

Cubic manganous telluride

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Manganous telluride (MnTe) thin films have been vapour-deposited onto cleaved sodium chloride and amorphous carbon substrates. At substrate temperatures between 150 and 400° C the MnTe grew with an epitaxial relationship to the NaCl, as a mixture of the cubic phase not previously observed in this temperature range, and the stable hexagonal phase. On carbon substrates only the hexagonal phase was observed. The appearance of the cubic phase appears to be associated with the cubic substrate, a phenomenon previously observed with CdS films on NaCl, but the relative MnTe cubic and hexagonal phase stabilities may also be influenced by the nonstoichiometric vapour beam.

1. Introduction

In recent years there has been considerable interest in the magnetic and electrical properties of the transition metal chalcogenides and particularly those of divalent manganese. The crystal structures of the manganous sulphide and selenide have been studied in some detail and while the stable form at room temperature is fcc [1-3], polymorphism is well established. The sulphide has several polymorphs including a hexagonal modification with the wurtzite structure [2]. The selenide is also reported to have an unstable hexagonal modification [4]. Manganous telluride on the other hand, with its much larger anion, has the hexagonal NiAs structure as its stable form at room temperature [5]. Although there has been little attention given to polymorphism in manganous telluride, a fcc modification similar to the sulphide and selenide has been reported at high temperature by Johnston and Sestrich [6] and Abrikosov *et al* [7].

Johnson and Sestrich, using differential thermal analysis and high temperature X-ray diffraction, found that the cubic modification of MnTe was stable above 1080° C and that on cooling it transformed back to the hexagonal modification at 1030 ± 4° C. The cubic phase had the NaCl structure and lattice spacing of $a = 6.026 \text{ \AA}$ at 1080° C. The lattice parameters of the hexagonal phase were $a = 4.148 \text{ \AA}$ and $c = 6.710 \text{ \AA}$ at 25° C. Abrikosov *et al* investigated the cubic-hexagonal transformation in MnTe again using high tempera-

ture X-ray techniques. They were able to detect a sharp attenuation in the intensities of the hexagonal reflections at 990 ± 3° C with increasing temperature. On decreasing the temperature from the melting point they were similarly able to detect the attenuation of the cubic intensities at 1020 ± 3° C but were not able to retain the cubic structure below this even with rapid quenching.

Hexagonal-cubic polymorphism similar to that discussed above, where a hexagonal → cubic transformation takes place at elevated temperatures, occurs in a number of materials. Cadmium sulphide undergoes a wurtzite → sphalerite transition of this type. Thin layers of the cubic (sphalerite) modification of CdS have been prepared by vapour deposition onto (100) cubic substrates, which has led to the suggestion that the appearance of this phase is due to the influence of the substrate structure [8-10]. This conclusion has been disputed by Holloway and Wilkes [11] but the later work by Wilcox and Holt [12] indicates that, at least on NaCl, the orientation of the substrate surface is important. The latter found that over a wide temperature range, vacuum deposition onto (100) and (110) NaCl surfaces gave the sphalerite structure, whereas deposition onto (111) NaCl gave wurtzite.

On the basis of the work discussed above it seemed possible that cubic manganese telluride might be obtained by vacuum deposition onto a cubic substrate. Thin films of MnTe were therefore deposited onto cleaved (100) NaCl substrates and

the structures compared with those of films deposited under similar conditions on amorphous carbon substrates.

2. Experimental

Manganese telluride was prepared with 99.99% manganese powder from the United Mineral and Chemical Corporation and 99.999% tellurium from the American Smelting and Refining Company. The tellurium was ground to -100 mesh and the elements were mixed in stoichiometric amounts. Vycor ampoules were filled to about one quarter capacity with this mixture and sealed under vacuum. The reaction between the elements was exothermic and tended to shatter the ampoule unless great care was taken. Therefore, the reaction was initiated by heating one end of the ampoule, held in the horizontal position, and allowed to self-propagate to the other end. The reacted mass was then again ground to -100 mesh and sintered at about 1100°C for 24 h in a second evacuated Vycor ampoule. X-ray examination showed that the resultant material had the hexagonal NiAs structure with $a = 4.148 \text{ \AA}$ and $c = 6.721 \text{ \AA}$.

Thin films of MnTe were prepared by vacuum evaporation of the compound from a tungsten surface emitting source onto cleaved $1 \text{ cm} \times 1 \text{ cm} \times 0.2 \text{ cm}$ (100) NaCl substrates and onto similar substrates covered with 300 \AA of amorphous carbon. The NaCl crystals were held on a stainless steel heater with small stainless steel clips and the temperature was monitored by a Chromel/Alumel thermocouple sprung onto the substrate face. Manganous telluride films were deposited at 10^{-6} torr after first annealing the NaCl substrates at 400°C for 1 h. The substrate was shielded from the source by a shutter which was removed when the emission from the source had stabilized and returned when the required film thickness had deposited. The deposition rate was approximately 30 \AA sec^{-1} .

Rather than making separate depositions on the carbon-coated substrates, single NaCl crystals half covered with carbon were used in most cases. In this way a direct comparison could be made of films deposited on the two substrates under identical conditions. The amorphous carbon was deposited from a resistance heated source immediately prior to the deposition of MnTe. The carbon deposition was restricted to half the substrate by a second shutter placed very close to the NaCl sur-

face. The resultant films were floated off the NaCl substrates onto water, mounted on grids, and examined using transmission electron microscopy and diffraction. The MnTe was found to be oxidized to MnO by the water used to float off the films. This problem was particularly severe with polycrystalline films and the flotation process was therefore effected as quickly as possible.

3. Results and discussion

Manganous telluride was deposited on freshly cleaved (100) NaCl at temperatures from 25 to 500°C . Above 400°C thermal etching and faceting of the substrate occurred which resulted in films with a lace-like appearance and an increasingly polycrystalline structure. At 400°C the MnTe films first developed a three-dimensional island structure and then became continuous as the channels between the islands filled in. The most obvious feature of the films was the presence of parallel fringe patterns oriented in two mutually perpendicular directions. This structure is shown in Fig. 1. The electron diffraction pattern from this film shown in Fig. 2, indicates a basic cubic symmetry with the (100) plane in the plane of the film but contains many extra reflections which cannot be indexed on this basis. The same basic orientation and structure was maintained down to 150°C , but below this temperature the orientation broke up and the films developed a polycrystalline component. The proportion of polycrystalline component increased down to room temperature, but even at room temperature significant orientation was still present. A diffraction pattern taken from a film deposited on NaCl at 100°C is shown in Fig. 3. The diffraction rings from the poly-



Figure 1 MnTe deposited on NaCl at 400°C .

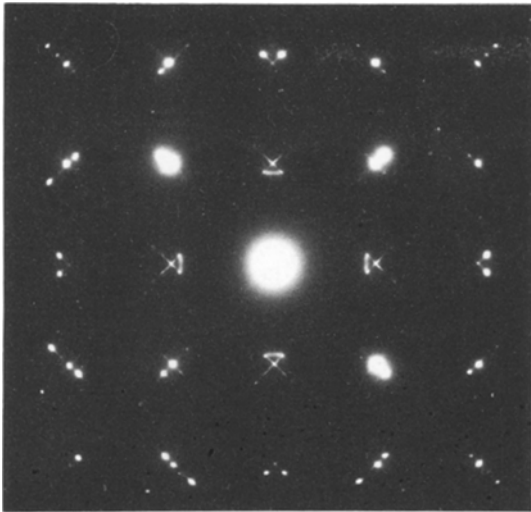


Figure 2 Electron diffraction pattern from MnTe deposited on NaCl at 400° C.

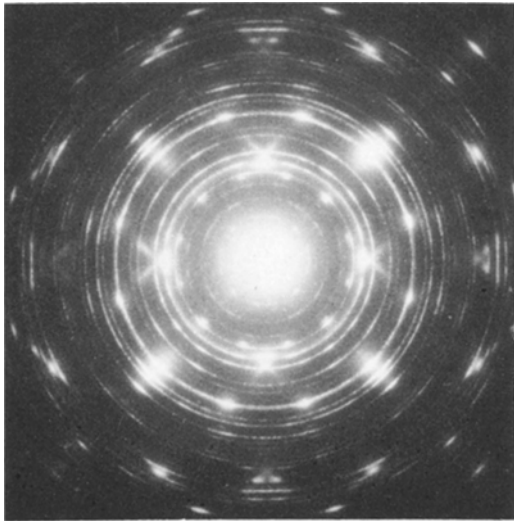


Figure 3 Electron diffraction pattern from MnTe film deposited on NaCl at 100° C.

crystalline component are not coincident with those from the basic cubic pattern.

An analysis of the diffraction pattern shown in Fig. 2 indicated that the basic structure was, in fact, fcc with a lattice constant, a , of 5.98 Å. This compares with a value of 6.03 Å for the fcc phase of MnTe at 1080° C by Johnson and Sestrich [6].

The reflections additional to those from the basic cubic MnTe lie along the $\langle 110 \rangle$ directions in the diffraction pattern. They can be interpreted in terms of extra reciprocal lattice points along the

$\langle 110 \rangle$ or $\langle 111 \rangle$ direction in reciprocal space. Interception of points along the $\langle 111 \rangle$ direction by the Ewald sphere would be caused by buckling of the film or elongation of the points in the direction of the surface of the sphere. Evaporated films of fcc metals also give extra reflections along the $\langle 110 \rangle$ directions which have been interpreted in terms of microtwins on the (111) planes together with double diffraction [13]. Such a structure can easily be shown to give rise to irrational reciprocal lattice points at $\pm 1/3 \langle 111 \rangle$ from the matrix reciprocal lattice points. With the electron beam parallel to the $\langle 100 \rangle$ axis only those reciprocal lattice points closest to the (100) reciprocal lattice plane would be close enough to the Ewald sphere to contribute to the diffraction pattern. This would give satellite spots at a distance of $\pm 1/6 \langle 110 \rangle$ around the matrix spots and obviously does not account for the pattern shown in Fig. 2.

As the stable bulk structure of MnTe below approximately 1100° C is hexagonal it seems possible that this structure could be present together with the cubic phase. Extra reflections in polycrystalline films of normally fcc metals [14] and in films of fcc cobalt [15] have been attributed to the presence of a small amount of metal with a hexagonal structure. Such structures have been discussed in detail by Pashley and Stowell [16]. The difference between the NaCl and NiAs structures is simply a change in stacking sequence from ABC.ABC. to ABAC.ABAC. in the $\langle 111 \rangle$ direction. This change in stacking sequence would give the special orientation relationship of $(0001)[100]_{\text{hex}} \parallel (111)[110]_{\text{cubic}}$ between the two phases. The pseudo-hexagonal spacing of 4.23 Å calculated for the (111) face of the basic cubic lattice and 4.15 Å measured by Abrikosov, *et al* [7] for the hexagonal lattice indicate the closeness of lattice matching in this direction.

A diagram showing the (100) reciprocal lattice plane for the fcc MnTe lattice is shown in Fig. 4. To this have been added points due to the change in stacking sequence proposed above, which lie close to the cubic (100) reciprocal lattice plane. Also included are further points which would result from secondary diffraction of the cubic $\{022\}$ reflections by the hexagonal lattice and secondary diffraction of the hexagonal $\{111\}$ reflections by the cubic lattice. These are probably due to the 45° inclination of the phase boundary to the electron beam. Comparison of Fig. 4 with the experimentally observed pattern

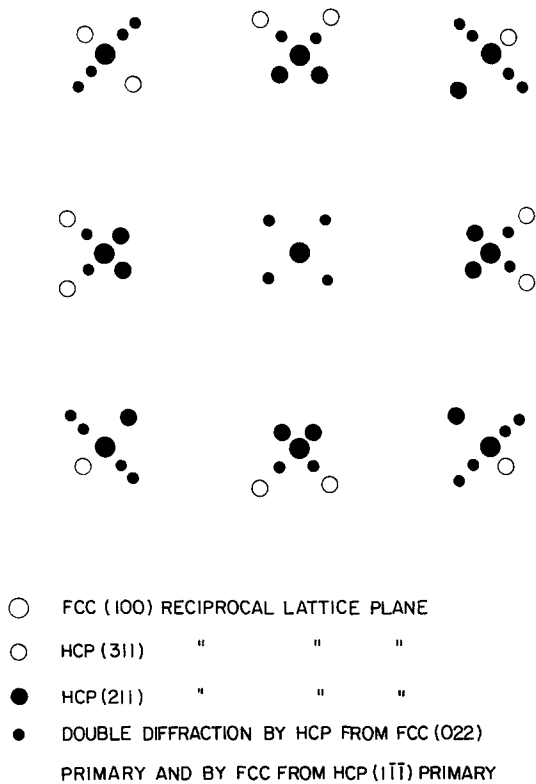


Figure 4 Diagram showing the MnTe (100) reciprocal lattice plane with extra reciprocal lattice points due to hexagonal plates with their {0001} planes parallel to the cubic {111} and double diffraction across the cubic-hexagonal boundary.

shows excellent agreement, with all the diffraction spots accounted for by the simple change in stacking sequence.

The parallel fringe patterns shown in Fig. 1 were oriented parallel to the $\langle 111 \rangle$ directions in the cubic film matrix. They appear to be due largely to displacement fringe contrast caused by the presence of stacking faults at the interface between the cubic and hexagonal phases. The fringes indicate that alternating platelets lie on or close to the cubic (111) planes, confirming the diffraction pattern analysis. The streaks in the diffraction pattern passing from the matrix spots through the satellite spots in the $\langle 111 \rangle$ directions would then be caused by a relaxation of the Laue conditions due to the small dimension of the platelets in this direction. Fig. 4, therefore, indicates that the films deposited above 150°C (shown in Fig. 1) are composed of grains or significant sections of grains with the hexagonal structure, grains or significant sections of grains of the cubic structure, and grains containing layers of both phases in close proximity. In the latter case

the phase boundaries are at 45° to the plane of the film and result in double diffraction effects. These structures are very similar to those observed by Wilcox and Holt [12] in CdS where the similar sphalerite-wurtzite transition is involved and which gives very similar electron diffraction patterns.

The calculated d spacings of the polycrystalline component of the diffraction pattern obtained from films deposited below 150°C (Fig. 3) are shown in Table I compared with the literature (ASTM) data for MnTe, cubic MnTe and MnTe₂. It is apparent that these low temperature films contain a significant fraction of MnTe₂. This suggests that in the course of evaporation from the molten state the MnTe in the vapour source can undergo a decomposition reaction of the type



and that the excess Mn remains in the liquid phase. This reaction results in a tellurium rich vapour and allows the formation of MnTe₂ at low substrate temperatures. At higher substrate temperatures, even in the presence of an excess tellurium vapour

TABLE I Lattice spacings for MnTe deposited on NaCl below 150°C and on carbon at 350°C

Polycrystalline film on NaCl $t_s^\dagger < 150^\circ\text{C}$	MnTe ₂ *	MnTe _(hex) *	Film on C $t_s = 350^\circ\text{C}$
6.94	—	—	—
4.97	—	—	—
4.00	4.01	—	3.54
3.50	3.48	3.36	3.39
3.11	3.11	3.17	3.17
2.85	2.84	—	—
2.46	2.46	2.46	2.45
2.30	2.32	—	—
2.16	—	—	—
2.10	2.10	2.08	2.08
1.93	1.93	1.90	1.90
1.86	1.86	—	—
—	—	1.77	1.77
1.74	1.74	1.74	1.74
—	—	1.68	—
1.58	—	1.59	1.59
1.54	1.52	—	—
—	1.48	—	—
—	—	1.41	1.40
1.33	1.34	1.34	1.32
1.30	1.29	1.31	1.30
1.28	1.27	1.26	1.25
1.23	1.23	1.20	—

*ASTM values (reflections with relative intensities less than 1% of most intense reflection not included).

$^\dagger t_s$ = substrate temperature.

flux, MnTe is the only stable phase and the excess tellurium re-evaporates from the substrate surface. Such changes in the stoichiometry of vapour deposited metal chalcogenide films with substrate temperature are not unusual [17].

On the basis of the discussion above it is evident that in these thin films the cubic phase of MnTe can exist far below the reported bulk transition temperature. The question of the possible role of the cubic alkali halide substrate in the nucleation and stabilization of this phase therefore arises.

As stated previously MnTe was also deposited on amorphous carbon films under conditions identical to those pertaining during the deposition onto NaCl. In fact even the morphology of the carbon layer was the same as the (100) NaCl surface underneath and only the atomic microstructure was modified. The chemical composition of the films on amorphous carbon followed the pattern observed for the films on NaCl, however, the crystallographic structure was not the same. Over the entire range of temperature where MnTe was obtained, the structure of the material was that of the stable bulk hexagonal phase. The microstructure and diffraction pattern of a typical film deposited at 350°C are shown in Figs. 5 and 6 and the d spacings are given in Table I. All the observed reflections can be accounted for on the basis of the hexagonal MnTe structure other than a weak line with a d spacing of 3.54 Å. There are no reflections which suggest the presence of MnTe₂ or cubic MnTe. It is probable that the 3.54 Å reflection is from a product of the previously discussed reaction of MnTe with water during the process of floating the film off the substrate. The micrograph

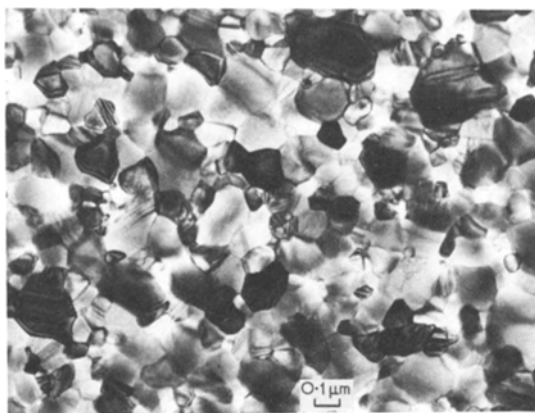


Figure 5 MnTe deposited on carbon at 350°C.

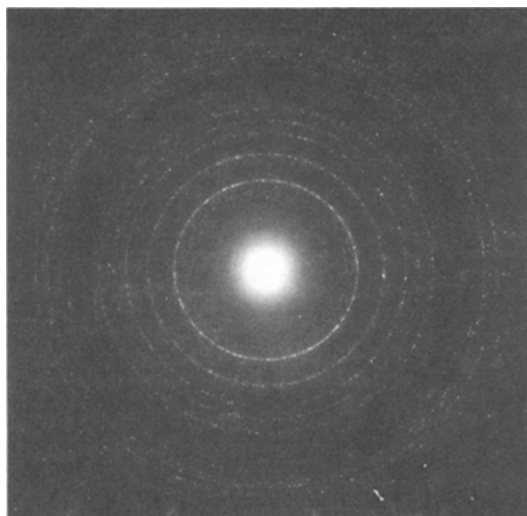


Figure 6 Electron diffraction pattern from MnTe film deposited on carbon at 350°C.

supports the conditions drawn from the diffraction pattern. The visible fringe structure within the grains generally follows the shape of the grain and appears to be largely due to grain boundaries at angles other than 90° to the plane of the film. There is little evidence of the stacking fault type contrast observed in the films deposited on NaCl.

As the topology of the substrate and the deposition conditions are identical for the films on NaCl and on carbon, the differences in the structure of the MnTe films must be related to the differences in the atomic geometry of the substrate surfaces. The geometry of the NaCl surface results in a directional ordering of the MnTe overgrowth lattice (epitaxy). In this case, as was claimed for the case of CdS [12], it also appears to exercise some control over the appearance of the metastable cubic phase. It should be noted that while the appearance of the cubic phase can be attributed to the substrate crystallography, the relative stability of the cubic and hexagonal phases may also be influenced by the excess tellurium in the impinging vapour beam and a possible non-equilibrium stoichiometry. No significant changes in lattice constants were, however, observed. In the films on NaCl the observed diffraction intensities indicated approximately equal proportions of the cubic and hexagonal phases.

4. Conclusions

By evaporating MnTe from an open boat source onto (100) NaCl and evaporated carbon substrates

it has been possible to form MnTe thin films at substrate temperatures above $\sim 150^{\circ}\text{C}$ and MnTe + MnTe₂ thin films below 150°C . This change in stoichiometry is probably due to an excess of Te in the vapour caused by decomposition in the evaporating melt. The MnTe films grew epitaxially on NaCl but were found to be a mixture of cubic (metastable) and hexagonal (stable) phases. The cubic phase has not been observed previously below 1000°C but it is possible that the relative free energies of the two phases may be influenced by the nonstoichiometry of the vapour. As the cubic phase was not detected on the carbon substrates, however, it is assumed that the cubic geometry of the substrate was responsible for the appearance of the cubic phase.

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