

Electron emission characteristics of sputtered lanthanum hexaboride

Susan J. Mroczkowski

Midwest Research Technologies, Inc., Milwaukee, Wisconsin 53218

(Received 17 September 1990; accepted 28 January 1991)

Magnetron sputtering was used to deposit a thin film of lanthanum hexaboride for cathode structures. The chemistry of the coatings was studied with x-ray diffraction, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. The work function and electron emission characteristics of the coating have been studied in a diode test cell using tungsten and rhenium as substrates and controls. After optimization of sputtering parameters such as sample bias, forward power, base pressure, and argon flow rates, coatings were obtained with a work function of 2.4–2.6 eV. At 1200 K, the emission density of a lanthanum hexaboride coated tungsten filament was 8.8 mA/cm² while the emission density of a clean tungsten filament was 9.7×10^{-12} A/cm². Coated tungsten filaments ran over 1000 h without any reduction in the emission current in a vacuum of 10^{-7} Torr. Coated filaments were flexed with moderate severity without microcracking, spalling, or a detectable difference in emission characteristics. After an initial activation, the lanthanum hexaboride-coated filaments were exposed to the atmosphere without a subsequent reduction in emission current density. Surface analysis indicated that the surface of the cathode was primarily lanthanum oxide.

I. INTRODUCTION

Thermionic emission is defined as the outflow of electrons from a substance into vacuum as a result of heat. The phenomenon of thermionic emission is related to the material work function—the minimum energy needed to remove an electron from the Fermi level of the substrate to infinity. At high temperatures, some electrons gain sufficient energy to overcome the work function (Φ) of the cathode material. The Richardson equation expresses the emission current density J from the cathode as:

$$J = AT^2 \exp(-e\Phi/kT) \text{ A/cm}^2 \quad (1)$$

where A is a constant which is a function of the material and T the emission temperature. For a tungsten filament at a typical operating temperature of 2700 K, J is equal to 1.75 A/cm² (assuming that $A = 60 \text{ A/cm}^2 \text{ K}^2$ and $\Phi = 4.5 \text{ eV}$).

Since the research of Lafferty¹ demonstrated the low work function of lanthanum hexaboride (LaB₆), it has been used as an electron source in various types of configurations. Higher brightness electron guns have been developed by Broers^{2,3} using a lanthanum hexaboride rod cathode with $J = 65 \text{ A/cm}^2$ at 1873 K with A equal to $40 \text{ A/cm}^2 \text{ K}^2$ and $\Phi = 2.4 \text{ eV}$. Either a rod of sintered LaB₆ or a single crystal of LaB₆ is indirectly heated to induce emission, or metal filaments such as tungsten, rhenium, and tantalum are electrophoretically coated with LaB₆, annealed and directly heated. Although very good emitters, both types of filaments are generally fragile and can withstand only a minimum amount of thermal shock; Indirectly heated LaB₆ electron sources complicate the design of electron guns and thereby increase the cost of the system. Single crystals of LaB₆ are moderately expensive. The price for a lanthanum hexaboride electron microscope filament assembly ranges from 400–600 dollars, contrasting with approximately 10 dollars for a simple tungsten hairpin assembly.

Metal filaments with an electrophoretically deposited

coating were described by Favreau.⁴ This type of filament, although simple in design and moderately successful as an emitter, is mechanically delicate. This problem can make installation difficult and/or reduce the lifetime of the structure. Research on electrophoretic coating with LaB₆ performed in 1969 and 1973 by Ford and Lichtman^{5,6} is similar to that reported in 1985 by Khairnar *et al.*⁷ These methods produce coated cathodes that are porous, rough, and prone to spalling because of weak coating adhesion. Preparation is difficult because pre- and post-coating heat treatments of the filaments are necessary. Khairnar carburized tantalum wire before coating to stop the diffusion of boron into the metal. Khairnar states that the LaB₆ coatings which were smooth, had a low porosity, and superior adhesion to the substrate gave better emission stability. LaB₆ deposited by sputtering should provide these characteristics.

Additionally, sputter-deposited LaB₆ coatings should be superior because there are no electrolytes used which can preferentially react with either the lanthanum or boron. Sputter-deposited ceramic coatings in general are more adherent, dense, and smoother than coatings deposited by electrophoretic methods. There is very little porosity. The coating is applied in a high vacuum environment so there should be significantly less outgassing than from plating methods. Diffusion barriers such as titanium nitride could be applied to tantalum filaments, perhaps avoiding the need for carburization.

A paper describing sputtered LaB₆ was published in 1971 by Cuomo⁸ at IBM. The work appears to have been successful. Using insulating substrates, he sputtered LaB₆ through a mask to form a thin filament pattern which was then connected with leads to appropriate power supplies. Although no other papers on sputtered LaB₆ from that group were found, there was a publication⁹ from a related group at IBM in 1985 dealing somewhat peripherally with laser sputtering of LaB₆.

Li and Wan¹⁰ deposited LaB₆ coatings onto tantalum us-

ing dc-diode sputter deposition and found that a high forward power resulted in poorly adhering films. They recommended heating during deposition and found interaction between the boron and the tantalum. Bessaraba *et al.*¹¹ compared LaB₆ films prepared by rf sputtering, resistive evaporation, and electron beam evaporation using reflection spectroscopy. No work function measurements were reported. A Soviet group led by Kondrashin¹² manufactured thin-film coatings of LaB₆ deposited by using a pulsed plasma accelerator. The authors claim to have "serious difficulties in industrial utilization." The coatings had a work function that ranged from 2.40 to 2.55 eV.

The research reported here was directed towards producing adherent, low stress thin films of LaB₆ using rf magnetron sputtering. The films manufactured were studied to reveal correlations between the structure, stoichiometry, and emission properties of the films and the conditions under which they were produced.

The potential commercial applications for the coating are diverse. Planar cathodes are found in electron guns for cathode ray tube applications. This structure could involve a rhenium metallic cup with a front surface that can be LaB₆ coated. Other applications involve special forms, such as the filaments used in electron microscopes or ionization gauges and the large cathodes used in power tubes like klystrons, magnetrons, and traveling wave tubes. In production, the cathode structures would be preformed and coated with the LaB₆.

II. EXPERIMENTAL METHOD

The research focused on sputtering thin films from a lanthanum hexaboride target. The source material was an 8 in. diam target composed of 99.9% LaB₆ manufactured by Cerac, Inc. (Milwaukee, Wisconsin) with a density of 70%–85%. The target was bonded to an OFHC copper backing plate and loaded into a Materials Research Corporation Model 822 rf magnetron sputtering system. The substrates included tungsten and rhenium ribbon (H. Cross Company, Weehawken, New Jersey, 99.97%, 0.040 in. wide × 0.005 in. thick × 1 in. long) for emission testing and glass slides and silicon wafers for subsequent chemical analysis. The samples were inserted through a vacuum loadlock chamber into the main chamber which was pumped with a cryopump to the low 10⁻⁷ Torr range. Quadrupole RGA analysis indicated that water was the predominant residual gas. The chamber was then throttled and backfilled with 99.999% argon via a calibrated MKS flow control system. A matrix of experiments was conducted. The argon backfill pressure varied from 2–50 mTorr, the rf forward power from 250–1500 W with a resultant target voltage that ranged from 75 to 380 V. Bias voltages were applied that ranged from 0% to 20% of the target voltage.

The coated samples produced were inspected with a JEOL 35C scanning electron microscope (SEM). A VG Escalab system was used to determine the surface composition of the coatings with Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). A General Electric diffractometer with a copper target and a nickel filter was used to determine the crystallography of the coatings.

The emission properties of the fabricated cathodes were tested by construction of a simple diode structure with a known geometry. Current versus voltage (*I*–*V*) curves were obtained in accordance with the Langmuir–Child Law

$$J = kE^{3/2} \quad (2)$$

where *k* is a constant which includes geometrical effects and *E* is the applied potential. This procedure was used to establish the proper cathode-to-anode voltage to insure that the current readings were true emission-limited values. The emission current as a function of filament temperature was then recorded. The cathode temperatures were obtained with a thermocouple-calibrated optical pyrometer. The Richardson Equation [Eq. (1)] was rearranged so that a plot of $\ln(J/T^2)$ vs $1/kT$ has a slope of $-\Phi$. In this fashion, the work function of the various filaments was obtained and the *y*-intercept is used to determine the value of the constant *A*.

III. RESULTS

A. Film deposition

Films that were deposited with a relatively low argon backpressure (< 15 mTorr) were porous and powdery, as were films deposited with a higher (> 30 mTorr) argon pressure. Between 18 and 28 mTorr, the films were dense, adherent, moderately reflective, and purple-gray in color. In that regime, the coatings showed no signs of residual stress. At 1000 W forward power, the deposition rate was approximately 1 μm per hour. A relatively low bias had no visible effect on the coatings; if the bias exceeded 15% of the target voltage, the coatings were again powdery. Changing the forward power from 250 to 1500 W also had no visible effect on the coating quality.

B. Analytical results

Utilizing SEM, it was found that the films usually had a dense, columnar structure as illustrated in Fig. 1. However,

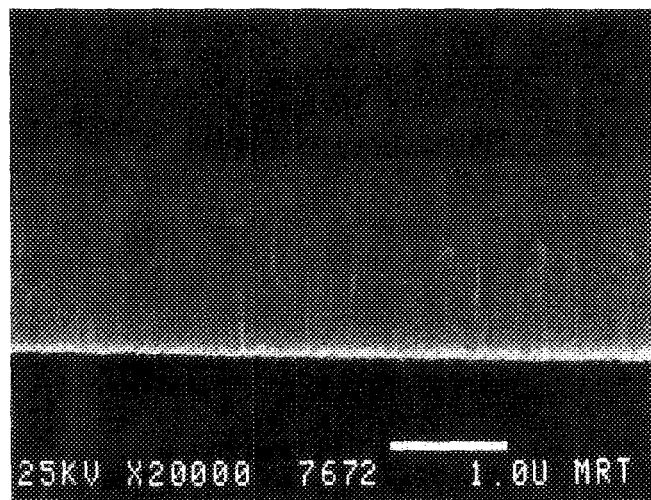


FIG. 1. Scanning electron micrograph of lanthanum hexaboride deposited onto silicon. The typical columnar structure, high density, and smooth surface are evident.

coatings deposited with 250 W forward power were amorphous. Depositions done with a substrate bias had a rougher surface than those without bias. Electron microscopic examination was performed after filament flexing experiments. Approximately $1\ \mu\text{m}$ of LaB_6 was deposited onto a 2 in. long segment of tungsten ribbon. The filament was flexed in the concave direction and in the convex direction a total of 20 times to a radius of curvature of $\frac{1}{2}$ inch. Inspection of the coating indicated that there was no microcracking or spalling after flexing. The flexed samples were later included in emission testing.

X-ray diffraction was used to compare the crystallography of bulk LaB_6 to the coatings deposited on silicon wafers as illustrated in Figs. 2(a) and 2(b). The pattern on the film matched the bulk material with a strong preferred orientation to the (200) plane. No peaks due to oxides of lanthanum or boron were detected.

The surface composition of the filaments was routinely determined with Auger electron spectroscopy and x-ray photoelectron spectroscopy. Polished fragments from the target were used as a standard and analyzed in parallel with the coated filaments. The films deposited in the range of 18–28 mTorr argon and without substrate bias were similar to the standard, as shown in Figs. 3(a) and 3(b). The fine structure of the lanthanum peaks is similar, with a predominant peak at 748 eV. Films deposited with a bias exhibited boron depletion with an approximate 4:1 boron-to-lanthanum ratio. Varying the power during deposition had no statistical effect on the ratio.

An XPS spectrum of the as-deposited coating was compared to that from a polished standard. The high resolution

lanthanum $3d_{3/2}$ and $3d_{5/2}$ peaks are illustrated in Figs. 4(a) and 4(b). From these scans, the surface of the coating contains a component of lanthanum oxide in addition to the lanthanum hexaboride.

C. Emission testing

Using the structure shown in Fig. 5, the cathode-to-anode potential difference during testing was in the range of 200–300 V. The test system pressure was typically 5×10^{-8} Torr. The current through the filaments was increased slowly and it was determined that an activation process was required that consisted of heating the coated filaments to approximately 1100 K for 30 min. After the initial period, the filaments could be turned off and on repeatedly or exposed to the atmosphere without requiring additional stabilization heating.

In order to study the changes in the coating during operation, filaments were heated to 1100 K for various lengths of time and the surface composition was obtained with AES and XPS. It was established that after the activation period, the surface was considerably lanthanum enriched. After approximately 50 h, the boron-to-lanthanum ratio was 2.5. After an emission test that lasted for 300 h, only a trace amount of boron was detected with AES [Fig. 3(c)]. High resolution XPS of the lanthanum 3d peaks of the 300-h test coating clearly showed that the coating at this time is primarily lanthanum oxide [Fig. 4(c)]. The observation of lanthanum surface enrichment agrees with the findings of Chambers and Swanson¹³ and Oshima and Aono.¹⁴

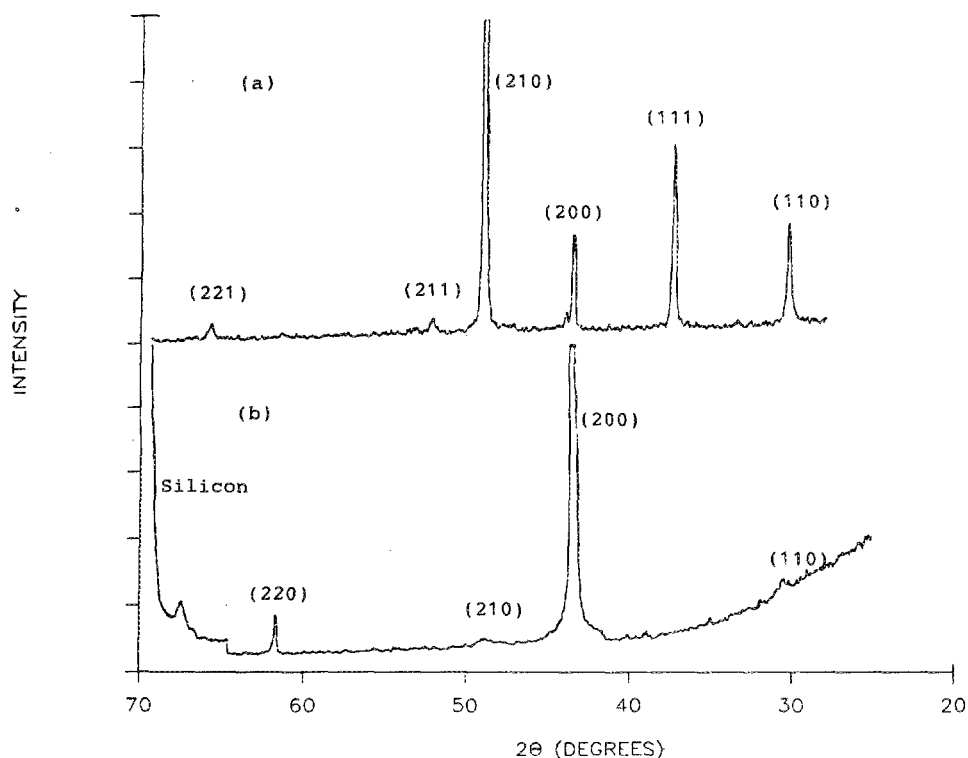


FIG. 2. X-ray diffraction patterns of (a) polycrystalline lanthanum hexaboride standard and (b) rf sputtered coating of lanthanum hexaboride on silicon substrate.

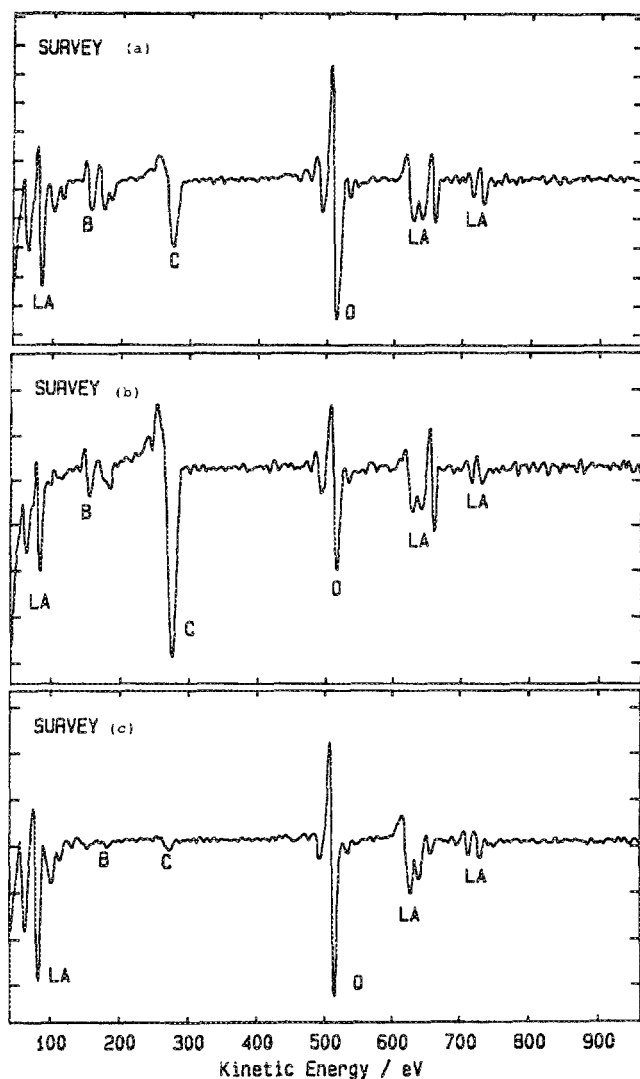


FIG. 3. Auger electron spectroscopy scan of (a) polycrystalline lanthanum hexaboride standard, (b) rf sputtered coating of lanthanum hexaboride, and (c) lanthanum hexaboride coating after 300 h of emission testing.

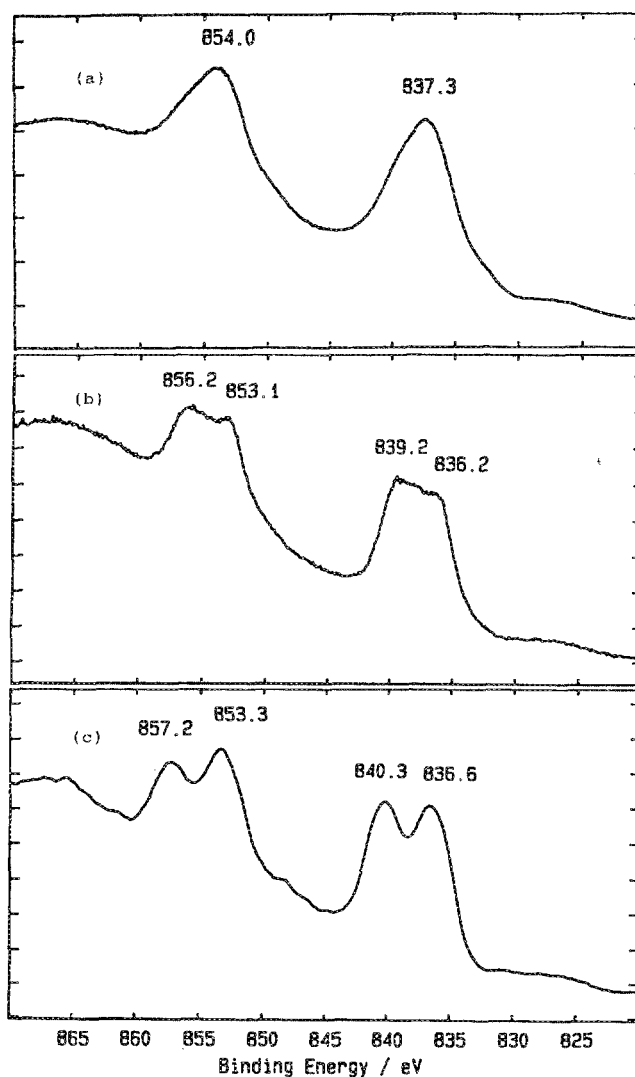


FIG. 4. X-ray photoelectron spectroscopy high resolution scans of the lanthanum 3d peaks from (a) polycrystalline lanthanum hexaboride standard, (b) as-deposited coating of lanthanum hexaboride, and (c) lanthanum hexaboride coating after 300 h of emission testing.

After the activation process, the filaments were heated and the emission current density was measured. At 1200 K, the emission density of a lanthanum hexaboride coated tungsten filament was 8.8 mA/cm^2 while the emission density of a clean tungsten filament was $9.7 \times 10^{-12} \text{ A/cm}^2$. Coated rhenium filaments behaved in an identical manner. Above 1300 K, this particular cathode/anode structure became space-charge limited with an emission current density leveling to 0.01 A/cm^2 .

The temperature was increased incrementally from 1000 to 1400 K. The emission values were converted so that they could be inserted into the rearranged Richardson equation and plotted as shown in Fig. 6. Also superimposed on the experimental data are the theoretical values for tungsten and lanthanum hexaboride. Most of the adherent, low stress lanthanum hexaboride-coated tungsten filaments yielded work functions of approximately 2.4 eV. Total emission cur-

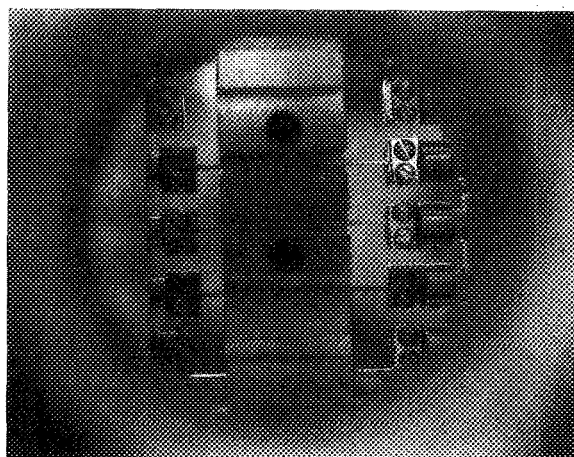


FIG. 5. Diode test cell with three coated filaments in place.

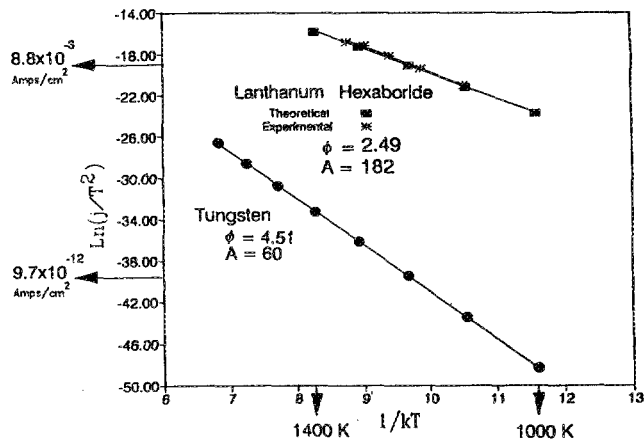


FIG. 6. Richardson equation plot from lanthanum hexaboride sputter deposited onto a tungsten support. Included for comparison are the theoretical plots for lanthanum hexaboride and tungsten.

rent regularly agreed with theoretical predictions for bulk lanthanum hexaboride. There were certain deposition conditions, however, where this agreement was not found. Coatings that were deposited with a low forward power (200–500 W) or a high bias (> 10% of the target voltage) had emission current densities an order of magnitude lower than predicted by theory. These lower emission levels could be due to an amorphous structure and a rougher surface as detected during electron microscope analysis.

Filaments that had been flexed before insertion were compared to filaments that had not been flexed. There was no difference in their electron emission current. A coated tungsten filament was lifetime tested at 1200 K; the output from a 1- μm thick coating was stable for over 1000 h. The test was halted at that time in the interest of performing other experiments and there was no evidence of deleterious substrate-coating interactions. Some of the coated filaments were exposed to the atmosphere after initial testing; after test chamber evacuation, the emission current resumed its preatmospheric exposure level. No additional activation was necessary.

IV. CONCLUSIONS

It was determined that a useful and practical electron source can be manufactured by coating metallic substrates

with lanthanum hexaboride deposited by radio frequency sputtering. Basic emission characteristics were measured by constructing a simple diode device and it was determined that thin film lanthanum hexaboride had emission currents that agreed with theoretical predictions for bulk LaB_6 material. Coated structures can be flexed for ease in installation. A room-temperature cathode could be exposed to the atmosphere without subsequent decrease in emission current. The data obtained thus far indicate that the improved electron source yields higher emission at lower temperatures with simpler electronics than currently many available cathodes.

ACKNOWLEDGMENTS

This work is supported by the State of Wisconsin Department of Development Grant TDF 9–2 and the University of Wisconsin-Milwaukee and was supported by the National Science Foundation award DMR-8760262. Helpful discussions with David Lichtman at the University of Wisconsin-Milwaukee and Norman Draeger at Midwest Research Technologies, Inc. are gratefully appreciated. John Kammer aided with the cathode manufacture and the electron microscopy analyses.

¹J. M. Lafferty, *J. Appl. Phys.* **22**, 299 (1951).

²A. N. Broers, *J. Appl. Phys.* **38**, 1991 (1967).

³A. N. Broers, *J. Physics E* **2**, 273 (1969).

⁴L. J. Favreau, *Rev. Sci. Instrum.* **36**, 856 (1965).

⁵R. R. Ford and D. Lichtman, *J. Appl. Phys.* **40**, 5088 (1969).

⁶R. R. Ford and D. Lichtman, *J. Appl. Phys.* **44**, 4378 (1973).

⁷R. S. Khairnar, P. W. Mahajan, D. S. Joag, A. S. Nigavkar, and P. L. Kanitkar, *J. Vac. Sci. Technol. A* **3**, 398 (1985).

⁸J. J. Cuomo, *IBM Tech. Disclosure Bull.* **13**, 3282 (1971).

⁹R. Kelly, J. J. Cuomo, P. A. Leary, J. E. Rothenberg, B. E. Braren, and C. F. Aliotta, *Nucl. Instrum. Methods Phys. Res. B* **9**, 329 (1985).

¹⁰X. Li and Y. Wan, *J. Zhejiang Univ.* **20**, 53 (1986).

¹¹V. I. Bessaraba, L. A. Ivanchenko, Yu. B. Paderno, A. V. Skosarev, L. I. Chernenko, and V. N. Shevtosov, *Poluch. Svoistva Tonkikh Plenok* **82**, (1982).

¹²A. A. Kondrashin, V. N. Cherynaev, V. F. Lorzo, and V. G. Blokhin, *Inorg. Mater.* **18**, 34 (1982). Translated from *Izv. Akad. Nank SSSR, Neorg. Mater.* **18**, 44 (1982).

¹³S. A. Chambers and L. W. Swanson, *Surf. Sci.* **131**, 385 (1983).

¹⁴C. Oshima and M. Aono, *J. Appl. Phys.* **51**, 997 (1980).