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Growth and Intercalation of Ag Evaporated onto (0001) Faces of TiS_2

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Intercalation of metal atoms from liquid media into van der Waals (vdW) gaps of layered transition metal dichalcogenide (TMD) crystals is a well known phenomenon (Friend and Yoffe, 1987). Recently, several cases of intercalation of metals evaporated onto cleavage faces of TMD crystals were observed by surface analytical methods (e.g., Weitering, 1991 and references therein). Since such specimens are very appropriate for the study of concommitant microstructural changes by microscopic methods we present a corresponding investigation of Ag on TiS_2.

TiS_2 crystals were grown by chemical vapor transport with iodine in a temperature gradient between 1070 and 990 K (Rimmington *et al.*, 1972). Ag was evaporated onto freshly cleaved (0001) faces of TiS_2 crystals at both high and ultrahigh vacuum conditions. Specimens with nominally 5–20 nm thick Ag layers grown at substrate temperatures between 300 and 600 K were examined by transmission electron and scanning tunneling microscopy.

At room temperature Ag grows on TiS_2 in the form of randomly oriented three-dimensional islands. Above 370 K Ag islands tend to assume polygonal shapes reflecting the symmetry of their (111) planes parallel to the substrate surface according to the observed parallel epitaxial orientation relationship. During annealing at elevated temperatures the amount of the deposit is substantially reduced (Fig. 1a and b) by diffusion of Ag into the vdW gaps of TiS_2. The diffuse reflections (Fig. 1c) corresponding to an $a\sqrt{3} \times a\sqrt{3}$ superstructure rotated by 30° with respect to the basic lattice indicate that Ag ions occupying approximately one-third of the octahedral interstices in vdW gaps are not completely ordered (Scholz, 1980). Ag intercalation can be accelerated by increasing the electron beam intensity during the observation in the microscope.

Intercalation of Ag proceeds even at room temperature as shown by microstructural changes observed several days after room temperature depositions (Fig. 2a). Besides the preexisting long and relatively straight glide dislocations small dislocation loops and long mobile dislocations are formed. The last can adopt quite arbitrary shapes and seem to delineate the areas of intercalated Ag. By cooling such specimens to about 130 K the superlattice reflections slowly sharpened and eventually became more intense than the main diffraction spots (Fig. 2b) indicating ordering of Ag ions within the vdW gaps.

These observations indicate that Ag atoms most probably diffuse into the vdW gaps straight through the S–Ti–S sandwiches. However, some of our STM images show that deposition of Ag causes some damage of the surrounding substrate surface which could facilitate the diffusion of Ag into the vdW gaps.

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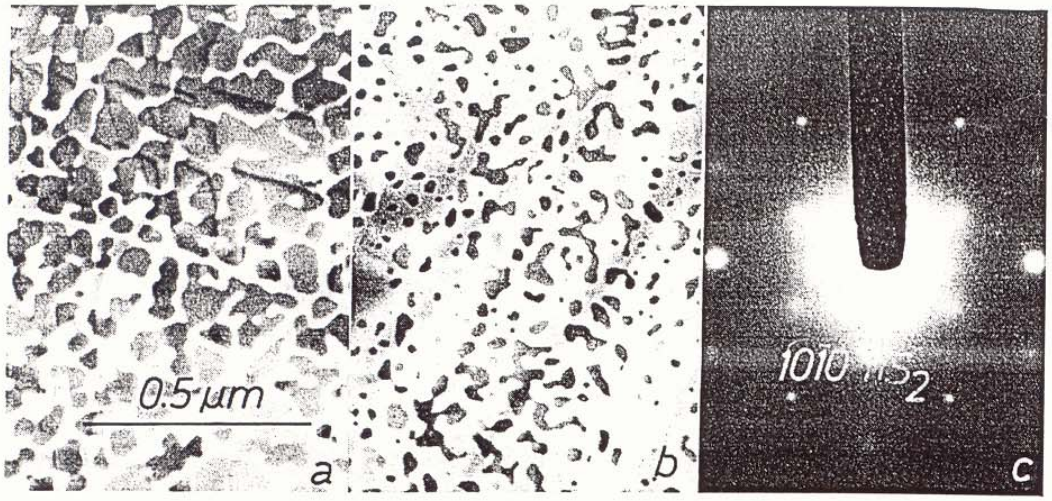

Fig. 1. A 10 nm Ag deposit grown at 470 K (a); and after a 3 hours anneal at 470 K (b); the corresponding diffraction pattern exhibits diffuse superstructure reflections (c).

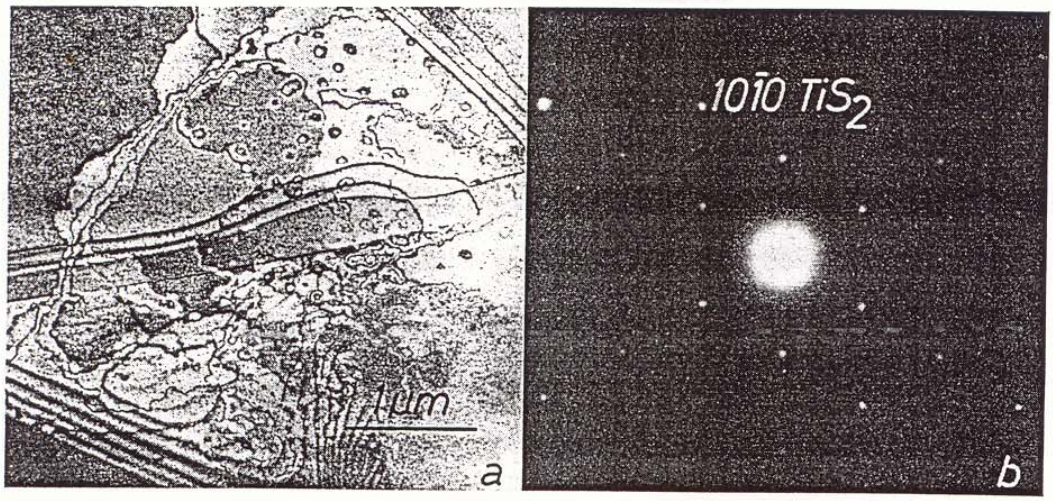

Fig. 2. Dislocations formed in TiS_2 during room temperature intercalation of Ag (a); sharp superstructure reflections due to ordering of Ag on cooling the specimen to 130 K (b).

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