Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

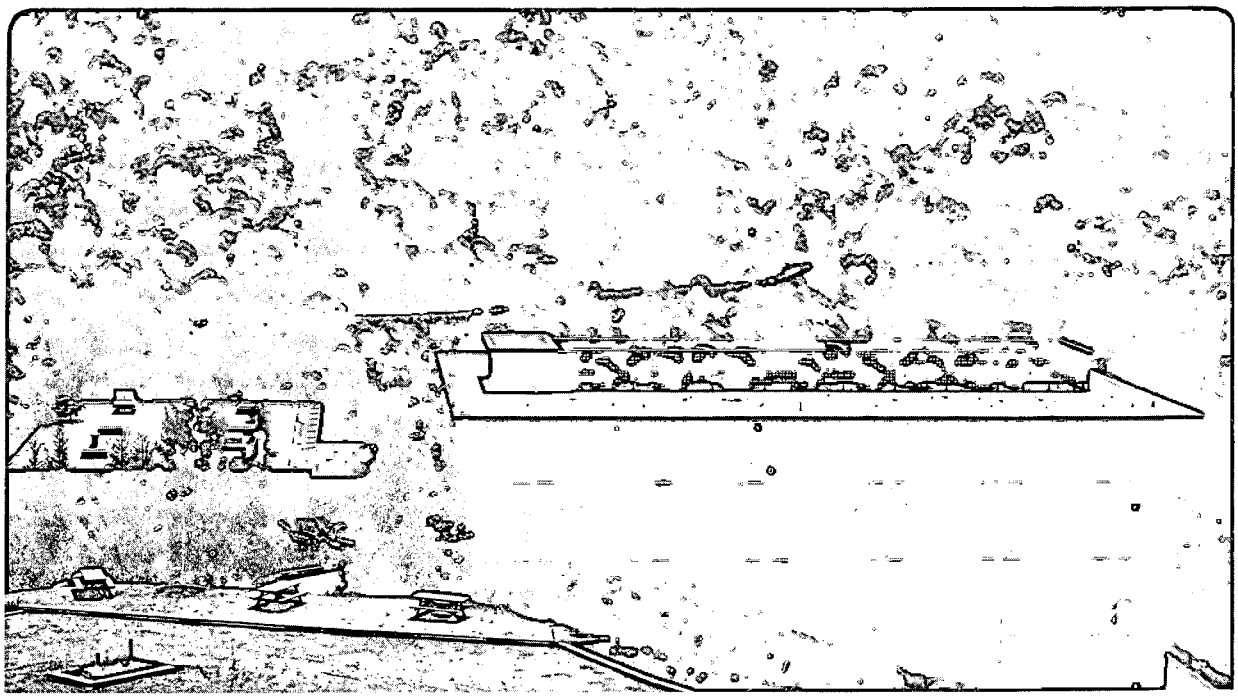
Materials Sciences Division

Presented at the Fall Meeting of the Materials Research Society, Boston, MA, December 2–6, 1991, and to be published in the Proceedings

Thermodynamic and Kinetic Characteristics of Variations in Shapes of Ridges Formed on {100} Lithium Fluoride Surfaces

J.W. Bullard, A.M. Glaeser, and A.W. Searcy

December 1991



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

LOAN COPY
Circulates
for 4 weeks
Bldg. 50 Library.
Copy 2
LBL-31567

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-31567

Thermodynamic and Kinetic Characteristics of Variations in Shapes of Ridges Formed on {100} Lithium Fluoride Surfaces

J.W. Bullard, A.M. Glaeser, and Alan W. Searcy

Department of Materials Science and Mineral Engineering
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

December 1991

This report has been reproduced directly from the best available copy.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

THERMODYNAMIC AND KINETIC CHARACTERISTICS OF VARIATIONS IN SHAPES OF RIDGES FORMED ON {100} LITHIUM FLUORIDE SURFACES

J.W. BULLARD, A.M. GLAESER AND ALAN W. SEARCY

Lawrence Berkeley Laboratory, University of California, Berkeley, Materials Sciences Division, and Department of Materials Science and Mineral Engineering, Berkeley, CA.

ABSTRACT

Channels with widths in the range from 5 μm to 25 μm were formed in {100} surfaces of LiF single crystals by a photolithographic technique. Specimens annealed at or above 0.90 T_m, where T_m is the melting point, and then quenched showed the channels and the ridges between them develop rounded profiles. Evolution of these profiles was evaluated for the various channel widths and for interchannel ridge spacings of 5 to 100 μm in terms of: a) an accepted theoretical model for a surface diffusion controlled process, and b) a model which assumes that shape changes depend only on the relative energies of attachment of atoms in surface sites with various surface curvatures. Either model is consistent with the experimental observations to within the reproducibility in measurements.

INTRODUCTION

From equilibrium thermodynamic considerations, one would expect ceramic crystals at low temperatures to be faceted since ceramics usually have highly anisotropic surface energies [1]. However, at typical sintering temperatures most ceramics form rounded particles, and most theories incorporating kinetic arguments, such as models of surface smoothing and grain boundary grooving, predict rounded morphologies. In some models the rounding has a thermodynamic basis; it results from assuming isotropic surface energy. In other models, surface anisotropy is assumed, but rounding results from assumptions about the rate limiting step in mass transport which is usually taken to be solid-state diffusion. The possibility that diffusion rates are sufficiently high that the profiles during surface smoothing reflect primarily the preferential rates of detachment from sites of highest energy and reattachment at sites of lowest energy has apparently not been considered.

This paper reports experimental observations of the influence of various heat treatments on the shapes of initially faceted ridges in {100} LiF surfaces and compares the observations to predictions made by assuming shape changes to be: a) kinetically controlled, or b) thermodynamically controlled.

Kinetic Considerations

Measurement of the amplitude decay of a sinusoidal surface profile of a single crystal is an established means of studying material transport on and near the surface of metals and ceramics. Mullins [2] set forth a theoretical model that incorporates both surface and bulk diffusion as possible transport mechanisms, and provides the following equation for the time dependence of the surface profile:

$$u(x,t) = a \sin(\omega x) \exp[-(C\omega^3 + B\omega^4)\, t] \qquad (1)$$

where a is the initial amplitude, ω is the wave number, $(2\pi/\lambda)$, x is the position along an axis parallel to the mean surface, and B and C are material and temperature dependent constants for surface and bulk diffusion, respectively. Equation (1) is strictly valid only when the orientation of the surface profile at any point varies only slightly from that of the mean surface. Mullins further postulates that any shallow, periodic surface shape can be represented as a Fourier series in which each of the terms decays independently of the others according to an equation like Eq. (1).

The above model has been used extensively for interpreting surface smoothing observations. Recently, Slamovich and Lange [3] have cited evidence that the rate limiting step of intermediate stage sintering of ≈1 μm alumina may be a near-equilibrium process. The possibility

that surface smoothing for micron-scale surface features may also be limited by a near-equilibrium process rather than by the diffusion rate should be evaluated.

Thermodynamic Considerations

If diffusion rates are high, then during the smoothing of sufficiently small-scale features etched into a ceramic surface, the shape resulting from a given amount of mass transfer may reflect primarily the most energetically favorable redistribution of that mass. In other words, the shape evolution may proceed along a path of minimum surface free energy. It is also possible that these evolving shapes may be rounded since entropy contributions make the high-temperature surface energies more isotropic [4]. These possibilities invite evaluation of the smoothing in terms of those differential shape changes which produce the maximum differential reduction in surface free energy.

EXPERIMENTAL PROCEDURE

Lithium fluoride crystals with dimensions 25 mm x 25 mm x 1mm were obtained with {100} faces and polished to a 0.1 μm finish. Atomic emission spectroscopy and x-ray photoelectron spectroscopy (XPS) analyses were performed to measure bulk and surface impurities, respectively, and no significant impurity concentrations were detected.

The photolithography/ion-beam milling technique used to produce the desired surface features follows closely that described by Rödel and Glaeser [5], and will be only briefly described here.

The pattern to be exposed in each LiF specimen consisted of 10 sets of 10 parallel channels and separating ridges. Within each set, hereafter called a profile, the channels had identical widths and the ridges had identical widths, which sometimes differed from the channel widths. The pattern was generated on a CAD system and transferred to a square 64 mm x 64 mm chrome-coated glass mask.

A layer of photoresist was applied to a (100) face of the crystals by spin coating. The resulting photoresist thickness was ≈1 μm. The crystal was then soft-baked at 95°C for 25 min. The crystal was next aligned and exposed in a 4:1 projection printer so that the vertical channel edge faces of the profile were also of {100} orientation (±≈1°). After exposure, the photoresist was developed by using a commercial developer concentrate. The crystal was then hard-baked at 120°C for 25 min.

In order to introduce the exposed pattern into the LiF, the photoresist was milled with an argon ion beam for 12 min. The milling rate was approximately 0.06 μm/min. The remaining photoresist was removed using a commercial resist remover (active ingredient n-methyl 2-pyrrolidone).

The crystals were annealed at 550°C for 15 h to remove surface contaminants and to relieve stresses caused by the processing steps. Following the anneal, the crystals were heat treated at temperatures between 680° and 770°C (0.81 and 0.91 T_m respectively) for varying time intervals. To prevent free evaporation and to achieve near-equilibrium conditions, two precautions were taken. First, the furnace chamber was evacuated to a pressure of 10^{-6} torr and then back-filled with 99.98% pure dry argon to 1 atm. Second, the crystal was placed on tungsten foil and another flat LiF crystal was positioned ≈1 mm above the profile. A type-K thermocouple was positioned on either side of the crystal to verify that temperature gradients were negligible.

Following the heat treatment, the crystals were quenched by removing them from the furnace and exposing them to ambient temperature. The cooling time is of the order of a few seconds. After cooling, each crystal was cut normal to the profile surface and mounted so that the profile cross-section could be studied directly by SEM. Photomicrographs representing a large sample of each of the profiles were collected. Typically, the dimensions of approximately six ridges in each profile were measured using an image analyzer and then averaged.

RESULTS

Each profile is identified subsequently by its intended channel width, *w*, and its intended channel spacing, *d*, in the following manner: *w/d*. By intended it is meant the dimensions designed into the mask reduced by a factor 4 to account for the 4:1 reduction during printing.

Representative morphologies of the initial profiles (following the 550°C anneal) are shown in Figure 1(a). The initial profiles are not perfectly rectangular; the channel walls slope somewhat (up to ≈30°), and there is some rounding of the corners. This configuration, which results in some high energy surfaces compared to the {100} type, is a result of the ion-beam milling procedure and has been reported by other investigators [6,7]. The profile depth and ridge cross-sectional areas were measured as indicated in Figure 1(b).

Profiles on a specimen that was annealed at 770°C for 4 h and quenched are shown in Figure 2(a). The profiles smoothed considerably compared to their initial geometries. The depth and cross-sectional ridge areas were measured with reference to the positive/negative curvature transition as shown in Figure 2(b). The initial depths and depth changes for profiles with a 10 μm ridge width are shown in Figure 3 , and the ridge areas and area changes for these profiles are shown in Figure 4. Both the depths and ridge areas decreased considerably from their initial values, but neither the depth changes nor the ridge area changes seem to depend on the profile geometry.

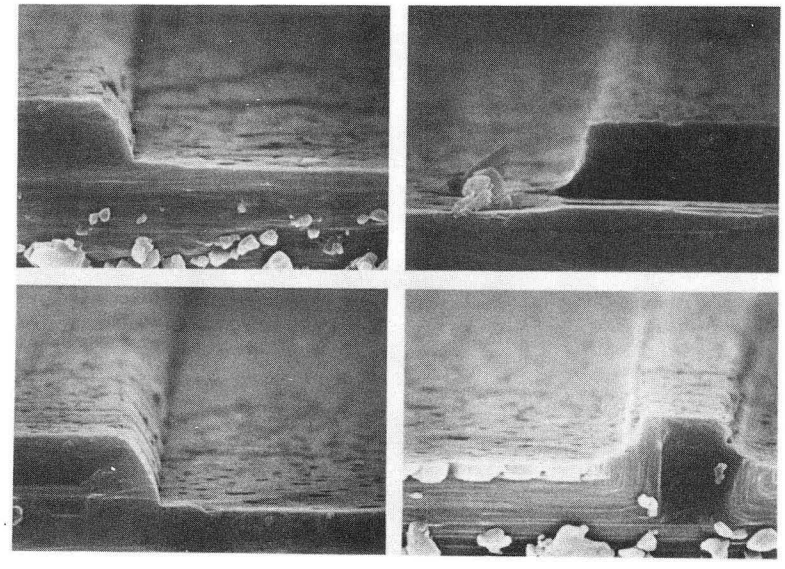
DISCUSSION

Examination of Figures 3 and 4 shows that, for constant ridge width, depths and areas of the rounded channels are reduced for the various geometries used, but variations in the measured geometries are large and no systematic variation with channel width or channel/ridge width ratio can be determined. The rounding of the profiles (and the decrease in depth and cross sectional areas at 770°C) is predicted by Mullins' model for sinusoidal decay, and therefore indicates that diffusion to surface sites may be the rate-limiting step in the process in this temperature range. By representing the profiles as a Fourier series, it is possible to predict the shapes of these initially faceted profiles at different times for a given temperature, as Mullins has indicated. This type of analysis was performed by assuming values for *B* and *C* in equation (1) and generating theoretical profiles with a computer. For typical values of *B* and *C*, surface diffusion is the dominant transport mechanism at this size scale. Measurements of cross sectional area and depth changes are displayed in Figures 5 and 6, respectively, and it appears that the theoretical and experimental data are in at least qualitative agreement. As stated earlier, this type of analysis is applicable only for small-slope profiles. Although the initial ridges are faceted, after a little smoothing takes place the small-slope assumption should be valid since, according to Mullins, this approximation applies to each Fourier term separately, and all but the high-frequency terms will have small slope for the profile geometries analyzed.

To see if the shape changes can arise from a near-equilibrium process, the shape evolution was also modeled by an energy minimization scheme. In this model the profile was composed of discrete elements or atoms arranged on a square lattice, and mass transport was simulated by repetition of a process in which a surface element with highest bonding energy is moved to an unoccupied surface site with lowest bonding energy. This model was examined using up to 5th-nearest neighbor interactions according to a coulombic potential.

Because relative rates of the diffusion and of the attachment and detachment steps were unknown, the shapes predicted by the two models were compared when their calculated ridge area reductions were equal to the experimental reductions (Figure 6). It is apparent by comparison with Figure 3 that both models agree with experimental data to within the experimental error. Both models give similar depth changes, but the depth change using energy minimization is, like the experimental data, less sensitive to profile geometry than in the Mullins model. Qualitatively, profile shapes produced by both models were very similar to the majority of profiles observed experimentally. The comparisons suggest that caution should be used when deriving kinetic data from surface smoothing experiments.

(a)



5 µm

(b)

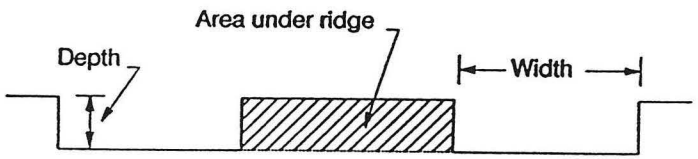
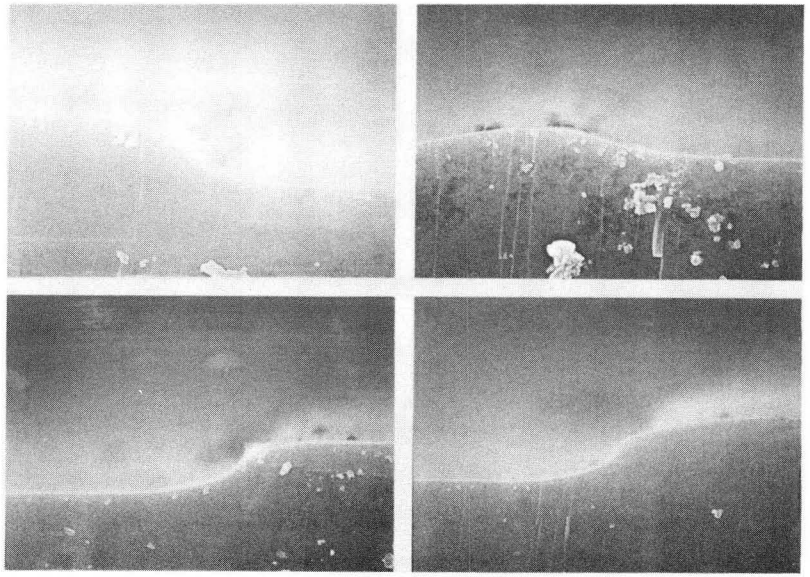


Figure 1 a) Representative initial profiles (following 550°C anneal), and b) dimensions measured for initial profiles.

(a)



5 µm

(b)

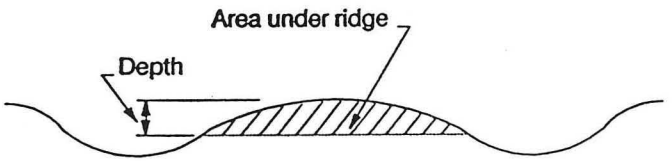


Figure 2 a) Representative profiles from a specimen heated at 770°C for 4 h and quenched, and b) dimensions measured for rounded profiles.

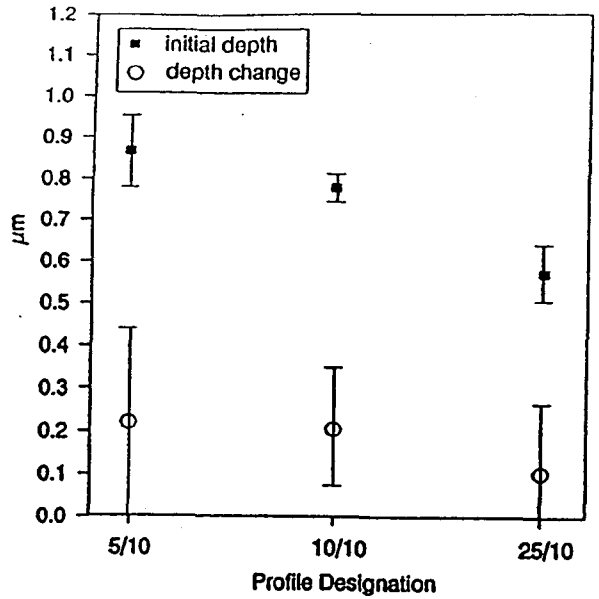


Figure 3 Initial depth and depth changes for profiles with a 10 μm intended ridge width. Error bars indicate 64% confidence limits.

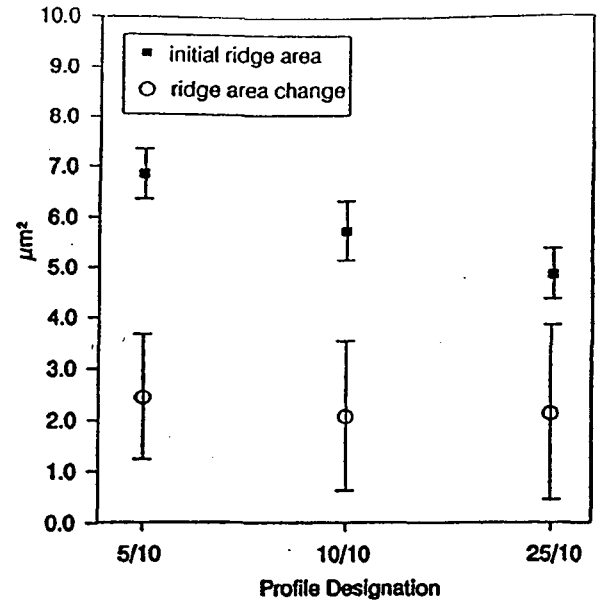


Figure 4 Initial ridge cross-sectional area and area changes for profiles with a 10 μm intended ridge width. Error bars represent 64% confidence limits.

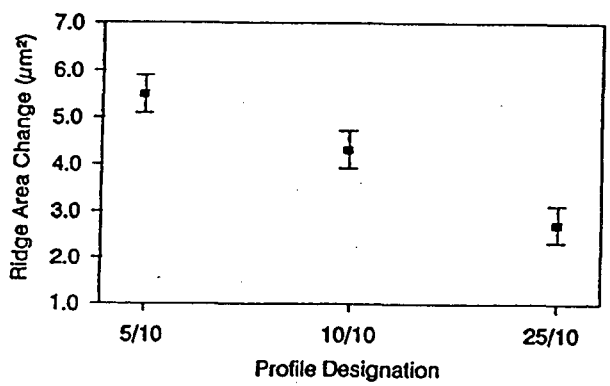


Figure 5 Ridge cross-sectional area changes for profiles with a 10 μm ridge width predicted by Mullins model.

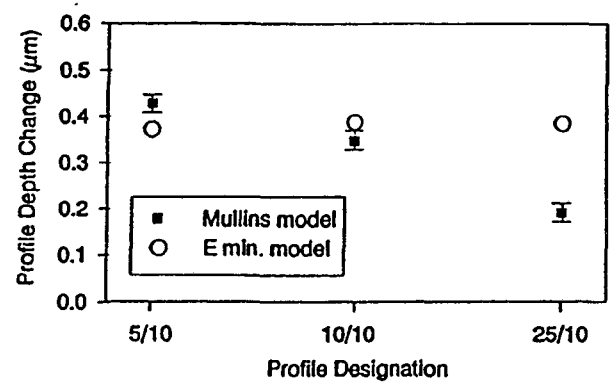


Figure 6 Comparison of profile depth change resulting from the Mullins model and a surface energy minimization model.

SUMMARY

The rate of evolution of rounded profiles in LiF {100} surfaces was dependent on the profile dimensions. Comparison of the results to both a diffusion-based model and an energy-based model indicated that profile shapes can evolve similarly regardless of whether diffusion or a near-equilibrium step of surface attachment or detachment is rate-limiting.

ACKNOWLEDGEMENTS

The authors wish to thank Russell Cinque and C.P. Burmester for their contributions to the energy minimization modelling. The research was supported by the Director, the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. J. E. Burke, in The Chemical and Mechanical Behavior of Inorganic Materials, edited by A. W. Searcy, D. V. Ragone, and U. Colombo (Wiley-Interscience, New York, 1970) pp. 413-441.
2. W. W. Mullins, in Metal Surfaces: Structure, Energetics, and Kinetics, (ASM, Metals Park, Ohio, 1963) pp. 17-65.
3. E. B. Slamovich and F. F. Lange, *J. Am. Ceram. Soc.*, 73, [11], 3368-75 (1990).
4. B. E. Sundquist, *Acta Metall.*, 12, 585-92 ((1964).
5. J. Rödel and A. M. Glaeser, *J. Am. Ceram. Soc.*, 70, [8], C172-C175 (1987).
6. P. G. Gloersen, *J. Vac. Sci. Tech.*, 12, [1], 28-35 (1975).
7. C. M. Melliar-Smith, *J. Vac. Sci. Tech.*, 13, [5], 1008-22 (1976).

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720