

phys. stat. sol. (a) **175**, 637 (1999)

Subject classification: 68.55.Jk; S9

## Structure Evolution of NdF<sub>3</sub> Optical Thin Films

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(Received April 16, 1999; in revised form July 2, 1999)

The structure evolution characteristics of NdF<sub>3</sub> thin films has been analysed concerning texture and grain morphology. The structure could be classified according to the structure zone models, and the growth mode could be related to zone T and zone II. Contamination of the films by residual gases was found to inhibit the migration of grain boundaries and therefore, zone II does not appear even at high substrate temperatures in contaminated films. Stratification by MgF<sub>2</sub> interlayers may also result in a decrease of grain size and a smaller surface roughness. The correlation between deposition conditions, stratification, growth mode and optical properties is discussed.

### 1. Introduction

NdF<sub>3</sub> thin films are used mainly as optical coatings in UV laser applications [1]. Beside their density, one important characteristics of the films is surface quality. This may be quantified by measuring RMS surface roughness or more completely the power spectral density (PSD) as obtained by atomic force microscopy (AFM). The latter quantity can be well associated with optical scattering measurements of the surface [2].

The surface topography of films depends on the growth morphology that is determined by the growth mode related to the different structure zones introduced by Movchan and Demchishin [3] for the morphology of evaporated films, and modified by Thornton [4] introducing zone T for the case of sputtering. The modified structure zone model of Thornton was applied for evaporation by Grovenor et al. [5] and further developed by Barna and Adamik [6] including the effects of additives and impurities, and the texture characteristics beside the morphology. This latter model will be applied in the present study. It has been shown that the growth of films can be altered by the codeposition of additives [6] or by the stratification of the films with a second material. That means the growth of the films is periodically interrupted by the deposition of thin layers of a second component. The stratification proved to be a useful tool for tailoring film properties through tailoring the film structure [7].

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In the present work, the structure evolution characteristics of single and stratified  $\text{NdF}_3$  optical thin films is analysed by cross sectional transmission electron microscopy (X-TEM), X-ray diffraction and atomic force microscopy (AFM). The investigations aim to reveal and explain the general behaviour of the films determined by the deposition conditions, on the basis of the structure zone models related to texture and growth morphology. The optical properties of the films are as well influenced by the structure, therefore a desired optical performance can be achieved by the understanding the structure forming phenomena and by selecting the proper deposition conditions.

## 2. Experimental

$\text{NdF}_3$  films at 400 nm thickness have been prepared by molecular beam deposition in an ultra high vacuum system [8]. The pressure of the vacuum system was lower than  $10^{-6}$  Pa. The starting materials were evaporated from high temperature effusion cells onto substrates kept at temperatures of 150, 300 and 500 °C. Deposition rate 2 to 3 nm/min, and thickness were controlled by a quartz microbalance. Stratified films were composed of 40 layers of 10 nm thick  $\text{NdF}_3$  and 40 layers of the stratifying material of 1 or 2 nm thickness deposited in sequence. The stratifying materials were  $\text{CaF}_2$  and  $\text{MgF}_2$  for two different types of samples. The stratified films were deposited at 300 °C substrate temperature. The films were deposited onto amorphous quartz substrates in order to study the growth structure of the films, not influenced by the orientation of the crystalline substrate. For comparison  $\text{CaF}_2(111)$  single crystal plates were also used as substrates in case of films deposited at 300 °C substrate temperature.

Films were deposited also in a conventional high vacuum system of base pressure of  $2 \times 10^{-4}$  Pa, in order to study the influence of contamination on the structure evolution of the films. In that case the deposited material was evaporated from a tungsten boat onto amorphous quartz substrates at  $1 \times 10^{-3}$  Pa working pressure and 2 nm/s deposition rate.

The morphology of the films was investigated by X-TEM, using conventional techniques of bright field and dark field imaging and selected area electron diffraction (SAED). X-TEM sample preparation was carried out by glancing incidence ion beam milling. In order to minimise heat and radiation artefacts, the sample holder of the milling unit was cooled by liquid nitrogen, and the ion energy for the sputtering was lower than 8 keV.

The texture measurements of the films were performed with a X-ray diffractometer in symmetric Bragg case reflection using  $\text{CuK}_\alpha$  radiation selected by a graphite focusing monochromator. The texture sharpness was evaluated with pole densities in ideal crystal directions. The pole density  $P_{hkl}$  is a measure of the relative volume of grains belonging to a given  $\langle hkl \rangle$  crystal direction compared to the respective volume in case of random crystalline distribution.

The surface morphology was investigated by atomic force microscopy (AFM). The roughness of the films and power spectral density PSD curves were determined on  $1 \times 1 \mu\text{m}^2$  areas.

Extinction coefficients were determined by measuring the transmission of the substrate and the transmission of the coated substrate at  $\lambda = 248$  nm wavelength.

### 3. Results and Discussion

#### 3.1 Single films

The morphology of single NdF<sub>3</sub> films exhibits a slightly V shaped columnar, fibrous structure (Fig. 1a) at a substrate temperature of 150 °C (0.25 of the melting point of NdF<sub>3</sub>) corresponding to zone T of the structure zone models. The growth of the films starts by the formation of a small grained structure, and the growth of slightly V shaped columns starts when the film becomes continuous. The V shape appears at the lower part of the film, since the faster growing grains impinge on each other and grow parallel after a certain thickness. The column diameter is 20 to 25 nm, and grain boundaries appear to be slightly porous indicated by the light contrast at the grain boundaries. This structure can be attributed to competitive growth of crystals. The V shape of the grains indicates that the grain boundary mobility is very low. The competitive growth of grains results in a multicomponent texture as expected for zone T [9]. The texture components are (111), (001), and (302) with the main component belonging to the (111) crystallographic plane (Fig. 2a, Table 1). The texture is weak therefore the SAED pattern shows practically random orientation (Fig. 1a). Surface topography and PSD curve are shown in Figs. 3 and 4, respectively.

Films deposited at 300 °C substrate temperature onto amorphous substrate show columnar structure with mainly parallel grain boundaries (Fig. 5a) or slightly V shaped grains. The column diameter 40 to 45 nm is apparently larger than in case of films deposited at 150 °C. This can be attributed to the larger self surface mobility of the depos-

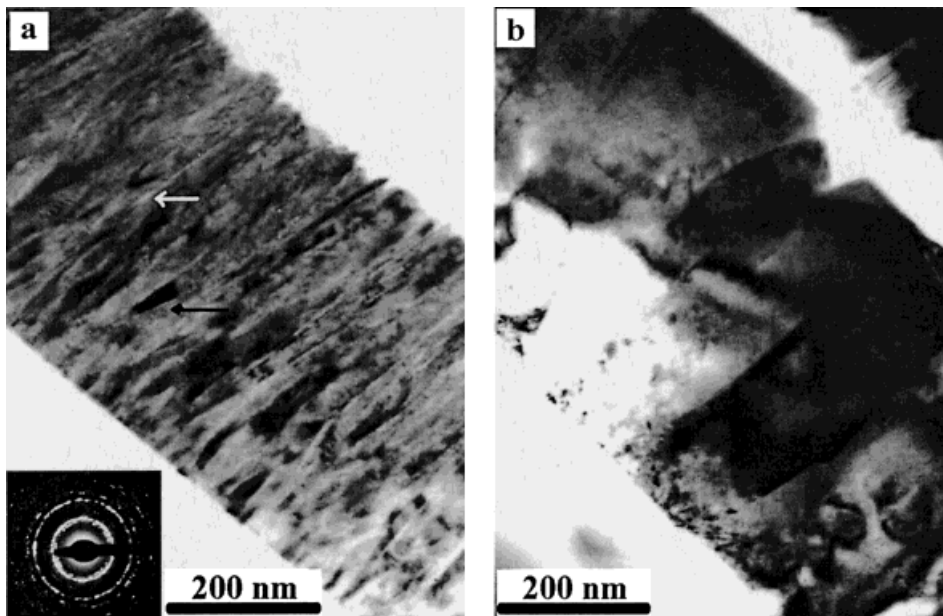


Fig. 1. X-TEM bright field images of single NdF<sub>3</sub> films deposited onto amorphous quartz substrates at a) 150 and b) 500 °C substrate temperature. A porous grain boundary, giving light contrast is indicated by a white arrow, and one of the V shaped grains is marked by a black one

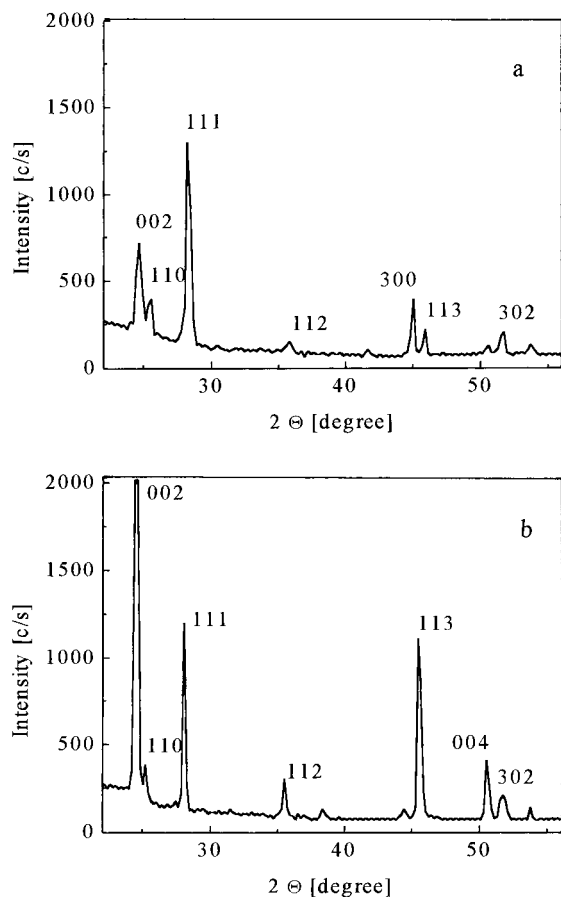


Fig. 2. X-ray diffraction patterns of single  $\text{NdF}_3$  films deposited onto amorphous quartz substrates at a) 150 and b) 500 °C substrate temperature

ited adatoms on the free surface. The film shows a small grained structure at the substrate–film interface, indicated by the white arrow. This morphology could be related to zone T. The main texture component belongs to the (113) crystallographic plane (Fig. 6a, Table 1), while other texture components are also present: (112) and (302). The SAED pattern exhibits even distribution of reflections along the diffraction rings, indicating random orientation distribution of crystallites due to the weakness of the texture components. The surface roughness is higher than that of the film deposited at lower substrate temperature (Fig. 3 and 7) what could be due to the increased grain size. The surface morphology and PSD curve are shown in Figs. 7 and 4, respectively.

Table 1  
Pole desities of 400 nm thick  $\text{NdF}_3$  films deposited by MBD

substrate temperature [°C]	$P_{002}$	$P_{110}$	$P_{111}$	$P_{112}$	$P_{300}$	$P_{113}$	$P_{302}$
150	1.7	0.5	<b>2.5</b>	0.6	1.1	0.8	1.5
300	–	–	0.7	2.1	0.2	<b>3.3</b>	2.0
500	<b>7.9</b>	0.2	1.3	2.8	–	3.0	1.0

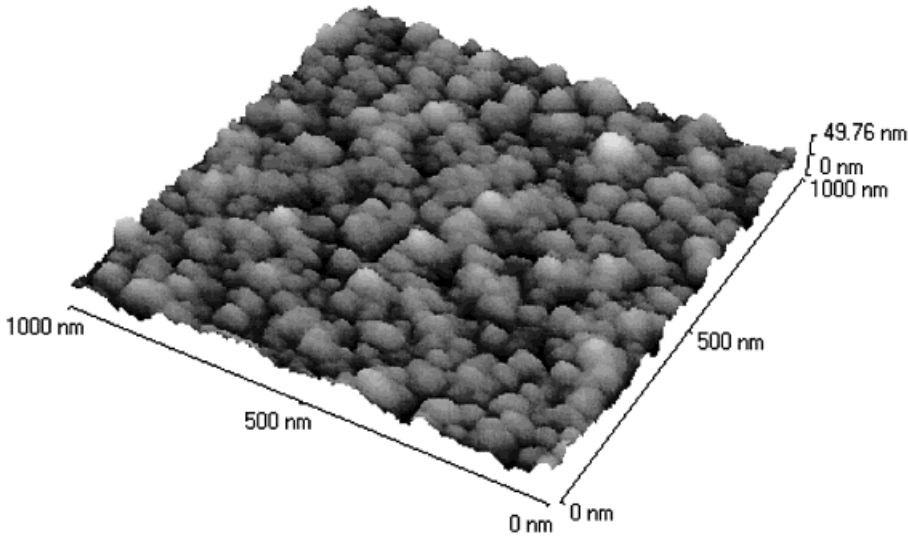


Fig. 3. AFM topography image of the NdF<sub>3</sub> film deposited at 150 °C substrate temperature

On CaF<sub>2</sub>(111) substrate the small grained structure at the substrate–film interface could not be observed, but large recrystallised grains, indicated by light contrast on the dark field image, are present in the film beside the V shaped ones (Fig. 5b). No diffraction rings are visible in the SAED pattern due to the large grain size. This structure is closer to the typical morphology of zone II.

A dramatic increase of grain size to 180 nm could be observed in the film deposited at 500 °C. The X-TEM bright field image (Fig. 1b) shows that the initial small grained structure observed at lower substrate temperatures is dissolved. This is the result of complete coalescence and grain boundary migration during the growth of the film at the elevated substrate temperature. The columnar structure is not completely regular, small grains are also present in the film mainly close to the substrate. This is probably

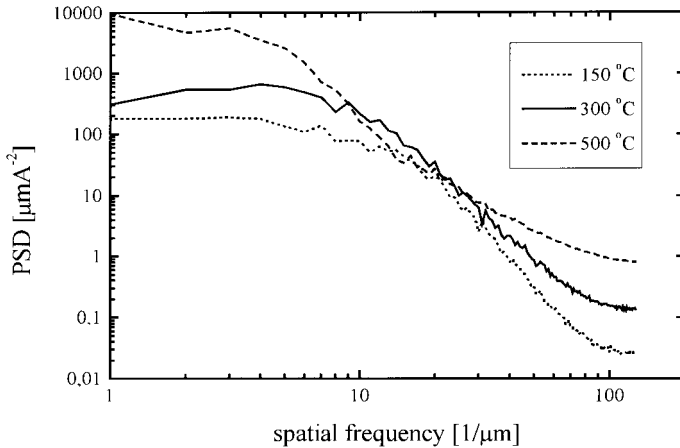


Fig. 4. PSD curves of single NdF<sub>3</sub> films deposited at 150, 300 and 500 °C substrate temperatures

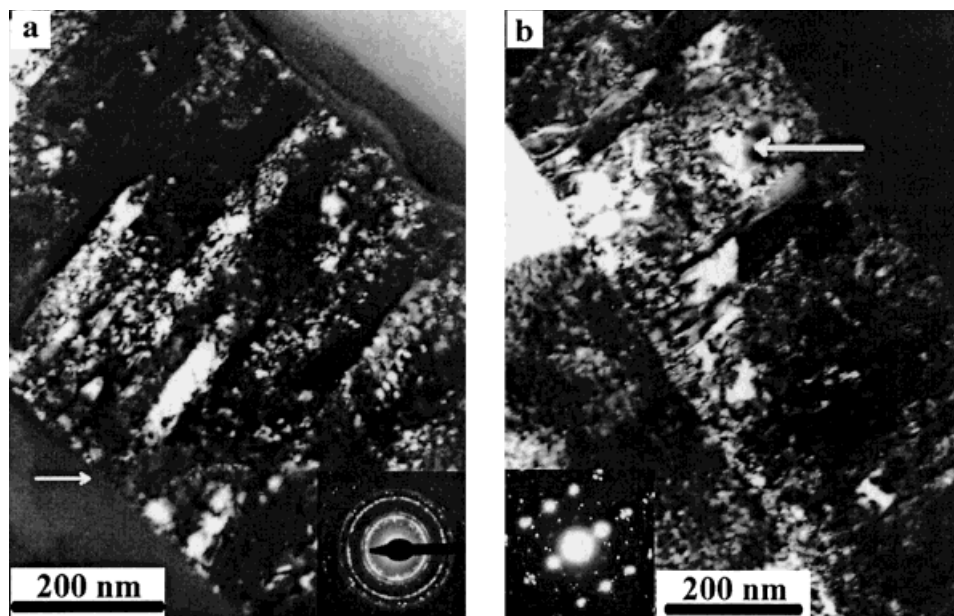


Fig. 5. X-TEM dark field images of single  $\text{NdF}_3$  films deposited at  $300^\circ\text{C}$  substrate temperature onto a) amorphous quartz and b)  $\text{CaF}_2(111)$  substrates. Substrate–film interface (a) and a recrystallised column (b) are indicated by white arrows. The inserts are the respective SAED patterns

due to impurities incorporated into the film during deposition [10] or due to the contamination present on the  $\text{SiO}_2$  substrate [11]. The main texture component belongs to the (002) crystallographic plane (Fig. 2b, Table 1) beside (112) and (113) and (111) texture components. The surface roughness is higher compared to films deposited at lower substrate temperatures (Figs. 8 and 4) what in the low frequency region is the result of the larger grain size, while in the high frequency region it might be related to macrosteps.

Single films deposited in normal high vacuum conditions at  $2\text{ nm/s}$  deposition rate and  $100$ ,  $230$ ,  $320$ , and  $440^\circ\text{C}$  substrate temperatures show main texture components of (302), (300), (113), and (113), respectively (Table 2). This result is in agreement with other measurements on films deposited in UHV, i.e. in the upper region of zone T the main texture component belongs to the (113) crystallographic plane. In the films deposited in HV, the (002) texture component mainly related to grain growth could not be observed even at high substrate temperature, probably due to the higher contamination level, indicated also by the smaller grain size in these films.

Table 2  
Pole desities of  $700\text{ nm}$  thick  $\text{NdF}_3$  films deposited by HV

substrate temperature [ $^\circ\text{C}$ ]	$P_{002}$	$P_{110}$	$P_{111}$	$P_{112}$	$P_{300}$	$P_{113}$	$P_{302}$
100	–	0.67	0.51	–	2.29	–	<b>3.64</b>
230	–	1.47	1.66	–	<b>2.49</b>	0.67	1.25
320	–	0.24	1.34	2.43	1.26	<b>2.44</b>	2.20
440	–	–	0.32	2.52	–	<b>4.17</b>	1.15

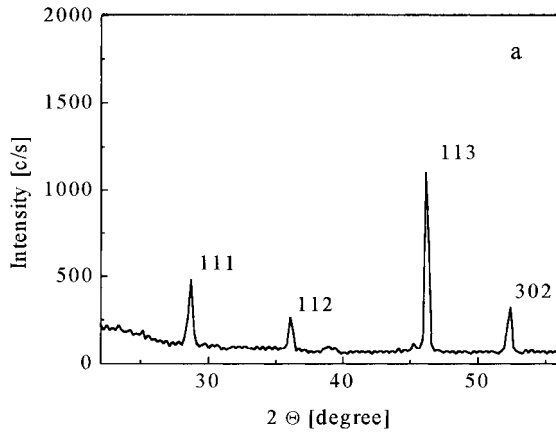


Fig. 6. X-ray diffraction patterns of a) single NdF<sub>3</sub> and b) stratified NdF<sub>3</sub>/MgF<sub>2</sub> films deposited onto amorphous quartz substrates at 300 °C substrate temperature

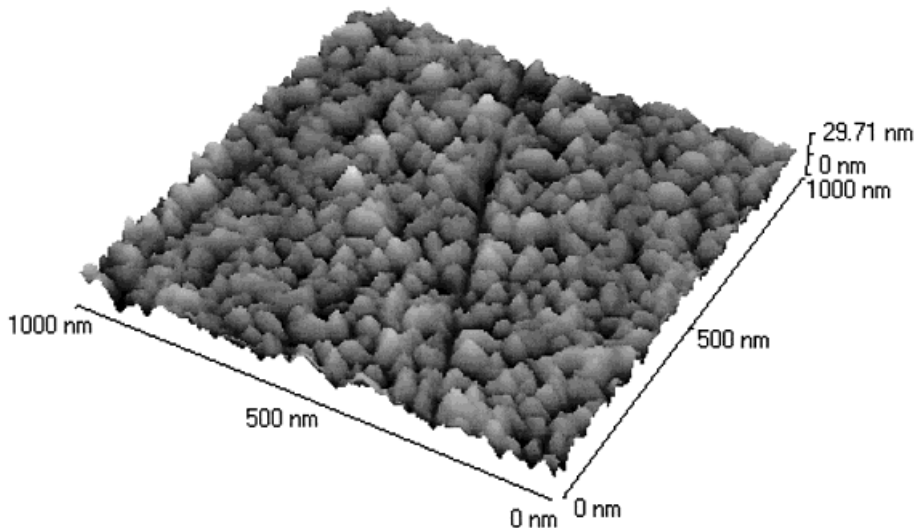
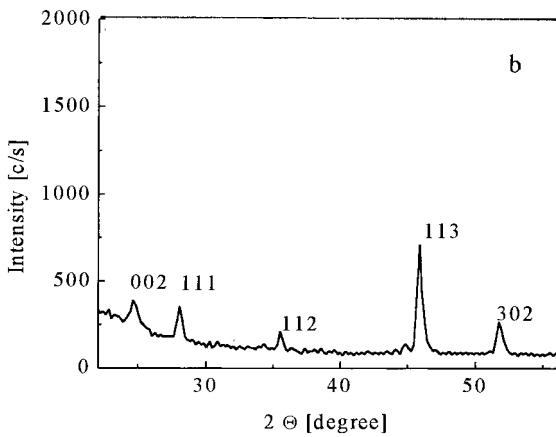


Fig. 7. AFM topography image of the NdF<sub>3</sub> film deposited at 300 °C substrate temperature

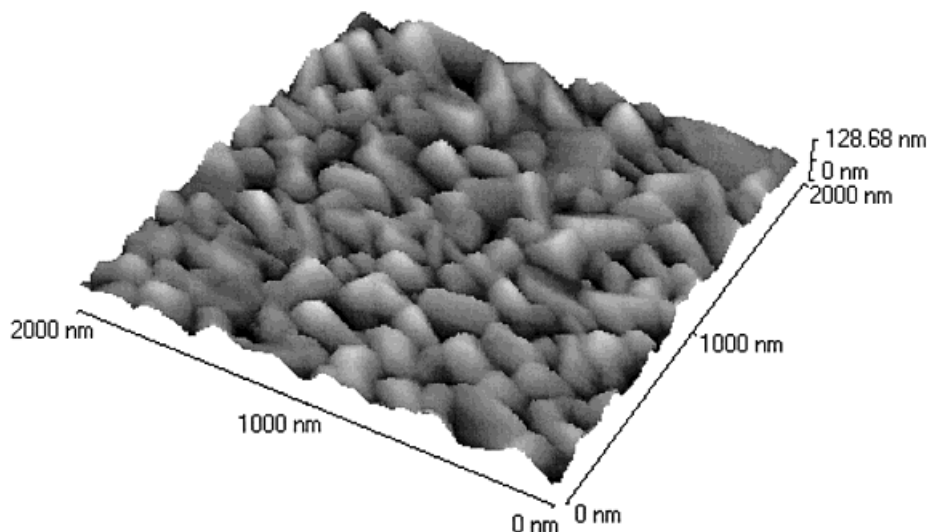


Fig. 8. AFM topography image of the  $\text{NdF}_3$  film deposited at  $500^\circ\text{C}$  substrate temperature

In hexagonal structures the (001) plane is supposed to have the lowest surface energy. This might be true also in the present case, although it is not known how the impurities may affect it. Therefore, the faceted surface of the films is presumably composed of the (001) crystal faces [12]. The minimisation of the free surface area requires low angles between the (001) crystallographic planes and the planes parallel to the substrate surface (Table 3). The order of the appearance of the observed texture components indicates a tendency to a decrease of the angles with increasing substrate temperature. Sharp facets composed of crystal faces with a large angle to the free surface could be observed in the cross section of the film deposited at low substrate temperature ( $150^\circ\text{C}$ ) (Fig. 1a). This is in accordance with the observation of texture components corresponding to the (111) and (302) crystallographic planes having large angle with that of the (001) index. At higher substrate temperatures the (112) and (113) texture components also appear composing smaller angles with the (001) plane, while (002)

Table 3

Angles between the detected crystallographic planes and the plane of lowest surface energy (001) in ascending order, calculated according to the crystallography of the hexagonal structure

$hkl$	$\varphi$ with (001) ( $d = 7.2 \text{ \AA}$ )
002	0.0
113	34.3
112	45.7
302	60.6
111	64.0
300	90.0
110	90.0



texture is observed at  $500^\circ\text{C}$ . The development of these texture components can be qualitatively related to the higher surface mobility of the impinging adatoms due to the elevated substrate temperature. At low substrate temperatures, where the surface migration of adatoms is limited, the main source of adatoms is the vapour phase, therefore the crystals showing larger surface area towards it might grow faster [13]. This way both the minimisation of the free surface energy, and the area of the surface influence the growth. At high substrate temperatures the adatom migration is decisive in the growth process, therefore the surface energy minimisation will be the dominating phenomenon of the structure evolution, resulting in the evolutionary selection of grains with smaller surface area, i.e. smaller angle with the (001) crystallographic planes.

The two main differences between UHV and HV deposited films are that the (002) component does not appear even at high substrate temperatures, and the second is that at low substrate temperatures in HV deposited films the (300) component is relatively strong. These differences could be the result of the effect of impurities, which could change the surface energies of the various crystal faces and suppress the growth of some crystal planes by segregation [9].

In single films the lowest extinction coefficient 0.0004 was observed in the film deposited at  $150^\circ\text{C}$  substrate temperature, which is in correlation with the results on the surface topography. The extinction coefficients are 0.0018 and 0.011 in the films deposited at  $300^\circ\text{C}$  and  $500^\circ\text{C}$ , respectively. These larger values can be due to the increased grain size and higher surface roughness at increased substrate temperature.

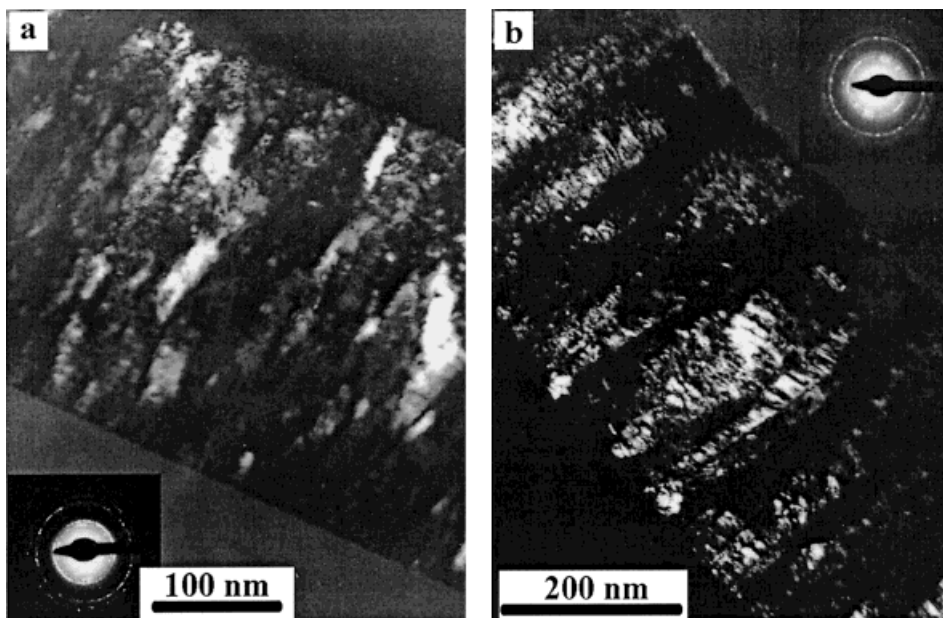


Fig. 9. X-TEM dark field images of a)  $\text{NdF}_3/\text{MgF}_2$  and b)  $\text{NdF}_3/\text{CaF}_2$  stratified films deposited onto quartz substrates at  $300^\circ\text{C}$  substrate temperature. Inserts are the respective SAED patterns

### 3.2 Stratified films

Stratification by 1 nm thick  $\text{MgF}_2$  interlayers results in a decrease of grain size to 25 nm on both substrates, compared to that observed in single films deposited at the same 300 °C substrate temperature. The morphology shows V shaped columnar structure similar to that in the single film deposited at 150 °C substrate temperature, which corresponds to zone T according to the structure zone models (Fig. 9a, 10a). The formation of the columnar structure can be related to discontinuities in the thin  $\text{MgF}_2$  layers. This is indicated by the disruption of the thin light lines of the  $\text{MgF}_2$  interlayers in Fig. 11. When thicker (2 nm)  $\text{MgF}_2$  interlayers are applied for the stratification, the development of columns is suppressed and a mainly globular grain structure can be observed (Fig. 10b). The smaller grain size is indicated also by the continuous rings of the respective SAED pattern.

The experiments show that in case of stratified films the substrate has no remarkable influence on the morphology of the films. The effect of stratification is similar to that of impurities or certain codeposited additives, in the way that the morphology reflects the characteristics of a structure zone corresponding to a lower substrate temperature. The PSD curves however indicate that the behaviour of surface morphology with stratification is different from that resulting from the variation of the substrate temperature during deposition (Fig. 12), although the decrease of surface roughness could be observed in both cases. In the case of stratification the PSD curves are shifted towards lower values roughly parallel to the curve corresponding to the single film. This shift is similar to that observed in case of single films deposited with different thickness [2]. The corresponding surface topographies are shown in Fig. 13a, b.

The main texture component belongs to the (113) crystallographic plane (Fig. 6b, Table 4) beside the (302) and (112) texture components like in the single film deposited

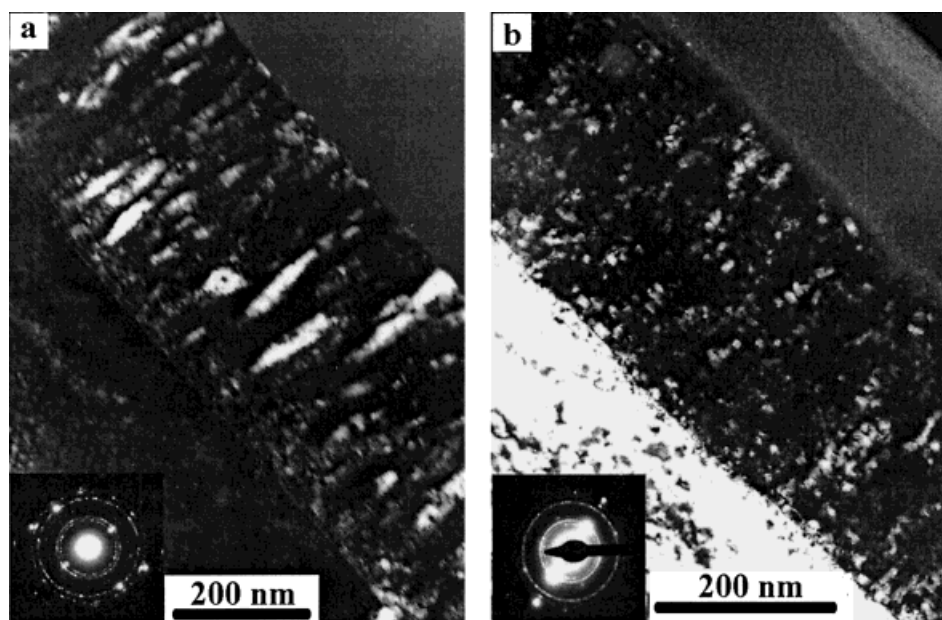


Fig. 10. X-TEM dark field images of  $\text{NdF}_3/\text{MgF}_2$  films stratified by a) 1 nm thick and b) 2 nm thick  $\text{MgF}_2$  interlayers, deposited onto  $\text{CaF}_2(111)$  substrates at 300 °C substrate temperature

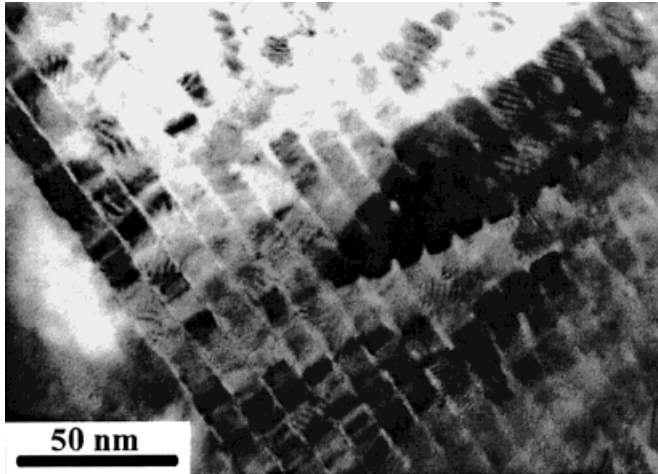


Fig. 11. X-TEM bright field image of an NdF<sub>3</sub> film stratified by 1 nm thick MgF<sub>2</sub> interlayers, deposited onto CaF<sub>2</sub>(111) substrate at 300 °C substrate temperature

at 300 °C substrate temperature, i.e. the stratification did not cause a remarkable change to the characteristics of the texture.

NdF<sub>3</sub> films stratified by 1 nm thick CaF<sub>2</sub> layers show a V shaped columnar morphology corresponding to zone T (Fig. 9b). The grain size is larger than in the single film at the same substrate temperature (60 to 70 nm). The surface roughness is only slightly changed compared to that in the single film deposited at the same substrate temperature. The main texture component belongs to the (113) crystallographic plane as in case of the single film, but the (112) and (302) components could not be observed.

Extinction coefficients are within measurement error the same as that of the single film deposited at 150 °C substrate temperature. They are 0.0006 and 0.0005 for the film stratified by MgF<sub>2</sub> and CaF<sub>2</sub>, respectively, what could be due to the similar grain struc-

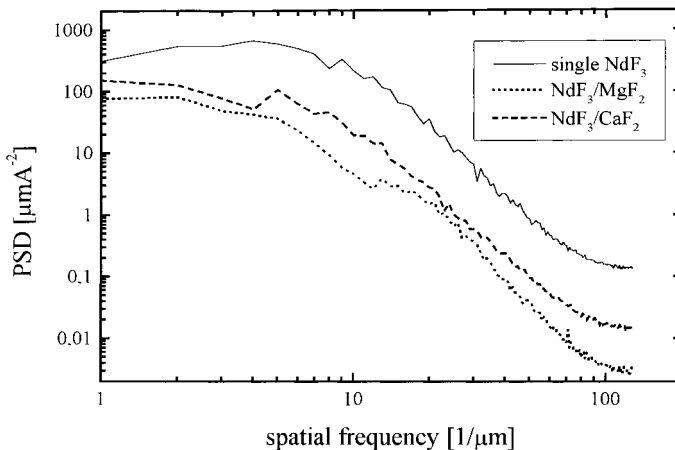


Fig. 12. PSD curves of single NdF<sub>3</sub> and stratified NdF<sub>3</sub>/MgF<sub>2</sub> and NdF<sub>3</sub>/CaF<sub>2</sub> films deposited at 300 °C substrate temperature onto amorphous quartz substrates

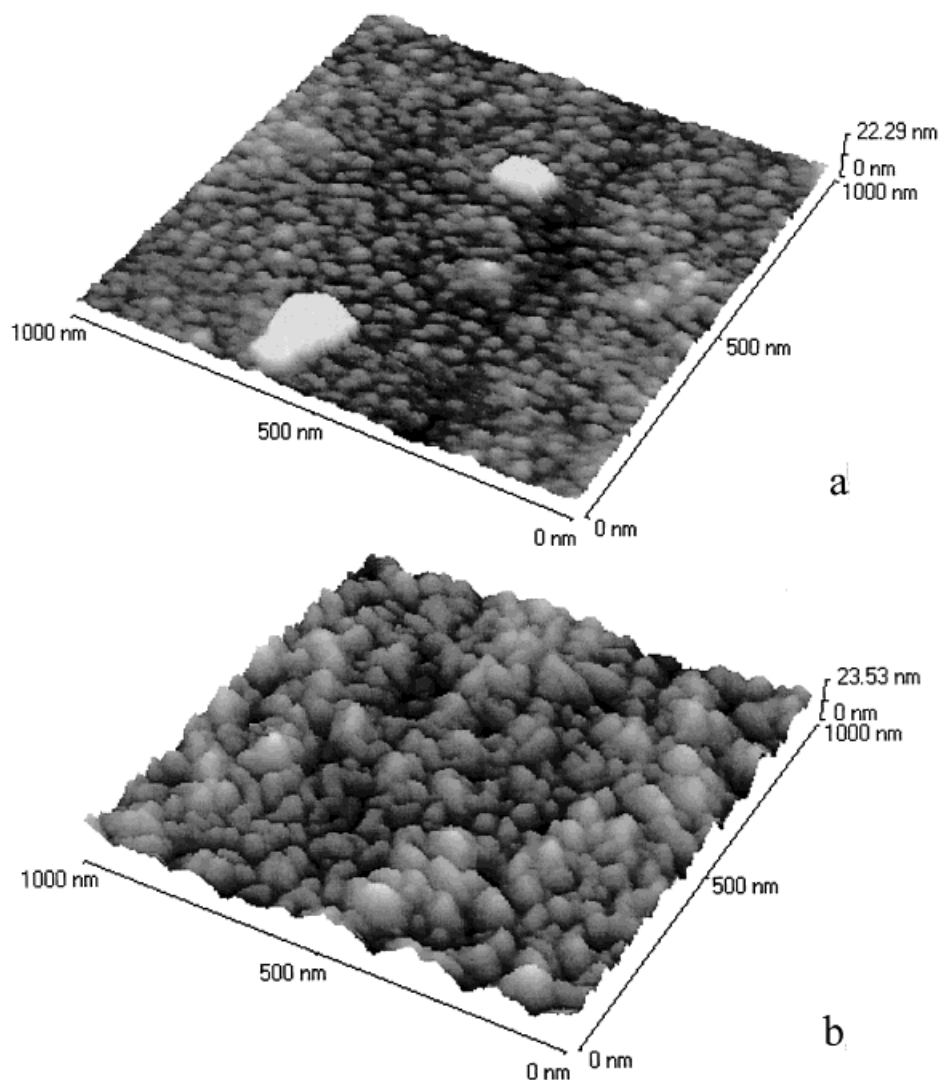


Fig. 13. AFM topography images of stratified a)  $\text{NdF}_3/\text{MgF}_2$  and b)  $\text{NdF}_3/\text{CaF}_2$  films, deposited onto amorphous quartz substrates at  $300^\circ\text{C}$

Table 4

Pole densities of 400 nm thick single and stratified  $\text{NdF}_3$  films deposited by MBD at  $300^\circ\text{C}$  substrate temperature

samples at $300^\circ\text{C}$	$P_{002}$	$P_{110}$	$P_{111}$	$P_{112}$	$P_{300}$	$P_{113}$	$P_{302}$
single film	–	–	0.7	2.1	0.2	<b>3.3</b>	2.0
stratified by $\text{MgF}_2$	0.4	0.4	0.5	1.2	–	<b>3.1</b>	1.6
stratified by $\text{CaF}_2$	0.3	0.8	–	–	–	<b>2.2</b>	–

ture and surface topography. The results indicate that the extinction coefficient is correlated mainly with the surface roughness decreasing both by decreasing substrate temperature and by stratification. The type of material applied as stratifying component had no remarkable influence on the properties.

#### 4. Conclusion

The morphology and texture of NdF<sub>3</sub> films depends on the substrate temperature and contamination level in a similar way as in metallic thin films in accordance to the structure zones. The decisive phenomenon in zone T is the crystal growth leading to various texture components. Their variation may be qualitatively related to the surface energy of the faceted crystal surfaces and to the mobility of adatoms, however the true understanding of the nature of texture evolution in this zone requires more detailed studies of surface processes during the growth of the film. In zone II (002) main texture was found for single films deposited under UHV conditions as a result of grain growth. In high vacuum the (002) texture component does not appear even at high substrate temperatures, since the grain growth is limited due to contaminants.

The main influence of stratification by MgF<sub>2</sub> and CaF<sub>2</sub> on the structure evolution of the NdF<sub>3</sub> films is the reduction of the grain size and the surface roughness. This results in low extinction coefficients observed in single films deposited at low substrate temperature. This method is therefore suitable for the deposition of thick optical films with low surface roughness and low optical losses.

**Acknowledgements** The authors thank G. Glazer, T. Bojinova and E. Hajmássy for their technical assistance. This work was supported by the Hungarian National Foundation OTKA under contract No. 1225 and W015179, by the Bulgarian National Found for Scientific Research under contract No. F-802/1998 in the frame of the co-operation agreement No. 9 of the Hungarian Academy of Sciences and Bulgarian Academy of Sciences, and by the Hungarian National Found for Technical Development (OMFB) in the frame of the German-Hungarian Intergovernmental S&T Co-operation Programme under contract No. 113.

#### References

- [1] U. KAISER, M. ADAMIK, G. SÁFRÁN, P. B. BARNA, S. LAUX, and W. RICHTER, *Thin Solid Films* **280**, 5 (1996).
- [2] C. RUPPE and A. DUPARRE, *Thin Solid Films* **288**, 3 (1996).
- [3] B. A. MOVCHAN and A. V. DEMCHISHIN, *Fiz. Metall.* **28**, 83 (1969).
- [4] J. A. THORNTON, *J. Vac. Sci. Technol.* **11**, 666 (1974).
- [5] C. R. M. GROVENOR, H. T. G. HENTZELL, and D. A. SMITH, *Acta Metall.* **32**, 773 (1984).
- [6] P. B. BARNA and M. ADAMIK, *Thin Solid Films* **317**, 27 (1998).
- [7] K. L. LEWIS, I. T. MUIRHEAD, A. M. PITT, A. G. CULLIS, N. G. CHEW, A. MILLER, and T. J. WYATT-DAVIES, *Appl. Opt.* **28**, 2785 (1989).
- [8] S. LAUX, U. KAISER, and W. RICHTER, *Proc. SPIE* **2253**, 455 (1994).
- [9] M. ADAMIK, P. B. BARNA, and I. TOMOV, *Thin Solid Films* **317**, 64 (1998).
- [10] P. B. BARNA and M. ADAMIK, in: *Protective Coatings and Thin Films: Synthesis, Characterisation and Applications*, Eds. Y. PAULEAU and P. B. BARNA, NATO ASI Series 3, High Technology, Vol. 21, Kluwer Academic Publishers, Dordrecht 1997 (pp. 279 to 297).
- [11] M. ADAMIK and P. B. BARNA, *Surf. Coat. Technol.* **80**, 109 (1996).
- [12] E. D. WILLIAMS and N. C. BARTELT, *Ultramicroscopy* **31**, 36 (1989).
- [13] A. VAN DER DRIFT, *Philips Res. Rep.* **22**, 267 (1967).

