

The Photoelectrochemical Properties of MoS₂ Single Crystals Grown in the Presence of Cobalt

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MoS₂ single crystals have been grown in the presence of cobalt. Photoresponse has been measured and compared with that from undoped MoS₂. The results are consistent with the segregation of cobalt on the surface edges of the doped crystals. © 1986 Academic Press, Inc.

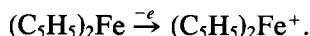
Introduction

Recently, Chianelli *et al.* (1) examined the surface of MoS₂ single crystals grown in the presence of cobalt. Results obtained using scanning Auger spectroscopy indicated that cobalt tended to segregate at the surface edges of MoS₂. Hall measurements reported by D'Ambra *et al.* (2), on crystals grown in the presence of cobalt, indicated that there was no appreciable change in the number of carriers. Hence, it was concluded that the cobalt was only present on the surface of the crystals and had not diffused appreciably into the bulk.

Since the work of Tributsch (3-5), there have been a number of studies (6-12) on the photoelectrochemical behavior of MoS₂ single crystals. Several of these studies (7, 9) have investigated *n*-type MoS₂ in non-aqueous solution using a wide variety of redox couples. From cyclic voltammetry

measurements, the positions of the valence and conduction band edges in MoS₂ were located.

In this study, it was of interest to compare the photoresponse from pure MoS₂ single crystals and those grown in the presence of cobalt as a means of ascertaining the presence of cobalt on the surface of the dichalcogenide. The magnitude of the photoresponse should be affected by the number of impurities present on the surface. Characterization of these crystals was carried out in acetonitrile solutions utilizing the fast, one-electron oxidation of ferrocene to ferrocinium ion



The definitive determination of the electronic state due to the presence of cobalt on or near the surface will not be attempted. Rather, the thrust of this study will be to relate changes in the photoresponse with the treatment of the crystal samples.

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Experimental

Crystal growth. Single crystals of MoS₂ were grown by chemical vapor transport both in the presence and absence of Co₉S₈ as described previously (2).

Electrode preparation. Photoelectrodes of MoS₂ crystals grown in the presence and absence of cobalt were prepared from as-grown samples. Some large crystals (~1 × 1 cm) of MoS₂ grown in the presence of cobalt were divided into two parts. One of the pieces was peeled with Scotch tape and electrodes were made from both the peeled and unpeeled portions.

Photoelectrodes were prepared by evaporating thin films of gold on the backs of the single crystals of MoS₂ to provide good ohmic contact which was established by measuring the current-voltage dependence between two such gold films. For mechanical support, the gold face of each crystal was attached to a disk of platinum foil with a drop of silver paint. The platinum foil had been soldered previously to a platinum wire which was sealed inside 6 mm Pyrex tubing. The electrodes were completed by applying a two-part epoxy to the platinum foil and wire so that only the front surface [(001)face] of the crystal was in electrical contact with the electrolyte solution. After curing the epoxy (13) and before each measurement, the electrodes were rinsed with acetonitrile (Baker HPLC Grade) and air dried.

Photoelectrochemical measurements. Photoelectrochemical measurements were carried out under potentiostatic control with a 150 W xenon lamp, a monochromator (Oriel 7240), and a current amplifier as described previously (14). A single compartment, three-electrode cell containing a flat Pyrex window was used with a platinum counter electrode. Potential measurements were made with respect to an Ag/Ag⁺ reference electrode. The Ag/Ag⁺ elec-

trode contained a silver wire immersed in a 0.01 M AgNO₃/0.1 M [*n*-Bu₄N]BF₄ acetonitrile solution. This electrode had a potential of +0.35 V versus SCE. For sampled current-potential measurements under steady-state conditions, bias was applied via a potentiometer and a voltage follower having a very low output impedance (<0.1 Ω).

HPLC grade acetonitrile (Baker) was dried by distillation from P₂O₅. Electrometric grade [*n*-Bu₄N]BF₄ (Southwestern Analytical Co.) was recrystallized from an ethyl acetate/pentane mixture (15) and dried under vacuum for 24 hr at 100°C. Ferrocene (Aldrich) was used without additional purification. The electrolyte solution consisted of 0.1 M [*n*-Bu₄N]BF₄/1 mM ferrocene in acetonitrile with a small amount of ferrocinium ion [ferrocene]⁺. The ferrocinium ion was electrochemically generated by oxidation of ferrocene at a platinum electrode. Cyclic voltammetry with platinum electrodes indicated that no electroactive impurities were present. For the sampled current-potential measurements, the electrolyte was vigorously stirred under nitrogen. At 0.0 V bias with respect to the counter electrode, the potential of the MoS₂ anode was -0.11 V versus Ag/Ag⁺.

Results

The photocurrents obtained from unpeeled crystals grown in the presence and absence of cobalt were compared. For large crystals grown in the presence of cobalt, the photoresponse of the peeled portion was compared with that of the unpeeled section.

The photoresponse observed for an MoS₂ single crystal grown in the absence of cobalt is shown in Fig. 1. The current-potential measurements were obtained under steady-state conditions. Photocurrents obtained in "white" light are plotted against the potential of the anode measured with respect to an Ag/Ag⁺ reference electrode.

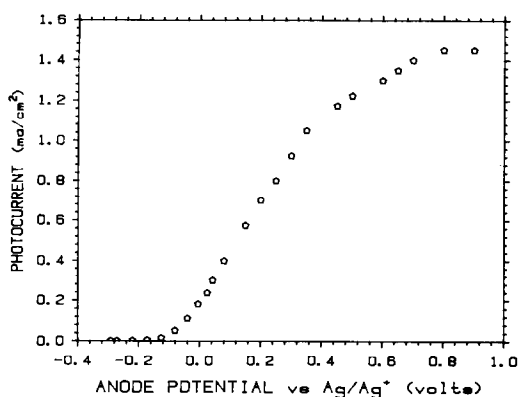


FIG. 1. Variation of photocurrent (in light, minus dark current) with anode potential under "white" xenon arc irradiation of 1.0 W/cm^2 in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{BF}_4$ containing [ferrocene] $^{+/\ominus}$ for a typical MoS_2 crystal grown in the absence of cobalt.

The onset of the photocurrent indicates a flat-band potential of approximately $+0.25 \text{ V}$ versus SCE, which is in good agreement with the previously reported value of $+0.21 \text{ V}$ (7).

The photoresponse observed for MoS_2 single crystals grown in the presence of cobalt is shown in Fig. 2. All three crystals originated from the same crystal growth experiment and exhibit very similar anodic behavior. The observed photocurrents for these crystals are appreciably lower than that found for pure MoS_2 (Fig. 1). Furthermore, unlike undoped MoS_2 , all three crystals exhibited at high anodic potentials ($>0.5 \text{ V}$ versus Ag/Ag^+) high dark currents that approached the magnitude of the observed photocurrent (Table I).

The photocurrent observed for peeled and unpeeled portions of a large MoS_2 crystal, grown in the presence of cobalt, is shown in Fig. 3; the crystal measured was obtained from a different crystal growth run than those reported in Fig. 2. It can be seen from Fig. 3 that the peeled portion gave an appreciably higher photoresponse than the unpeeled section. In fact, the photoanodic behavior of the peeled crystal resembles

TABLE I
PHOTOCURRENTS AND DARK CURRENTS FOR
 MoS_2 CRYSTALS

Compound ^a	Anode potential vs Ag/Ag^+ (V)	Photo-current (mA/cm^2)	Dark current (mA/cm^2)
MoS_2	0.9	1.5	0.2
MoS_2 (Co)	0.9	0.6	0.7
MoS_2 (Co)	0.85	0.8	0.7
MoS_2 (Co)	0.9	0.6	0.4
MoS_2 (Co) peeled	0.9	1.5	1.0
MoS_2 (Co)	0.9	0.7	0.7

^a Unless indicated, crystals are unpeeled.

that found for undoped MoS_2 which is also shown in Fig. 3. However, the dark current at high potentials for the peeled crystal (Table I) resembles that found for unpeeled samples.

Discussions

The results presented in this study suggest that cobalt is on the surface of MoS_2 and modifies the photoanodic behavior of

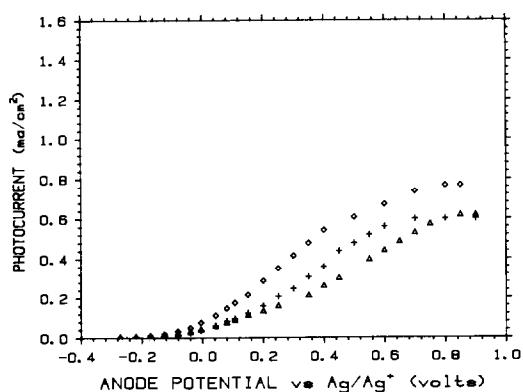


FIG. 2. Variation of photocurrent (in light, minus dark current) with anode potential under "white" xenon arc irradiation of 1.0 W/cm^2 in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{BF}_4$ containing [ferrocene] $^{+/\ominus}$ for three MoS_2 crystals grown in the presence of cobalt.

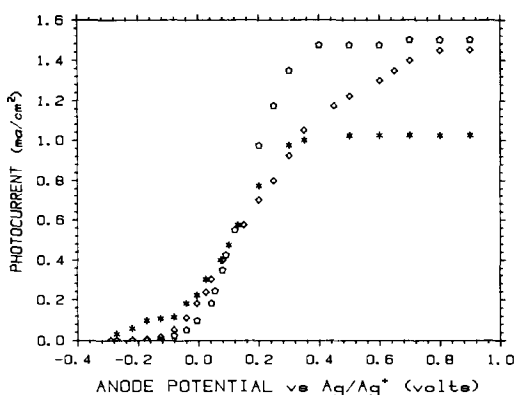


FIG. 3. Variation of photocurrent with anode potential under "white" xenon arc irradiation of 1.0 W/cm² in CH₃CN/0.1 M [n-Bu₄N]BF₄ containing [ferrocene]^{+/0} for peeled (□) and unpeeled (*) portions of a MoS₂ crystal grown in the presence of cobalt compared with an unpeeled crystal (◇) grown in the absence of cobalt.

the dichalcogenide. The results shown in Figs. 1–3 are for randomly chosen crystals. Peeling of undoped MoS₂ crystals does not appreciably modify the photoresponse. Moreover, the photoresponse of the peeled crystals doped with cobalt shows essentially the same level of photocurrent as the undoped crystals. The unpeeled cobalt-doped crystal shows a significantly lower photoresponse. These findings are consistent with the Hall measurements which were reported previously (2) in which the cobalt was found to exist only on surface steps. Furthermore, the results found in this study support the scanning Auger analysis reported by Chianelli *et al.* (1) who indicated that cobalt tended to segregate at the surface edges of MoS₂.

Cobalt (*d*⁷) for Co(II) found at these edges provides a source of delocalized electrons and, hence, recombination centers on the surface of the dichalcogenide. Evidence for this conclusion can be found in both the decreased photoresponse and higher observed dark currents. Recovery of the photoresponse is observed when the surface of

the doped crystal is peeled with Scotch tape. This process evidently removes a large part of the cobalt. However, despite peeling, some dark current persists because some of the original surface steps remain after this peeling. The scope of this investigation was directed toward determining the usefulness of the photoelectrochemical technique in corroborating the presence of impurities on the surface rather than in the bulk of crystals which show a photoresponse.

Acknowledgments

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