop across this contact is also negligible. Contact 3 senses the potential just inside the semiconductor. Variation of the current through contacts 1 (and 2) and 4 yields the $J-V$ characteristic of contacts 1 and 2 and the contact resistivity. The specific contact resistivity is defined by

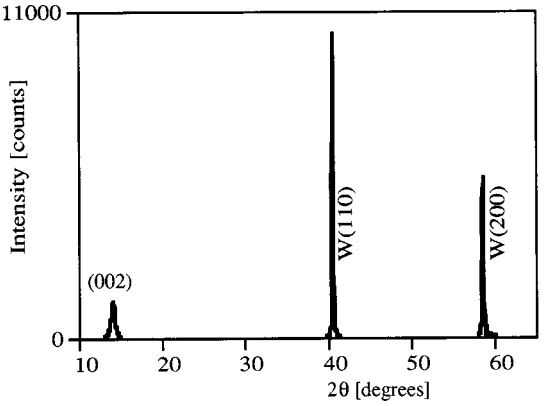

FIG. 2. XRD diagram of a MoS_2 film grown on a randomly oriented tungsten sheet at $T=1073$ K for $t=30$ min (thickness of the film: 500 nm).

$$\rho_c=\left(\frac{\partial J}{\partial V}\right)^{-1}_{V=0}=(A_cR_c)\quad(\Omega\ \mathrm{cm}^2), \tag{2}$$

where A_c is the contact area and R_c the contact resistance.

III. EXPERIMENTAL RESULTS

The objective of this work is to obtain textured MoS_2 films without the help of additive atoms such as Ni. For a first study we have used two kinds of tungsten substrates, randomly oriented sheets and sheets oriented with the (200) plane parallel to the substrate, in order to show the influence of the orientation of tungsten on the texture and the crystal structure of the MoS_2 films. Figures 2 and 3 report results for MoS_2 films obtained in the same run. It can be seen that, after annealing at $T=1073$ K for 30 min, the MoS_2 films obtained on a randomly oriented tungsten sheet (Fig. 2) are very badly crystallized. When a tungsten sheet (200) oriented is used, far better results are obtained (Fig. 3). In that case, the MoS_2 films are not only crystallized in the 2H–MoS_2 structure, but the (00ℓ) peaks are predominant. The preferential orientation factor $F(00\ell)$ varies from 0.8 to 1. So the results described below concern only the films obtained on tungsten sheets (200) oriented.

The atomic composition of the MoS_2 films has been measured by microprobe analysis. Before annealing, 75 at %

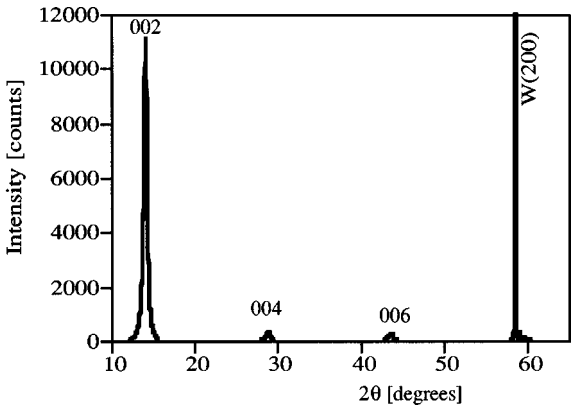

FIG. 3. XRD diagram of a MoS_2 film grown on a tungsten sheet (200) oriented at $T=1073$ K for $t=30$ min (thickness of the film: 500 nm).

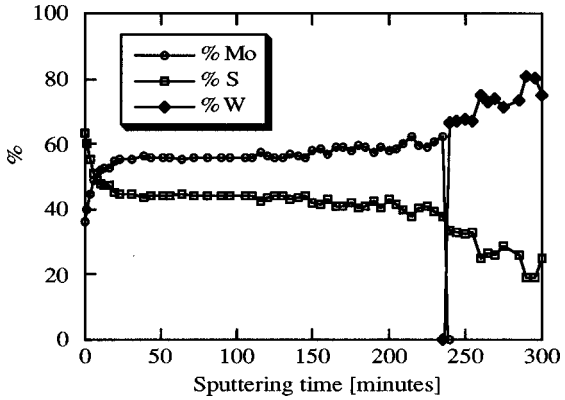

FIG. 4. XPS depth profiling of a MoS_2 film obtained on a tungsten sheet (200) oriented by annealing at 1073 K for 30 min (thickness of the film: 500 nm).

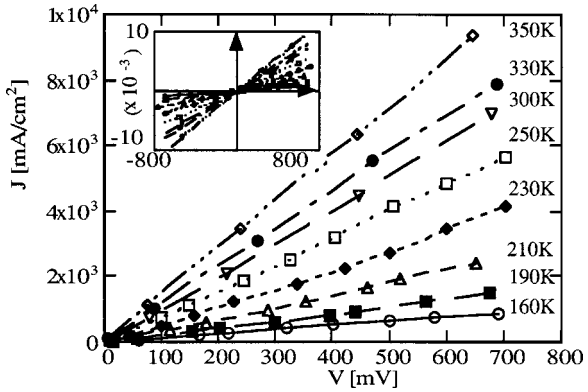

FIG. 6. $J-V$ characteristics of the $W/MoS_2/W$ structure as a function of the temperature.

of sulfur were present. After annealing the films were stoichiometric (66 at $\% \leqslant S \leqslant 67$ at %). The stoichiometry and the contamination of the films have been checked by XPS. It was established that the films were stoichiometric and the absence of bulk contamination by oxygen and carbon was verified during XPS depth profiling. On the surface, binding energy of the C 1*s* peak (284.4 eV) matched the reference binding energy of the spectrometer used. The binding energies of the S $2p$ and Mo $3d_{5/2}$ core levels in the films are 162.24 and 229.34 eV, respectively, identical to the values observed in the reference powder, which confirms that the bond offset is negligible. Depth profiling of MoS_2 is reported in Fig. 4. It is well known that the sputtering yield of sulphur is higher than that of molybdenum. Therefore, after etching, the relative sulfur concentration decreases. However, as usual in the case of sputtering, after a rapid decrease during the first etchings, the sulphur concentration decreases very slowly. It could be seen that, at the W/Mo interface, while Mo disappears rapidly when W appears, the evolution of the S concentration is not strongly modified by the crossing of the Mo/W interface. It can be concluded that at the MoS_2/W interface, some WS_2 has grown. Therefore the sulfur excess has partly diffused into the W substrate.

After this characterization, upper electrodes of tungsten were deposited by sputtering onto the MoS_2 film in order to study the electrical properties of the W/MoS_2 contact. A small contact resistance between the metallic film and the photoabsorbant material is necessary for the fabrication of a solar cell. The contact resistance adds a serial resistance which diminishes the performance of the solar cell. A value less than 0.2 Ω cm^2 is necessary for the contact resistance.[12] Figure 5 shows that the $J-V$ characteristic at room temperature is linear, so the contact is ohmic. The value of the resistivity ρ through the MoS_2 film is about 7 Ω cm^2. The value of the contact resistivity ρ_c is on the order of 0.06 Ω cm^2. One can assume that there is a potential drop through the MoS_2 due to the spreading resistance beneath the contact. In that case ρ_c would be the addition of the contact resistivity and the spreading resistivity. In any case we have $\rho_c \leqslant 0.06\,\Omega\,\text{cm}^2 \ll 0.2\,\Omega\,\text{cm}^2$. Figure 6 shows the temperature dependence of the $J-V$ characteristics which are linear whatever the temperature is. The strong increase of the conductivity with the temperature proves the semiconducting behavior of the MoS_2 film in the $W/MoS_2/W$ structure.

The variation of the contact resistivity ρ_c with temperature has been analyzed on the basis of thermoionic emission above the potential barrier (Fig. 7) such as

$$\rho_c = \frac{k}{qA^*T}\exp\left(\frac{q\phi_b}{kT}\right). \tag{3}$$

From Fig. 7 one can deduce a barrier height of about 120 meV, which is a typical value obtained in MoS_2 films.[9] One

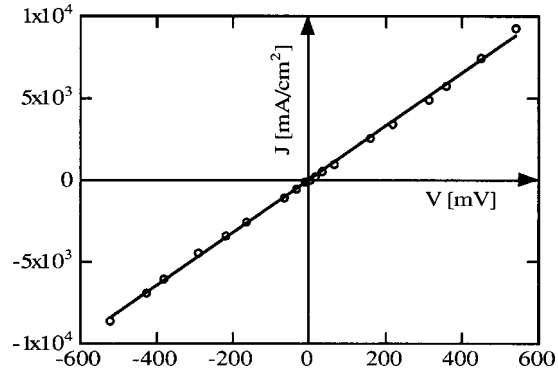

FIG. 5. $J-V$ characteristic of the $W/MoS_2/W$ structure at room temperature.

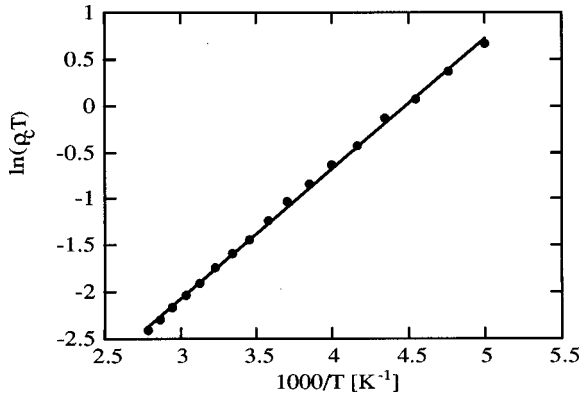

FIG. 7. $\ln(\rho_c T)$ vs $1000/T$ of the W/MoS_2 contact.

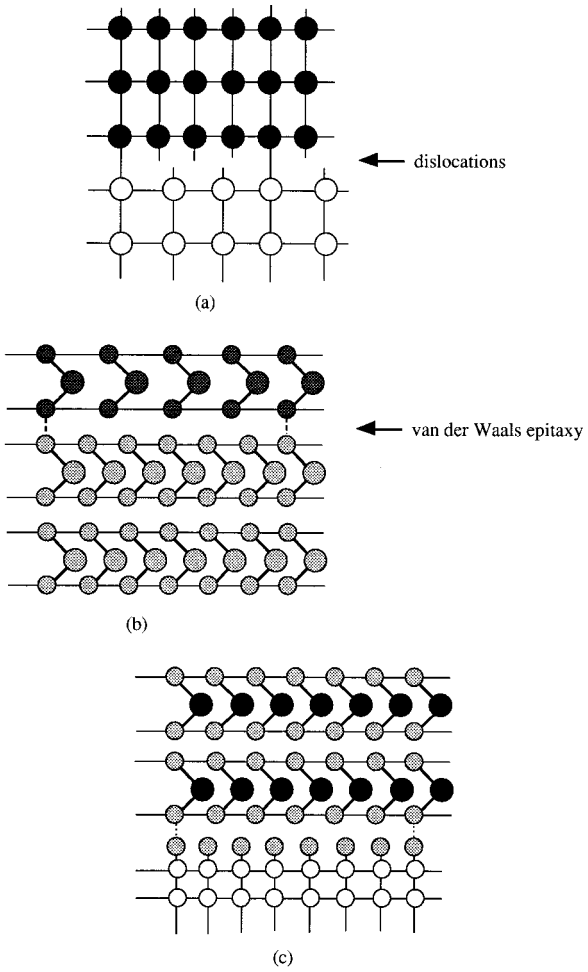

FIG. 8. Schemes for different interconnected interfaces: (a) covalent bonds, (b) van der Waals surfaces, (c) satured surface connected with van der Waals surface.

can conclude that the contact resistance between the W and the MoS_2 film is sufficiently small to avoid the trapping of the carriers and that the resistance of the film predominates.

IV. DISCUSSION

We have shown that textured films can be obtained without adatoms such as Ni, Co,... and, in that case, the crystalline state of the substrate is determined. The substrate's influence is usual in the case of epitaxial deposition. Therefore by analogy, even if in the present work we have not epitaxial but only textured films, we will discuss the results with the help of epitaxial growth.

It is well known that, in the case of covalent semiconducting materials, the lattice matching condition is especially severe. This comes from the fact that dangling bonds on the surface of the substrate should be connected to atoms of the growing layer, which is not easy in the case of lattice misfit since the length and the angle of the covalent bonds cannot be changed easily. The strong bonds formed between the dangling bonds of the substrate and the growning film introduce distortions and nucleate dislocations in the overlayer when the lattice matching condition is not satisfied [Fig. 8(a)].

There are, however, materials having no dangling bonds on their cleaved faces. MoS_2 is a material which crystallizes in a layered structure. In such material, strongly bonded two-dimensional S–Mo–S sandwiches are loosely coupled to each other by weak van der Waals bonds. These van der Waals planes are inert chemically without dangling bonds. The epitaxial growth on such surfaces of another lamellar compound proceeds with van der Waals strength and has been called van der Waals epitaxy [Fig. 8(b)].[13–15] In this case, the lattice matching condition has been found to be relaxed drastically. Thin films with their own lattice constant can be grown by van der Waals epitaxy even under the existence of lattice mismatch as large as 50%.

Moreover it has been shown that van der Waals epitaxy can occur on dangling-bond terminated surfaces.[13] Usually dangling bonds on a surface prevent good heteroepitaxial growth of layered material on it. However, van der Waals epitaxy becomes possible if regular termination of the surface dangling bonds is accomplished [Fig. 8(c)] and if it is kept stable at the temperature required for the epitaxial growth. It has been shown in the case of GaAs that treated surface sulfide allows van der Waals epitaxy since, at the surface, dangling bonds are terminated with sulphur atoms.[14,15] Such epitaxial growth of $MoSe_2$ on $(NH_4)_2S_x$ treated GaAs(111) surfaces has been tried successfully.[14] Other authors[16] have shown that copper, silver, and gold films were found to grow epitaxially on WS_2. Here also sulfur appears to play a decisive role since it is present in the first metal layers.

In the present work, since the substrate is not a single crystal but only textured, only textured grown films could be obtained. However the analogy, with the quasi-van der Waals epitaxy described above, is clear and we call the present process quasi-van der Waals texturation. As in the cases described above, quasi-van der Waals texturation becomes possible by terminating surface dangling bonds with some sulphur excess in the upper layer. We have shown that sulphur diffuses through the surface of the tungsten sheet. Since the tungsten is highly reactive with sulphur, the dangling bonds of the real surface of the substrates will be satured by suphur atoms. The MoS_2 and the WS_2, being lamellar compounds, can grow epitaxially on a dangling-bond terminated surface. Therefore after the diffusion of sulphur in tungsten, some WS_2 forms while the real surface of tungsten is passivated by sulphur. When the local microscopic crystallites in tungsten are oriented, van der Waals epitaxy is possible, which macroscopically induces the growth of textured films: first the WS_2 interfacial film then, by van der Waals epitaxy, the MoS_2 film.

However, epitaxy is obtained on a heated substrate during the deposition process while, in the present work, crystallization takes place during the annealing process. It has been shown[8,17] that the van der Waals surface allows a second crystallization[18] which may induce the growth of textured films. It has been shown that, by analogy with graphite,[17] the presence of nickel allows high quality textured films during the second step of the crystallization process. In the present work, it appears that nickel is not necessary when the oriented W substrate is used: a van der Waals

texturation process occurs as described in Fig. 8(c). When a randomly oriented tungsten substrate is used, small domains are randomly juxtaposed which induces crystallization of the upper layer without texturation.

The good crystallinity of the films is confirmed by the barrier height deduced from the electrical measurements. The barrier height (120 meV) is of the same order as that of MoS_2 films obtained with Ni,[9] and smaller than that of MoS_2 films obtained without Ni on randomly oriented substrates (150 meV).[10] A smaller barrier height indicates a better crystallinity and homogeneity of the films.

V. CONCLUSION

We report the growth of textured MoS_2 films obtained without any additive atoms such as Ni, Co. The crystalline quality of the films obtained on textured tungsten W(200) is similar to that of the films obtained on Ni coated substrates. The main advantage of these new textured films is that secondary effects induced by nickel phases, such as short circuit effect in sandwich structures, can be avoided. Therefore we have succeeded in growing textured MoS_2 films on oriented tungsten substrates. Obtaining a W/MoS_2 ohmic contact is very promising for the realization of a solar cell. It also opens up a new way to apply van der Waals surface properties to growth textured layered materials as the MX_2 family (M=Mo, W; X=S, Se, Te).

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