CHAPTER-IV

Structural Properties of Mn - Oxide Films.

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STRUCTURAL PROPERTIES OF Mn-OXIDE FILMS

4.1 Introduction :

In the study of thin films of any material it is essential to study the transport and optical properties. The electrochemical effect depends on these two properties. Under the transport properties the electrical conductivity is important. In the transition metal oxides it is affected by substrate temperature and stoichiometry. The deposition parameters affect the optical absorption due to the crystal growth process and variation of grain size, etc. Discrepancies occuring in theoretical and experimental values of n and k are generally due to lack of homogenity, surface asperites, etc., which may arise due to structural changes. Thus the study of structural properties is important. In this chapter transmission micrograph, X-ray diffraction patterns are used for the study of structural properties. Also the effects of substrate temperature and concentration on the structural properties are studied.

4.2 Experimental setups for Structural Properties :

In the present investigation microstructures of the films were observed with the optical microscope - Carl Zeiss Jena make. Such microscope is useful in the study of structure and grain size of any material under investigation. This instrument depends on photomicrography. The aim of photo micrography is achieved by producing the photograph on an

enlarged scale of reproduction. This can be done by (1) the photographic lens which forms an image of the object directly and (2) an optical system which enlarge the image and projected into the image plane. The photomicrographic instrument consists of an attachment camera, a horizontal and a vertical camera and camera microscopes. In this microscope "MF" photomicrographic equipment is used which is attachment type camera. This instrument has series of eyepieces with low magnificatioin ranging from x5 to x20. The microscope objective has focal length from 15 mm to 45 mm. The total magnification of the microscope is given as

$$M = M_{objective} \times M_{projective}$$

The exposure times can be adjusted for the camera from 1/100 sec. to 1 sec. For 35 mm photomicrographs, the 24 x 36 "MF" camera attachment is used.

Mn-oxide films are structurally characterized by observing their X-ray diffraction patterns. For diffraction pattern Philips XRD model PW 1730 was used. CuK_{α} was used as a target metal and Ni as a filter. The chart speed was maintained at 1 cm/min and that of scanning at 1°/min.

4.3 Results and Discussion :

a) Transmission Micrograph

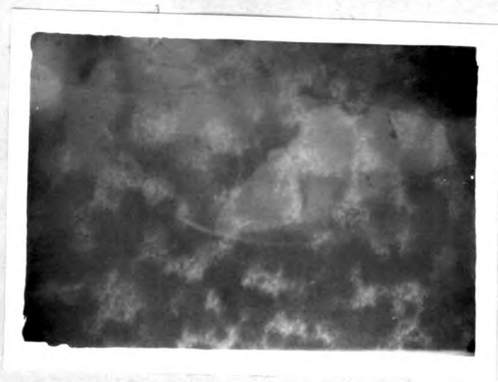
The microstructure of the sprayed films depends on the following parameters: (1) geometry of the nozzle (2)spray

rate (3) nature of the substrate (4) velocity, size and geometry of the droplets and (5) substrate temperature and temperature profile during deposition process and kinetics and thermodynamics of the pyrolytic reaction. Out of these five parameters, the first two are fixed. Thus micrographs are affected due to the remaining three parameters.

Fig. 4.1 shows micrographs for the films which are deposited on nonconducting glass substrates having temperatures 350,375,400,425 and 450°C respectively. The micrographs become planer as the substrate temperature increases. This may be due to the overlaping of diffused grains. The nature of the micrographs for films prepared at substrate temperatures 350 and 375°C may be different from the nature for films prepared at substrate temperatures 400, 425 and 450°C. This may be attributed to incomplete decomposition and oxide formation at lower substrate temperatures. This change in nature is supported by XRD study as discussed latter on.

The transmission micrographs give only information about the grain size. Thus the effects of substrate temperature, concentration and spray rate on the grain size can be studied. Here only one parameter is considered i.e. substrate temperature.

Fig. 4.2 gives the variation of grain size with substrate temperatures. The grain size decreases with increase in the substrate temperature. This may be attributed to increase in momentum, decrease in the size of droplet and



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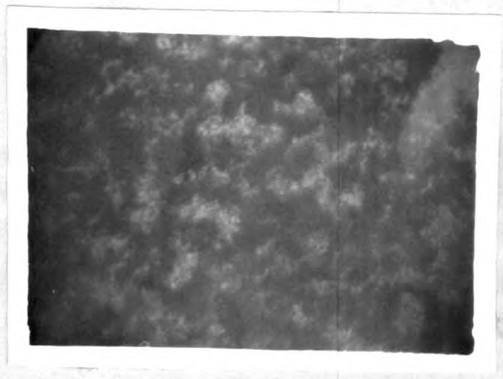

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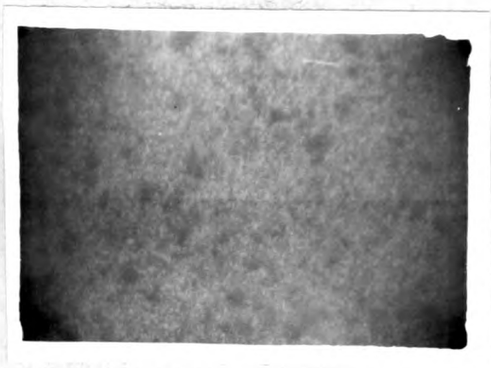

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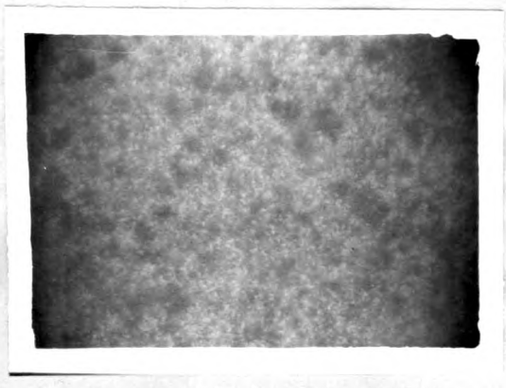

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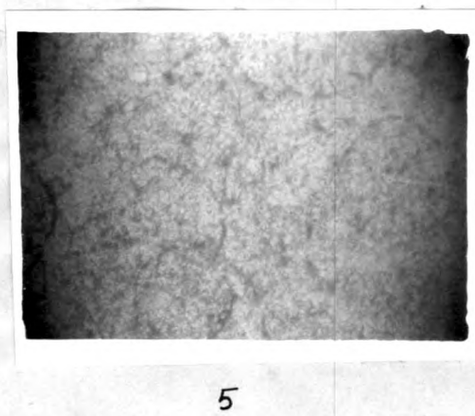

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Fig. 4.1 Transmission micrographs with magnification 600, for films prepared on nonconducting glass substrates at different substrate temperatures. (1) 350°C (2) 375°C (3) 400°C (4) 425°C and (5) 450°C.

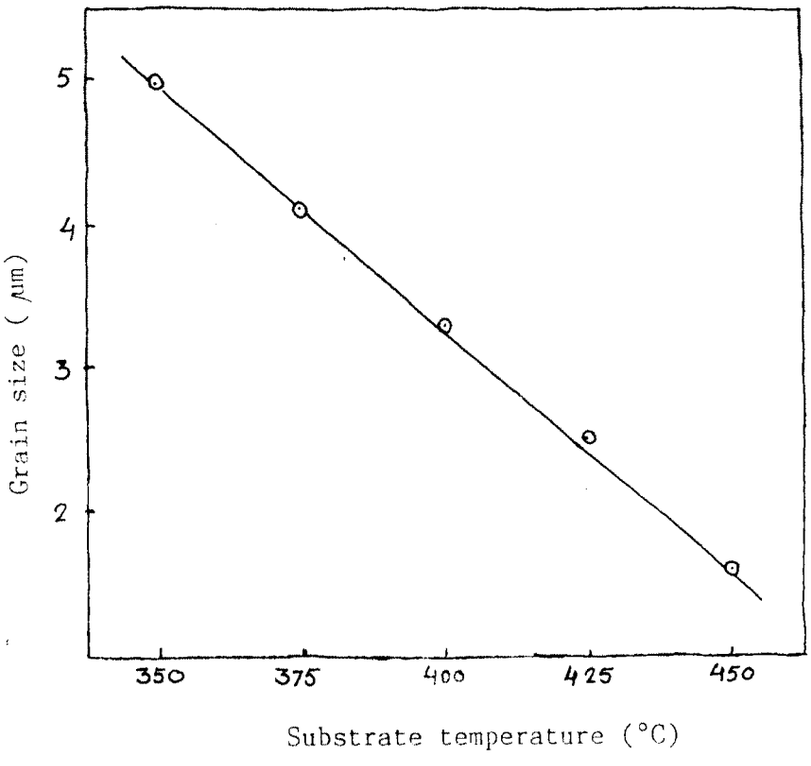


Fig. 4.2 Variation of grain size with substrate temperature.

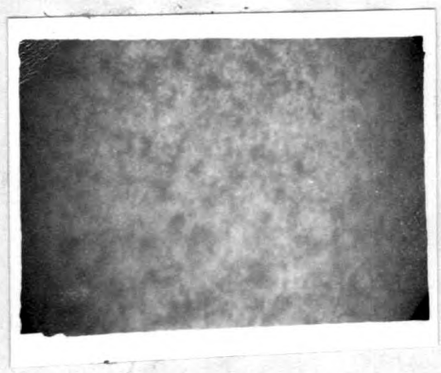
decrease in surface tension with increase in substrate tempe rature. This result is similar to findings reported by other workers /1-4/.

The transmission micrographs were taken for the film deposited on nonconducting and conducting glass substrate at a particular substrate temperature (400°C).

Fig. 4.3 shows the micrographs for the films deposite on non-conducting and conducting glass substrate, and fo the films deposited on conducting glass substrate before an after the heat treatments. The film on non-conducting glas is rather planer than the film on conducting glass. Afte the heat treatments the film becomes planer as compared t the same film before heating. From the grain size melasure- ments it was found that the grain size for the film deposited on conducting glass substrate is less than that for the fil deposited on nonconducting glass. This may be attributed t the roughness of the surface of the substrate and temperature gradient of conducting glass substrate. The comparison betwee the grain size of the film deposited on conducting glass subs trate before and after heating for three hours shows decrease in grain size after heating. This may be due to change i stoichiometry after heating.

b) X-ray Diffraction Patterns

The X-ray diffraction patterns are very useful fo identification of crystalline substance than the transmission



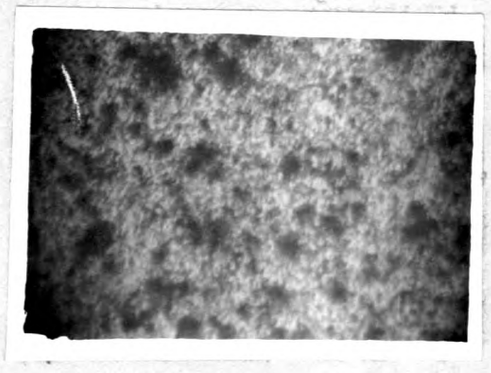


Fig. 4.3 Transmission micrographs with magnification 600, for films prepared on conducting glass substrates at 400°C substrate temperature with heat treatment.
(1) before heating (2) after heating the film.

micrograph. Even when complete structure determination is not possible, however much valuable information of a less detailed character may be obtained by X-ray methods. The pattern obtained by X-ray diffraction is used to identify crystalline substances, in the same way as the optical emission spectra is used to identify elements, or infrared absorption spectra to identify molecules. Each crystalline substance gives its own characteristic pattern. Thus X-ray diffraction patterns of different substances generally differ so much from each other that visual comparison is usually sufficient for identification, if patterns taken with the same camera are available for comparison with published patterns, measurement of the positions of recorded diffractions and conversion into standard units are necessary.

In any laboratory using crystallographic methods, it would be mistake to rely on X-ray methods alone, the combination of evidence given by X-ray diffraction patterns with that given by optical poperties, habit, cleavage and so on, may lead to valuable conclusiions /5/.

The concentration effect on XRD is shown in fig.4.4(a). The nature of XRD for 0.5 M ($S_{0.5}$) and 1 M (S_1) concentration be nearly the same but with slight change in peak intensity. For 0.25 M ($S_{0.25}$) concentration some peaks are absent e.g. peaks corresponding to 2 θ = 29,31,44.5,48.7,54,60.8,64.5°, etc. and some peaks are divided into two e.g. peak corresponding to 2θ = 36°. This change in XRD for 0.25 M concentration

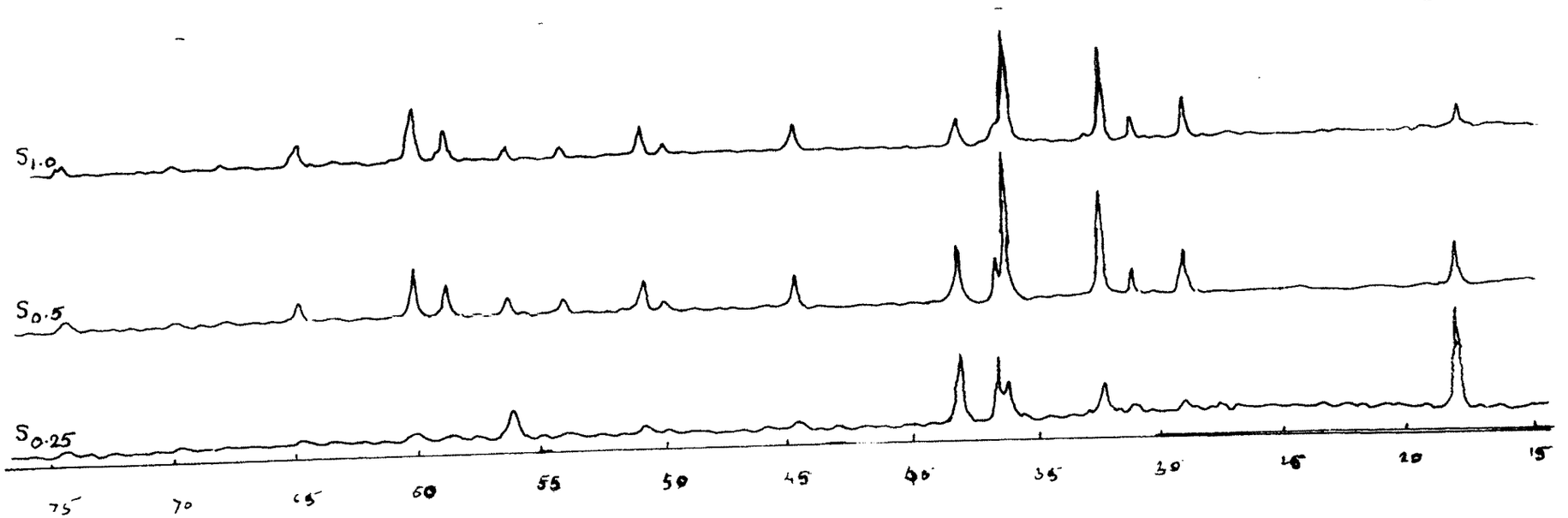


Fig. 4.4(a) Variation of XRD pattern with concentration of spraying solution (1) 0.25 M (2) 0.5 M (3) 1 M.

may be due to the change in stoichiometry. This is supported by the electrical conductivity measurements which are discussed latter. In transition metal oxides the electrical conductivity is highly affected by stoichiometry /6/.

From X-ray diffraction pattern 'd' the interplaner spacing, I/I_o the relative intensity [where I is diffracted intensity and I_o is the direct intensity] and the two parameters 'a' and 'c' are calculated with the help of relations /7/

$$n\lambda = 2\ d\ \sin\theta \qquad \ldots (4.1)$$

where, n is the order of diffraction pattern, λ is wavelength of CuK_α radiations and θ is the angle corresponding to a particular peak.

$$d = \frac{a}{\sqrt{h^2+k^2+l^2(a^2/c^2)}} \qquad \ldots (4.2)$$

where 'a' and 'c' are optic axes and h,k and l are indices.

The calculated values of d and the standard 'd' values with corresponding planes and intensity ratio /8/ are listed in table 4.1. The standard 'd' values exactly match with calculated 'd' values. Thus the film prepared at 400°C substrate temperature with 1M concentration has the composition Mn_3O_4. The calculated optical axes a = b = 5.63A° and c = 9.45 A°are in good agreement with standard values a = b = 5.57 A° and c = 9.42 A°. Thus the structure of the film is tetragonal. Also in Chapter I structure of Mn_3O_4 is given as tetragonal.

Table No. 4.1

Standard 'd' values and calculated 'd' values for a particular sample with corresponding planes and intensity ratio.

$d_{obs.}$ in A°	$d_{cal.}$ in A°	Planes	Intensity ratio I/I_o
4.9745	4.9740	101	20
3.0998	3.0997	112	31
2.8847	2.8846	200	8
2.7798	2.7799	103	63
2.4947	2.4946	211	100
2.3781	2.3781	004	13
2.0433	2.0432	220	15
1.8029	1.8028	105	18
1.7050	1.7050	312	5
1.6447	1.6447	303	5
1.5777	1.5776	321	50
1.5488	1.5488	224	50

Number of molecules per unit cell is 4 (i.e. Z = 4) and compound is $MnO.Mn_2O_3$.

The external structures of different types of Mn-oxide are as shown in fig. 4.6 /9/.

Fig.4.4(b) gives the variation of intensity ratio with concentration for particular values of interplaner spacings. These particular values of interplaner spacings are selected on the basis of higher intensity ratio (70% to 90%) for MnO, Mn_2O_3 and Mn_3O_4. Since Mn_3O_4 is always a mixture of Mn_2O_3 and MnO as given in Chapter I /10-11/. For MnO and Mn_3O_4 the intensity ratio increases with concentration while for Mn_2O_3 the intensity ratio decreases with concentration. The effect of concentration on the intensity ratio shows maximum percentage of Mn_2O_3 than MnO and Mn_3O_4 for 0.25 M concentration. While for 0.5 M and 1 M concentrations the percentage of Mn_2O_3 is less than MnO and Mn_3O_4. Since Mn_2O_3 shows better conductivity /12/ than Mn_3O_4, the 0.25 M concentration may be useful to prepare films.

Fig. 4.5(a) shows the effect of substrate temperature on XRD pattern. There is change in location and intensity of peaks in XRD patterns with change in substrate temperature. XRD for the film deposited on substrate having temperature 375°C is different from the others due to additional peaks corresponding to 2θ = 44.5, 50.7, 58.6, 60, 64.6°, etc., and single peak for 2θ = 36°. This figure shows that the

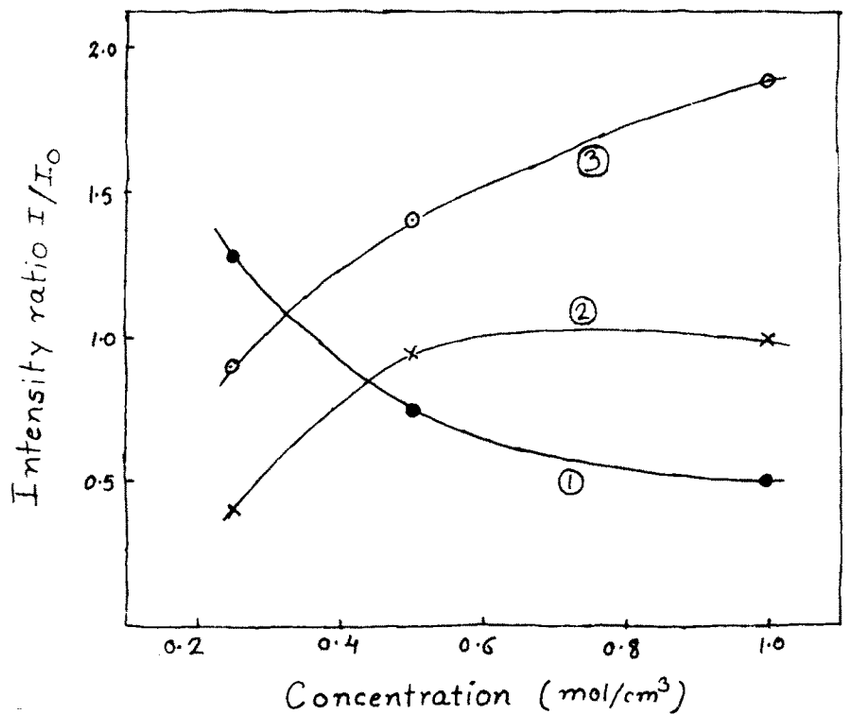


Fig. 4.4(b) Variation of intensity of peaks with concentration of spraying solution for (1) Mn_2O_3 (2) MnO (3) Mn_3O_4.

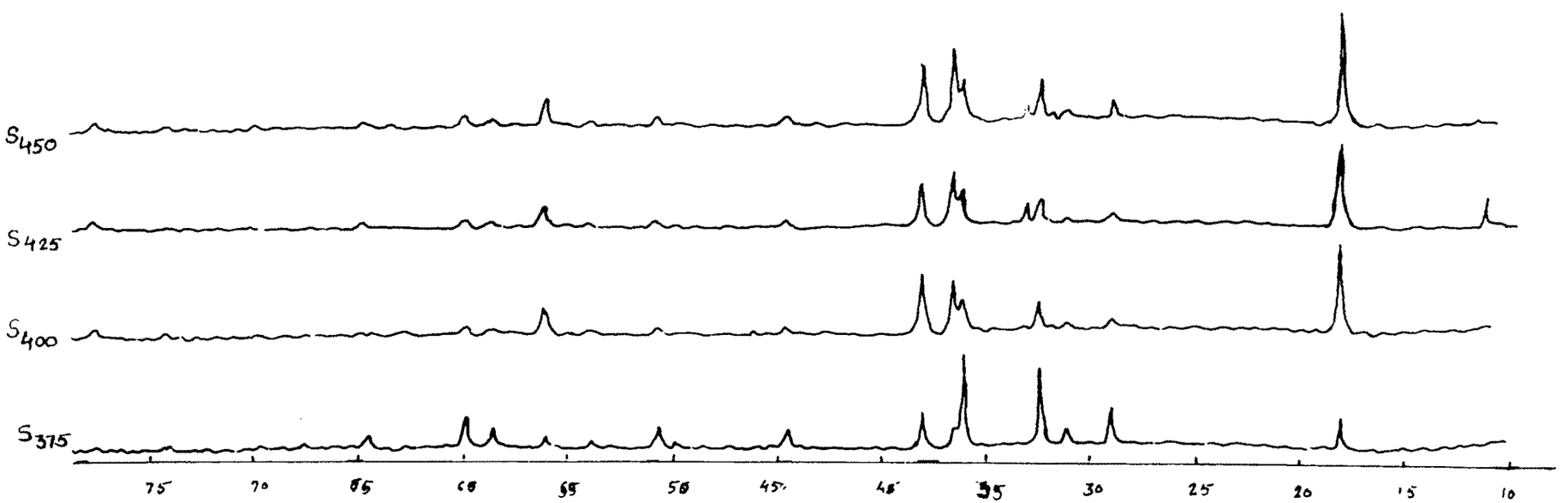


Fig. 4.5(a) Variation of XRD pattern with substrate temperatures.
(1) 375°C (2) 400°C (3) 425°C (4) 450°C.

stoichiometry for the films having substrate temperature 400, 425 and 450°C be the same as there is slight change in peak intensity only for these films. The additional peaks for the film deposited on the substrate having temperature 375°C shows different stoichiometry than the other films. The comparison between XRD of the film which is deposited by spraying the solution of 0.25 M concentration on the glass substrate having temperature 375°C with the XRD the films having substrate temperature 400°C and deposited with the solutions having concentrations 0.5 M and 1 M respectively, show that they have the same stoichiometry. The change in stoichiometry may be attributed to the incomplete decomposition. Thus the XRD patterns are affected by the concentration of the spraying solution and substrate temperatures. These patterns also show that the Mn-oxide films are polycrystalline.

Fig. 4.5(b) shows the variation of intensity ratio with substrate temperatures. The intensity ratio decreases for MnO and Mn_3O_4 with increase in substrate temperature but shows increase in intensity ratio at substrate temperature 450°C. While for Mn_2O_3 the intensity ratio increases with substrate temperature but slightly decreases for the substrate temperatures more than 400°C. The figure shows maximum percentage of Mn_2O_3 than MnO and Mn_3O_4 for 400°C

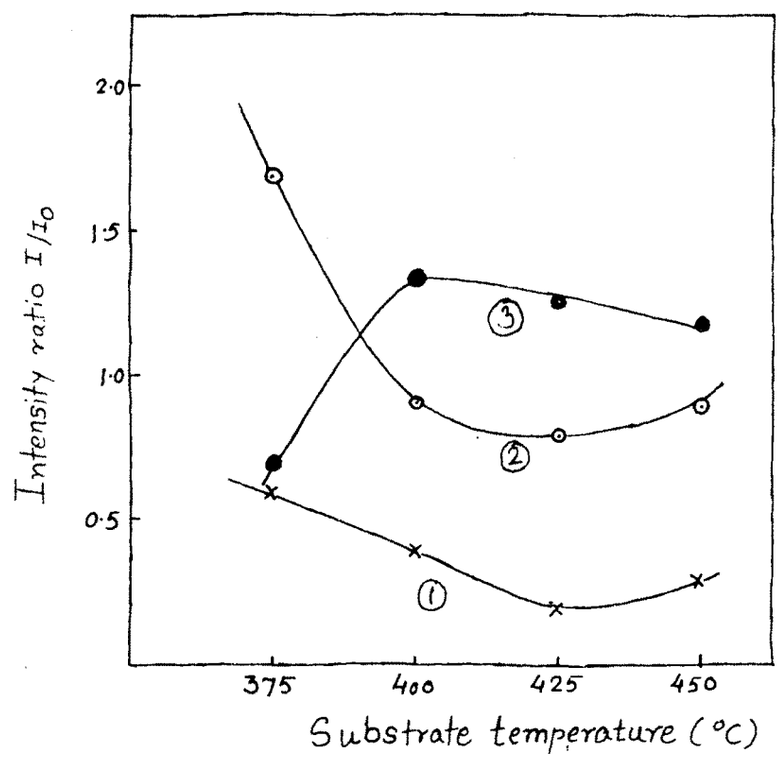


Fig. 4.5(b) Variation of intensity of peaks with substrate temperatures for (1) MnO (2) Mn_3O_4 (3) Mn_2O_3

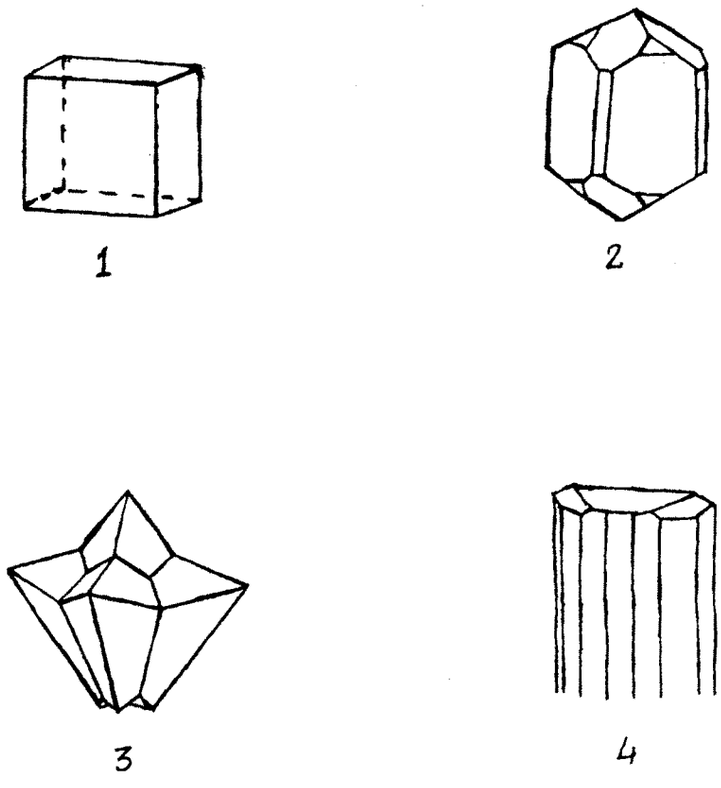


Fig. 4.6 External structures of different types of Mn-oxides
(1) Rock-salt (2) Rutile (3) Hausmannite (4) Manganite.

substrate temperature than 425 and 450°C. XRD patterns show that crystallinity is less for films having substrate temperature 425°C and 450°C than the film having substrate temperature 400°C. This result is supported by transmission micro graphs. For the films having substrate temperature less than 400°C, percentage of Mn_3O_4 is more than Mn_2O_3 and MnO. Thus for 0.25 M concentration, 400°C substrate temperature may be proper substrate temperature to produce good quality of films.

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