EPITAXIAL GROWTH OF MnO FILMS OBTAINED BY IMPURITY DIFFUSION

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ABSTRACT: The epitaxial growth of MnO obtained by impurity diffusion from volume to surface in NaCl is studied. Films were obtained by annealing of NaCl single-crystals doped with manganese at 550°C. Change in the orientation of MnO nuclei on the NaCl surface as film thickness increases are discussed. It is found that in the early stages nuclei have ten preferent orientations which are eliminated when the thickness increases. Finally, the continuous film is randomly oriented. The elimination of preferent orientations is discussed in terms of the number of nuclei per unit area that are generated in the early stages.

I. INTRODUCTION

As it has been previously reported[1] the manganese impurities contained in NaCl crystals migrate by diffusion from volume to surface when crystals are annealed. Once on the surface manganese ions oxidise. Then an epitaxial layer of MnO (fcc) is produced on the NaCl surface.

The present paper describes how the orientation of MnO thin films changes on the NaCl surface when their tickness increases. In this growth technique the film thickness increases with the annealing period at a constant temperature.

2. EXPERIMENTAL RESULTS

The Kyropoulos method in the open atmosphere-modificated by Muñoz et al[2] was used to grow NaCl with an impurity of 1% manganese in NaCl. Samples of $0.5 \times 0.5 \times 0.15$ cm. were cleaved and annealed in a tubular furnace in air at 550 °C in periods ranging from 30 min to 12 hours. Crystals were cooled at a rate of 300 °C/hour. MnO produced on the NaCl surface were stripped by flotation on water and observed in the electron microscope.

The preferential orientations in the textured deposit have been observed in MnO nuclei grown on the NaCl surface. In order to describe those orientations the subscripts n and s are used respectively for planes and directions of the MnO nuclei and the substrate. The orientations are:

a) $(001)_n // (001)_s$ and $[100]_s // [100]_n$

b) $(001)_n // (001)_s$ and $[100]_n // [110]_s$

c) $(111)_n // (001)_s$ and one $\langle 110 \rangle_n //$ to one $\langle 110 \rangle_s$

d) $(111)_n // (001)_s$ and one $\langle 110 \rangle_n //$ one $\langle 100 \rangle_s$.

There are four different orientations of each c) and d).

Electron diffraction patterns of MnO films with an average thickness respectively of 25,100 and 1500 Å are shown in figures 1–3.

The annealing periods were 30 min., 90 min and 12 hours. In figure 1 the ten preferred orientations can be observed, but orientation a) is more prominent than b). Similarly, orientation b) is more prominent than c) and d). The slightly arced spots in the diffraction patterns indicate that there are small deviations of some nuclei with respect to the preferred orientations. Figure 2 shows that preference for a) decreases when films reach a thickness of 100 Å but it increases from b) to d) and several non-preferred orientations are presented at this stage of growth. Finally, diffraction patterns of the continuous film do not show preferred orientations and films are randomly oriented (figure 3).

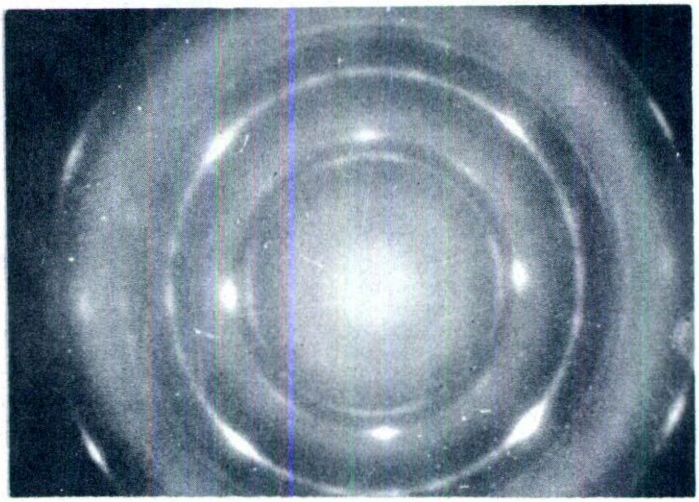

Fig. 1. Electron diffraction patterns from MnO films with 25 Å in average thickness.

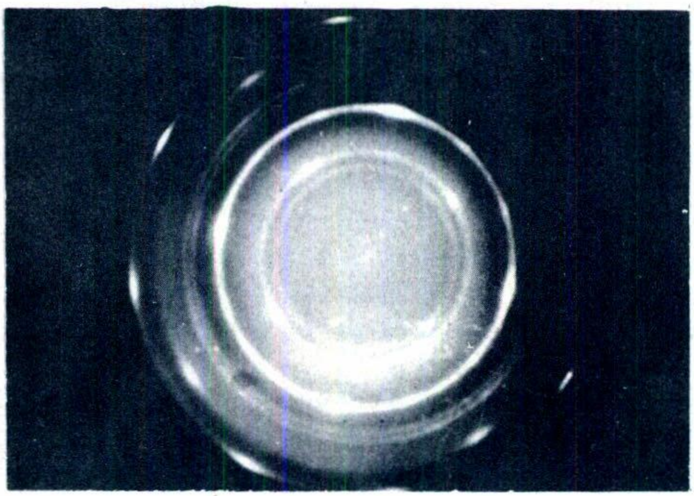

Fig. 2. Electron diffraction patterns from MnO films with 100 Å in average thickness.

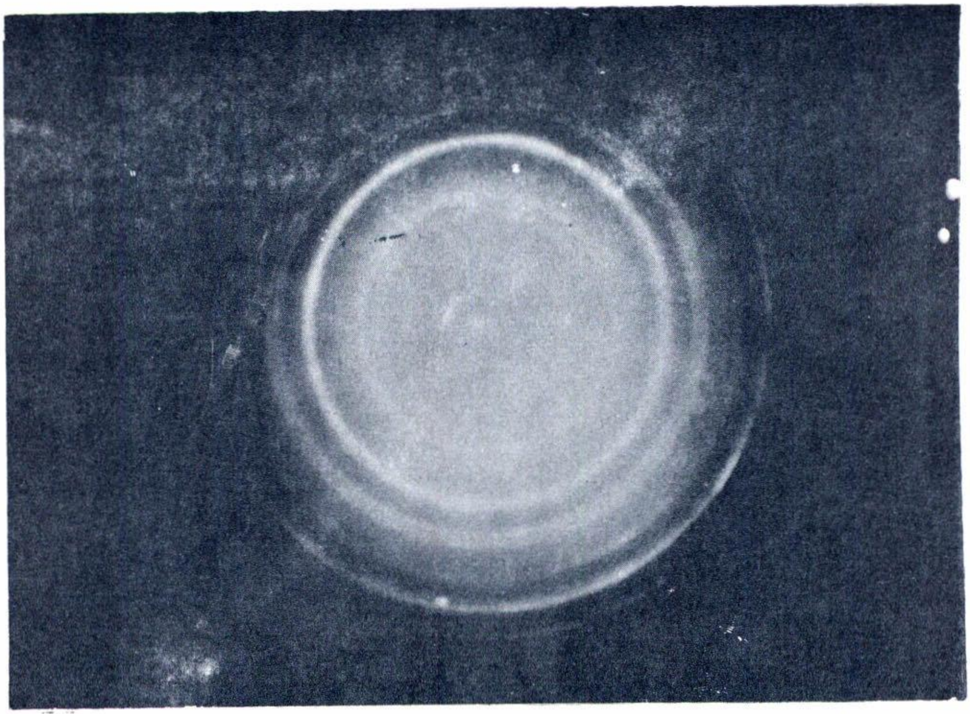

Fig. 3. Electron diffraction patterns from MnO films with 1500 Å in average thickness.

3. DISCUSSION

The results presented above show that preferred orientations are eliminated as the film thickness increases. Elimination of orientation a) takes place principally because of the rapid growth of the (III) nuclei. The growth observed of the MnO films is similar to the growth of evaporated metal films on clean NaCl surfaces. In a series of experiments on the deposition of gold on NaCl, Matthews et al[3] found that any process which increases the number of nuclei formed per unit area in the early stages, will aid the growth of single crystal films. The number of nuclei generated is small in clean NaCl surfaces and as the thickness increases, gold films become randomly oriented.

In MnO the ratio of the molar volumes of oxide to metal is greater than unity[4]. Oxide films then tend to be continuous. The MnO molecules in the early stages of nucleation have the tendency to form larger nuclei. As a result of this, the number of nuclei formed per unit area is small. Thus the growth of a randomly oriented film is favored.

The diffusion of manganese impurities may be discussed as follows: When the NaCl: Mn is annealed, Mn^{2+} ions have the tendency to migrate into the NaCl matrix. Some of the ions which are in position closer to the surface emerge on them. On the surface, ions oxidise immediately and the MnO mole cule that is formed remains on the substrate. This produces a concentration gradient of impurities along the NaCl volume which results in a flux of ions toward the surface. Since oxidation occurs more rapidly than diffusion the gradient is maintained. So the problem is reduced to the nucleation of a diffusion flux of particles into a substrate in the same way as in that of evaporated films.

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REFERENCES

1. M. J. Yacamán and E. Pedrero, J. of C. Rys: Growth, Vol. 7 (I) (1970) 259.
2. E. Muñoz, C. Ruiz and H. Riveros, J. Appl. Phys. Vol. 39 (1968) 3654.
3. J. W. Matthews, J. Vac. Sci. and Tech. Vol. 3 (1966) No. 3.
4. L. Holland, Vacuum Deposition of Thin Films, Chapman and Hall Ltd., London (1966).

RESUMEN

Se estudia el crecimiento epitaxial de películas delgadas de MnO obtenidas por difusión de impurezas del volumen a la superficie en NaCl. Las películas fueron obtenidas por calentamiento a 550 °C de monocristales de NaCl que contenían impurezas de manganeso. Los cambios en la orientación de los núcleos de MnO en la superficie del NaCl a medida que aumenta el espesor de la película son discutidos. Se encuentra que en los estados iniciales los núcleos tienen diez orientaciones preferentes, las cuales se eliminan a medida que aumenta el espesor de la película. Finalmente, cuando la capa es contínua es totalmente policristalina. La eliminación de las orientaciones preferentes es discutida en términos del número de núcleos generados por unidad de área en los estados iniciales del crecimiento.