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The Growth and Perfection of Epitaxial Mn_3O_4

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Uniform single crystals of Mn_3O_4 have been grown over a wide range of growth conditions by vapour hydrolysis of manganese chloride onto (001) cleavage faces of magnesium oxide in an air/water vapour atmosphere. The growth has been shown to be much less temperature dependent than other transition metal oxides grown by this technique, and, in contrast, is markedly dependent on the ratio of air pressure to water vapour pressure.

The crystals have been examined by optical and X-ray diffraction techniques, revealing their growth characteristics and perfection, and are compared with other crystals grown by similar techniques. The lattice parameters have been shown to vary by only 0.1 % over the range of growth conditions used, with an average value of $a = 5.762$, $c = 9.463$ Å.

1. Introduction

The structure, electrical and magnetic properties of transition metal oxide semiconductors are of considerable interest theoretically, and the work presented in this paper forms part of a programme on the study of the growth and physical properties of transition metal oxides [1-6]. Previous investigations on Mn_3O_4 have largely been conducted on polycrystalline samples, and, in this respect, it was of interest to prepare good quality single crystals of Mn_3O_4.

The present work on the epitaxial growth of Mn_3O_4 follows similar investigations by the present authors into the epitaxial growth of other transition metal oxides [4, 5]. Mn_3O_4 has a tetragonal structure with $a \sim 5.76$, $c \sim 9.42$ Å, but is commonly described as a tetragonally distorted spinel with $a \sim 8.15$, $c \sim 9.42$ Å, the precise lattice parameters depending on the mode of preparation [7].

Previous investigations into the growth of single crystal Mn_3O_4 by the Verneuil (e.g. [7]) and the arc transfer (e.g. [8]) techniques, suffer from the problems of high temperature phase changes and gross deformations, problems which are not encountered in the relatively low temperatures used in epitaxial techniques. The variation of crystal thickness over a wide range of growth conditions has been investigated in the present work, and the subsequent crystals examined by optical and X-ray diffraction techniques in order to ascertain their crystallographic orientation and perfection.

2. Epitaxial Growth

2.1. Experimental

The experimental arrangement is basically the same as that used previously [4, 5], and is similar to that used by Cech and Alessandrini [9]; growth occurring by the vapour hydrolysis of $MnCl_2$ onto freshly cleaved (001) surfaces of an MgO substrate. The substrate was held at the same temperature as the chloride and located above it ensuring the "open" nature of the system as described previously [4, 5] essential to the free access of the surrounding vapours to the substrate surface. The growth temperature and water vapour pressure were varied as before, and, in addition, a controlled air leak was introduced to increase the oxygen content in the growth atmosphere, enabling the optimum growth conditions to be established for good surface quality, singularity and thickness. In order to compare the quality and thickness of the overgrowth under different growth conditions, a fixed starting charge of $MnCl_2$ was used in all the growth runs. The mass of chloride used was 1 gm, and the mass of the deposit at maximum thickness was 0.01 gm, representing an efficiency of 1.6% for conversion of chloride to epitaxially deposited oxide.

2.2. Observations

Initially, the crystals were grown under fixed conditions of water vapour pressure (25 mm Hg) and the growth temperature was varied between 600 and 700°C. In general, the crystals were

fairly clear and glassy in appearance, and the Mn_3O_4 overgrowths were consistently about 1 μm thick, whereas, in the cases of NiO [4] and CoO [5], the thickness varied considerably over this range of temperature. Increasing the water vapour pressure resulted in somewhat broken and discontinuous surfaces, undoubtedly a result of insufficient oxygen to promote the formation of Mn_3O_4. Hence, an additional supply of oxygen (namely air) was used. The ratio of air pressure (pa) to water vapour pressure (pw) was obviously an important factor for growth, and this pa : pw ratio was varied from virtually zero to about 80, at a fixed growth temperature of 650°C. The thicker, better quality surfaces corresponded to the upper range of pa : pw. Some of the results are presented in table I, where it can be seen that crystals up to 20 μm thick were produced in single deposition. The rate of growth depends on the growth parameters, and varied from 2 to 20 μm per hour, the latter figure representing the rate under optimum conditions for maximum thickness.

TABLE I Variation of crystal thickness with pa : pw ratio at a fixed growth temperature of 650°C

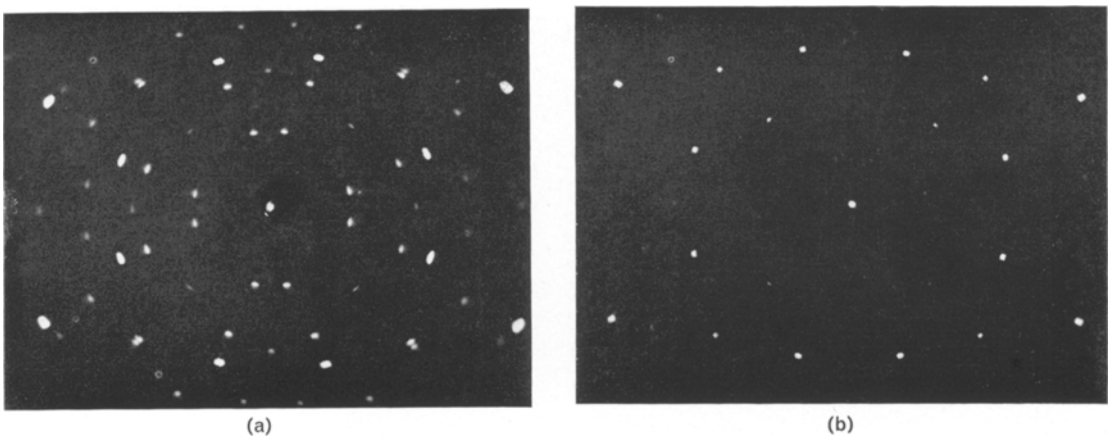
pa : pw	Thickness (μm)	Surface
0	~1	Discontinuous, growth mainly along cleavage facets.
1	~1	Even growth, surface tends to be slightly dull.
2	1-2	Fairly even growth.
7	2-3	Good surface, somewhat broken in places.
10	5	Good surface, even growth.
80	6	Excellent surface, very clear glassy and uniform.
80	10	Good quality crystal, surface slightly pitted.
80	20	Excellent surface, good quality crystal.

These results can be compared with the recent work of Caslavska and Roy [10] (the only other work on the epitaxial growth of Mn_3O_4), who grew good quality 1 μm thick crystals under optimum conditions of air pressure 3 to 4 mm and water vapour pressure ~ 1 mm (representing a pa : pw ratio of about 4 to 1). Their experimental set-up is a more complex variation of the Cech arrangement, and is detailed by Robinson *et al* [11], where the substrate was held at 650°C and the chloride crucible at 250°C (both of these were held at 650°C in the present work). While agreeing with their results, inasmuch that crystals of comparable thickness and quality were grown under comparable conditions, increasing the pa : pw ratio in the present work resulted in much thicker crystals without loss of quality. Their full range of growth parameters is not presented, and it must be realised that it is difficult to compare results quantitatively, since the relative locations of the experimental constituents will obviously affect the ultimate conditions for good growth.

3. Crystal Perfection

The Mn_3O_4 crystals were examined by optical and X-ray diffraction techniques, in order to ascertain the thickness and quality of the overgrowths, their orientation and overall perfection relative to the substrate. Laue transmission photographs were taken of each specimen on its substrate (the weak high angle reflections prohibited reasonable back-reflection photographs) where the Mn_3O_4 reflections were superimposed on those of the MgO (see fig. 1). The sharpness of the reflections confirm the crystalline quality of the overgrowth and reveal a four-fold symmetry axis normal to the substrate surface. Rotation photographs using Cr Kα radiation confirmed the Mn_3O_4 structure, with the $<110>$ axes of the tetragonal unit cell parallel to the $<100>$ axes of the MgO substrate; the (001) planes of both being parallel. It should be pointed out that if the larger distorted spinel unit cell is considered, then the $<100>$ axes are parallel to the $<100>$ axes of the MgO. This is the expected orientation, since the oxygen atoms of the Mn_3O_4 are in identical arrangement to the oxygen atoms of the MgO, with a lattice misfit of about 3% (Mn_3O_4 > MgO).

It is well known that the lattice parameters of Mn_3O_4 can differ by more than 1% depending on the conditions of growth in different techniques [7], and they were measured in the present work in order to see whether the growth conditions affected the parameters. It was extremely difficult to make accurate measurements using the single crystals, and a selection were microtomed, 3 μm slices being removed, and powder photographs taken. This method had the advantage that the reliability of the results could be checked, since the inevitable presence of MgO in the microtomed slices could be used as an internal standard. The parameters were measured to an accuracy of $\pm$ 0.002 Å and varied from

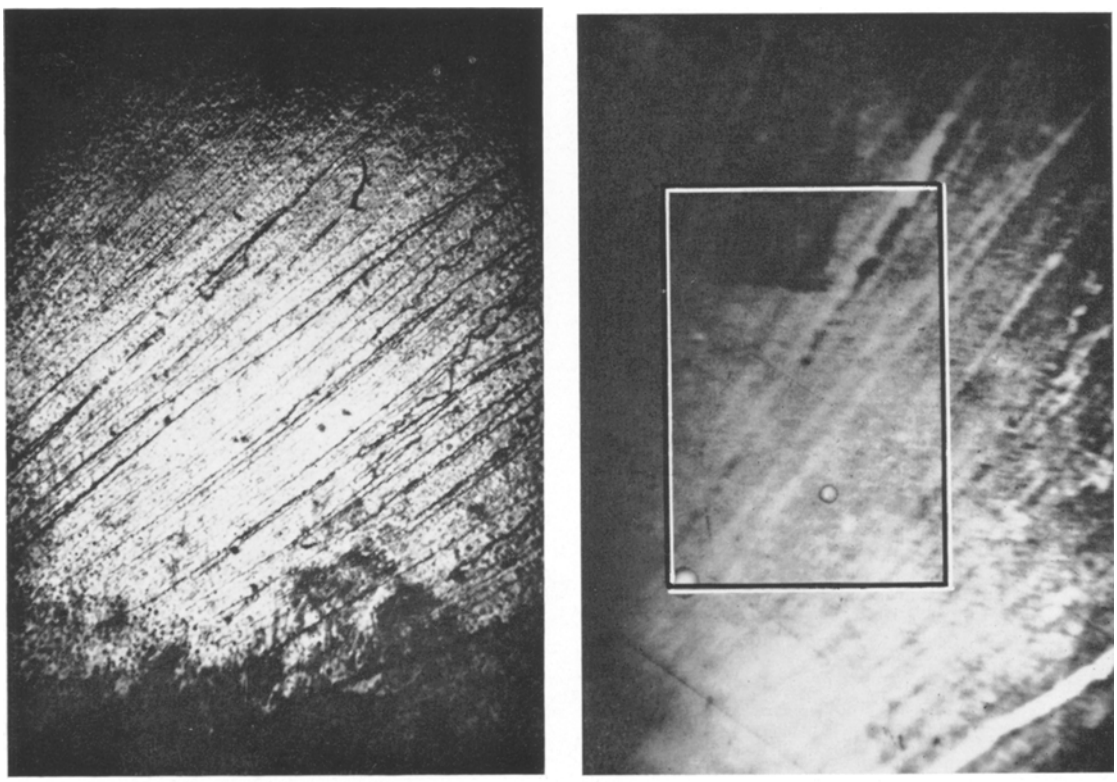


(a) (b)

Figure 1 (a) Transmission Laue photograph of Mn_3O_4 overgrowth on MgO substrate, revealing crystalline quality of overgrowth, and (b) Laue photograph of MgO alone for comparison.

$a = 5.759$, $c = 9.457$ Å to $a = 5.76_1$, $c = 9.471$ Å with a consistent c/a ratio of 1.642 (this ratio is higher than that reported for previous measurements [7]). The variation in parameters is thus only about 0.1 %, and the only correlation with the growth conditions was a tendency to increase with crystal thickness.

X-ray topographs of the specimens were taken by the Berg-Barrett technique [12], using the (004) reflections of Mn_3O_4 and Cr Kα radiation from a Hilger microfocus generator. Topographs were also taken of the MgO interface through the Mn_3O_4 overgrowth using the (002) reflections. In this way, the relative conditions of both over-

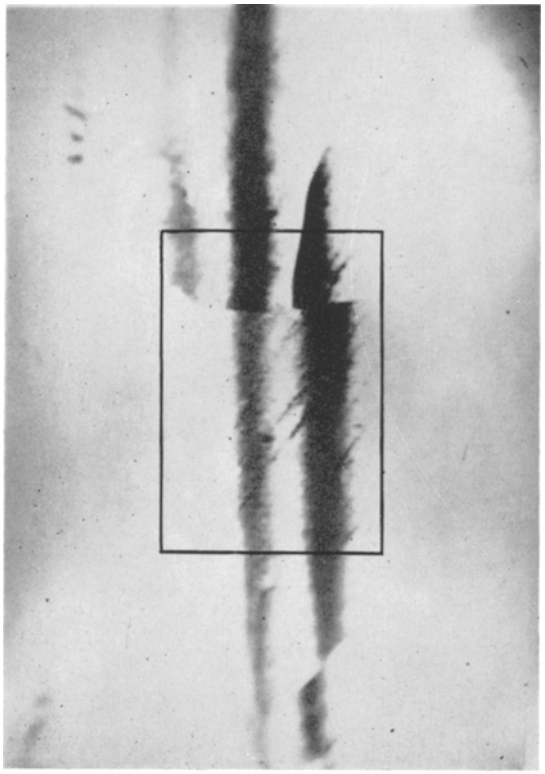


(2a) (2b)

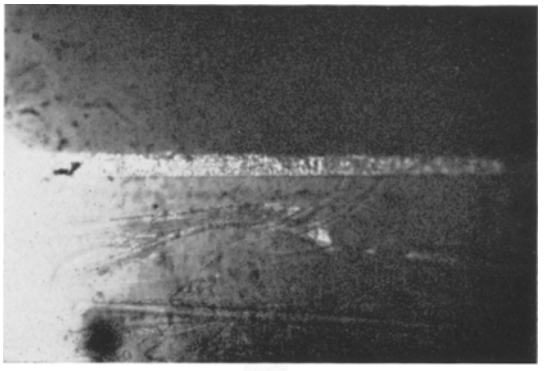
growth and substrate could be examined. The quality of the specimen is reflected in the quality of the topograph (see fig. 2b), and there was no evidence of grossly misoriented regions or any ordered dislocation networks in either overgrowth or substrate. All the overgrowths had a concave curvature, as evidenced from the large area topographs obtained, in common with previous work on transition metal oxides [4, 5]. We concluded in those works that the stresses due to differential thermal contraction between overgrowth and substrate on cooling from the growth temperature were responsible for this curvature, since it did not depend on the degree or sign of the lattice mismatch between the oxide and the MgO. Since the mismatch is positive and much larger (3%) in the case of Mn_3O_4, it seems reasonable to adopt the same conclusion, although no calculations could be done owing to lack of knowledge of the physical constants of Mn_3O_4. This conclusion is supported by the recent work of Abrahams *et al* [13] on Ga As, who show that bending due to large mismatch is unlikely. In addition, there was never any indication of curvature in the MgO itself, as proved by the narrow $K\alpha_1/K\alpha_2$ images obtained (see fig. 2c), furthermore, there was no evidence of cleavage as there was in the case of NiO, in both overgrowth and substrate. Hence, any stress relief which occurs in these relatively thin crystals takes place by bending in the bulk of the overgrowth; the interface and substrate are not bent owing to the relative thickness of the substrate, the curvature in the overgrowth is thus greatest at its free surface. The topographs of figs. 2b and c also indicate the extension of substrate defects into the overgrowth. The areas outlined in these figures clearly show the cleavage facets and low angle boundaries common to both the overgrowth and the substrate.

Optical examination of the surfaces and cross-sections showed little in the way of growth characteristics, apart from the extension of substrate defects, such as cleavage facets, mentioned previously, as illustrated in fig. 2a, and the overgrowths were generally very clear and glassy, except for some discontinuities under conditions

Figure 2 Micrographs showing the prominent features of the epitaxial growth of Mn_3O_4.
(a) Optical micrograph of Mn_3O_4, revealing overall glassy mosaic growth and defects propagated by faults in the MgO substrate (× 23).
(b) X-ray topograph of same region of Mn_3O_4, showing the same defects as (a). The concave curvature of the specimen is evidenced by the large area topograph (× 23).
(c) X-ray topograph of MgO substrate of same region as (a) and (b), showing identical faults in the MgO surface (the outlined area on the topographs clearly shows the common cleavage facets and low angle boundaries of the substrate and overgrowth). The narrow $K\alpha_1/K\alpha_2$ doublet is an indication of the flatness of the substrate (× 23).
(d) Optical micrograph of the cross section of the same specimen, revealing the uniformity of the Mn_3O_4 overgrowth (× 235).



2(c)



2(d)

of excess water vapour (low pa : pw). Once continuous growth occurred, uniformly thick crystals were obtained over the whole substrate, an example of this being given in fig. 2d. Finally, it should be emphasised that there was no evidence of a second phase in any of the techniques used in this work.

4. Conclusions

Uniformly thick single crystals of good quality Mn_3O_4 can be grown epitaxially onto (0 0 1) cleavage faces of MgO over a wide range of growth conditions, thicker crystals being grown at relatively high ratios of air pressure to water vapour pressure. The characteristics of the overgrowths from X-ray and optical observations show that (a) the crystals have uniformly thick cross sections, once continuous growth occurs, (b) stress relief occurs by bending in the overgrowth but not in the substrate, (c) there is no evidence of plastic deformation or cleavage, (d) the crystals have a concave curvature although the mismatch is relatively large and positive, indicating that differential thermal contraction is the major source of stress, (e) the lattice parameters have an average value of $a = 5.762$, $c = 9.463$ Å, with a variation of only 0.1% over the range of growth conditions used, and (f) there is no evidence of the presence of a second phase.

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