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Preparation and Electronic Properties of MoS_2 and WS_2 Single Crystals Grown in the Presence of Cobalt

D. M. D'AMBRA, J. V. MARZIK, R. KERSHAW, J. BAGLIO,* K. DWIGHT, AND A. WOLD†

*Department of Chemistry, Brown University, Providence, Rhode Island 02912, and *GTE Laboratories, Inc., Sylvan Road, Waltham, Massachusetts 02254*

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Single crystals of MoS_2 and WS_2 were grown by chemical vapor transport in both the presence and absence of cobalt. Hall measurements indicate that cobalt cannot diffuse appreciably into the bulk of MoS_2 or WS_2 and, therefore, can be present only on the surface. Similar results were obtained for as-grown crystals annealed or sulfided in contact with Co_9S_8 or sulfided after being dipped in a 0.1 *M* $CoSO_4$/methanol solution. © 1985 Academic Press, Inc.

Introduction

Recently, extended X-ray absorption fine structure (EXAFS) of cobalt-promoted MoS_2 hydrosulfurization catalysts has demonstrated that they contain a sulfided molybdenum phase which is structurally similar to crystalline MoS_2 (*1–3*). However, within a S–Mo–S sheet the average coordination number for the Mo–Mo coordination shell appeared to be reduced relative to that of bulk MoS_2. Additionally, Huntley *et al.* (*2*) and Parham *et al.* (*3*) indicated that a reduced coordination number was found for the first coordination shell of sulfur about molybdenum. These results suggest that the molybdenum is present in the form of very small crystallites (~10–15 Å) of MoS_2.

The nature as well as the promotional effect of the cobalt associated with these MoS_2 crystallites is less clear. Schrader and Cheng (*4*) have indicated that the function of cobalt was to facilitate the reduction of oxysulfide phases during the sulfiding of the oxide precursor and also to prevent formation of well-crystallized MoS_2. However, they were unable to identify by Raman spectroscopy what cobalt phase(s) were present. Topsøe, using a number of techniques including Mössbauer emission spectroscopy, has proposed the existence of a distinct Co–Mo–S phase (*5, 6*). When dispersed on alumina, this MoS_2-like phase consists of single S–Mo–S sheets with cobalt atoms located on surface positions. Furthermore, for both bulk (*7*) and supported (*8*) Co–Mo sulfide catalysts, the catalytic activity appears to be related to the amount of cobalt associated with this Co–Mo–S phase.

Other models have been proposed to ex-

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† To whom all correspondence should be addressed.

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plain the promotional effect of cobalt. Delmon (9) has proposed a synergistic effect resulting from intimate contact between Co_9S_8 and MoS_2 (contact synergy model). Voorhoeve and Stuiver (*10*) introduced the intercalation model in which nickel was partially intercalated into the van der Waals gap (between sulfur–sulfur layers) of WS_2. The model was extended to cobalt promoted MoS_2 hydrosulfurization catalysts by Farragher and Cossee (*11*). This pseudo-intercalation model restricted the intercalation of cobalt to the edges of MoS_2.

If any appreciable quantity of cobalt were to diffuse into bulk MoS_2 or WS_2, then there should be a measurable change in the number of carriers as obtained from Hall measurements. However, if the cobalt remains primarily associated with the surface, then there would be no significant change. In this study a number of different methods were used to prepare single crystals of cobalt-promoted MoS_2 and WS_2. Hall measurements were made on crystals grown in both the presence and absence of cobalt.

Experimental

Crystal growth. Single crystals of MoS_2 and WS_2 were grown by chemical vapor transport both in the presence and absence of Co_9S_8. Chlorine was used as the transport agent. Molybdenum (Gallard–Schlesinger, 99.99%) and tungsten (Gallard–Schlesinger, 99.995%) were both reduced at 800°C for 8 hr in a dry 85%/15% Ar/H_2 atmosphere to remove oxygen. Sulfur (Gallard–Schlesinger, 99.999%) was resublimed in vacuum at 80°C before use. Co_9S_8 powder was prepared at 450°C as described previously (*12*).

For crystals grown in the absence of cobalt, large single crystals of MoS_2 and WS_2 were prepared as described in an earlier publication (*13*). For crystals grown in the presence of cobalt, 1 wt% Co_9S_8 was added to the charge. Growth conditions identical to those for undoped crystals were followed. A chlorine concentration of 3 mg/ml was used. The effect of slow cooling or annealing the as-grown crystals was determined. At the end of the growth process, some transport tubes were cooled at a rate of 10°/hr to room temperature; others were cooled to a temperature of 450°C and the crystals annealed for one week at that temperature. All crystals grown in the presence of cobalt were washed and dried with acetone to remove surface cobalt halide.

Some crystals of MoS_2 and WS_2, grown in the absence of cobalt, were placed in silica tubes and totally covered with Co_9S_8 powder. The tubes were evacuated and the samples annealed at 450°C for one week.

Other crystals covered with Co_9S_8 were placed in a vertical silica reactor and sulfided for 4 hr with H_2/H_2S (40 : 1 v/v) at 450°C. The reactor tube was then air quenched to room temperature. Further details of this sulfiding procedure have recently been reported (*12*).

Still other crystals were divided into two parts. One of the pieces was dipped into a freshly prepared 0.1 *M* $CoSO_4$/methanol solution and air-dried. The dipped portions were then placed in the vertical reactor and sulfided as described above.

Electrical measurements. Prior to performing any measurements, crystals grown in the absence of cobalt were peeled with Scotch tape to remove silicon and oxygen impurities (*13*). Crystals grown in the presence of cobalt were also peeled, but in addition, a comparison was made with unpeeled samples. Crystals treated in intimate contact with Co_9S_8 were initially measured unpeeled. Surface peeling and remeasurement of the same sample followed subsequently. The electrical properties of crystals portions that were dipped in $CoSO_4$ and sulfided were compared with those of the undipped sections.

TABLE I

ROOM TEMPERATURE HALL MEASUREMENTS OF MoS_2 AND WS_2 CRYSTALS GROWN IN ABSENCE OF COBALT

Compound	Carrier type	No. carriers (/cm^3)
MoS_2	*n*	$0.8(1) \times 10^{16}$
	n	$1.3(1) \times 10^{16}$
WS_2	*n*	$1.6(1) \times 10^{15}$
	n	$1.5(1) \times 10^{15}$

Room temperature resistivity and dc Hall effect were measured in the basal plane of the single crystals using the van der Pauw technique (*14*). Contacts were made by the ultrasonic soldering of indium directly onto the samples, and ohmic behavior was established by measuring current–voltage characteristics.

Results

Crystals of MoS_2 and WS_2, grown in the absence of cobalt, were subjected to emission spectrographic analysis which indicated less than 100 ppm total impurities of which the transport agent formed the major portion. The electrical properties obtained for the undoped MoS_2 and WS_2 crystals (Table I) agree well with those values reported in the literature (*13, 15*). Hall data for crystals grown in the presence of cobalt are shown in Table II. There appears to be no variation in the sign of the carrier and little in the number of carriers for both MoS_2 and WS_2 crystals grown in either the presence or absence of cobalt. Surface peeling of crystals grown in the presence of cobalt has no significant effect on their electrical properties. Furthermore, for crystals grown by chemical vapor transport in which the tube was either slow-cooled or annealed, little change in the Hall measurements was observed.

TABLE II

HALL MEASUREMENTS OF MoS_2 AND WS_2 CRYSTALS GROWN IN PRESENCE OF COBALT

Compound	Preparation[a]	Treatment	Carrier type	No. carriers (/cm^3)
MoS_2	(a)	Unpeeled	*n*	$2.1(2) \times 10^{16}$
		Peeled	*n*	$1.9(3) \times 10^{16}$
	(b)	Unpeeled	*n*	$1.5(2) \times 10^{16}$
		Peeled	*n*	$0.7(1) \times 10^{16}$
	(c)	Unpeeled	*n*	$1.1(1) \times 10^{16}$
		Peeled	*n*	$1.1(1) \times 10^{16}$
WS_2	(a)	Unpeeled	*n*	$3.1(3) \times 10^{15}$
		Peeled	*n*	$3.9(4) \times 10^{15}$
	(b)	Unpeeled	*n*	$1.6(2) \times 10^{15}$
		Peeled	*n*	$2.9(4) \times 10^{15}$
	(c)	Unpeeled	*n*	$2.1(1) \times 10^{15}$
		Peeled	*n*	$2.9(2) \times 10^{15}$

[a] (a) Allowed to cool in furnace overnight. (b) Slow-cooled at 10°C/hr to room temperature. (c) Annealed at 450°C for 1 week.

The Hall data are summarized in Table III for as-grown crystals treated with either Co_9S_8 or $CoSO_4$. The MoS_2 ans WS_2 crystals annealed in Co_9S_8 show no significant change in the number of carriers let alone in their sign. Surface peeling also has no effect. Similar results were obtained for crystals covered with Co_9S_8 and sulfided. Portions of the crystals dipped in a cobalt sulfate/alcohol solution, removed, dried,

TABLE III

HALL MEASUREMENTS OF MoS_2 AND WS_2 CRYSTALS TREATED IN Co_9S_8 OR DIPPED/SULFIDED WITH $CoSO_4$

Compound	Preparation[a]	Treatment	Carrier type	No. carriers (/cm^3)
MoS_2	(a)	Unpeeled	*n*	$2.8(2) \times 10^{16}$
		Peeled and remeasured	*n*	$2.8(4) \times 10^{16}$
	(b)	Unpeeled	*n*	$0.7(1) \times 10^{16}$
		Peeled and remeasured	*n*	$1.3(1) \times 10^{16}$
	(c)	Undipped	*n*	$2.9(4) \times 10^{16}$
		Dipped	*n*	$1.9(2) \times 10^{16}$
WS_2	(a)	Unpeeled	*n*	$1.7(1) \times 10^{15}$
		Peeled and remeasured	*n*	$1.8(1) \times 10^{15}$
	(b)	Unpeeled	*n*	$2.1(1) \times 10^{15}$
		Peeled and remeasured	*n*	$4.4(1) \times 10^{15}$
	(c)	Undipped	*n*	$2.0(2) \times 10^{15}$
		Dipped	*n*	$2.1(1) \times 10^{15}$

[a] (a) Annealed in Co_9S_8 at 450°C. (b) Sulfided in Co_9S_8 at 450°C. (c) $CoSO_4$ dipped and sulfided at 450°C.

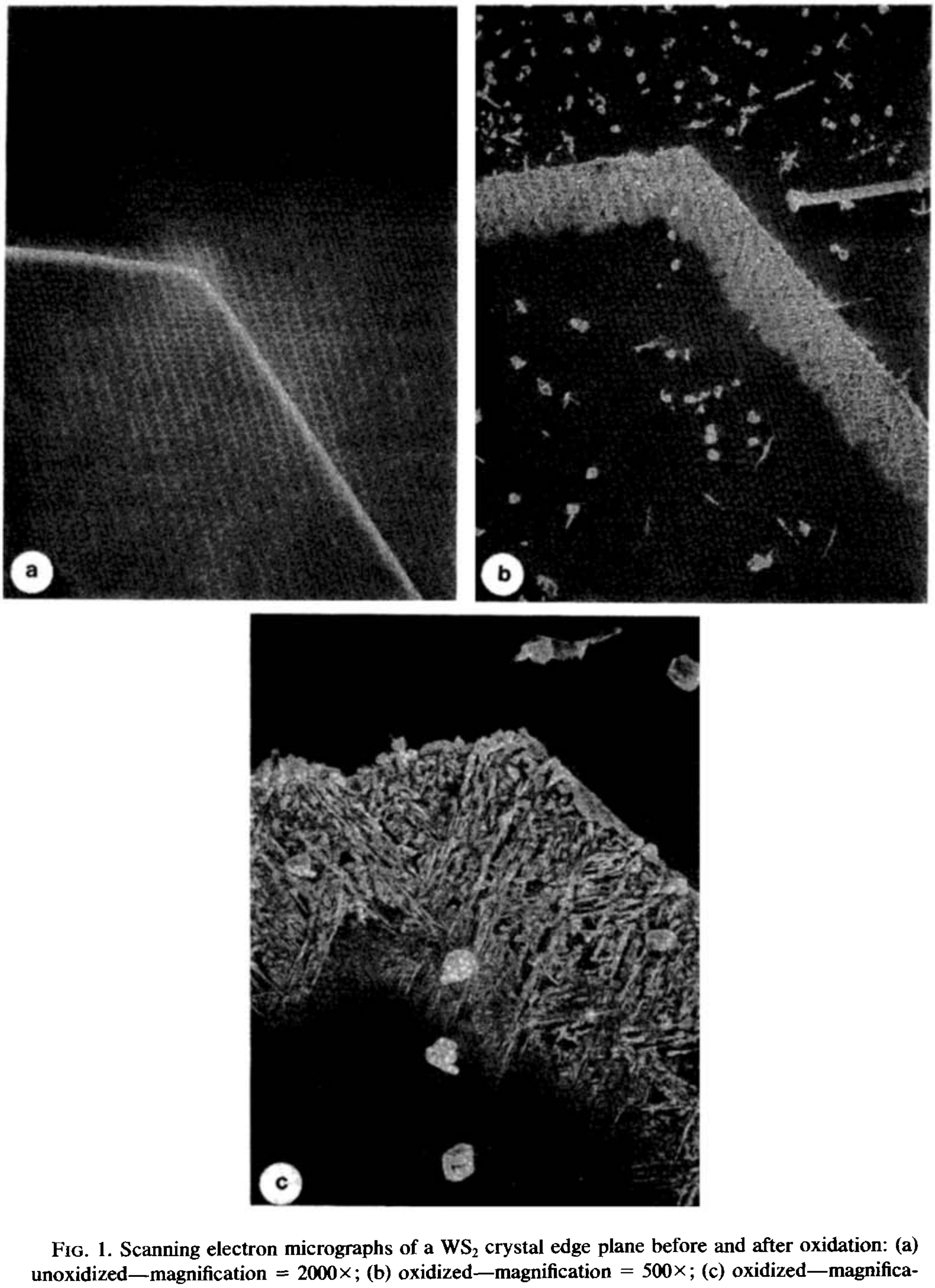

FIG. 1. Scanning electron micrographs of a WS_2 crystal edge plane before and after oxidation: (a) unoxidized—magnification = 2000×; (b) oxidized—magnification = 500×; (c) oxidized—magnification = 2000×.

and sulfided in a H_2/H_2S at atmosphere showed no meaningful change in the number of carriers compared to undipped portions.

Sulfiding of cobalt sulfate under the conditions specified would be expected to produce Co_9S_8 (*12*). Visual examination of these crystals revealed the presence of a black phase on the crystal surface. Identification of this phase was obtained by repeatedly placing drops of $CoSO_4$ solution onto an undoped crystal, followed by drying. This produced a sufficiently thick $CoSO_4$ coating which, after sulfiding, could be removed and characterized. X-Ray powder diffraction of this phase indicated the presence of single-phase Co_9S_8. Despite the presence of Co_9S_8 on the surface, no variation in the electrical properties could be determined.

Discussion

Hall measurements provide a sensitive method for detecting the presence of impurity atoms within the bulk. If cobalt atoms were to diffuse appreciably into the bulk of MoS_2 or WS_2, a change in the number of carriers would be expected. The results presented in this study suggest that no appreciable change occurs regardless of the method used to try to introduce cobalt.

Wentrcek and Wise (*16*) have reported that when cobalt is diffused into the bulk of naturally occurring MoS_2 crystals, a change from *n*- to *p*-type behavior is observed. This observation could not be reproduced on the pure synthetic dichalcogenides prepared in this study.

Recently, Chianelli *et al.* (*17*) have examined the chemistry of single crystal edge planes in MoS_2. Results obtained using Auger spectroscopy indicated that crystals grown in the presence of cobalt tended to show a segregation of cobalt at the surface edges of MoS_2. Furthermore, Chianelli *et al.* indicated that oxidation occurred preferentially along these edge planes. Previously, Bahl *et al.* (*18*) reported similar findings for surface oxidation of naturally occurring MoS_2 crystals. Surface oxidation of synthetic WS_2 crystals in a CO_2 atmosphere has also been found to give preferential edge plane oxidation (Fig. 1). It does appear that cobalt impurities accumulate at the edges and reactions, e.g., hydrodesulfurization, could occur along these edge planes.

Hall measurements indicate that cobalt can be present only on the surface of MoS_2 and has not diffused appreciably into the bulk. Topsøe has indicated that for cobalt-promoted molybdenum hydrodesulfurization catalysts the cobalt occupies surface positions in an MoS_2-like structure which he identifies as a Co–Mo–S phase (*6*). The lack in variation of the number of carriers found in MoS_2 and WS_2 single crystals containing small quantities of surface cobalt sulfides is consistent with this "surface phase."

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