JOURNAL OF MATERIALS SCIENCE 1 (1966) 336–345

Growth of Transition Metal Oxide Crystals by Halide Vapour Hydrolysis

L. B. ROBINSON, W. B. WHITE*, RUSTUM ROY*
Materials Research Laboratory, Pennsylvania State University, Pennsylvania, USA

Received 3 June 1966

Single crystals of NiO, CoO, FeO, Co_3O_4, and Fe_3O_4 have been epitaxially deposited on MgO single-crystal substrates by the hydrolysis of anhydrous metal bromides in the gaseous phase. All of the crystals were grown at temperatures below 700° C and at a total pressure of less than 25 torr. The deposition was usually complete after approximately 30 min, and the crystals were of uniform thickness with a glassy-clear, smooth surface. Depending on the number of depositions, these crystals can be formed in various thicknesses ranging from approximately 5 μm to 1 mm. The crystals were found to deposit in parallel alignment with the (100) cleavage plane of MgO. A substantial increase in chemical purity is observed, and only 10^3 to 10^5 dislocations/cm^2 were observed in all NiO crystals. A reaction mechanism is proposed which involves:
(i) the formation of a hydroxybromide transport phase with fluid properties;
(ii) adsorption of the transport phase on the MgO substrate; followed by (iii), the chemical disproportionation-crystallisation of the intermediate phase to the oriented, solid oxide phase.

1. Introduction

The growth of single crystals of the transition metal oxides has been the object of much research in the solid-state materials area, as is evidenced in the literature. This interest stems from the magnetic and electrical properties observed in some of the transition metal oxides and arises from the knowledge that these properties can be best studied on single crystals. The fact that many of the transition metal oxides melt at very high temperatures, and that some of the metal ions present may adopt one of several valencies introduces severe limitations on the usual, high-temperature, crystal growth techniques [1]. Other problems that may be associated with the melting methods are: the attainment and control of high temperatures; contamination by the crucible, flux or solvent materials; and the complexity of the equilibrium phase relationship in the melting region. The complexities and problems associated with phase equilibria studies involving transition metal oxides and, in particular, iron-containing compounds have been reviewed by Muan [2].

Epitaxially grown metal and semiconductor single crystals have proved to be quite valuable in studying materials behaviour, principally because of the relatively low temperature required in their formation, the attainment of high purity, the absence of grain boundaries and their definite orientation. Although Cech and Alessandrini [3] reported a method by which oxide crystals could be grown epitaxially, this has not been fully exploited and consequently little is known of the formation conditions and the mechanism involved in the growth process. The purpose of this study is, therefore, to provide information on the epitaxial growth of crystals by a vapour pyrohydrolysis method and to demonstrate its usefulness in providing oxide crystals of various dimensions suitable for a variety of research studies. The deposition parameters which were investigated included the temperature of the substrate, the deposition rate, the condition of the substrate, the concentration of the reactants in the gaseous atmosphere, the total gas pressure and the flow rate of the gas. In practice, a flat, uniform, glassy-

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*Also associated with the Department of Geochemistry and Mineralogy.

like surface structure of the epitaxial layer is desired. An evaluation of the quality of crystals produced by a technique is essential, and established analytic techniques were used throughout this study in determining crystal perfection.

2. Formation and Growth of Oxides on Magnesium Oxide

2.1. Experimental Procedure

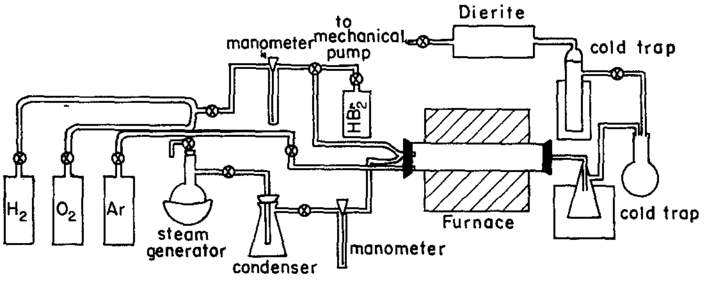
2.1.1. *Crystal Growth System*

The apparatus used in preparing the oxides is shown schematically in fig. 1. It consists of a split furnace provided with a vycor reaction tube into which water vapour and other gases are continuously passed. The water vapour was produced in a distilling flask and then passed through a condenser at room temperature. The vapour could then be passed through unheated tubing to the manometer and the reaction tube without excess moisture condensation. When other gases were required in conjunction with water vapour, then a predetermined amount of the gas was mixed with the water vapour at the entrance of the reaction tube. A vacuum pump was connected to the system and used to transport the reaction products away from the reaction area, and also to pump the system continuously at any desired total pressure by means of a suitable stopcock arrangement. The water vapour and gaseous reaction products were removed before entering the mechanical vacuum pump by dry-ice acetone cold-traps, Todds universal adsorbent, dierite, and magnesium perchlorate.

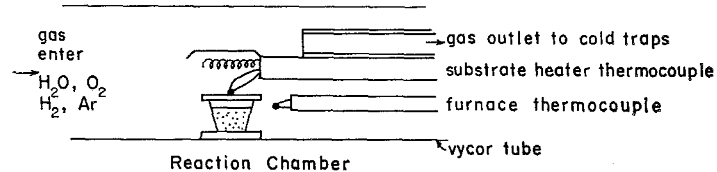
The substrate was separately heated by an internal-wound platinum-wire resistance heater. Above the substrate heater was a platinum radiation shield to radiate the heat onto the substrate crystal. Measurement of the temperatures was by means of two Pt–Pt 10% Rh thermocouples positioned to measure the temperature on the substrate and the vaporising temperature of the halide.

2.1.2. *Starting Materials and Preparation*

The chemicals used in this study were the anhydrous purified bromides of Ni, Co, and Fe. Since these compounds are very hygroscopic, it was necessary to dry them at 150° C in vacuum for 24 h prior to use. They were then stored in a desiccator. MgO single-crystal blocks oriented for cleaving along the (100) planes were obtained from Semi-Elements Inc, and used as substrates in all runs. The substrate surface is of critical importance for the preparation of epitaxial deposits, since this surface plays a major role in the nucleation process taking place during the initial stages of growth. A freshly cleaved substrate provides a very active surface which is easily poisoned by atmospheric gases. Therefore, the freshly cleaved crystal was stored under reagent-grade carbon tetrachloride. The substrates were approximately 1 mm thick by 1 cm



EPITAXIAL DEPOSITION SYSTEM



Reaction Chamber

Figure 1 Schematic drawing of epitaxial deposition system.

square. No cleaning, etching or polishing techniques were used on any substrate.

2.1.3. *Formation Conditions and Reactions*

In the formation of the transition metal monoxides, only a water vapour atmosphere was used, except in the case of wüstite in which a mixture of water vapour and hydrogen was needed. Water vapour plus pure oxygen was used in the preparation of Co_3O_4, and air was used for magnetite. The temperatures involved in all preparations were between 600 to 700° C. The system pressure at which vapour growth is achieved is critical. Preferably, the system pressure should be below 30 torr for good growth. In practice, a pressure of 15 to 25 torr was usually maintained.

2.1.4. *Crystal Analysis*

Two techniques were used consistently to determine the quality of the overgrowth layers: optical microscopy and X-ray diffraction. Electron microscopy was used occasionally to investigate continuity and microstructure by replication techniques. The identification and crystallinity of the deposits were determined by utilising a Norelco X-ray diffractometer. Using this method of analysis, the composition, orientation, and crystallinity of the deposit could be obtained. The overgrowth layer was examined in reflected, transmitted, and polarised light, when applicable. In addition to looking at the general character of the deposit (uniformity, continuity, pits, voids, and crystallinity), features such as spiral-growth step patterns, subgrain boundaries, and defects in substrate-deposit interfaces were continually sought. In order to prevent contamination of the cleaved MgO surface by the atmosphere and by excess handling, the thickness of specimens was measured, after runs, with a micrometer capable of measurement to 0.015 mm. Therefore, the thicknesses given in the tables are only approximate. Dislocation etch-pit density in the deposited layers of NiO was determined by etching the surface with hot nitric acid followed by a counting procedure under the microscope.

3. Experimental Results

3.1. NiO Epitaxy

3.1.1. *Investigation of Growth Parameters*

The growth parameters which were investigated and considered important have been listed below.

(a) Spacing between source and substrate.
(b) Halide vapour pressure or deposition rate.
(c) Substrate temperature (temperature of decomposition and oxide growth).
(d) Total gas pressure.
(e) Condition of substrate.
(f) Flow rate of gas.

The importance of the distance between the halide source and substrate may not be immediately obvious. Several runs were made in which the substrate was first placed 1 to 1.5 cm above the source, and then, secondly, in a horizontal position with respect to the source in order to have the reacted vapours flow over the substrate. Neither of these modes of deposition gave significant results. A mean-free-path calculation considering both the ambient pressure and the temperature indicated the source-substrate separation should be approximately 2 to 3 mm for deposition. Therefore, in all runs, the substrate was placed directly above the halide source (see fig. 1), with a 2 to 3 mm separation.

In determining the optimum conditions for growing single crystals of NiO, experiments were carried out at various sublimation and substrate temperatures at a water vapour pressure of 25 torr. The duration of each run was only 15 min at the desired temperatures, since the major portion of the deposition occurs within this time and the main objective was to get a continuous, clear, crystalline layer. In the first series of six runs, the sublimation temperature was varied to determine a halide pressure at which good growth could be expected. A substrate temperature of 600° C was maintained for this series. At 520° C, a very thin film formed, the film thickness increased with increasing temperature. At 600° C, the sublimation and substrate temperatures being the same, the character of the deposit seemed very poor. The deposit was thin and had a dull appearance. Upon increasing the sublimation temperature along with the substrate temperature to 625° C, the deposit became thicker but still lacked clarity. At 650° C, a thick crystalline deposit formed with a trace of powder covering the surface.

Taking 600° C as the temperature at which $NiBr_2$ has an appreciable vapour pressure for a critical evaluation of growth under various conditions, the substrate temperature was then varied from 600 to 680° C. The temperature of the substrate is an important parameter in that it controls surface diffusion of the adsorbed vapour species. With the substrate at 624° C, a good deposition was obtained. However, the crystal was neither very clear nor uniform. By increasing the temperature further, to 650° C, the overgrowth became smooth, continuous, and uniform. As the temperature of the substrate was raised even higher, there was diffusion of material to the cooler edges, and the centre of the deposit gradually became thinner. At approximately 680° C, the entire area of the substrate immediately exposed to the halide source was completely devoid of overgrowth. These data are tabulated in table I.

TABLE I Effect of the substrate temperature on NiO overgrowth (water vapour pressure, 25 torr; temperature of sublimation, 600° C; duration of runs, 15 min).

Substrate temperature (° C)	Approximate thickness (μm)	Remarks on deposit
600	20	Poor, dull surface, uneven, higher in the centre
625	30	Fair, improved surface appearances
650	30 to 40	Very good, uniform, clear, glassy
670	—	Non-uniform, clear, but diffusion of NiO away from the centre of MgO substrate toward edges
680	none	NiO present around the edge of MgO

In another series of runs, the vapour pressure of water in the reaction tube was varied from 5 to 40 torr. A substrate temperature of 650° C and the sublimation temperature of $NiBr_2$, 600° C, were used. As shown in table II, at approximately 15 torr of water vapour, a maximum thickness of NiO was reached, followed by a continuous decrease in thickness with further increase in pressure. At 40 torr, little-to-no NiO crystal growth was observed.

Having established an optimum water vapour pressure for growth, another series of runs were made varying both substrate and sublimation temperatures as in the previous experiments. The data in these experiments as well as the results of all runs have been summarised in table III. As will be seen, in some runs, the NiO crystals obtained were thicker for high $NiBr_2$ pressures, but the quality of these crystals is not as good as the quality of those prepared at 600° C. A typical high-quality crystal is illustrated in fig. 2. The partial pressures of $NiBr_2$ given in column three were calculated from the equation below [4]:

TABLE II Effect of water vapour pressure on NiO deposition (temperature of sublimation, 600° C; temperature of substrate, 650° C; duration of runs, 30 min).

Water vapour pressure (torr)	Approximate deposit thickness (μm)	Remarks
5	10 to 20	Fair
10	30 to 50	Very good
15	50 to 100	Very good
20	> 50	Good
25	50	Good
35	10 to 20	Dull
40	film 1 to 5	Very cloudy and dull surface

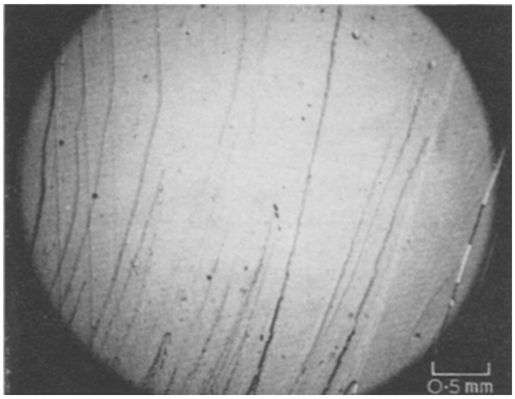


Figure 2 Photomicrograph of high-quality crystal surface. Grown at: 600° C, sublimation temperature; 650° C, substrate temperature; $p_{H_2O} = 15$ torr.

$$\log P(\text{atm}) = 16.6805 - 13111.9/T - 1.7112 \log T - 0.3497 \times 10^{-3}\, T$$

The flow rate of the water vapour through the system does not appear to be a critical parameter in the deposition. However, if the flow is drastically reduced to an almost static condition, the NiO formed is not glassy-clear but translucent, and its surface is continuous but slightly wrinkled. Fig. 3 is a photomicrograph of a specimen. If the flow rate is very rapid, the deposit thickness is reduced.

In this study, it was noticed that, if a cleaved

TABLE III Synopsis of formation conditions used for various sets of NiO crystals deposited on MgO.

Set No.	Source temperature (° C)	p $_{NiBr_2}$ (torr)	p $_{H_2}$ (torr)	Substrate temperature (° C)	Deposit thickness (μm)	Remarks
1	520	0.006	25	600	film	—
2	560	0.034	25	600	film	—
3	600	0.16	25	600	$\sim$20	Poor growth, dull
4	625	0.39	25	625	40 to 50	Fair, lacks clarity
5	650	0.91	25	650	$\sim$70	Good, some powder
6	600	0.16	25	625	20 to 30	Lacks clarity and smoothness
7	600	0.16	25	650	$\sim$30	Good, very uniform
8	600	0.16	25	670	—	Thin deposit at centre
9	600	0.16	25	680	none	NiO along edge only
10	600	0.16	15	600	30 to 40	Non-uniform, poor
11	600	0.16	15	625	$\sim$40	Fair, uneven
12	600	0.16	15	650	40 to 60	Very good, glassy-clear
13	625	0.39	15	650	$>$50	Very good
14	650	0.91	15	650	70 to 100	Good
15	600	0.16	10	650	40 to 50	Very good, glassy-clear
16	625	0.39	20	650	$\sim$60	Good

Figure 3 Photomicrograph of the surface of a crystal grown under static conditions: 600° C, sublimation temperature; 650° C, substrate temperature; p_{H_2O} = 15 torr.

MgO surface was left exposed to the atmosphere for several hours, a layer of $MgCO_3$ was formed by a process of chemisorption. This carbonate layer is sufficient to poison the surface against epitaxial growth. Removal of this layer can be accomplished by heating the substrate in vacuo (350° C), in which case the complex decomposes to give carbon dioxide and oxygen, or by treating the surface with dilute hydrochloric acid. This latter method does not render the surface unsuitable for crystal growth, as is the case when orthophosphoric or sulfuric acid is used.

3.1.2. *Crystal Perfection*

The appearance of the surface of a specimen consisting of a single-crystal NiO overgrowth is similar to that of the original MgO surface. A photomicrograph of an as-grown NiO surface on MgO viewed in transmitted light is shown in fig. 2. It can be seen that the NiO grows continuously over the cleavage steps of the MgO and is an exact replica of the cleaved surface. Fig. 4 shows the uniform thickness with which these NiO crystals can be deposited on a substrate, provided the temperature of the substrate is correct.

The epitaxially grown layers have been frequently examined by X-ray diffraction to establish their single crystallinity and orientation. The normally grown layers are invariably

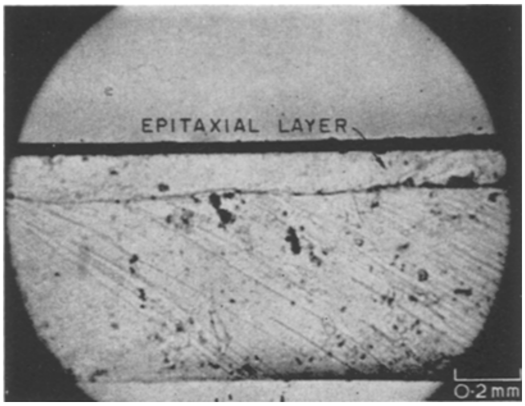


Figure 4 Photomicrograph of cross-section of NiO overgrowth, illustrating uniformity of thickness in epitaxial layer.

oriented in the same crystalline plane as the substrate. A complete diffraction pattern gave only two intense peaks at hkl values of (200) and (400) for NiO.

In addition to the X-ray technique, a chemical etch was used to reveal etch pits in the deposited layers. The external shapes of the pits are square pyramids and are consistent with the symmetry of the (100) plane. Both of these techniques show that the layers are highly crystalline and oriented in the same sense as the substrate, i.e. the mode of epitaxy is:

(100) NiO/ /(001) MgO and [100] NiO/ /[100] MgO

The etching procedure merely consisted of submerging the crystal for 15 min, in a hot solution of 1 part nitric acid to 1 part water by volume. In good deposits, the number of dislocations in the layer is primarily determined by the dislocations inherent in the substrate rather than by ones introduced during the growth process. It has been found that dislocation etch-pit density in the overgrown crystal is strongly dependent on the condition of the substrate, i.e. on how well the substrate has been cleaved. An average of 10^3 to 10^5 dislocation/cm^2 was observed. Densities ranging from 10^5 to 10^7/cm^2 have been reported for annealed crystals of NiO made by the flame fusion method [6].

3.1.3. *Multi-deposition and Substrate Removal*

Thick NiO crystals (> 0.5 mm) were grown by repeated deposition on the initial NiO layer. After each deposition, the crystal was cooled in vacuum and then placed in carbon tetrachloride until the crucible was refilled with bromide. Interrupting the deposition by removing the crystal from the furnace and later continuing the growth did not produce an obvious separation between the two deposits. In growing thick NiO crystals by repeated deposition, there does appear to be a separation of the overgrowth from the substrate as previously noticed by Cech and Alessandrini [3]. Also, cracks are found in the thick NiO overgrowth. These cracks, however, are believed to be caused by the rapid cooling from the deposition temperature and temperature cycling employed in multi-deposition.

The NiO removal is easily accomplished by suspending the crystal in hot 85% orthophosphoric acid with only the substrate fully submerged. Phosphoric acid is preferred to nitric acid in this process because it does not readily attack the NiO crystal. The use of this acid does, however, have the very serious drawback of forming $Mg_2P_2O_7$ patches on the crystal surface.

A NiO crystal removed from the substrate clearly shows antiferromagnetic domain patterns when viewed in polarised light.

3.2. Cobalt Oxides' Epitaxy

3.2.1. *Preparation of CoO*

CoO crystals grown under similar conditions to the NiO were glass-clear and reddish-brown. The optimum conditions were found to be a substrate temperature of 625° C, sublimation at 600° C, and a 15-torr water-vapour partial pressure. If these conditions are changed slightly, quite a different CoO surface is obtained. For example, at a substrate temperature of 600° C, sublimation of $CoBr_2$ at 550° C, and in a water-vapour atmosphere, the deposit has a grey metallic lustre. This crystal is uniform, smooth, and continuous throughout the exposed area, with a thickness of approximately 50 μm.

Heating the substrate to a higher temperature only results in the diffusion of material from the centre of the substrate to the cooler edge. This is the same effect observed in the case of the NiO growth.

Increasing the sublimation temperature to 610° C and examining the resulting crystal under the optical microscope suggested the production of the epitaxial deposit by solidification of a liquid intermediate. As shown in fig. 5, droplets of a liquid had collected along the substrate cleavage steps and at preferred sites on

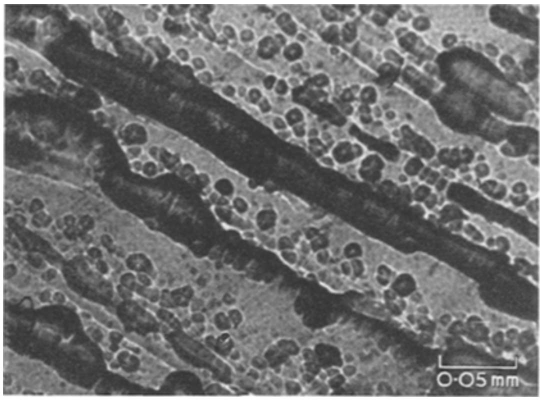


Figure 5 Formation of CoO by solidification of liquid intermediate; reflected light.

the MgO surface. Many CoO crystals under high magnification exhibit small hills of concentric rings and spirals. These hillocks have been observed by other authors in the vapour growth of ice crystals in a diffusion cloud chamber [7].

An electron probe analysis was performed on these samples to determine if any difference in composition existed in the deposit at the cleavage steps from that on the flat areas. The results indicated that the CoO overgrowth was completely homogeneous with respect to Co in both of these regions.

3.2.2. *Formation of Co_3O_4*

From the thermochemical considerations, it was evident that oxygen gas must be added to water vapour in order for the Co_3O_4 to form according to the reaction:

$$3CoBr_2(g) + 3H_2O(g) + \tfrac{1}{2}O_2(g) = Co_3O_4(s) + 6HBr(g)$$

In this reaction, anhydrous $CoBr_2$ was sublimed at 550° C in a water vapour (10 torr) and oxygen (15 torr) atmosphere. The temperature of the substrate was at 570° C. Under these conditions, the crystal deposit was uniform and black. The formation of Co_3O_4 occurred on the MgO substrate if the temperature was below 600° C. Above this temperature, only CoO resulted. There are two limitations that must be considered in the Co_3O_4 formation. One of these is that the total gas pressure should not exceed 30 torr for good results, and, secondly, at the low decomposition temperature, equilibrium between the oxygen gas and oxide phase must be attained. Fig. 6 is a plot of the experimental results showing the regions of CoO and Co_3O_4 formation.

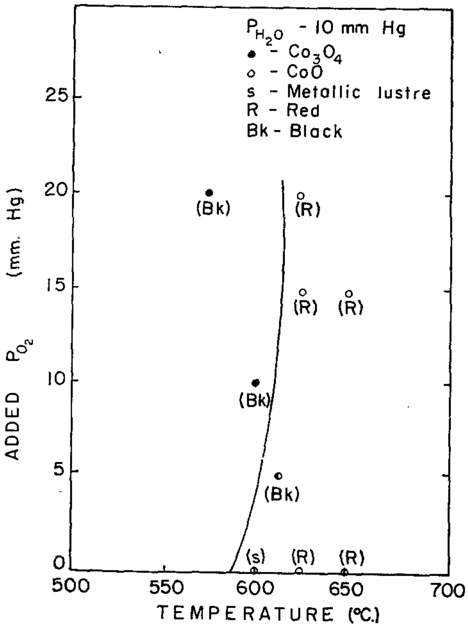


Figure 6 Conditions for deposition of CoO and Co_3O_4 as a function of p_{O_2} and temperature.

3.3. Iron Oxides' Epitaxy

3.3.1. *Preparation of FeO*

An important requirement in the preparation of wüstite is that the atmosphere of water vapour and hydrogen must be in the proper ratio to be in equilibrium with the monoxide phase. The required p_{H_2O}/p_{H_2} ratio was obtained from a diagram of Muan [2], illustrating stability relationships among the Fe oxides as a function of the temperature. At a substrate temperature of approximately 700° C, the p_{H_2O}/p_{H_2} ratio should be between 0.45 and 1.0, in order for FeO to be a stable phase. The very short range of FeO stability at this temperature made the experimental procedure very tedious and reproducibility very difficult. In most cases, a mixture of FeO plus magnetite was formed, because of the condensation of some water vapour before it entered the reaction tube. Such losses of water-vapour cannot be precisely compensated for.

3.3.2. *Formation of Fe_3O_4 Spinel in Various Atmospheres*

Magnetite was grown using atmospheres of water vapour-hydrogen and water vapour-air at a total pressure of 20 torr. In the former, the p_{H_2O} and p_{H_2} values were 12 and 8 torr respectively. The usual procedure was followed in which the anhydrous $FeBr_2$ was sublimed at 600° C and the substrate heated to 700° C. After approximately 30 min at this temperature, a thin, uniform, shiny-black deposit had formed on the MgO crystal. It seemed that the best results were obtained when the flow rate was constant, and the proper gas ratio maintained with as little fluctuation as possible. The growth was not very thick, and consequently both X-ray and electron diffraction techniques were used in the analysis. An extraction replica was made of the surface of the specimen on the MgO, and fig. 7 shows what is believed to be misfit dislocation in the (001) oriented film. On this same specimen, the crystalline overgrowth was separated from the substrate by a quick-freezing method in liquid nitrogen. Selected area diffraction of a very thin crystal, using an aluminium standard for calibration, gave a pattern which was analysed to be Fe_3O_4 with a calculated lattice constant of 8.403 Å.

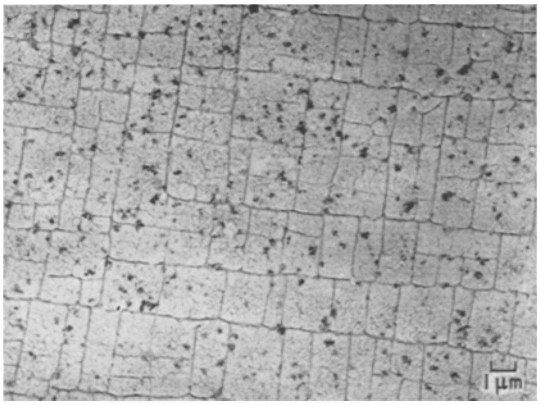


Figure 7 Misfit dislocation on Fe_3O_4 overgrown on MgO.

The growth of magnetite crystals in an atmosphere of water vapour and oxygen (air) is according to the reaction:

$$3FeBr_2(g) + 3H_2O(g) + \tfrac{1}{2}O_2(g) = Fe_3O_4(s) + 6HBr(g)$$

This reaction was derived from purely thermochemical considerations. Experimentally, $FeBr_2$ was sublimed at 600° C, with the substrate temperature set at 650° C, and a water vapour (10 torr) and air (5 torr) mixture continually flowing through the system. A very thick, black, strongly magnetic deposit formed which, when X-rayed, was found to be an oriented overgrowth of the Fe_3O_4–γFe_2O_3 solid solution. This crystal was not glassy and smooth as was the case in the other oxide crystals. The deposit was uniform, glossy, and had a coarse, grainy texture. A replica of the surface clearly showed growth steps. In this experiment, the partial pressure of $FeBr_2$ under the growth conditions was calculated to be 4 to 5 torr [8]. The oxygen partial pressure was estimated to be approximately 1 torr. Therefore, we can write the following reaction to account for the observed deposition:

$$5FeBr_2(g) + 5H_2O(g) + O_2(g) = Fe_3O_4(s) + \gamma Fe_2O_3 + 10\ HBr(g)$$

In order to reduce the formation of γFe_2O_3 in the deposit, the experimental conditions were changed slightly: a substrate temperature of 630° C and the partial pressure of air maintained at 2 to 3 torr.

4. Discussion and Conclusions

In general, there seems to be good agreement between this work on the monoxides of the transition metals and that of Cech and Alessandrini [3]. However, a much stronger influence of the substrate temperature on the epitaxy and character of the deposit, than was previously noticed, has been demonstrated. The growth spirals as reported by these authors were never observed on any of the monoxide crystals. Photomicrographs of several NiO and CoO crystals indicated the formation of a liquid-like intermediate, which appears to disproportionate and crystallise on the substrate. When the temperature of the substrate was such, that this fluid spread uniformly over the surface, an exact replica of the substrate was obtained. As shown in fig. 5, the predominance of material along the steps is probably the result of the additional binding provided by the step, which results in an enhanced probability of nucleation of the step relative to the free surface. Other imperfections in the MgO substrate, such as point and line dislocations, will also be preferred nucleation and growth sites.

The crystal nucleation process was not specifically studied in these experiments. However, observations of the course of crystal growth during the various runs permitted some qualitative conclusions to be made regarding the growth process. These observations were made: (a) The extreme sensitivity of the adsorbed species to small, substrate temperature changes of 10 to 20° C.

(b) The remarkably liquid-like behaviour (high mobility, etc.) and the appearance of the final product.

(c) Surface features indicating growth occurring from a vapour with relatively high degree of supersaturation.

(d) The deposition of MO which is confined exclusively to the MgO substrate.

All of the above observations can be accounted for by assuming droplets of a complex, of the form $MO_xH_yBr_z$, which possess fluid properties. These small droplets are the result of multiple collisions and condensation in the vapour phase and are quasi-stable under the growth conditions. This concept of such an intermediate metastable phase in crystal growth was suggested by Grisdale [9] for the growth of ferrite crystals by vapour hydrolysis of halides. Recently, Messier [10] studied the kinetics of high-temperature hydrolysis of MgF_2, and proposed a three-step mechanism which included a hydroxyfluoride intermediate.

According to Grisdale, the stability of the complex is a function of both the hydrogen and halogen content, and, as these decrease, the fluidity and vapour pressure of the complex must decrease until the end member, the solid oxide, is reached. Beyond a possible, critical oxygen content, solidification occurs and crystallisation of the oxide may take place by disproportionation. This may account for the unusual formation and stability of magnetite in an atmosphere originally consisting of water vapour and air. For example, a reaction sequence may be written as follows:

$$2M(\mathrm{II})Br_2(g) + 3H_2O(g) = M_2(\mathrm{II})(OH)_3Br(l) + 3HBr(g)$$

and on the MgO substrate we get:

$$3M_2(\mathrm{II})(OH)_3Br + \tfrac{1}{2}O_2 = 2M_3O_4(s) + 3HBr + 2H_2O + H_2$$

Here, we are assuming that the metal halide reacts more readily with water vapour than with oxygen, to form a hydroxy-compound which subsequently disproportionates.

Cech's conclusion that the halide decomposition was catalysed by MgO was based solely on the observation that the metal oxides deposit only on the MgO in the reaction chamber. Again, if one accepts the above criteria of complex stability and the existence of a critical oxygen content, then the environment outside the crucible may clearly represent an unstable condition in which a complex cannot form and metal oxide deposition would not be expected.

Then, it is supposed that a process of "spontaneous nucleation" occurs as described by Pashley [12]. A spontaneous nucleation mechanism occurs via an intermediate stage, which could be one of an amorphous or liquid state. When the amount of deposited material is increased to a certain value, a crystallisation process occurs and nuclei are spontaneously formed. This crystallisation process is considered to be the disproportionation of the intermediate complex, as mentioned above. It is well known that the condition and nature of the substrate can significantly influence the shape and distribution of the condensed phase, as well as its orientation.

On the basis of our work, the inability of Cech and Alessandrini to regrow on an NiO crystal may be accounted for by the chemisorption of CO and CO_2 gases on the freshly formed surface.

Frank and van der Merwe [13] suggested that the misfit between crystals with different lattice parameters would be accommodated partly by strains in the lattices and partly by a grid of misfit dislocations. These dislocations have been observed by Matthews [14], and such grids have been observed here between a film of magnetite on MgO.

The development of Cech's vapour growth process into a reliable epitaxial method for the preparation of oxides crystals required, as investigation of several process parameters, an examination of the overgrown crystal by established analytic techniques, and a consideration of the growth mechanism. The optimum growth conditions were found to depend primarily on: (i) the nature of the substance deposited; (ii) the condition of the substrate; (iii) the temperature of the substrate; (iv) the halide vapour pressure; (v) the water vapour pressure; and (vi) the total system pressure. Since this vapour process is one of sublimation or distillation, it is in itself a purifying process, and a substantial increase in purity of the crystals over the starting materials is observed.

Probably the most important advantage of this method is the relatively low temperature required in the crystal growth. The necessity of such a low-temperature method is very evident when one realises that higher temperatures tend to dissociate the higher valence oxides and to require more complicated systems. The equipment requirements are very modest in comparison to the usual epitaxial systems. This method has the added advantage that deposition occurs only on the substrate and not throughout the reaction tube. The process also has an advantage over the chemical transport method for oxide growth in that the process is very rapid and does not involve the direct use of corrosive HBr or HCl atmospheres.

The main limitation in this work has been the lack of an identification of the transport species. The enhanced volatility of many compounds in the presence of steam is well known. However, little quantitative data are available, and the chemical composition of the volatile species is seriously in doubt in most cases. Therefore, for several reactions, assumptions had to be made on the formulae of both the sublimed species and the intermediate liquid phase.

Acknowledgement

This work was supported by the Advanced Research Projects Agency of the US Department of Defense under contract SD-132.

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