Reports

Edge Surfaces in Lithographically Textured Molybdenum Disulfide

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Lithographic techniques were used to expose edge surfaces in layered molybdenum disulfide single crystals. This microstructuring produced ideal samples for the study of the surface morphology and electronic structure of this catalytically important material. The optical absorption that was measured at mid-gap increased by two orders of magnitude after texturing. This increase resulted from reduced molybdenum at surface defects that are located on edge planes, as shown by photoemission spectroscopy. This information cannot easily be obtained on conventional crystals with predominantly basal plane surfaces.

The layered transition metal dichalcogenides have applications in areas as diverse as lubrication (*1*), catalysis (*2*), and electrochemistry (*3*). The usefulness of these materials results from their highly anisotropic structure, in which tightly bound two-dimensional layers are held together by weak van der Waals forces between layers. Single crystals of these materials have two types of surfaces that have very different characteristics. Basal plane surfaces are parallel to the layers; edge surfaces are perpendicular. The basal surfaces contain sulfur atoms that are bound to three metal atoms. The sulfur atoms provide physical adsorption sites for intercalates but are otherwise chemically inert (*4*). On the other hand, the edge surfaces can be formed only by breaking bonds within the layer and have been shown to be chemically and catalytically active (*5*). The structure of these edge surfaces, which lies at the heart of the chemical properties of these materials, is poorly understood at present.

The catalytic properties of these materials are usually studied by using highly disordered powders (*6*). We have recently shown (*7*) with microcrystalline molybdenum disulfide (MoS$_2$) samples that edge surfaces have a distinct optical absorption spectrum. However, conventional growth techniques yield materials with relatively low edge area because growth occurs primarily in the direction parallel to the layers. A well-ordered edge surface is difficult to create by cutting or polishing because the layers fold and break irregularly. We report here a new way of preparing chemically reactive surfaces with lithographic fabrication methods. Single crystals of MoS$_2$ prepared in this way have a surface that consists primarily of edge planes, which allows exceptional control of the surface morphology. These microstructures are also ideal for fundamental studies of edge surface properties with techniques such as optical or photoemission spectroscopy. Spectral features with molybdenum binding energies lower than those of the bulk indicated the presence of defects. These lower binding energies are consistent with the presence of sulfur deficiencies at the surface. The structural control that could be achieved by lithographic processing allowed high-resolution transmission electron microscopic studies to be performed on the same sample.

Microstructures can be prepared lithographically in a virtually limitless range of shapes and sizes. We used natural lithography (*8*), which allowed easy processing over a large area. A thin film of MoS$_2$ was cleaved parallel to the basal plane from a synthetic single crystal. This sample was placed on a substrate and covered with a monolayer of monodisperse polystyrene spheres (0.2 μm in diameter) as an etchant mask (Fig. 1). The structure was then exposed to an argon ion beam (500 eV, 0.3 mA/cm^2) that removed the material between the spheres and left "posts" of MoS$_2$. The use of such closely packed submicrometer features was necessary to produce a sufficient area of edge surfaces. Any residual polymer on the surface was removed by an oxygen ion beam that selectively removed hydrocarbons (*9*). This procedure left a surface oxide that was removed with a final brief argon or SF$_6$ ion milling. The penetration depth (*10*) of the ions at this energy was less than 15 Å (this estimate included the effect of the angle between the beam and the surface) so that this technique produced a well-ordered MoS$_2$ lattice. Figure 2 shows a single post and a magnified view of the edge surface. The individual layers were flat and uninterrupted across the entire width of the post, and they continued to within $\sim$5 Å of the surface, where they terminated abruptly.

These materials are ideal for studying the electronic structure of the edge planes, which can be revealed through optical absorption measurements. We used photothermal deflection spectroscopy (*11*), a calorimetric technique that relies on the deflection of a laser beam. The absorption spectra of a 0.7-μm-thick sample are shown in Fig. 3. The solid line is the spectrum before texturing; only bulk and basal surface absorption was observed. The peaks at 1.83 and 2.0 eV are the exciton features (*12*). The broad shoulder at lower energies is caused by the indirect band gap (*13*) at 1.22 eV. The fine structures present at the lowest energies are interference fringes caused by reflections at the surfaces.

The absorption observed below 1.2 eV would not be present in perfect single crystals of MoS$_2$ and was caused by defects. When the sample was textured to introduce edge surfaces, this absorption increased by up to two orders of magnitude (Fig. 3). This dramatic effect was not observed on samples that were ion-bombarded without the etchant mask; thus this spectrum is not simply that of a damaged layer. The inset of Fig. 3 shows the absorption at 0.8 eV both before and after texturing for a series of samples of different thicknesses that were all cleaved from the same single crystal. Before texturing the absorption coefficient was constant, which indicated that the absorption is caused by bulk defects, perhaps grain

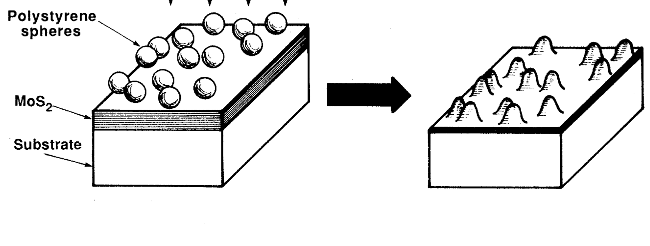

Fig. 1. Lithographic technique for the preparation of MoS$_2$ edge surfaces.

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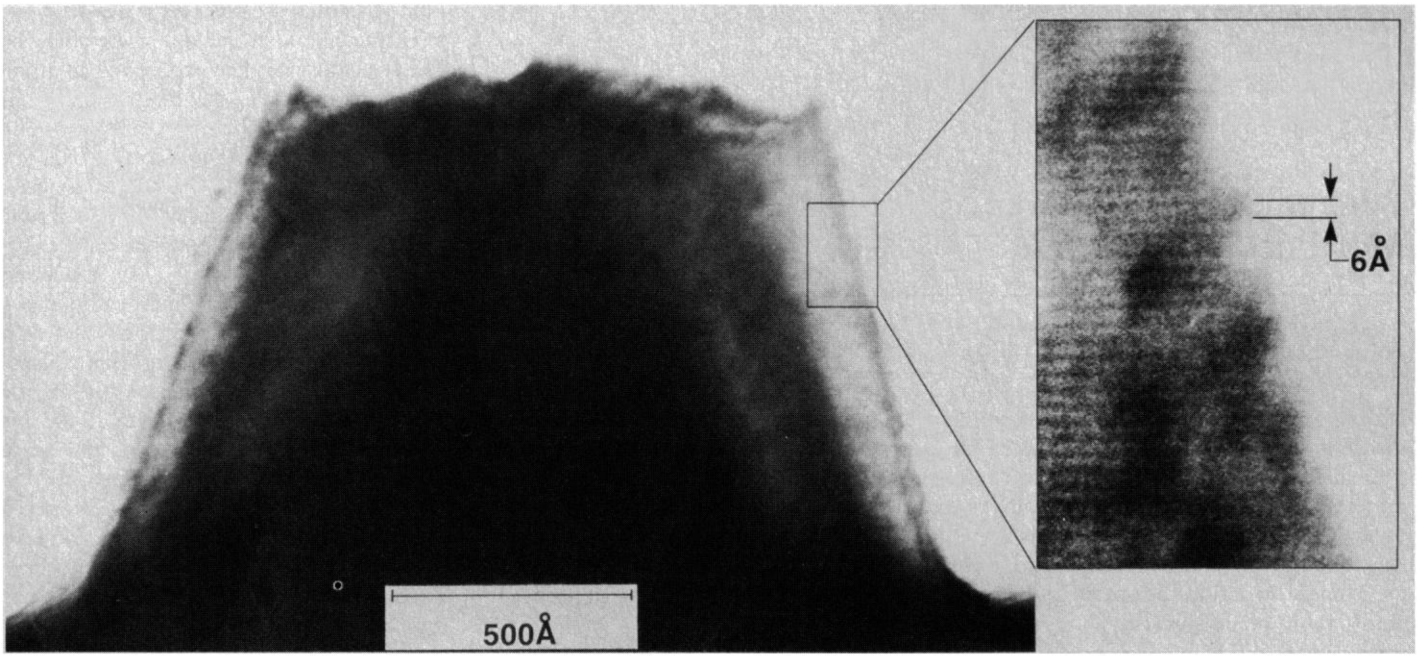

Fig. 2. Transmission electron micrograph of a post that is 2000 Å in diameter. The inset shows a magnified section of the edge surface.

boundaries or dislocations. As expected, after texturing α was inversely proportional to the sample thickness ℓ. This result showed that the absorbance (αℓ) was constant and indicated the presence of a surface effect. The shape of the optical absorption was virtually identical to that observed on the edge surfaces of microcrystalline MoS_2 (*7*).

A series of control experiments showed that this absorption was intrinsic to the edge surface and not caused by damage or contamination. The textured samples showed the same absorption after a wet etch in hydrochloric acid that removed the top surface. The same spectrum was observed when the sample was treated in 15% H_2–85% H_2S at 300°C (to remove surface oxygen) and measured immediately without exposure to air.

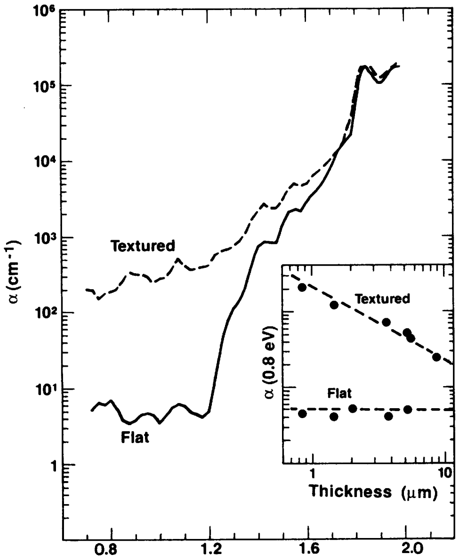

Fig. 3. Optical absorption spectrum of a 0.7-μm-thick MoS_2 sample before (flat) and after (textured). The inset shows the absorption coefficient at 0.8 eV (averaged through interference fringes) for a number of samples of different thicknesses.

These surface defects can also be observed in x-ray photoemission spectroscopy. Figure 4 shows the molybdenum 3*d* core levels of a flat basal plane and of a lithographically textured crystal. Also evident at lower energies is the sulfur 2*s* level. The textured sample was treated in H_2-H_2S at 350°C to reduce and resulfide the surface. This decreased the amount of oxygen observed by a factor of 70. The edge surface spectrum is considerably broader than the spectrum for the basal surface and is also shifted to lower energy. Each of the molybdenum core levels can be separated into two components as shown in Fig. 4. The more intense peak has a Gaussian shape; it is centered at 229.0 eV and is 1.10 eV wide. It was observed for both samples. The spectrum for the textured sample has an additional component that is shifted 0.8 ± 0.05 eV to lower energy. These two components gave a good fit to the entire spectrum and showed that the edge defects contain molybdenum that is reduced relative to the bulk. The shift of 0.8 eV is about that expected for reduction of Mo^{4+} to Mo^{3+} in sulfide compounds (*14*).

The actual microscopic structure of the reconstructed MoS_2 surface is still uncertain. The presence of Mo^{3+} would imply a deficiency of sulfur at the surface relative to the bulk. Such sulfur vacancies, or "dangling bonds," are well known in conventional semiconductor interfaces (*15*). These defects commonly absorb light near mid-gap (*16*), as we observed on MoS_2 edge surfaces. Ultraviolet photoemission spectroscopy measurements showed that the Fermi level moved 0.80 eV closer to the valence band upon texturing. Because this shift is nearly as large as the band gap (1.2 eV), the Fermi level of the edge surface must be within ~0.3 eV of the valence band maximum. This implies that most of the edge surface defects within the band gap would be unoccupied, and that optical transitions would involve the excitation of electrons out of the

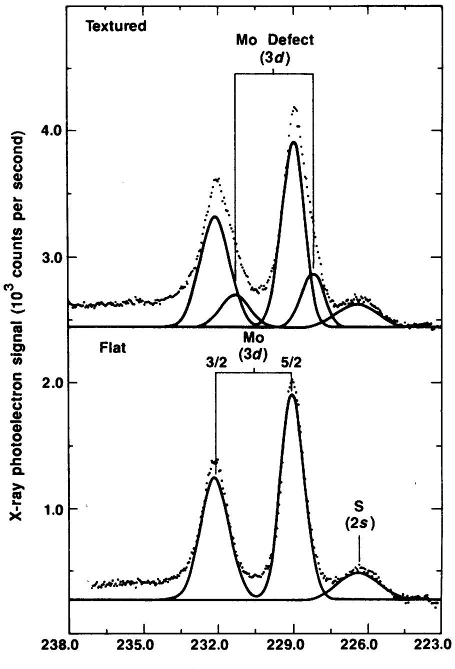

Fig. 4. X-ray photoemission spectra of MoS_2 single crystals before (bottom) and after (top) texturing. Photon energy, 1253.6 eV; resolution, 0.2 eV.

valence band into the defect level. Such transitions would lead to the monotonic increase in absorption with photon energy that we observed. The strength of the absorption observed [a cross section of 6×10^{-17} cm^2 per exposed molybdenum atom (*7*)] is consistent with other similar defects if every surface site undergoes transitions.

These data on the electronic structure of the edge surface have important implications for our understanding of catalysis in the transition metal sulfides. Such reactions are known to occur on the edge surface (*17*) and are correlated with the optical absorption we have observed (*7*). The presence of reduced molybdenum species such as Mo^{3+} at the surface is consistent with the "sulfur vacancies" that are often hypothesized as catalytically active sites (*18*). In fact, W^{3+} (which is isoelectronic with Mo^{3+}) has been correlated with activity in sulfide catalysts in electron spin resonance studies (*19*).

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Solar Irradiance Change and Special Longitudes Due to *r*-Modes

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Sluggish global oscillations, having a periodicity of months and trapped in the sun's convection zone, modulate the amount of energy reaching Earth and seem to impose some large-scale order on the distribution of solar surface features. These recently recognized oscillations (*r*-modes) increase the predictability of solar changes and may improve understanding of rotation and variability in other stars. Most of the 13 periodicities ranging from 13 to 85 days that are caused by *r*-modes can be detected in Nimbus 7 observations of solar irradiance during 3 years at solar maximum. These modes may also bear on the classical question of persistent longitudes of high solar activity.

TWO SOLAR PROBLEMS OF HIGH INTEREST early this century were never solved. The challenging observations had no convincing explanations. Perhaps as a consequence, their study became unfashionable at the main research centers. First, solar activity (sunspots and flares) tends to occur at certain preferred longitudes, and second, it seems multiperiodic, at periods other than the 11- or 22-year cycle. Although few investigators thought that many true periods were plausible, some did accept the evidence for preferred (*1*) and rigidly rotating (*2*) longitudes, in spite of the paradoxical nature of this idea in a gaseous sphere whose surface so clearly fails to rotate rigidly. Today, new explanations are possible that involve convection and global oscillations of its mass (*3*). These oscillations rotate like rigid bodies, creating special longitudes with their nodes and antinodes. The sun's heat rises by convection through a layer thought to occupy at least the outer 25% of its radius. At depth, these flows are massive and have the energy to dominate the thin surface layers, affecting the local brightness and the number and location of surface blemishes. All this can be modulated by a system of global oscillations that corresponds with measured periods in the sun's irradiance and is consistent with rotation of large surface features. Our results demonstrate that periodic global oscillations, called *r*-modes, are indeed strong enough to modulate convection, making irradiance and surface blemishes similarly periodic in longitude and time.

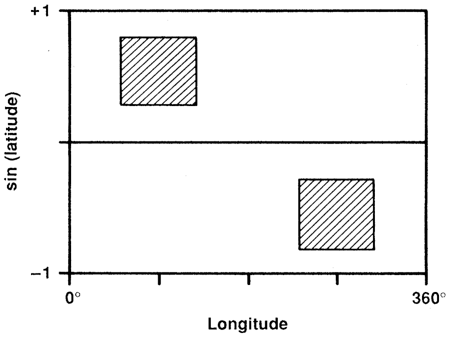

Fig. 1. Map of a complete solar surface showing schematically the areas (shaded) of atypical brightness where convection tends to be enhanced by a family of *r*-modes. The pattern rotates rigidly at a known rate. Smaller scale structure is ignored because of its lesser influence on irradiance, which is an integral over a solar hemisphere.

An *r*-mode (*4*) is a toroidal oscillation of swirling horizontal motions whose period is at least as long as the star's rotation period. "*r*-Modes," "Rossby waves," and "inertial oscillations" are basically the same physical phenomenon differing in geometric approximations or history of derivation. The restoring force (Coriolis) conserves angular momentum while other forces (compression and buoyancy) are negligible. Such modes have been studied for a uniformly rotating star (*5–7*) and specifically for the sun (*8*). Their strong interaction with convection is almost certain because the size, vorticity, and period of the *r*-mode are all comparable (*8*) with that of large deep convection cells. This would cause the sun's total luminous output to fluctuate and parts of its surface to change brightness on long time scales derivable from *r*-modes, contradicting the widespread assumption that convection is stochastic over intervals that much exceed the turnover time of a typical cell (*9*). As a test, one can ask: Does solar energy reaching Earth display periodicities consistent with the surface distribution of *r*-modes and their rotation law?

The apparent (synodic) rotation rate of an *r*-mode is (*8, 10*)

$$\nu = \nu_s \left[1 - \frac{2}{\ell(\ell+1)}\right] - \nu_e \qquad (1)$$

where ν_s is the mean sidereal rotation rate of the sun's envelope, $\nu_e = 31.7$ nHz is the orbital rate of Earth and ℓ is the principal

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