# Observation of intercalate domains in Ag-TiS<sub>2</sub>

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The Ag distribution in partially intercalated stage-2 Ag/TiS<sub>2</sub> was determined by measuring the Auger signals of elements on surfaces of cleaved crystals. The results show that the intercalant is distributed in fairly regular "channels" which extend from the crystal edge to the intercalation front and have an average spacing of about 10  $\mu$ m. The results provide evidence for a regular Daumas-Hérold domain model of intercalation staging.

#### INTRODUCTION

One of the most remarkable properties of intercalated layered materials is the staging phenomenon. Staging refers to a long-range one-dimensional ordering of sheets of intercalated atoms which are located between the host layers. For a stage-n compound, the period of the ordering consists of an intercalate layer followed by n host layers. Experimental and theoretical studies of staging have attracted a great deal of recent interest, 1-8 but the phase transition which allows the stage index n to change has no satisfactory explanation in terms of simple staging, since it is known that the intercalant cannot pass through the layers of the host.<sup>9</sup> In order to understand staging transitions, Daumas and Hérold<sup>10</sup> proposed a simple but elegant staging model known as the domain, or Daumas-Hérold (DH), model. The model is shown in Fig. 1 for a stage-2 compound. In this model, the intercalation compound consists of regular microscopic domains, such that within any domain the intercalate layers ("islands") are continuous and, together with the host layers, form a staged sequence, but in adjacent domains the intercalant layers lie between different pairs of host layers. Thus, a macroscopic crystal can be stage-n almost everywhere and, at the same time, globally there can be an equal amount of intercalant between every neighboring pair of host layers. This model allows the stage index to change via the movement of islands of intercalant between adjacent domains. Although the domain model is widely accepted as the only reasonable explanation for many ex-



FIG. 1. Daumas-Hérold domain model for a stage-2 intercalated compound. The lines represent the host, and the circles represent atoms making up the intercalant islands. The results established in this work are consistent with the surface islands having one-half the intercalant concentration of the subsurface islands (due to cleaving effects), as shown. perimental results, 11-13 there has been little direct evidence for the existence of any kind of a regular domain structure and little direct information on the lateral extent and shape of intercalation domains. Such information is essential for a complete understanding of the intercalation process and the two-dimensional diffusion mech-anism. Thomas *et al.*,<sup>14</sup> using high-resolution electron microscopy, showed the existence of isolated islands of intercalant in a residue compound of FeCl<sub>3</sub>-intercalated graphite. Recently, Levi-Setti et al., 15 using a focussed ion beam and secondary-ion mass-spectroscopic mapping, observed randomly distributed beadlike regions of intercalant on the surface of cleaved stage-2 and stage-4 SbCl<sub>5</sub>-intercalated graphite. However, Bretz and Clarke<sup>16</sup> submitted that these regions were a result of the surface-exposed intercalant migrating and selectively decorating the graphite surface.

In this article, we report a study of the surface distribution of intercalant on a cleaved stage-2 Ag-intercalated  $TiS_2$  single crystal. We believe that our observations provide the first direction evidence for the existence of a regular island structure in a staged intercalation system.

## EXPERIMENTAL PROCEDURE AND RESULTS

Pure TiS<sub>2</sub> crystals were prepared by the iodine-vaportransport method and the crystals used for intercalation were obtained by cleaving the as-grown crystals. The cleaved crystals were  $1-3 \ \mu m$  thick, as measured by an optical interference microscope, and had lateral dimensions of about 1000  $\mu$ m. Using a solution of 0.05M AgNO<sub>3</sub> in water, an open circuit potential of 110 mV was observed, and crystals could be electrointercalated by completing the external circuit. Two types of stage-2 intercalated systems were prepared: (i) by placing an opposing voltage of about 50 mV in the external circuit the crystals were intercalated directly as stage 2, (ii) by shorting the external circuit the intercalation proceeded via a stage-2 region followed by a stage-1 region. Upon disconnecting the circuit the stage-1 region converted to stage 2 within several hours.<sup>5</sup>

Information on the quality of the stage-2 system studied is essential when attempting to interpret results in terms of a DH model. Figure 2 shows an x-ray



FIG. 2. X-ray diffraction pattern from a partially intercalated Ag/TiS<sub>2</sub> crystal. The arrows indicate the peak positions for pure stage 1 and pure stage 2. The strong peak at  $15.61^{\circ}$  is from the unintercalated region of the crystal. Auger data on this sample are presented in Fig. 4.

diffraction pattern from the partially intercalated crystal (obtained by a conversion from stage 1) shown later in Figs. 4(a) and 4(b). The diffraction shows a strong peak at  $2\theta = 15.61^{\circ} \pm 0.02^{\circ}$  from the unintercalated portion of the crystal. A smaller peak is seen at  $2\theta = 14.50^{\circ} \pm 0.05^{\circ}$ from the intercalated region at the edge of the crystal. The intercalation peak is weak due to the relatively small intercalated region of the crystal. X-ray diffraction patterns from only the intercalated region of similar crystals reveal only the single "stage-2" peak so we can safely assume that no portion of the unintercalated (15.61°) x-ray peak is from the intercalated region of the crystal. The arrows in Fig. 2 indicate where the peaks for pure stage 1 and pure stage 2 are expected for the intercalation technique used here.<sup>8</sup> Figure 2 shows that the intercalated region is predominantly stage 2. An analysis<sup>17</sup> based on the intercalated peak shift, assuming a one-dimensional model with random stacking of the stage-1 and stage-2 cspacings of 12.890 and 12.145 Å, respectively, indicates that the intercalated region is a mix of stage 1 and stage 2 with the proportion of stage 1 in the intercalated region estimated to be  $(10\pm6)\%$ . The intercalation peak in Fig. 2 is slightly asymmetrical, suggesting that there may be two peaks, one due to pure stage 2 and one due to the random mix of stage 1 and stage 2. This could account for a peak broadening that is somewhat greater than expected from a random stacking model. Some stage-1 content is not surprising, considering that the stage-2 system was created via conversion from stage 1. A small quantity of stage 1 cannot be expected to significantly affect the results to be presented, and the data are interpreted in terms of a pure stage-2 system.

The crystals were partially intercalated into selected edges by covering the other edges with silicone rubber. Once intercalated, the crystals could be left indefinitely, since stage-2 Ag/TiS<sub>2</sub> is stable at room temperature.<sup>9</sup> The intercalated crystals were mounted on a copper substrate, then cleaved in air and put immediately into the ultrahigh vacuum of a Perkin-Elmer model 595 Scanning

Auger Microprobe. The direction of cleaving was from the unintercalated region of the crystal toward the intercalated region, since the crystals tended to cleave best in this direction. The spatial distributions of elements on the surface of the freshly cleaved intercalated crystal were determined by measuring the Auger signals of the elements as the electron beam was rastered through a set of points over a selected region of the crystal. The electron beam remained for 20 msec on each point. Rastering through a set of points once is termed a cycle and the number of cycles used was determined from signal-tonoise considerations. The Auger peaks examined were S (152 eV), Ag (351 eV), and Ti (387 eV). The electronbeam voltage and current were 3 kV and 15 nA, respectively, and the beam diameter was 0.22  $\mu$ m. Preliminary work using smaller beam currents (5 nA) gave the same results as the higher beam current, so the latter was used to increase the signal-to-noise ratio.

Figure 3 shows the relative concentrations of S, Ti, and Ag as a function of distance as measured along a straight line across the surface of a stage-2 crystal obtained by transition from stage 1. The direction of this line scan was, to within 10 deg, perpendicular to the crystal edge. The data were obtained by a series of point measurements taken 0.7  $\mu$ m apart, and the duration of a cycle was 4 sec. As can be seen in Fig. 3, at a distance of about 30  $\mu$ m from the crystal edge the Ag distribution consists of a series of maxima and minima on a scale of about 10-15  $\mu$ m, and both the S and Ti distributions are clearly anticorrelated to the Ag distribution. Small-scale variations within the Ag and Ti distributions are considered to be noise. The anticorrelation of S and Ti with Ag shows that the Ag oscillations are not caused by contamination on the crystal surface.

Due to the symmetry of the cleaving process, it can be expected that the Ag divides equally on an atomic scale onto both of the newly created surfaces. This view is supported by the ratio R of the Ag maxima to the Ag mini-



FIG. 3. Auger line scan across a freshly cleaved surface of a partially intercalated stage-2 Ag/TiS<sub>2</sub> crystal. The stage-2 system was obtained through conversion from stage-1. The arrow denotes the intercalation front and the crystal edge is located at  $-5 \,\mu$ m.

ma from Fig. 3. The data in Fig. 3, when averaged over the four maxima and minima extending from 30  $\mu$ m to the intercalation front, give  $R = 1.7 \pm 0.2$ . Theoretically, the Auger signal I from a layer of Auger emitting atoms m+1 layers below the crystal surface varies as<sup>18</sup>

$$I \approx N_{m+1} \prod_{m} \{1 - X_m + X_m \exp[-1/\sigma \cos(\theta)]\}$$
, (1)

where  $N_{m+1}$  is the concentration of atoms in the Auger emitting layer,  $\sigma$  is the escape depth of Auger electrons measured in monolayers, and  $\theta$  is the angle (with respect to the crystal surface normal) at which the Auger electrons are collected. The product  $\prod_m$  is carried out over all m atomic layers between the Auger emitting layer and the crystal surface, and  $X_m$  is the fraction of a monolayer in the atomic layer m. Note that Eq. (1) takes into account the absorption of all layers above the (m+1)th layer. For the energy of the Ag Auger electrons the value of  $\sigma$  is about 3.9±1 monolayers, <sup>18</sup> and in our experiments  $\theta$ is 42 deg. Referring to Fig. 1: for TiS<sub>2</sub>, each host layer consists of a S-Ti-S "sandwich," and so is equivalent to three atomic layers, and each atomic layer is one complete monolayer; the subsurface islands in stage-2  $Ag/TiS_2$  are equivalent to 0.4 of a monolayer, and the surface islands, which are one-half the concentration of the subsurface islands, are equivalent to 0.2 of a monolayer.<sup>19</sup> Using the model in Fig. 1, and summing the Auger signals from all islands within domains to obtain the maximum and minimum Ag Auger signals gives R = 1.6, with an uncertainty of +0.5 and -0.2. Calculations using a model with no surface Ag (or with the surface island concentration equal to the subsurface island concentration) gives R = 2.8, with an uncertainty of +1.2and -0.5. Thus, the model of surface Ag islands with one-half the concentration of the subsurface Ag islands (due to an atomic dividing of Ag upon cleaving), as shown in Fig. 1, provides the best agreement with the observed experimental ratio of 1.7, and so the data in Fig. 3 are interpreted using this model. We have found no other model of a stage-2 system which gives a value of Rwhich agrees with Fig. 3 other than that shown in Fig. 1. Note that the value of R provides information on the three-dimensional (3D) distribution of intercalant.

The distribution of Ag on the surface of another stage-2 crystal obtained by transition from stage 1 is shown in Fig. 4(a). In this case the S signal was measured rather than Ag because of a better signal-to-noise ratio. The map was obtained by a series of point measurements taken 1.7  $\mu$ m apart in both directions, and the duration of a cycle was 128 sec. Light-colored regions correspond to a strong S Auger signal and dark-colored regions correspond to a weak S Auger signal. Line scans in the map area showed that the S and Ag are anticorrelated, so the dark regions in Fig. 4(a) correspond to the presence of surface Ag. Thus Fig. 4(a) shows that the Ag distribution consists of a series of "channels" which are approximately perpendicular to the crystal edge. The width of the channels are about 5  $\mu$ m, and the spacing between channels is about 10  $\mu$ m. Figure 4(b) is a computer-enhanced version of Fig. 4(a) and clearly shows the channel-like structure. Some channels appear to meander and divide

as they extend in from the edge of the crystal toward the intercalation front. This could (at least in part) be due to a change in channel contrast due to small cleavage steps across the channels: a monomolecular cleavage step would result in a channel contrast reversal (a bimolecular cleavage step would give no contrast reversal). This type of channel-like Ag distribution was also seen in crystals intercalated directly as stage 2. The structure of separate line scans taken across Auger maps are well correlated with the map features. In particular, we have done a line scan approximately perpendicular to the channels for a region adjacent to that in Fig. 4 and find good correlation between the line scan and the map. Maps or line scans similar to those in Figs. 3 and 4 have been observed consistently in more than ten different samples. Even though the line scan in Fig. 3 was nominally perpendicular to the



FIG. 4. (a) Two-dimensional Auger distribution of S on a freshly cleaved surface of a partially intercalated stage-2 Ag/TiS<sub>2</sub> crystal showing a channel-like structure. The stage-2 system was obtained through conversion from stage 1. Light regions correspond to a strong S signal, and dark regions correspond to a weak S signal, caused by Ag on the surface. The arrow denotes the direction and extent of the intercalation front. The crystal edge is approximately parallel to the intercalation front and just out of the figure to the left. The length of the scale bar is 20  $\mu$ m. (b) Computer-enhanced image (two-level grey scale only) of the data of (a) clearly showing the channel-like structure. Scale as in (a). The channels are about 10  $\mu$ m apart.

intercalated edge of the crystal, the development of the Ag maxima and minima as the beam progresses in from the crystal edge can be realized as the crossing of the line scan over channels which curve and divide as intercalation proceeds from the crystal edge. This is consistent with the fact that the Ag maxima and minima in Fig. 3 are wider than the channels in Fig. 4. Secondary-electron images and optical microscopy of the examined regions showed no evidence for crystal steps or cracks parallel to the channels which could account for such a channel structure.

As mentioned previously, the cleaving direction of the intercalated crystals used for Figs. 3 and 4 was from the unintercalated region toward the intercalated region, so that the direction of the channels was approximately parallel to the direction of cleaving. To show that these channels are not an artifact of cleaving, Ag was intercalated into two adjacent edges of a crystal, the angle between the edges being 60°. When cleaving such a crystal, one cannot simultaneously cleave in a direction perpendicular to both intercalated edges. Auger analysis on such samples<sup>20</sup> yielded Ag channels which were perpendicular to their respective edges. The only region where channels were not observed was the corner where the two edges met, and this can be explained in terms of the channels from the two edges interfering with each other during intercalation. It should be noted that both Figs. 3 and 4 show that the width of the Ag channels is approximately the same as the spacing between channels. This is consistent with a stage-2 domain structure and also with the observed macroscopic Ag distribution (5- $\mu$ m channel width) not being affected by an atomic dividing of Ag upon cleaving. These results, combined with the fact that the value of R calculated from Fig. 3 is consistent with surface Ag islands being one-half the concentration of the subsurface islands, provide convincing evidence that the Ag channel structure is not an artifact of cleaving.

We have observed that the oscillating Ag structure (Fig. 3) tends to disappear within 12-24 h of cleaving. This is expected due to diffusion of Ag on the surface and diffusion of subsurface Ag caused by the relaxation of the surface host layer after cleaving. However, the observed distributions are reproducible up to about 6 h in ultrahigh vacuum after cleaving. Since all results were obtained within a few hours of cleaving, we believe the results in Figs. 3 and 4 represent the distribution of Ag immediately after cleaving and thus provide information on

the Ag distribution of the bulk crystal.

A complete channel domain model of a crystal as indicated in Fig. 1 requires 3D evidence of the channels. The value of R discussed above provides some 3D information in that it gives evidence of the Ag distribution down to a few Ag layers below the surface. Additional evidence for a 3D channel model was obtained by cleaving a crystal twice. This process revealed channels in nominally the same region of the crystal with essentially the same spacing at two different levels in the crystal. Recent data have been obtained on a sample which reveals two cleavage steps perpendicular to the channel direction: across each step a contrast reversal of channels is observed, as expected for a 3D channel model.

### DISCUSSION

The work presented demonstrates that the Ag distribution in stage-2 Ag-intercalated TiS<sub>2</sub> consists of regions in the form of fairly regular "channels" which extend from the crystal edge toward the intercalation front. The channel separation is about 10  $\mu$ m. We also provide evidence for 3D Daumas-Hérold channel domains within stage-2 Ag-intercalated  $TiS_2$ . In this case, such a form for domains is appealing in that it minimizes the domain-wall energy and allows the individual atoms of intercalant to "flow through" the channels during intercalation and stage transition. The model does not require the movement of intercalant between adjacent domains during stage conversion, but only requires that the channels grow in extent in the intercalation direction. We believe these channels provide a good model of the transition from stage 1 to stage 2 during deintercalation, where stage 2 is observed to propagate in from the edge of the crystal.<sup>9</sup> Kirczenow has observed similar behavior in Monte Carlo computer simulations of deintercalation.<sup>7</sup>

It can be expected that such channels may exist in other intercalated materials, and further work is being carried out on the intercalation and deintercalation of  $Ag/TiS_2$  and other intercalation systems.

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FIG. 4. (a) Two-dimensional Auger distribution of S on a freshly cleaved surface of a partially intercalated stage-2 Ag/TiS<sub>2</sub> crystal showing a channel-like structure. The stage-2 system was obtained through conversion from stage 1. Light regions correspond to a strong S signal, and dark regions correspond to a weak S signal, caused by Ag on the surface. The arrow denotes the direction and extent of the intercalation front. The crystal edge is approximately parallel to the intercalation front and just out of the figure to the left. The length of the scale bar is 20  $\mu$ m. (b) Computer-enhanced image (two-level grey scale only) of the data of (a) clearly showing the channel-like structure. Scale as in (a). The channels are about 10  $\mu$ m apart.