

The behavior of LiF-coated metal anodes in pulsed electric fields

P. R. Schwoebel and J. A. Panitz

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

(Received 30 September 1991; accepted for publication 18 November 1991)

Investigations of ion emission from LiF-coated metal anodes subjected to pulsed electric fields are reported. For LiF films having a thickness greater than 1000 Å, catastrophic vacuum arcs are initiated by electric-field pulsing. With films having a thickness less than 500 Å field-stress-induced film removal proceeds direct field evaporation of Li^+ from the anode surface.

I. INTRODUCTION

The search for ion sources suitable for light-ion inertial confinement fusion (ICF) reactors has followed several avenues.^{1,2} Given the present capabilities of pulsed-power technology, ion-beam/target-interaction considerations indicate that Li^+ is the preferred ion species for light-ion ICF.² As part of the ion source development effort, the production of ions from LiF films subjected to large, pulsed electric fields is being investigated.²

The behavior of alkali halides in large dc electric fields has been the subject of investigation for many years. Studies range from the characterization of fundamental dielectric breakdown phenomena³ to the investigation of thermally assisted field desorption of ions.⁴ Ion emission studies from LiF-coated field-emitter tips were initiated previously.⁵ Although ion emission was observed in these experiments, mass analysis of the species was not performed.

In this paper we report the ions species produced when vapor-deposited LiF films are subjected to pulsed electric fields. The experimental results are rationalized through simple theoretical considerations.

II. EXPERIMENT

The experimental chamber is essentially an UHV imaging atom probe mass spectrometer⁶ operating in the low 10^{-10} -Torr range. The anodes were annealed (~ 3000 K) tungsten emitter tips having an end radius of curvature on the order of 2000 Å and coated with LiF by vapor deposition in a separate high-vacuum system. The LiF-coated emitter tips were imaged in a transmission electron microscope (TEM) prior to and following ion emission experiments. The electric fields on the anode surface before coating with LiF were characterized by Fowler-Nordheim analysis, through which the standard field-voltage relation⁷ for well-annealed emitter tips, $F = V/5r$, where F is the magnitude of the electrostatic field at the tip apex, V is the applied voltage, and r is the emitter tip end radius, was found to be adequate.

Voltage pulses having an ~ 3 -ns rise time, 20-ns duration, and maximum magnitude of 25 KV were applied to the anode tip using a spark-gap-switched, cable-discharge pulse generator. Ion species were determined with time-of-flight (TOF) mass spectrometry by digitizing the channel-electron multiplier output signal versus time. The presence

of the channel plate backed by a phosphor screen allowed for simultaneous viewing of the ion's spatial distribution.

III. RESULTS

A. Film morphology characterization

LiF was vapor deposited onto the W field-emitter tips in vacuums of $\sim 10^{-7}$ Torr from a heated W coil containing LiF. The tip was aligned coaxially with the axis of the coil, and was maintained at room temperature. The deposition rate of ~ 500 Å/s was not varied; only the deposition time was used to control the film thickness. Under these conditions, subsequent film morphology characterization in a TEM showed basically three distinct film "types."

For thicknesses d less than ~ 500 Å, the film is smooth on a nanometer scale [see Fig. 1(a)]. Although electron-diffraction experiments were not performed, other literature suggests that such films are predominately polycrystalline, with a slight preference towards a [100] orientation.⁸

With films of intermediate thickness, $500 \text{ Å} < d < 1000 \text{ Å}$, the nucleation of crystallites begins on the underlying smooth film [see Fig. 1(b)]. Further deposition results in the nucleation and growth of more crystallites.

As the films become thicker, $d > 1000 \text{ Å}$, whisker growth, with most likely a [111] orientation,⁸ becomes the dominant mode of film growth [see Fig. 1(c)]. These characteristics of film growth are apparently associated with an increasing diffusion coefficient for the incident LiF molecules. For the thin films ($d < 500 \text{ Å}$), good thermal contact with the room-temperature W emitter tip results in relatively rapid thermal accommodation and therefore in the growth of very small crystals. As the film thickness increases, the thermal contact is degraded by the presence of a thicker LiF film, resulting in greater diffusion coefficients. Crystallite growth is followed by whisker growth as the diffusion coefficient is increased further.

B. LiF-pulsed electric-field results

1. Thick films ($\geq 1000 \text{ Å}$)

With thick LiF films, electric-field pulsing always leads to the initiation of catastrophic vacuum breakdown. The resulting arcs cause melting of the emitter tips (see Fig. 2). These arcs saturate the channel-plate detector making species identification difficult. Typically it appears as though the first ions to arrive at the detector correspond to a

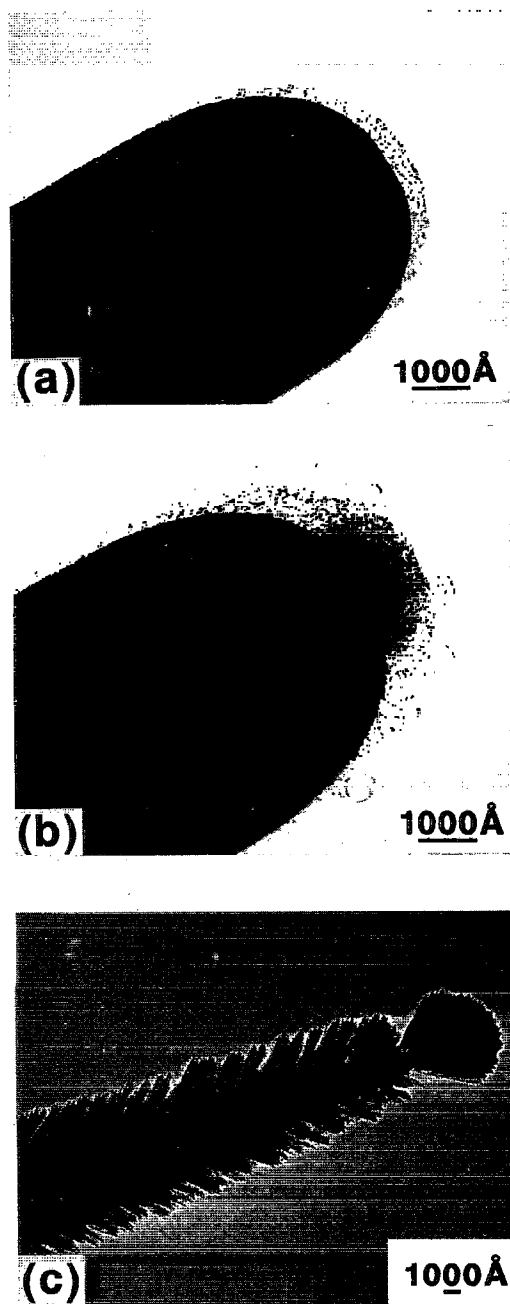


FIG. 1. TEM micrographs showing the change in LiF film morphology as a function of film thickness: (a) 400-Å LiF film; (b) 800-Å LiF film; and (c) ~5500-Å LiF film.

charge to mass ratio of 7, very possibly Li^+ . Due to the complex film morphology, it is difficult to make a good estimate of the electric fields in or at the surface of the LiF when vacuum breakdown occurs. However, the electric field at the surface of the uncoated LiF emitter tip would be on the order of $1 \text{ V}/\text{\AA}$ when vacuum breakdown is initiated. This implies that the electric field in the LiF film is at least several MV/cm.

2. Thin films ($d \lesssim 500 \text{ \AA}$)

Thin films of LiF typically yielded mass spectra as a function of applied electric field like those shown in Fig. 3.

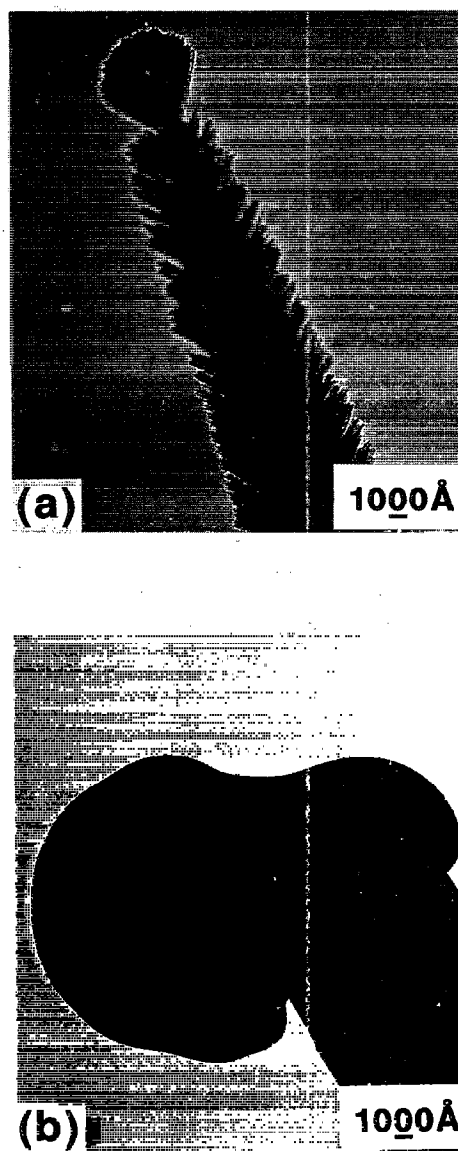


FIG. 2. The emitter tip of Fig. 1(c): (a) prior to field pulsing, and (b) following voltage pulsing at 4.3 kV at which point a vacuum arc was initiated. The melting of the tungsten substrate is evident.

As the applied field is increased from zero, initially no ions are observed. At fields on the order of $0.36 \text{ V}/\text{\AA}$ on the LiF surface ($0.04 \text{ V}/\text{\AA}$ inside the LiF) protons are observed. Often not much change in the proton signal is seen with increasing fields. Once fields at the surface of the LiF film are on the order of ~ 1.0 – $1.5 \text{ V}/\text{\AA}$, Li^+ -ion emission is observed, with an intensity that increases with increasing applied field. At fields of $\sim 1.5 \text{ V}/\text{\AA}$, up to 10 pulses at constant voltage have been applied with no significant change in the Li^+ intensity.

It was very interesting to find that subsequent imaging of the thin-film-type anode tips in the TEM always showed a bare emitter tip surface, i.e., the LiF layer was totally removed from the tip surface (see Fig. 4). Several experiments were conducted in which the magnitude of the pulsed electric field was increased just until Li^+ -ion emis-

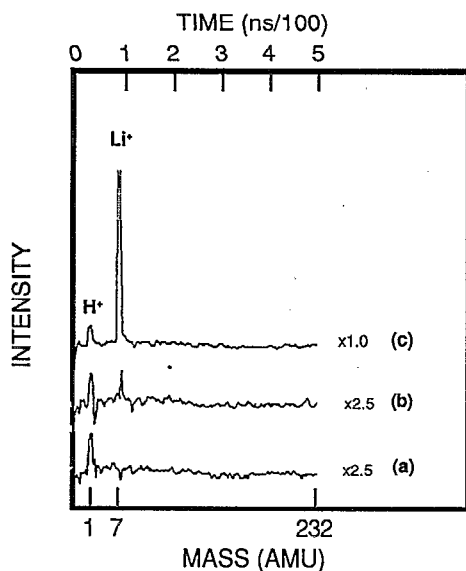


FIG. 3. A typical TOF mass spectrum obtained from LiF films ≤ 500 Å in thickness. The voltages of curves (a), (b), and (c), correspond to 13.5-, 14.4-, and 15.3-kV voltage pulses, respectively. The TEM image of this tip is shown in Fig. 1(a); W tip radius of 2200 Å, and a LiF layer thickness of 400 Å.

sion was distinct. Pulsing was then stopped yet subsequent TEM imaging still showed no trace of a LiF film on the emitter tip surface. The TOF spectra in Fig. 3 and the TEM images in Fig. 4 correspond to such an experiment.

To aid in interpretation of the film removal/ Li^+ production mechanism, an emitter tip was revoltage pulsed after TEM verification of prior film removal. Interestingly enough, H^+ followed by Li^+ emission was again observed at fields (voltages) comparable to those at which such ion emission was observed before TEM verification of the film removal.

Typically, in all cases with thin LiF films the ion emission spatial distribution was uniform; i.e., the phosphor screen showed homogeneous illumination.

3. Intermediate films ($500 \text{ Å} < d < 1000 \text{ Å}$)

Films of intermediate thickness behave either as thick or thin films. In certain cases voltage pulsing leads to vacuum breakdown as discussed above for thick films. In other cases, the results are basically identical to those typical of thin films. No distinct characteristic of the intermediate-thickness LiF films has been identified that would allow one to predict which mode of behavior will be observed upon applying pulsed fields.

IV. DISCUSSION

A. Background

There are several physical phenomena worthy of discussion prior to interpreting the results obtained with the LiF films discussed above.

The dielectric breakdown of alkali halides has been investigated quite extensively.⁹ Rather definitive experimental work was done by von Hippel³ in the 1930s. From

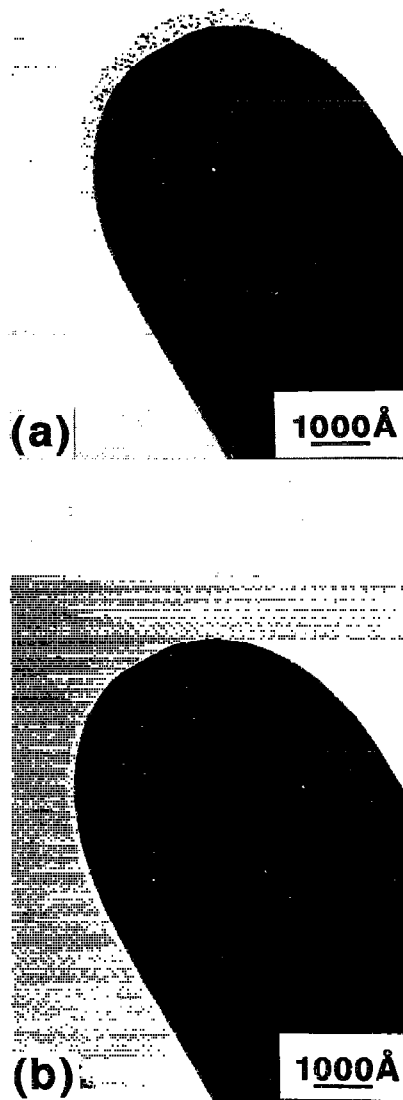


FIG. 4. A TEM micrograph of the emitter tip used for the TOF mass spectrum shown in Fig. 3: (a) prior to field pulsing, and (b) following pulsing to 15.3 kV. The LiF layer has been totally removed.

such data the dielectric breakdown field for bulk LiF is found to be on the order of 3 MV/cm. Although no strong dependence upon film thickness has been found in the past experimentally, data for films on the order of several 1000 Å in thickness or less could not be found.

Local-field strengths at the surface of the LiF films is another important consideration. For example, in the case of whiskers having a given height-to-width ratio, what is the resulting field enhancement factor at the whiskers apex? In order to address such questions we have investigated the field enhancement factor as a function of eccentricity for a dielectric ellipsoid. Using the electrostatic potential associated with a dielectric ellipsoid oriented such that its major axes is in the direction of an applied electrostatic field,¹⁰ one can calculate the field enhancement factor just outside the surface at the ellipsoid's apex. A very in-

teresting result of this calculation is that the field enhancement factor asymptotically approaches the dielectric constant of the ellipsoid as the ellipsoid's eccentricity approaches 1 (i.e., as it becomes "needlelike"). Thus, for LiF the maximum field enhancement factor to be found just above its surface is 9, LiF's dielectric constant.

Finally, we note that the stresses associated with electric-field strengths on the order of a $0.1 \text{ V/\AA}$, applied to the surface of LiF single crystals, are in the range of the mechanical yield strength of this material.¹¹

B. Interpretation of results

1. Thick films

The vacuum arcing associated with the thick films is, of course, indicative of large quantities of ions and/or electrons being injected into the vacuum gap. The exact cause is difficult to clarify since several possible factors may enter into initiating the vacuum breakdown process. Recall that the electric fields which would be present on the emitter tip surface, assuming that no LiF were present, are on the order of $1 \text{ V/\AA}$ when vacuum breakdown is observed. Even ignoring the field enhancement factors at the LiF surface due to roughness, this implies that the electric field inside the LiF exceeds that required for bulk dielectric breakdown. In addition, the fields on the surface of the LiF layer are on the order of those associated with the mechanical yield strength of the bulk material. Finally, one would expect that the bonding at the W/LiF interface could be less than that associated with the LiF/LiF bonding in a bulk sample of LiF crystal. If this is the case, then yielding of the LiF layer near or at the interface could also be expected to occur in the fields present when vacuum breakdown is initiated. The results of our experiments do not allow one to determine conclusively which of these phenomena, if any, are dominant in initiating the observed vacuum breakdown with thick films.

2. Thin films

As the ion emission from thin films under the pulsed field conditions is well behaved, the mechanisms of film removal/ion formation are somewhat easier to clarify.

From Fig. 3 we see that no catastrophic ion emission occurs as the magnitude of the pulsed field is increased. Initially, Hr^+ is observed, followed by Li^+ emission at fields of $1\text{--}1.5 \text{ V/\AA}$. Such a result indicates that dielectric breakdown of the LiF layer does not occur in the thin films, since one would expect to see a characteristic ion spectra associated with the dielectric breakdown event. The observation of Li^+ in fields of $1\text{--}1.5 \text{ V/\AA}$ is consistent with direct field desorption of Li^+ from Li-coated W field-emitter tips.¹² This indicates that the LiF layer is removed from the W substrate by field stresses associated with small enough fields that no significant ion formation occurs; the layer removal event is then undetectable by our TOF mass spectrometer which is only sensitive to charged particles. Following layer removal, some Li is left behind on the W surface and this is subsequently field desorbed in fields approaching $\sim 1.5 \text{ V/\AA}$.

V. CONCLUSION/FUTURE EXPERIMENTS

These experiments indicate that field desorption of Li^+ from intact LiF coatings is not possible using LiF-coated metal anodes at room temperature. For the thin films field-stress-induced removal of the LiF coating occurs before fields necessary for ion formation are achieved. Subsequent emission of Li^+ occurs from LiF residue on the anode surface. With thick films catastrophic vacuum arcs are initiated prior to the onset of any controllable ion emission process. Experiments should be conducted in which field pulsing is done in tandem with TEM imaging of thin films. This would allow one to quantify the field at which the LiF layer is removed. In addition, it would aid in the interpretation of the aforementioned results if the dielectric breakdown strength of single-crystal thin ($< 1000 \text{ \AA}$) films of LiF was quantified.

It would be surprising if substrates other than W, or emitter-tip/LiF-coating annealing treatments, would drastically alter the general behavior we have observed. With these considerations in mind, a valuable future experiment would be to study LiF-coated field-emitter tips under pulsed field operation at elevated temperatures. If dielectric breakdown can be suppressed with very thin films of LiF, it may be possible to reduce the activation barrier to field desorption sufficiently at elevated temperatures that Li^+ emission can be achieved without field-stress-induced layer removal.

ACKNOWLEDGMENTS

This work was supported by Sandia National Laboratories under Contract No. 75-4246, and in part by the United States Department of Energy under Grant No. DE-FG04-88ER45348.

- ¹J. P. Vandevender and D. L. Cook, *Science* **232**, 801 (1986).
- ²R. A. Gerber, in *The Physics and Technology of Ion Sources*, edited by I. Brown (Wiley, New York, 1989), Chap. 18.
- ³A. von Hippel, *J. Appl. Phys.* **8**, 815 (1937).
- ⁴F. Okugama, S. S. Wong, and F. W. Röllgen, *Surf. Sci. Lett.* **151**, L131 (1985).
- ⁵J. A. Panitz, A. L. Pregonzer, K. W. Bieg, and R. E. Olson, *J. Appl. Phys.* **67**, 7556 (1990).
- ⁶J. A. Panitz, *Prog. Surf. Sci.* **8**, 219 (1978).
- ⁷R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, MA, 1961).
- ⁸L. G. Schultz, *J. Chem. Phys.* **17**, 1153 (1949).
- ⁹R. Stratton, in *Progress in Dielectrics 3*, edited by J. B. Birks and J. Hart (Wiley, New York, 1961), p. 235.
- ¹⁰J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), p. 213.
- ¹¹E. Gillam, *Materials Under Stress* (CRC, Boca Raton, FL, 1969); J. J. Gilman and W. G. Johnson, in *Solid State Physics: Advances in Research and Applications 13*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), p. 148.
- ¹²V. M. Gavriluk and V. K. Medvedev, *Sov. Phys. Tech. Phys.* **11**, 1282 (1967).