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The Reactivity of MoS_2 Single Crystal Edge Planes

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The reactivity of the edge planes of MoS_2 have been studied on single crystals. MoS_2 edge planes have been shown to be reactive toward oxygen by both optical and scanning Auger studies. In addition it has been shown that Co incorporated at low levels into single crystals tends to surface segregate at MoS_2 edge planes.

INTRODUCTION

The potential importance of the edge planes of layered hydrotreating catalysts, such as MoS_2 and WS_2, has long been recognized.[2] That these planes should be important in the reactivity of these solids arises naturally from the inherent chemical anisotropy residing in these solids. The transition metal is bound to six sulfurs in trigonal prismatic coordination, which forms the basic building block of the structure. Each sulfur atom in the extended lattice is strongly bound to three molybdenum atoms to form two-dimensional sheets. These triply bonded sulfur atoms form the basal planes of the crystal. Because the sulfurs are so strongly bonded the basal planes are chemically quite inert and the bonding between layers is extremely weak. It is this property which is thought to be at the basis for the exceptional lubricating properties of MoS_2. In hydrotreating, on the other hand, it is thought that the active sites for many types of reactions are sulfur vacancies, and the inertness of the sulfur atoms in the basal plane would make the formation of a sulfur vacancy a very high energy process. Thus, the formation of a vacancy could occur easily only at the edge of a layer where the sulfur coordination is incomplete, and therefore the sulfur is chemically labile.

Evidence for the reactivity of the edge planes in MoS_2 can be found in the linear correlation between O_2 chemisorption and the hydrodesulfurization (HDS) of dibenzothiophene (DBT). An attempt to correlate the HDS activity to BET surface area fails, presumably because the physical adsorption of N_2 occurs on both basal and edge planes, whereas the O_2 preferentially adsorbs on edge planes, or edge-like defects (*3*). Evidence for oxygen interaction with edge planes comes from the earlier work of Bahl *et al.* (*4*). They showed that when MoS_2 was heated in 10 Torr O_2 in the range 400–600°C, oxidation takes place preferentially at edge planes, or dislocation steps. Reactions other than HDS also appear to proceed on the edge planes such as isomerization and hydrogen exchange (*5*). Hydrogenation of benzene and cyclohexene on WS_2 (which is isostructural with MoS_2) catalysts was studied by Voorhoeve and Stuiver (*6–8*). The authors concluded that both reactions took place on edge-like defects: cyclohexene hydrogenation on singly unsaturated W defects (edge sites) and benzene hydrogenation on doubly unsaturated W defects (corner sites). These authors also introduced the concept of

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[2] For two recent reviews see Refs. (*1, 2*).

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"pseudointercalation" of Ni atoms at the edge of WS_2 planes to increase the number of benzene hydrogenation active sites (*7*, *8*). This "pseudointercalation model" was extended to HDS and to Co/MoS_2 catalysts by Farragher and Cossee (*9*). Both studies emphasized the role of the MoS_2 (or WS_2) edge planes in the promotion phenomenon. The term "pseudointercalation" is used to make the point that MoS_2 and WS_2 do not normally intercalate most metals as do other layered sulfides such as NbS_2 and TaS_2. To pseudointercalate means to insert Co or Ni between the layers in octahedral holes near the edge. Other promotion models have also been presented which emphasize the role of Co or Ni at the MoS_2 or WS_2 edge planes (*2*). New evidence for the presence of Co at the edges of MoS_2 has recently appeared (*10*, *11*).

In this paper we report the results of a series of chemical and physical studies on the edge planes of synthetic MoS_2 and Co-doped MoS_2 crystals. The purpose of these studies is to further elucidate the chemical reactivity of MoS_2 edge planes and the interaction of Co with these edge planes. In the first part, we investigate the reaction of wet air with MoS_2 edges at elevated temperatures, following the work of Bahl *et al.* (*4*). In the second part, we study the interaction of O_2 and Co at ambient temperature using the scanning Auger technique.

EXPERIMENTAL

A. Optical microscopy study of the oxidation of crystalline MoS_2. The MoS_2 crystals employed in this study were prepared in sealed silica tubes by chemical vapor transport, using sulfur vapor at 1050–1100°C. The sulfur vapor density was 5 mg/cm^3 corresponding to a sulfur pressure of approximately 10 atm. The as-grown crystals were small (50–100 μm) and exhibited hexagonal symmetry.

The MoS_2 used in the crystal growth experiments was prepared from the elements: molybdenum wire from Material Research Corporation, VP grade; sulfur pieces from Alfa-Ventron, 99.999% purity. A stoichiometric ratio of molybdenum and sulfur plus an excess of 5 mg/cm^3 of sulfur were sealed in an evacuated silica tube. The tube was heated for 1-day intervals beginning at 450°C. The temperature was incremented daily by 50°C until it reached 900°C. The reaction was allowed to proceed at 900°C for 8 days. The resultant MoS_2 was ground up, and the powder used as a charge in the crystal growth experiments. Oxidation studies were carried out using a Leitz Ortholux-pol II microscope fitted with a 1350°C hot-stage for transmitted and reflected light. Air saturated with water by bubbling was passed through the hot stage as the reactive gas.

B. Scanning Auger study of Co-doped MoS_2 single crystals. Single crystals of Co-doped MoS_2 were grown by the following method. Molybdenum powder (Gallard-Schlesinger, 99.99%) was reduced in a dry 15% H_2/15% Ar atmosphere for 8 h at 800°C to remove oxygen impurities. Sulfur (Gallard-Schlesinger, 99.999%) was resublimed *in vacuo* at 80°C before use. Large single crystals of MoS_2 were prepared by chemical transport using a concentration of 8 mg/cm^3 of bromine as the transport agent. A melting-point capillary containing the calculated weight of bromine was sealed at a pressure of 10^{-3} Torr and placed in an H-tube filling apparatus (*12*). The charge consisted of 0.4797 g molybdenum, 0.3206 g of sulfur (corresponding to 5×10^{-3} mole), and 0.005 g Co_9S_8, which had been previously prepared from the elements (*13*). After sealing off the charge under vacuum of 10^{-5} Torr, the bromine capillary was opened, and the bromine distilled onto the charge. The silica transport tube (1.6 cm diam. × 28 cm long) was then sealed off and placed in a transport furnace. The furnace was operated so that the empty portion of the tube, or growth zone, was heated to 1150°C while the charge end was heated to 700°C. This temperature profile was maintained for 15 h, allowing the powder charge to react, and back transport to clean the growth zone of unwanted nucleation sites. The charge zone was then raised to 1150°C over a 5-h period. The temperature of the growth zone was then lowered to 1100°C at 1°C/h. Crystal growth was allowed to proceed for 6 days, after which the furnace was turned off. The transport tube was removed when cooled, opened in a glove box under N_2, and the crystals washed with CCl_4 to remove Br_2. Crystals as large as 4 × 5 mm were grown using this technique. No particular precaution to eliminate oxygen were taken upon transferring the crystals to the Auger spectrometer.

Co-doped MoS_2 single crystals were analyzed using a Physical Electronics Scanning Auger Microprobe (SAM-590). The instrument is equipped with a coaxial electron gun and a single-pass cylindrical mirror electron energy analyzer. Auger spectra and elemental mapping were carried out with a beam diameter of 2 μm and primary electron beam energy of 5 kV. To minimize changes in the chemistry of the surface, the beam current was kept low ~50 nA. Secondary electron micrographs were taken at a beam size of 0.2 μm for best resolution. During measurements, the residual pressure in the system was maintained at 5×10^{-10} Torr using ion and titanium sublimation pumps. A differentially pumped ion gun and argon gas was used for sputter etching of the surface. This gun has the advantage of low contamination of the surface during and after sputtering. The sputter rate of the gun was 300 Å/min calibrated for a tantalum oxide standard, and all thickness measurements reported are given with respect to this standard. The method used for calibrating the sensitivity factors of the Auger signals in terms of atomic percentage are according to the method outlined in Ref. (*14*) using an Ag standard.

RESULTS

Initial experiments were performed to determine conditions for controlled oxidation of the crystals, which would permit the process to be followed photographically. It was found that the optimum temperature range was from 545 to 590°C. At temperatures above this range, the reaction proceeded too rapidly to follow, and below this range the reaction was too slow to follow conveniently. In the optimum range the crystals showed perceptible changes within a reasonable amount of time (1–5 min). For example, Fig. 1 shows a crystal before and after exposure to the reactive gas for 1 min at 590°C. The reactivity of the edge planes with respect to oxidation is clearly indicated in Fig. 1b. We may speculate that the oxidation appears to take place in two steps: first, a topotactic oxidation of MoS_2, probably to MoO_2, indicated by the darkened area at the edge of the reacted crystal (Fig. 1b); and second, by loss of material from the crystal by sublimation of MoO_3. It is clear from these studies that MoO_3 is subliming from the edges. The formation of the intermediate MoO_2 requires further investigation. The results of this reaction sequence are indicated schematically in Fig. 2. Further, we see by comparing the dimensions of the reacted crystal with the dimensions of the unreacted crystal, that the oxidation may be anisotropic with respect to the edges themselves. The crystallite dimensions were measured using a cross-hair scale in the eyepiece of the microscope.

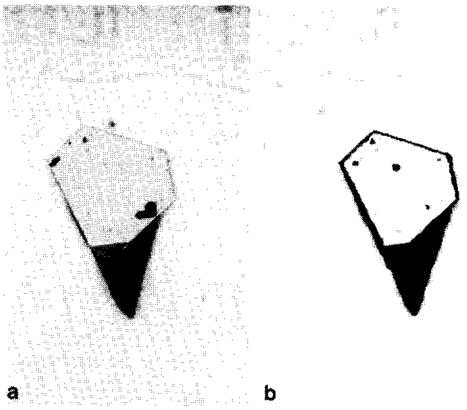

FIG. 1. (a) Unoxidized crystal of MoS_2, (b) oxidized crystal of MoS_2 (dimensions of crystal shown in Fig. 2).

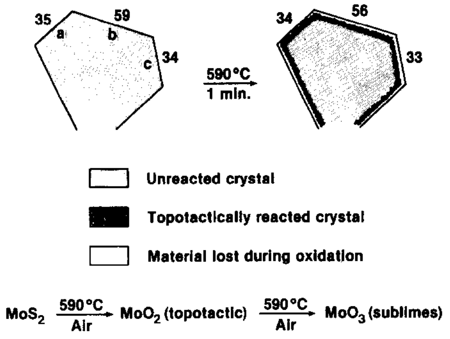

FIG. 2. Schematic diagram of the oxidation of the MoS_2 crystal show in Fig. 1. Numbers on crystal faces are in micrometers.

FIG. 3. SEM of MoS_2 showing smooth edge planes. In this micrograph the edge planes are from 1 to 2 μm thick. Arrow indicates edge plane.

The position of the face of the crystal which is lying flat on the microscope stage can be estimated to ±0.5 μm. The face dimensions were first determined on the unreacted crystal and then on the reacted crystal. In Figs. 1 and 2, it can be seen that faces a and c have reacted more rapidly than face b. Although this requires more confirmation,

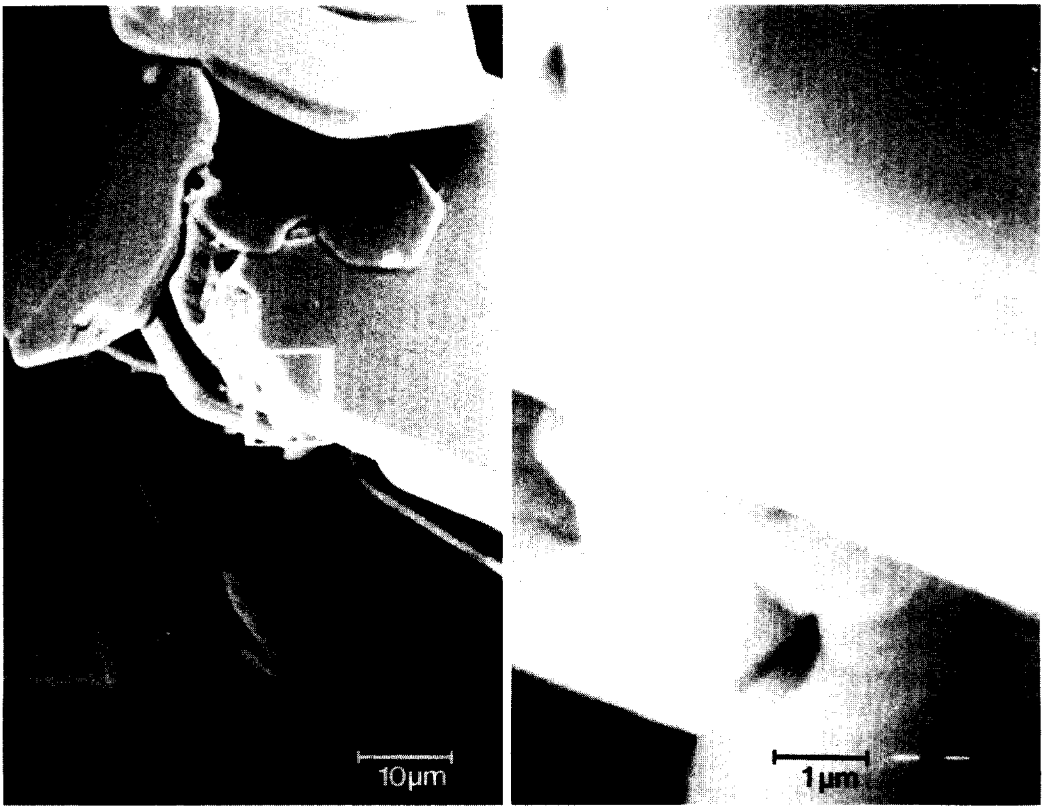

FIG. 4. SEM of oxidized MoS_2 crystals showing reacted edge planes and oxidation pits in the basal plane. Arrow indicates edge plane.

we note that the structure of MoS_2 demands that alternate edge planes terminate in different ways.

However, from the point of view of this paper, we wish to indicate that oxidation of MoS_2 at high temperatures occurs by attack, preferentially along the edge planes (Fig. 4). A similar SEM photograph of an unreacted crystal (Fig. 3), shows that the edge planes are quite smooth. In Fig. 4 the striations and steps caused by oxygen attack at the edge planes are quite apparent, whereas the basal planes seem to be unattacked, except where edge-like defects appear. At these points, oxidation takes place rapidly outward. These results indicating selective oxidation at edge planes or step defects on the basal plane are in complete agreement with the work of Bahl *et al.* (*4*) using a different technique.

Figure 5a shows an SEM micrograph of a freshly prepared MoS_2 crystal doped with approximately 1% Co. Clearly visible are well-defined basal planes, edge planes, and other features typical of the layered transition metal dichalcogenides, and specifically of MoS_2. Figure 5b shows a corresponding micrograph for undoped MoS_2; the edge planes or step heights are greatly reduced compared with the Co-doped crystals. However, we may note that there are many more edge-like defects in a given area. Similar observations for vapor-grown crystals have previously been reported without additional comment (*8*). Presumably, the interaction of Co with the basal plane near the edges of MoS_2 increases the interaction between successive layers of MoS_2 causing the crystals to grow thicker. In fact, crystals grown without Co were too thin for Auger analysis, and, at this writing, we have been unable to obtain synthetic MoS_2 crystals which are thick enough for edge plane studies. The thickness of the Co-doped crystal at the edge (Fig. 5a) is ~50 μm at the large edge and ~25 μm at the smaller edge. The edges in the undoped crystals though more numerous are only 1–2 μm high.

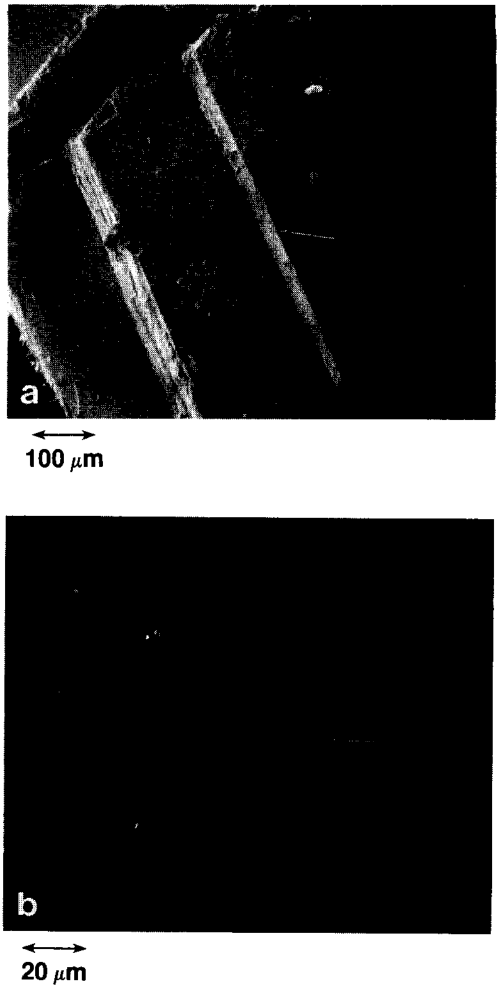

FIG. 5. (a) Secondary electron micrograph of as-received MoS_2 (1% Co) crystal showing characteristic terraced structure on the basal planes. (b) Same undoped crystal showing only weak terracing. Arrow indicates edge plane.

An Auger spectrum from a basal plane (Fig. 6), shows the presence of Mo, S, C, and O, with a trace of Co. The carbon, oxygen, and cobalt appear to be surface contaminants, since the signals disappear after removal of about 100 Å of material by sputtering (Fig. 6). After continued sputtering of the basal plane, no prominent cobalt Auger signals were seen, suggesting that cobalt was not present on or between the basal planes within the limits of detectability of the instrument.

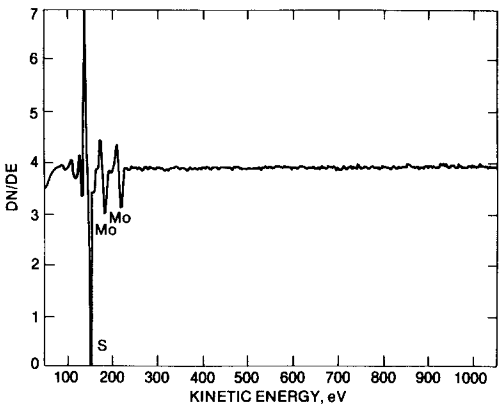

FIG. 6. Auger spectrum from basal plane after removing ~100 Å of the top surface layer.

An Auger spectrum from an edge plane initially shows peaks corresponding to Mo, S, C, O, and Co. However, sputtering off of the top layer 100 Å clearly reduces surface O and C contaminants as shown in Fig. 7. Also we can see from this figure that the cobalt signals is clearly enhanced after surface cleaning. Elemental mapping, which only give differential contrast and not absolute atomic concentrations, for Co and O confirmed that these elements are segregated along the edges of the crystal facets (Figs. 8a and b). Some of the contrast in the Auger maps could be due to the morphology of the sample, but a comparison of maps for Co and O with those for Mo and S give convincing evidence of significant segregation only along the edges of the crystal facets (Figs. 8c and d). Also the crystal is tilted approximately 45° to the beam which would tend to eliminate geometric enhancement. Sputtering of edge planes to 1500 Å removed almost all Co and O from the edge planes, which is further evidence for edge segregation of these elements. Depth concentration profiles were obtained along edge planes at a sputter rate of ~50 Å per minute, which is the depth resolution for sputter etching (indicated schematically in Fig. 9). It is clear from the profile that the edges are rich in Co and O and deficient in Mo and S for the first 800 Å of the surface. It is interesting to note that though the crystal has less than approximately 1% Co, the level of Co is 10% or greater 800 Å into the crystal. We believe that this distribution into the crystal is real but qualitative due to the inherent limitations of this technique. Further evidence to support this conclusion comes from a recent TEM and electron diffraction study (*15*). That the Co is distributed throughout the crystal at some low level and tends to enrich at the edge is further demonstrated by the fact that most of the Co is removed from the edge by extensive sputtering (after 1500 Å of sputtering). Interestingly, upon exposure of the sputtered region to 1×10^{-6} Torr of O_2 for 15 min, the enrichment in Co and O along the edges is restored, albeit not up to the original concentration levels. This observation suggests the oxygen adsorption along the edges enhances cobalt segregation. H_2S also appears to enhance cobalt segregation to the edges, since crystals treated at 400°C in H_2/15% H_2S showed enrichment at the edges without sputtering.

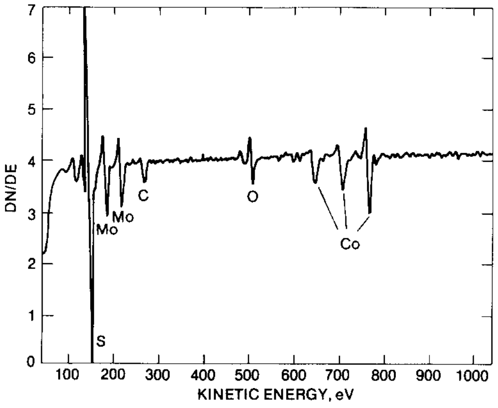

FIG. 7. Auger spectrum from an edge of the crystal after removing ~100 Å of the top surface layer. Co, O, and C are present in addition to Mo and S.

Irregularly shaped, noncrystallographic edges produced by crystal cleavage showed no evidence for Co, or O segregation. Similar negative findings were obtained on edges exposed by ion beam sputtering to form a shallow crater in a crystal facet. It may be concluded, therefore, that segrega-

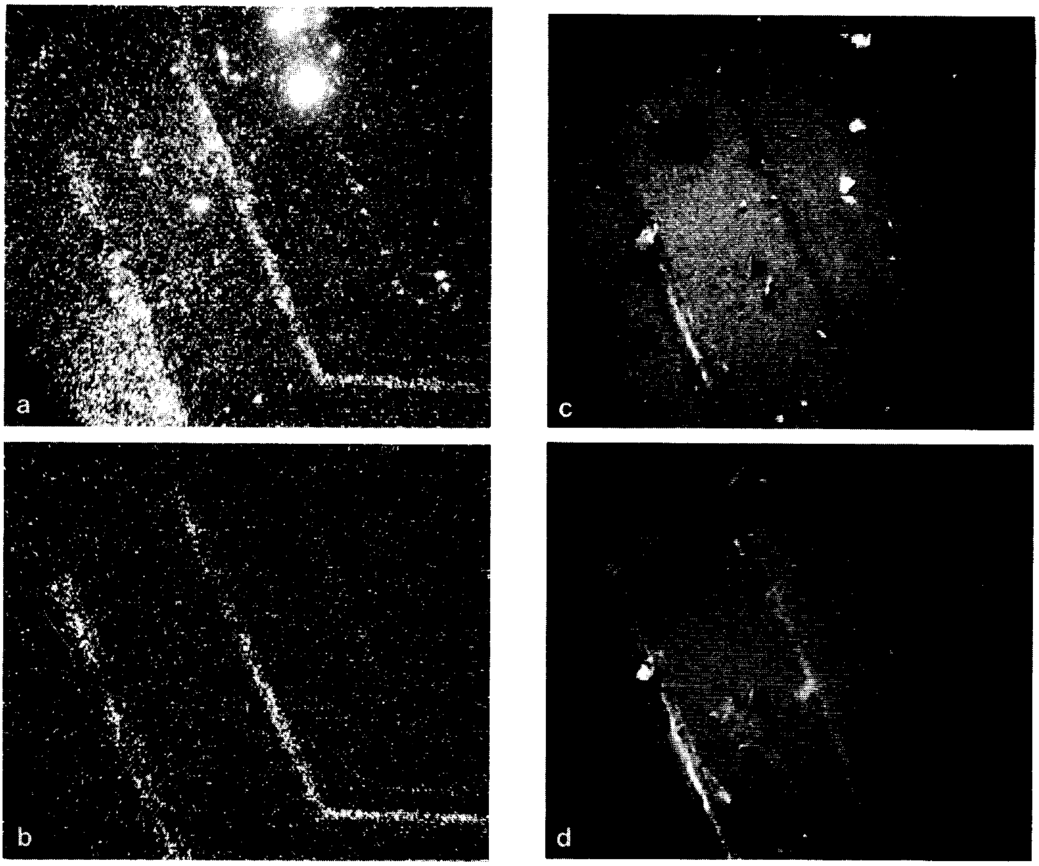

FIG. 8. Auger elemental spatial mapping showing enrichment of Co, and O on the surface. (a) Oxygen map, (b) cobalt map, (c) molybdenum map, (d) sulfur map.

tion of Co and O occurs only along crystallographically aligned edges of the original as-grown faceted structure, which suggests a link between segregation and crystal growth. Perhaps cobalt segregation facilitates edge migration across the basal planes during crystal growth. Also, if surfaces are sputter cleaned, exposure of these faces to a reactive gas such as O_2 or H_2S causes Co segregation. Although the annealing experiments described above indicated that H_2S caused strong Co segregation to crystallographically aligned edges, equivalent experiments on cratered basal planes have not yet been performed. However, it would be expected that such annealing would trans-

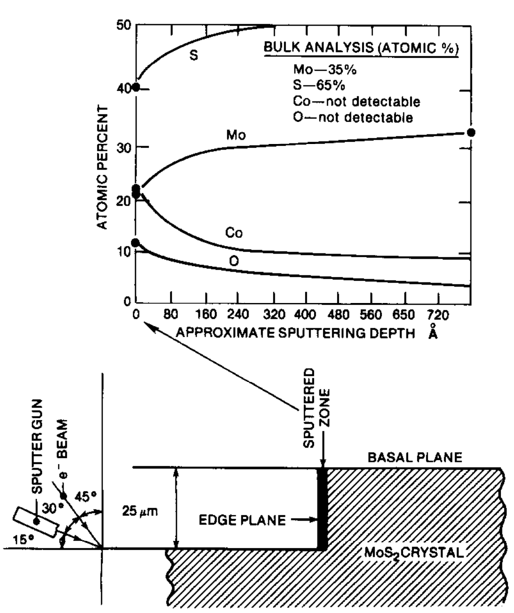

FIG. 9. Schematic diagram of sputtered edge indicating results of depth profiling.

form sputtered craters into crystallographically aligned edges enriched in Co.

DISCUSSION

In this paper we have confirmed that the edge planes of crystalline MoS_2 are reactive toward oxidation at elevated temperatures. Further, that the edge planes of MoS_2 react with Co thus becoming enriched with Co. This enrichment tends to cause MoS_2 planes to grow thicker in the presence of Co (and presumably Ni) than crystals in the absence of Co. Co-enriched edge planes also adsorb oxygen at room temperature as has been reported in supported catalysts (*16*).

The present study indicating Co enrichment near the edge planes of MoS_2 lends support to those theories of promotion which require interaction of Co at MoS_2 edge planes. Voorhoeve and Striver (*6–8*) have proposed that the Co resides between the layers near the edge (pseudointercalation) and Ratnasamy and Sivasanker (*2*) have proposed that the Co terminates the MoS_2 layer at the edges. Although this study cannot structurally pinpoint the Co, it does locate the Co at the MoS_2 edges. The location of the Co in these theories could cause the thickening of the crystals noted in this study. We may also note that the ratio of Co : Mo : S near the edge is quite close to 1 : 1 : 2 (if we include the oxygen with the sulfur). This again is consistent with the "pseudobinary" theory of electronic promotion proposed by Chianelli et al. (*17*) which postulates that the energy of a vacancy is "adjusted" by having a sulfur atom, connected to both a Co and a Mo atom. Topsøe *et al.* (*16*) have discovered the physical signature of the "promoting Co" and have stated that this Co can be located at the edge plane of MoS_2. More detailed studies will be required to define the exact structure of the Co/Mo sulfide located at the MoS_2 edge planes but a better picture of this structure should lead to a detailed understanding of the promotion phenomenon. Additionally, future studies will concentrate on the surface chemistry of the MoS_2 edge planes, which are so important to the catalytic activity of MoS_2 in many reactions.

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