Intercalation islands and stage conversion in Ag-TiS$_2$

D. Kaluarachchi* and R. F. Frindt

Physics Department, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

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The conversion of stage 1 into stage 2 for thin TiS$_2$ crystals partially intercalated with Ag has been observed at room temperature using electron microprobe x-ray fluorescence. The results are consistent with the Daumas-Hérold island model for staging and show that in the stage conversion the stage-1 region acts as a source of moving stage-2 Ag islands. A simple regular island configuration with wedge-shaped intercalation fronts is used to determine an island size around 130 Å for stage-2 Ag in TiS$_2$.

There has been much interest in intercalated graphite and the intercalated transition-metal dichalcogenides, particularly with regard to the occurrence of staging transformations. Staging refers to the phenomenon where the intercalated species occupies the space between the host layers in an ordered sequence. The stage number n refers to the number of host layers between the intercalant layers. In 1969 Daumas and Hérold[1] proposed an island model to explain transformations between stages of intercalated graphite. In the Daumas and Hérold (DH) model, intercalant is found between all of the host layers in the form of domains of regularly stacked islands, and a transition between stages involves a lateral redistribution of intercalant within a given layer, with no motion perpendicular to the layers being required. Although experiments on stage transformation are quite satisfactorily explained in terms of the DH model[2-4] no direct observation of DH domains is available. Perhaps the most convincing evidence to date in support of the DH model is given by a high-resolution electron microscope study on FeCl$_3$ in graphite,[5] where an isolated island and various interpenetrating stages are evident. In addition, the existence of intercalate islands has been used to explain deviations from expected stoichiometry for nickel chloride and manganese chloride in graphite, with x-ray line broadening indicating island sizes in the range 100 to 200 Å.[6] In contrast to these results, an in-phase coherence distance in excess of 1 μm was obtained from an x-ray study on stage-4 Br in graphite.[7] If the DH model is applicable here, the indications are that a wide range of island sizes can be expected, depending on a number of factors such as the elastic properties of the host, stage number, temperature, size of the intercalant, and possibly the method of intercalation used. From a theoretical viewpoint, the stability of the pure stage DH model relative to mixed or randomly staged compounds has been demonstrated,[8] and recently the interaction of DH domain walls has been discussed[9] where it is shown that stage-2 DH domains should strongly bind to each other, again demonstrating the inherent stability of the model.

We present here the results of an electron microprobe study of the intercalation of silver (Ag) into thin single crystals of the layered compound titanium disulphide (TiS$_2$). In this system both stage 1 and stage 2 have been observed in electrointercalated crystals,[10] and it is known that the Ag intercalates into TiS$_2$ via the propagation of stage 1 and then stage 2 in from the crystal edge.[11] In our study we used partially intercalated crystals where we observed a rapid conversion of stage 1 into stage 2 at room temperature. A moving island model based on the DH model is required to reasonably explain the observations and, using the model,

we obtain a value for the size of the stage-2 Ag islands.

The importance of using thin crystals in such experiments must be emphasized. We have found that severe strain-induced crystal cracking occurs both along and perpendicular to the layers when crystals greater than a few microns thick are intercalated. Similar cracking of large TiS$_2$ crystallites has been observed on intercalation with Li.[12]

The TiS$_2$ crystals used in the experiments were cleaved from as-grown crystals which were prepared by the iodine vapor transport method. The thicknesses of the crystals were in the range of 1–2 μm (micrometers) and the lateral dimensions were usually less than 1000 μm. The cleaved crystals were mounted on pieces of cover glass and the thicknesses were measured by use of optical interference fringes. They were then allowed to electrointercalate partially only from one edge by covering the other edges with silicone rubber. A solution of $0.1M$ AgNO$_3$ in glycerol was used as the electrolyte. The relative intercalated Ag content as a function of distance in from the crystal edge was determined by observing electron beam stimulated fluorescent x-ray emission from scans along a line perpendicular to the edge of the crystal. The scans were point measurements taken about 5 to 20 μm apart with an electron beam size of typically about 2 μm. The counting time per point was typically about 3 min. The emitted fluorescent x rays were analyzed by an energy-dispersive spectrometer and the x-ray intensity of the Ag $L\alpha$ peak was measured relative to the intensity of the Ti $K\alpha$ peak using a window of width of 0.30 keV. A 20-kV electron beam was used and at this voltage the maximum depth for detectable Ag fluorescent x rays in TiS$_2$ was determined to be about 2 μm from measurements on pure TiS$_2$ crystals on a Ag substrate.

After partial intercalation, the crystals were scanned repeatedly and it was found that the stage-1 silver converts into stage-2 silver within hours, as shown in Fig. 1. All of the graphs obtained for the distribution of Ag in different samples showed that the stage-1 and stage-2 intercalation fronts have a finite width. In addition, when the final stage-2 front resulting from the stage-1 to stage-2 conversion was stabilized, the width of the stage-2 front (r) was found to be approximately twice the widths p and q of the initial stage-1 and stage-2 fronts. In addition to the electron microprobe results, we have shown, using radioactive tracers, that none of the Ag in the stage-1 region migrates to the final stage-2 front.[13] This means that the only plausible model that can be used to explain the evolution of stage 1 into stage 2 is an island model, and we propose the moving island model shown in Fig. 2 to interpret our observations. Figure 2(a) shows the upper half of a partially inter-
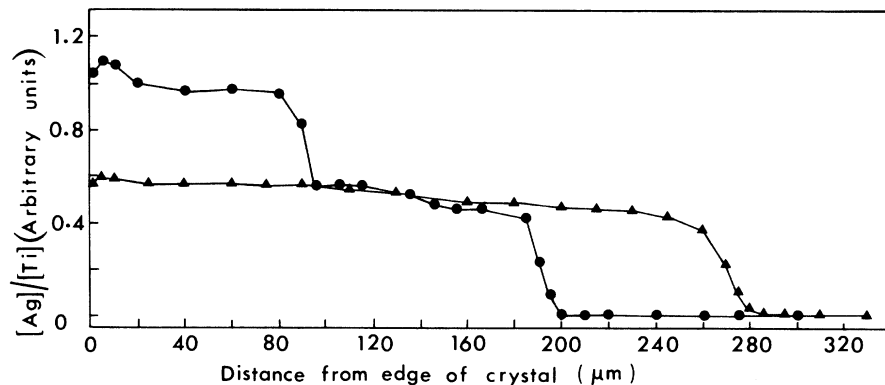
FIG. 1. Distribution of Ag in a partially intercalated TiS_2 crystal at room temperature. ●—started 45 min after intercalation, showing stage 1 and stage 2. ▲—data taken after two days, showing only stage 2. The lengths p, q, and r are the widths of the intercalation fronts.

calated crystal. In a complete crystal, the islands are arranged in such a way that the stage fronts are V shaped. Sloped fronts are required to reduce crystal strain and the linear or V-shaped front is consistent with our microprobe results and also with crystal surface topology as determined by interference fringes.[11] It should be noted that the kinks in the host layers in Fig. 2 are exaggerated since x-ray results show that the host layer spacing increases by 6.5% on intercalation.[10]

In the conversion from stage 1 to stage 2, it is apparent from the model that stage-2 islands are generated at the stage-1–stage-2 interface and that the empty crystal is penetrated by the motion of the islands. In Fig. 2(a), both the stage-1 and stage-2 intercalated fronts have the same width (p and q) and the front width doubles [r, Fig. 2(b)] as the stage 1 converts to stage 2. In the model of Fig. 2, the intercalation fronts are steplike. Noting that for a crystal of N host layers (for large N) there are $N/2$ steps associated

with the fronts in Fig. 2(a), the size (L) of the stage-2 islands can be related to the width of the intercalation fronts as

$$L_p = \frac{2p}{N}, \quad L_q = \frac{2q}{N}, \quad L_r = \frac{r}{N} \qquad (1)$$

for large N, where p, q, and r refer to the front widths as shown in Fig. 2. Note in Fig. 2 that the front width r is twice that of p and q. The value of N can be determined from the original crystal thickness and the c lattice parameter of pure TiS_2 of 5.696 Å.[10] Values for front widths p, q, and r for ten samples were obtained from electron microprobe scans and the calculated values for the stage-2 island width (L) are presented in Table I.

The measured stage front widths p, q, and r in Table I are consistent with the model given in Fig. 2 in that the front widths increase with time and the stage-1 front width r is approximately twice the stage-2 front width p. A time of
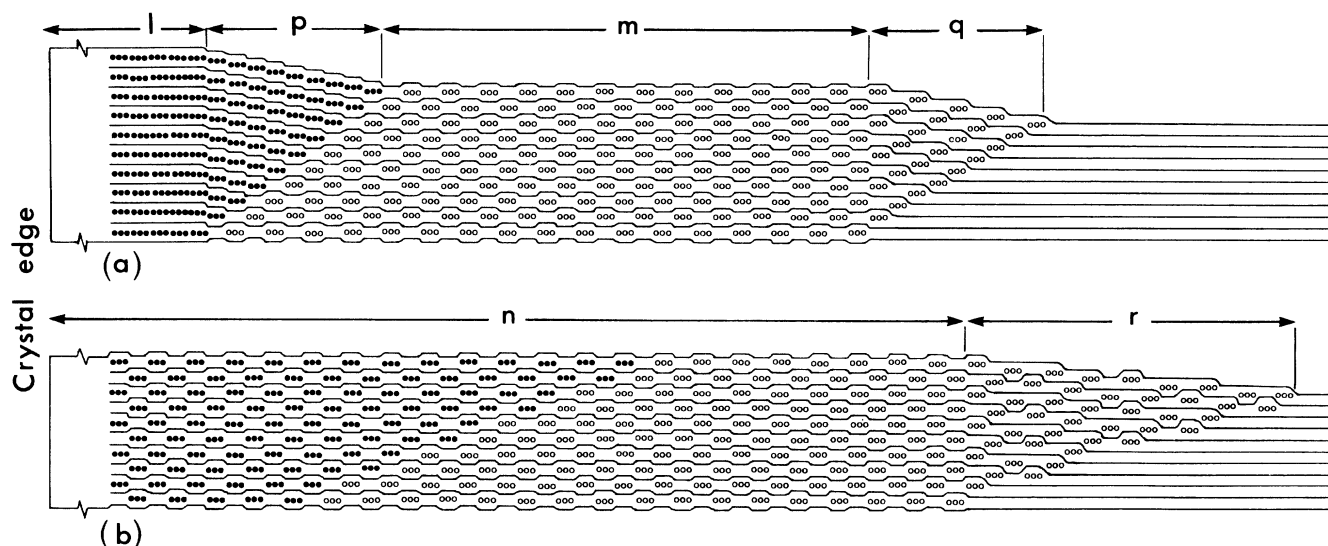

FIG. 2. Island model showing a cross section of one-half of a partially intercalated crystal. This is a schematic diagram where the host layers are depicted by lines and the circles depict regions of intercalated Ag (the circles do not depict individual Ag atoms). Dark circles are the originally stage-1 Ag. Light circles depict Ag in stage-2 islands. (a) The crystals with stage 1, stage 2, and empty regions. l, p, m, and q are the widths of the pure stage-1 region, stage-1 intercalation front, initial pure stage-2 region, and initial stage-2 intercalation front, respectively. (b) The crystal after the conversion to stage 2. n and r are the widths of final stage-2 region and final stage-2 intercalation front.

TABLE I. Electron microprobe results for Ag distribution in TiS$_2$ crystals. L is the Ag island size and the other symbols are defined in Fig. 2.

Crystal thickness ±0.07 (μm)	l (μm)	p (μm)	m (μm)	q (μm)	n (μm)	r (μm)	Stage-1 front (p) (h)	Stage-2 front (q) (h)	Stage-2 front (r) (days)	L_p (Å)	L_q (Å)	L_r (Å)
							Time (T)[a]					
0.89	83	12	100	15	265	20	1.25	2	2–3	155	190	130
1.10	40	13	90	16	170	30	1.25	2	2–3	135	165	155
1.18	20	15	60	17	100	25	1	1.75	2–3	145	165	120
1.18	35	13	100	15	170	30	1.25	2	2–3	125	145	145
2.00	70	22	110	23	255	37	1	2	2–3	125	130	105
1.18	85	15	112	20	· · ·	· · ·	1.25	2.5	2–3	145	195	· · ·
1.77	50	20	55	25	· · ·	· · ·	1.25	1.75	2–3	130	160	· · ·
1.47	130	15	210	22	· · ·	· · ·	1.25	2.5	2–3	115	170	· · ·
1.18	· · ·	· · ·	· · ·	· · ·	95	30	· · ·	· · ·	2–3	· · ·	· · ·	145
2.00	· · ·	· · ·	· · ·	· · ·	260	38	· · ·	· · ·	2–3	· · ·	· · ·	110

[a]Time interval between the start of scanning the corresponding front and the stop of the intercalation.

$2\frac{1}{2}$ to 3 h was required to complete a scan across the sample so that values for p were determined before the values for q. Since the silver in the stage-1 region was moving during this period, the values for q are expected to be a little higher than p. As a result, the values for L_q are less reliable and are higher than L_p and L_r, as shown in Table I. The average values for L_p and L_r from Table I are 135 and 130 Å, respectively, with all of the values lying within 20% of the averages. We thus conclude that within the constraints of the model the island size for stage-2 silver in TiS$_2$ is of the order of 130 Å. Note that no consistent variation in island size with crystal thickness is observed.

Our model gives only one dimension of the two-dimensional islands. A number of different ordered island shapes are possible. Hexagonal or circular islands are possibilities; however, hexagons and circles cannot be stacked in stage 2 without leaving significant unintercalated regions. Triangular or square islands can be efficiently stacked in stage 2; however, both of these would introduce a large amount of bending strain in host layers. Since a minimum amount of host bending is expected, it would seem that islands that are striped (or highly elongated), with the stripes lying parallel to the crystal edge, are a reasonable possibility. If this is the case, our measurements give the width of the island stripes.

Further work is required to fully characterize island formation in Ag-TiS$_2$ and to see if the model presented is applicable to other intercalation systems.

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