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Grain growth and texture development in lithium fluoride thin films

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We have studied grain-growth and texture development in polycrystalline lithium fluoride thin films using dark-field transmission electron microscopy. We demonstrate that we can isolate the size distribution of $\langle 111 \rangle$ surface normal grains from the overall size distribution, based on simple and plausible assumptions about the texture. The $\{111\}$ texture formation and surface morphology were also observed by x-ray diffraction and atomic force microscopy, respectively. The grain-size distributions become clearly bimodal as the annealing time increases, and we deduce that the short-time size distributions are also a sum of two overlapping peaks. The smaller grain-size peak in the distribution corresponds to the $\{111\}$ -oriented grains, which do not grow significantly, while all other grains increase in size with annealing time. A novel feature of the LiF films is that the $\{111\}$ texture component strengthens with annealing, despite the absence of growth for these grains, through the continued nucleation of new grains.

I. INTRODUCTION

The structure of polycrystalline thin films has significant influence upon their performance in almost all applications. Porosity, grain shape, grain size, grain-size distributions, grain-boundary or triple-junction networks, and grain orientations all influence the film properties and stability. These characteristics of grain structure are developed via grain growth occurring during thin-film deposition and postformation processing such as annealing; extensive research has been done on grain growth in thin films.¹⁻⁴ Insulating films including polycrystalline alkali fluorides have recently been investigated as promising materials for applications in electronics and optics.^{5,6} Among the alkali halides, LiF thin films are of commercial and scientific interest for a variety of reasons including their possessing the largest band gap among solid crystals and having point defects that can be optically active at room temperature.^{7,8} In the past few years, attention has been given to the structural and optical characteristics of polycrystalline LiF thin films as a function of growth conditions.^{9,10} In a recent study,¹¹ we have identified the growth conditions required to make fully dense films. Grain growth has been studied in bulk¹² and thin-film LiF,¹³ and prior investigators have determined that the grain-growth exponent is anoma-

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JOURNALS

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lously low for ceramics¹⁴ and nanocrystalline materials.^{15,16} Although they have suggested several possible reasons for these exceptionally low grain-growth exponent values, they are not fully understood yet.

Techniques available for texture analysis include x-ray diffraction (XRD), which provides information about the crystal orientation distribution of a large region of the sample, but does not provide microstructural information,^{17,18} and transmission electron microscopy (TEM) Kikuchi patterns from individual grains provide the means for relating orientation and grain size directly, but do not provide meaningful statistics about the texture or the grain-size distribution. Electron backscatter pattern analysis provides both kinds of information but requires extended data collection times.

In this study, we applied a dark-field (DF) TEM method to characterize the grain-growth kinetics of specific sets of diffracting grains to obtain grain-growth and preferred orientation information, with meaningful statistics, for polycrystalline LiF films.

II. EXPERIMENTAL PROCEDURES

The 50-nm-thick, fully dense polycrystalline LiF thin films were grown by thermal evaporation onto amorphous, 50-nm-thick Si_3N_4 membrane window substrates supported by single-crystal Si wafers in a standard evaporator. The background pressure was $2-3 \times 10^{-4}$ Pa, and the LiF powder charges of 99.98% purity were heated in a tungsten boat. The evaporation rate was

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monitored by a quartz-crystal oscillator, and kept to 1-2 nm/s to obtain homogeneous and crack-free films. The substrates were placed above the source, and the distance between the substrate and source was 10 cm. The substrate temperature was measured with a chromelalumel (K-type) thermocouple that was in contact with the substrate, and the accuracy of the temperature was about ±1 °C. The LiF powder was always preheated in the vacuum to eliminate moisture and impurities, and the substrates were also preheated in the vacuum to eliminate adsorbed water. A quartz-crystal thickness monitor was used to measure the thickness of the LiF thin films. The 50-nm-thick LiF thin films were deposited with substrate temperatures from 300 °C [0.51 melting temperature $(T_{\rm m})$] to 423 °C (0.62 $T_{\rm m}$) and annealed in situ, without breaking the vacuum, for 0, 10, 30, 60, 120, or 180 min before ramping down to room temperature. The substrate temperatures used in this study are all in the range that produces fully dense films, thus minimizing the possibility that pores may impede grain growth.

LiF is a very good electrical insulator; thus, carbon was sputtered onto the specimens used for TEM to prevent charge buildup, which can cause the specimen to drift and crack under the electron beam. In the center of each substrate is a transparent Si_3N_4 window, which enables the examination of the film structure in the transmission electron microscope (JEM 2000FX; JEOL, Tokyo, Japan).

The transmission electron microscope was operated at an accelerating voltage of 200 kV to obtain bright-field (BF) images, DF images, and diffraction patterns. In the DF images, individual, strongly diffracting grains show up brightly, and are easily discriminated for size analysis using standard stereological tools. The grain-size measurements were made from DF images at 60,000× magnification using Gatan Digital Micrograph (Pleasanton, CA) software, version 3.65, to determine the average grain size and the grain-size distribution. At least 500 grains were measured per sample.

XRD was performed using a conventional Bragg– Brentano geometry Siemens (New York, NY) diffractometer, to assess any preferred orientation within the films. The x-ray source is Cu K_{α} (40 kV and 20 mA), and the incident beam direction is fixed. The scan rate was 5°/min for 2 θ varying between 35° and 50°. These diffraction measurements collect information only from lattice planes parallel to the film surface, in contrast with TEM, which collects information from planes perpendicular to the film surface.

A Digital Instruments (Woodbury, NY) multimode atomic force microscope (AFM) was used, in tapping mode, to observe the surface morphology. AFM measurements were carried out with a Digital Instruments Dimension 3100 controller with NanoscopeIII software. The tip and cantilever are an integrated assembly of single-crystal silicon that is produced by etching. The spring constant and resonant frequency were 30 N/m and 300 kHz, respectively. The nominal tip radius of curvature was 5–10 nm, and the cantilever length was 125 μ m. The scanner had to travel 5 μ m in the *z* direction and 500 nm in the *x* and *y* directions.

III. DATA ANALYSIS

All of our DF images were obtained using segments of the closely spaced $\{111\} + \{200\}$ rings or the isolated $\{220\}$ diffraction ring tilted onto the optic axis of the objective lens, employing the smallest objective aperture to exclude any rays diffracted by other grains, as shown in Fig. 1. Grain sizes are represented as the mean equivalent grain diameters, determined from the DF images obtained at a magnification of 60,000×.

IV. RESULTS

Figure 2 shows a typical set of images representative of those used in this research. The BF and DF images provide an indication of the grain growth that occurs with annealing. More quantitative analysis is presented below.

A. Shape of the grain-size distribution

Figure 3 shows the development of the grain-size distribution determined from the DF images in the TEM, as a function of time at 423 °C (0.62 $T_{\rm m}$). For the data collected from the {220} images, the distribution is monomodal for the as-deposited condition and for short annealing times, but it becomes distinctly bimodal at longer annealing times. The small-size peak moves only very slowly to larger grain sizes, but the large-size peak moves more rapidly. We surmise that this grain-size distribution can be understood as the sum of two peaks, which overlap at short annealing times and separate as



FIG. 1. Sequence in obtaining a DF and a BF image.



FIG. 2. The plan-view BF and DF images and diffraction patterns (DPs) as a function of annealing time at 423 °C ($0.62 T_{\rm m}$).



FIG. 3. {111} + {200} and {220} diffracting grain-size and subtracted distributions as a function of annealing time from 0 to 180 min at 423 °C (0.62 $T_{\rm m}$).

the microstructure develops. In contrast with the results from the $\{220\}$ DF images, the grain-size distributions obtained from the $\{111\} + \{200\}$ images are primarily monomodal, within the limits of sample noise, at all an-

nealing times. To interpret these results, we note that, as shown in Table I, grains contributing to a $\{100\}$ texture can be observed in $\{200\}$ and $\{220\}$ DF images. Grains that contribute to a $\{110\}$ texture can be seen in all three

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J. Mater. Res., Vol. 23, No. 2, Feb 2008

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TABLE I. The possible textures that may include the diffracting planes.

Diffracting planes	Possible textures (surface normal planes)		
	{100}	{110}	{111}
{111}	Not visible	Visible	Not visible
{200}	Visible	Visible	Not visible
{220}	Visible	Visible	Visible

diffracting conditions, and {111} grains can only be observed in the {220} DF images. If we assume that these three orientations contribute more significantly than any others to the overall texture, the {111} grain-size distribution can be inferred by comparing the data from {220} DF images with that from the $\{111\} + \{200\}$ DF images. We can obtain the {111} grain-size distributions by normalizing and subtracting the distribution of the $\{111\}$ + {200} diffracting grains from that of the {220} diffracting grains, yielding the results shown in the third row of Fig. 3. The {111} grain-size distribution deduced in this manner clearly corresponds in its location and shape, to the small-size peak in the {220} grain-size distribution. We conclude that the distinguishing feature of the smallsize peak in the grain-size distribution is that it corresponds primarily to grains that exhibit a {111} texture.

Our procedure leads to some physically unrealistic negative values in the grain-size distribution attributed to the {111} grains. This results from normalizing the distributions from the two sets of DF images to the same total number of grains, where they should be different, because one set includes more orientations than the other and, therefore, more grains.

Grain-size distributions for films annealed at 338 °C (0.55 $T_{\rm m}$) and 300 °C (0.51 $T_{\rm m}$) are shown in Figs. 4 and 5, respectively. These show features essentially similar to those seen in Fig. 3, as described above.

B. Trends in the as-deposited films

Basic information about the grain sizes measured in our as-deposited films is provided in Table II. All of the grain-size distributions are monomodal in the asdeposited condition, and the average grain diameter increases with increasing substrate temperature for both the $\{111\} + \{200\}$ and $\{220\}$ diffracting grains. The width of the distribution also increases with increasing substrate temperature.

The mean grain diameter of the $\{220\}$ diffracting grains is always smaller than that of the $\{111\} + \{200\}$ diffracting grains, which corresponds to the finding that the $\{220\}$ data include a distinct small-diameter component.



FIG. 4. {111} + {200} and {220} diffracting grain-size and subtracted distributions as a function of annealing time from 0 to 180 min at 338 °C (0.55 $T_{\rm m}$).



FIG. 5. {111} + {200} and {220} diffracting grain-size and subtracted distributions as a function of annealing time from 0 to 180 min at 300 °C (0.51 $T_{\rm m}$).

Substrate temperature (°C)	Counted grains (No.)	Diffracting grains	Mean equivalen grain diameter (nm)
423 (0.62 T _m)	608	$\{111\} + \{200\}$	82.4
	555	{220}	68.7
338 (0.55 T _m)	634	$\{111\} + \{200\}$	63.7
	804	{220}	60.1
$300 (0.51 T_{\rm m})$	890	$\{111\} + \{200\}$	52.6
	924	{220}	49.7

TABLE II. The grain size measurement information.

All grains were counted from 60 DF images.

C. Effects of annealing

JOURNALS

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The grain-size distributions obtained from the {220} DF images can all be fitted with reasonable accuracy to a sum of two normal distributions, as shown for a single case in Fig. 6. As discussed above, the smaller diameter peak should correspond to {111}-oriented grains, and the larger diameter peak corresponds to most other orientations.

Figure 7 shows the growth of the average grain sizes with annealing time for the separated data, corresponding to the two fitted peaks in the grain-size distributions. During annealing, the sizes of the grains other than those with the {111} orientation increase. However, the



FIG. 6. {220} diffracting grain-size distribution fitted to two normal distributions. This film is deposited at 0.62 $T_{\rm m}$ for 180 min.

 $\langle 111 \rangle$ surface normal grains exhibit only very slow growth, stagnation, or even shrinkage. The grain-growth time exponent, *n*, was calculated for the growing component of the microstructure by fitting the mean grain sizes to the empirical grain-growth law:

$$d(t) = kt^n \quad , \tag{1}$$

456



FIG. 7. Average grain size as a function of annealing time for three different temperatures: (a) 0.62 $T_{\rm m}$; (b) 0.55 $T_{\rm m}$; (c) 0.51 $T_{\rm m}$; (d) ln k versus 1/T.

where d(t) is the mean grain diameter at time t and k is a constant. The grain-growth exponent was 0.21 for 0.62 $T_{\rm m}$, 0.20 for 0.55 $T_{\rm m}$, and 0.19 for 0.51 $T_{\rm m}$. The corresponding values of k yield an activation energy of 16.77 kJ/mol, or 0.2 eV per molecule for this component of the grain growth in our films, as shown in Fig. 7(d).

A more detailed analysis of the growth of the {111} grains is obtained from the grain-size distributions that were deduced by subtraction of the two sets of DF image data, as shown in Figs. 3–5. The residual peaks, ascribed to {111} grains, can be fitted with reasonable precision to lognormal distributions. This allows us to find the modal grain size and also to estimate the full width of the distribution at half of its maximum height.

Figure 8 illustrates the development of the grain-size distributions of the $\langle 111 \rangle$ surface normal grains with time for each temperature. In these plots, the filled symbols represent the modal grain diameters, and the open symbols represent the upper and lower limits of the distribution at half of its peak height. At 0.51 $T_{\rm m}$, the {111} grains initially grow but then shrink marginally after 30 min of annealing. At 0.55 $T_{\rm m}$, there is continuous growth of {111} grains throughout the experiment. However, at 0.62 $T_{\rm m}$, the grain size clearly decreased for the first 30 min. In this case, we remeasured the {111} grainsize changes using a new set of specimens and obtained the same result, within a very small error.

The number density of $\{111\}$ grains was estimated from the grain-size distributions obtained from the $\{220\}$ DF images, accounting for the fact that the objective aperture only intersects 7.3% of the diffraction ring, and we thus only count this percentage of the {111} grains. The number density of {111} grains is shown as a function of annealing time in Fig. 9. These data are rather noisy, but the best-fit linear regressions suggest that the number density of the {111} grain increases by an amount between 6.8×10^7 and 1.6×10^8 grains/m²/s from the lowest to the highest temperature investigated in this study. The area fractions represented by the {111} grains are also shown as a function of annealing time for three different temperatures in Fig. 10. The linear regression data also indicate that the area fraction of a {111} grain increases by an amount between 3.2×10^{-8} and 1.3×10^{-7} per second.

The XRD spectra obtained from specimens annealed for various times at 0.62 $T_{\rm m}$ are shown in Fig. 11. The {111} peak strength increased and the {200} peak intensity decreased with the annealing time. The {111} texture was strongly dominant, and the {200} peak is almost absent at 0.62 $T_{\rm m}$.

As shown in Fig. 12, there is a surface morphology change with increasing temperature. At higher temperatures and longer annealing times, we observed faceted surfaces, while at lower temperatures and shorter annealing times more rounded and macroscopically rough surfaces are typically observed.

V. DISCUSSION

A. Porosity and grain structure of the films

Our films are essentially pore free,¹¹ and the mean grain size is greater than the film thickness; so, the grains

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FIG. 8. Average grain size of $\langle 111 \rangle$ surface normal grains as a function of substrate temperature and annealing time: (a) deposited and annealed at 423 °C (0.62 $T_{\rm m}$); (b) deposited and annealed at 338 °C (0.55 $T_{\rm m}$); and (c) deposited and annealed at 300 °C (0.51 $T_{\rm m}$).

are predominantly columnar and their growth is twodimensional. The relationship between the substrate temperature and the initial grain size has been studied extensively, and is explained by the interactions among nucleation, growth, and coalescence.^{19–21} The competition between island growth and nucleation, prior to coalescence, leads to an increase of grain size at the point of coalescence with increasing substrate temperature. A similar relationship between the substrate temperature



FIG. 9. The number density of {111} grains as a function of annealing time for three different temperatures: (a) 0.62 $T_{\rm m}$; (b) 0.55 $T_{\rm m}$; and (c) 0.51 $T_{\rm m}$.

and grain size is found for our LiF films, as illustrated in Fig. 7.

B. Grain-growth kinetics

Our results show that no obvious grain growth took place for $\langle 111 \rangle$ surface normal grains at any annealing temperature. However, the grains other than those with a $\langle 111 \rangle$ normal surface grew during annealing, as shown in Figs. 7 and 8. The growth exponent range for these grains is from 0.19 to 0.21. According to the accepted models for two-dimensional grain growth,^{22,23} the time

458

CAMBRIDGE JOURNALS

J. Mater. Res., Vol. 23, No. 2, Feb 2008



FIG. 10. The area fraction of {111} grains as a function of annealing time for three different temperatures: (a) 0.62 $T_{\rm m}$; (b) 0.55 $T_{\rm m}$; and (c) 0.51 $T_{\rm m}$.

exponent should be 0.5. Observed time exponents are usually somewhat less than 0.5, as in our LiF films, and this is commonly considered as evidence that the growth process is restrained due to solute segregation, secondphase particles,²⁴ or surface pinning in thin films.²⁵ The presence of a preferred orientation can also have an influence on the grain-size distribution and, hence, can affect the growth exponent. Because the grain growth in these cases is accompanied by texture alterations,²⁶ the energy and mobility of the grain boundaries of the surviving grains have to change with time. However, in this particular case, we may infer that the low value of the



FIG. 11. XRD patterns of LiF films as a function of annealing time from 0 to 60 min deposited and annealed at 423 °C (0.62 $T_{\rm m}$).

grain-growth exponent is due to the increase of the nucleation effect of the $\langle 111 \rangle$ surface normal grains as the annealing temperature and time increase.

Recently, small values of *n* have been reported in a few cases. An exponent of 0.083 has been reported for mullite by Schmücker et al.,²⁷ 0.02 for Nb₃Al + Nb by Suryanarayana and Koch,²⁸ and 0.05 for nanocrystalline pure iron by Koch and Malow.²⁹ In our case, analyzing the results on the basis of a single average grain size, including both the {111} and the "other" grains, would yield a grain-size exponent in the range of 10^{-2} , but this does not accurately reflect the kinetics of the process.

The activation energy for grain growth, calculated in the temperature range from 0.51 to 0.62 $T_{\rm m}$ is approximately 1/10 of that reported for lattice diffusion in LiF (211.9 kJ/mol or 2.2 eV per molecule).³⁰ This may indicate that the growth of the grains other than those with $\langle 111 \rangle$ surface normal grains is not controlled by lattice diffusion, but by surface diffusion, grain-boundary diffusion, triple-junction diffusion, or a combination of these three.

C. Texture development

Texture can develop in polycrystalline thin films as a result of nucleation at preferred sites and/or the growth of grains with a preferred orientation. The topography and crystallographic orientation of the substrate may provide preferred sites and orientations for adatoms forming nuclei, and contaminants adsorbed on the surface of the substrate can also influence this type of oriented nucleation.^{31,32} Preferential growth can occur as a result of: (i) surface-energy minimization^{33,34}; (ii) elastic-deformation energy minimization³⁵; (iii) plastic yield-energy minimization.³⁷

In the case of our LiF films, a {111} texture develops in the early stages of annealing, which is consistent with

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FIG. 12. AFM surface morphology images of LiF films: (a) deposited at 300 °C (0.51 $T_{\rm m}$); (b) deposited at 423 °C (0.62 $T_{\rm m}$); (c) deposited at 338 °C (0.55 $T_{\rm m}$); and (d) deposited and annealed for 1 h at 338 °C (0.55 $T_{\rm m}$).

the observations by Baldacchini et al.³⁸ However, Monterealis et al.³⁹ detected {111} and {100} textures, and Kaiser et al.⁴⁰ observed a weak {100} texture, depending on the deposition parameters. It is rather unlikely that the texture observed in our experiments arises as a result of surface-energy minimization, because {111} surfaces are polar in LiF, exposing only cations or anions, and thus have high energy. It is also difficult to explain the {111} texture based on the elastic strain-energy minimization. We can calculate the ratio of the appropriate planar elastic moduli because the compliance data⁴¹ of LiF and direction cosines in cubic the lattice are known; on the basis of these, the ratio of the moduli is calculated as $E_{100}/E_{110}/E_{111} = 0.74:0.87:1$. The elastic strain energy depends on the mean elastic moduli acting in the plane *hkl.*³⁵ It is expected, therefore, that the strain-energy term will be smaller for the {100} orientation than for the {110} and {111} orientations. The yield points for the different orientations can be calculated by possible slip plane angles and burgers vector angles based on the favored slip system of LiF films, which are $\langle 110 \rangle$ {110} and $\langle 110 \rangle$ {100}. If all of the grains in LiF films have reached their yield stress, the texture that minimizes the strain energy would also be {100}. Strain-energy effects have been minimized in our experiments by the fact that we did not cool our specimens between deposition and annealing. This avoids the generation of thermalmismatch stresses, although other mechanisms can generate stress in the films. These might include shrinkage stresses associated with the sintering of pores, but, again, our experiments have been carried out in a manner that minimizes this effect.¹¹ Where additional stresses are

present in LiF films, we might expect to see an increased presence of the {100} texture.

The grain-size data shown in Figs. 7 and 8 indicate that the $\langle 111 \rangle$ surface normal grains are small and undergo essentially no growth at longer annealing times, although they undergo some unusual size changes (both positive and negative) earlier in the annealing process, as shown in Fig. 8. We surmise that the {111} texture derives from some preferred nucleation process giving rise to large numbers of small {111} grains, which are then constrained from growth by their unfavorable surfaces and strain energy. We were not able to identify the process by which these grains nucleate, but it is clear that their number of density continues to increase with annealing time (as seen in Fig. 9) and there is a corresponding increase in the strength of the {111} texture, as seen in Fig. 11.

Figure 7 shows that the grains other than those with $\langle 111 \rangle$ surface normal grains may grow conventionally, extending to the longest annealing times. The growth exponent for these grains is approximately 0.2, rather than the theoretically expected value of 0.5, and this may result from the pinning of the boundaries of the growing grains by the stagnant {111} crystallites, in addition to the other pinning effects that occur in thin films.

D. Surface morphology development

The development of faceted surface morphologies in our higher temperature films is consistent with the observations of Cosset et al.,⁴² who also found that when the LiF films were deposited onto substrates at temperatures higher than 300 °C, well-defined facets appeared. There is no clear explanation of the relationships among

JOURNALS

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faceting, the growth of the {111} peak, and the suppression of the {100} XRD peak, which both occur at higher annealing temperatures.

VI. CONCLUSIONS

The grain-size distribution that develops during postdeposition annealing of LiF thin films is strongly bimodal, with a sharply defined, largely immobile peak at small grain sizes, accounting for the {111} grains. A broader peak at larger grain diameters exhibits conventional grain growth with a growth exponent of approximately 0.2 and an activation energy of 0.2 eV per molecule.

The {111} texture in LiF thin films strengthens with annealing temperature and time through the continuous nucleation of new $\langle 111 \rangle$ surface normal grains, rather than by their growth.

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