Lifetime of ferroelectric $Pb(Zr,Ti)O_3$ ceramic cathodes with high current density

M. Einat, D. Shur, E. Jerby, and G. Rosenman[a)]
Tel-Aviv University, Faculty of Engineering, Department of Electrical Engineering-Physical Electronics, Tel-Aviv 69978, Israel

(Received 22 June 1999; accepted for publication 3 October 2000)

Electron emission from ferroelectric cathodes is investigated, it is commonly suggested as an electron source for different applications due to its special characteristics such as high current density, easy treatment, and operation. In this experimental research, a lifetime of lead zirconate-titanate ceramic cathode with composition related to a ferroelectric phase was studied. The strong plasma emission from the cathode was excited in a nonreversal (nonswitching) mode by application of unipolar high stress. Severe damage to the cathodes was observed, especially in a high repetition rate. An upper limit of the lifetime of the ferroelectric cathode with plasma-induced emission was estimated at about $\sim 10^6$ pulses of $\sim$200 ns each at $\sim$100 Hz repetition rate. Possible applications of the limited lifetime ferroelectric cathode are discussed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1329350]

I. INTRODUCTION

Ferroelectric cathodes are attractive cold electron emission sources, allowing the generation of high-electron-emission current density up to 100 $[A/cm^2]$.[1–15] The cathodes can be handled and operated in poor vacuum conditions and do not require heating or activation process before operation. Intensive studies of the ferroelectric electron emission effect associated with the reversal of spontaneous polarization,[16,17] as well as ferroelectric cathodes were conducted.[1–15] A great difference of the emission current density was reported. A weak electron current of 10^{-7} A/cm^2 was measured in the study[16,17] using electron multipliers while the published data[1–15] reported huge emission currents reaching 100 A/cm^2.

Some basic parameters of the ferroelectric cathodes such as electron-emission current density,[2] brightness,[3] and perveance[4] were studied properly. These studies demonstrated fairly good figures of merit of these cathodes in comparison with classical electron sources. In 1993 destruction of electrodes and ferroelectric ceramics of cathodes for high-electron emission was observed.[5] However, the lifetime and reproducibility of the ferroelectric cathodes with high current density were not investigated. These cathode parameters are the most critical, determining the applications suitable to employ the ferroelectric cathodes in various electronic devices.

In this article we report on experimental studies of the lifetime and reproducibility of the $Pb(Zr,Ti)O_3$(PZT) ceramic ferroelectric cathode with high current density. The problem of the ferroelectric cathodes lifetime and reproducibility has come to the forefront after recent publications presenting observations of a light emission[5,8,14] and erosion of deposited switching electrodes and ferroelectric surface,[5,7] observations of ion currents,[4,6,14,18] and other evidences of a surface flashover formation.[6,9]

It was shown[6,10] that the ferroelectric cathodes, generating strong emission current, may be operated in two different modes. The first mode is a reversal mode. The applied bipolar voltage pulses cause periodic spontaneous polarization reversal followed by the strong electron emission extracted from the surface plasma. This type of surface plasma is of a ferroelectric origin. It emerges in the ferroelectric phase under the polarization switching. For example, it was generated in ferroelectric triglycine sulfate (TGS) crystals at a temperature less than the Curie point that is in the ferroelectric phase only.[6] In this case the plasma is ignited by the weak ferroelectric emission.[16,17] A similar effect was also observed from ferroelectric PLZT 7/65/35 ceramics.[5,10]

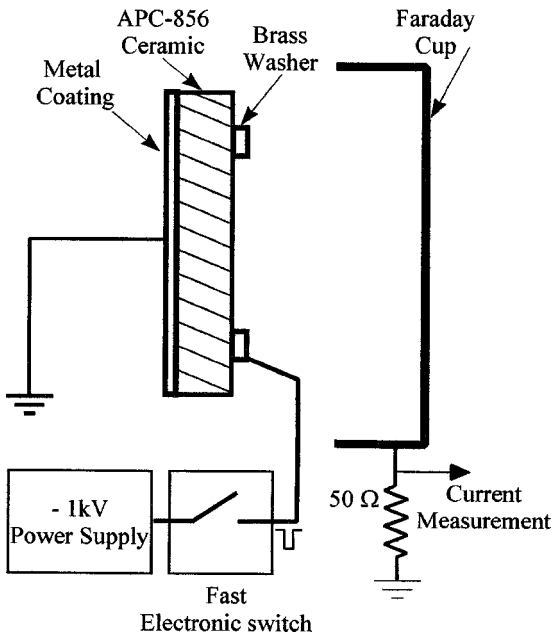

FIG. 1. The experimental setup of the PZT ferroelectric cathode.

[a)]Electronic mail: gilr@eng.tau.ac.il

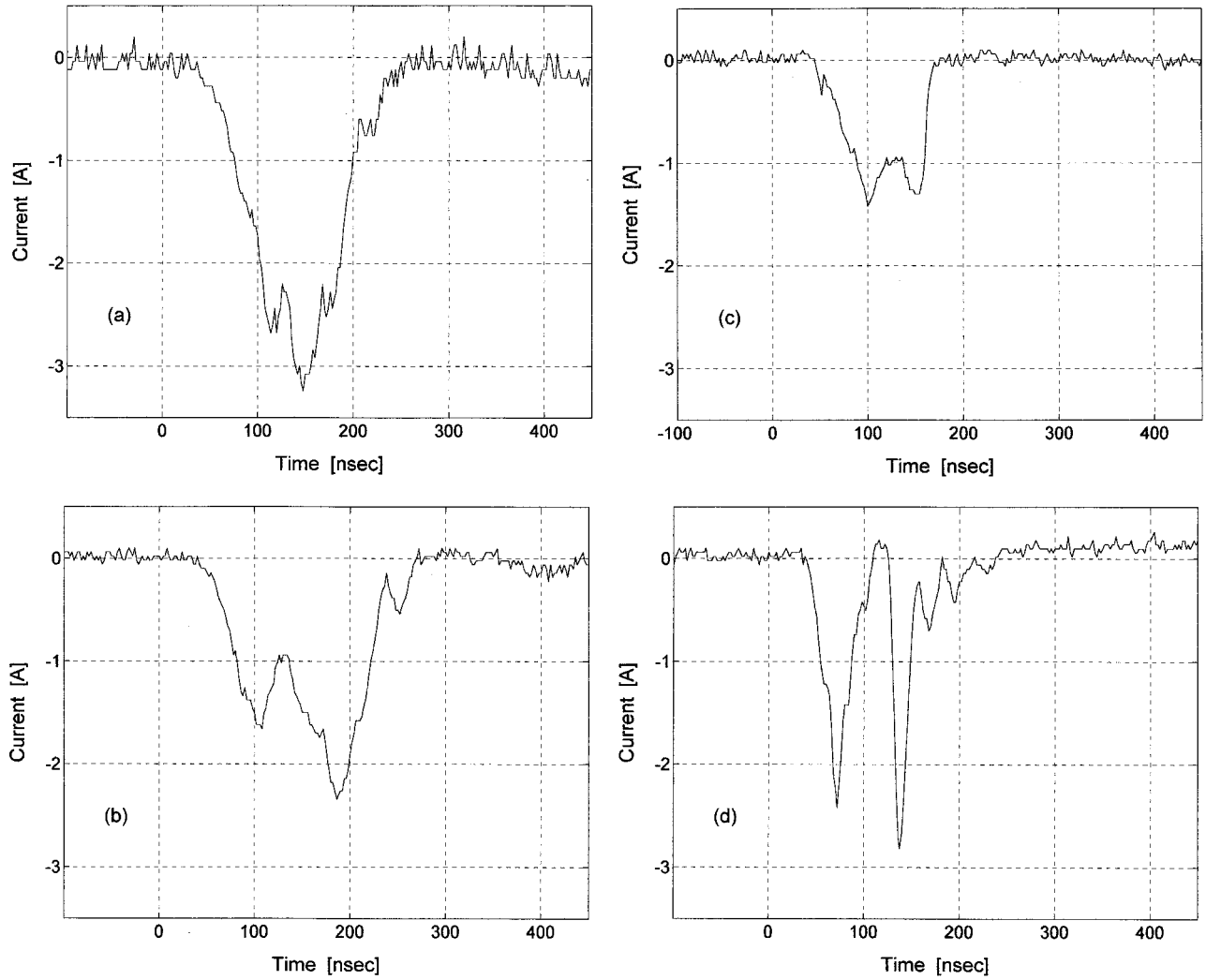

FIG. 2. Emitted current pulses from APC 856, excited by 250-ns trigger voltage pulses starting at $t=0$, after various numbers of shots: (a) Initial shots, (b) after $\sim 6\times 10^3$ shots, (c) after $\sim 2\times 10^5$ shots, and (d) after $\sim 5\times 10^5$ shots.

The second mode of the strong emission generation is a nonreversal mode. It is observed in any linear dielectrics[11] and in ferroelectrics in any phase state.[8,10,14] This mode of the emission excitation occurs with unipolar applied high-voltage stress. The direction of the applied trigger voltage coincides with the direction of macroscopic spontaneous polarization and therefore cannot cause any polarization reversal. However, the field intensity should be high enough to ignite the surface plasma by field emission from triple junctions.[4,10,11] This nonreversal mode was used in the strong emission cathodes based on ferroelectric ceramics PLZT,[10] PZT, and $BaTiO_3$.[14,15]

It may be assumed that the surface flashover plasma of any origin should cause a damage to the ferroelectric cathode surface, influence the reproducibility of the emission current, and limit the cathode lifetime.[5] Thus the main motivations of the undertaken studies were (a) to estimate some critical parameters of the ferroelectric cathodes such as reproducibility and lifetime, and (b) to evaluate the applicability of ferroelectric cathodes with high current density in real electronic devices. We conducted this research with conventionally used ferroelectric PZT ceramics. The emission was excited in the nonreversal mode.

II. MATERIALS AND EXPERIMENTAL SETUP

Ferroelectric ceramics lead zirconate-titanate (PZT) (APC-856)[19] were investigated. This material is related to a ferroelectric phase and possesses macroscopic electric spontaneous polarization. A lifetime test was performed by the use of $10\times 10\times 1$ ceramic samples. The experimental setup is shown in Fig. 1. The emission current was measured by a Faraday cup in a 3-mm distance from the cathode. All experiments were conducted in a vacuum of $\sim 10^{-5}$ Torr. The surface damage was inspected by reflected optical microscopy.

The setup was comprised of a traditional configuration for ferroelectric cathode electrodes. The nonemitting rear side of the ferroelectric ceramic PZT sample was metal coated and connected to the ground. A brass washer with an internal diameter of 3.4 mm was glued by silver paint to the emitting front side. The cathode was subjected to unipolar

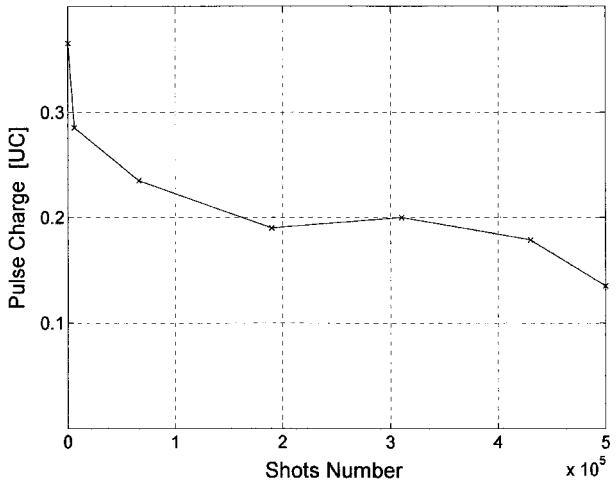

FIG. 3. The current-pulse charge degradation.

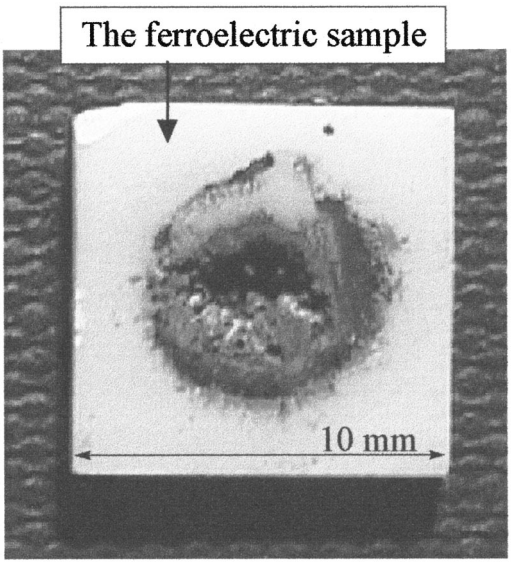

FIG. 4. Damages to the ferroelectric cathode on the front emitting side.

negative rectangular voltage pulses (<1 kV), with repetition rates of 100 or 200 Hz and a rise time of less than 100 ns applied to the electrode of the emitting side. Application of the unipolar high-voltage pulses provided the ferroelectric cathode operation in the nonreversal mode only.

Six consequent test cycles of 10 min each were performed. The reproducibility of the electron emission current was investigated after each consequent cycle. The damage to the sample was inspected after 20, 40, and 45 min of the cathode operation.

III. EXPERIMENTAL RESULTS

First high-voltage pulses were applied manually for verification of the emission current parameters. Several stable electron-emission current pulses of $I=3$ A were obtained. The periodic operation with a repetition rate of $f=100$ Hz caused a decrease in the electron current. Figures 2(a)–2(d) illustrate experimental traces of the generated electron currents for different stages of the test. The initial electron current trace $I(t)$ [Fig. 2(a)] is similar to the previously published experimental results,[8] i.e., a high-voltage 250-ns pulse (starting at $t=0$) causes the electron-emission current generation after a definite delay time of 50–70 ns. The maximum peak value of the electron current was $I=3.1$ A. A subsequent testing of the cathode PZT (APC 856) with a frequency of $f=100$ Hz led to a gradual degradation of the electron current parameters. After 1 min of the cathode operation (6×10^3 shots) [Fig. 2(b)], two distinct peaks were observed. The maximum current decreased to two thirds and it became $I=2.2$ A. Subsequent testing showed [Figs. 2(c) and 2(d)] that the emission current pulse duration τ_{dur} decreased from $\tau_{dur}=200$ ns in the first 6×10^3 shots to $\tau_{dur}=120$ ns after 190×10^3 shots. A continuous cathode operation of 1.5 h caused changes in the electron current shape. A two peak current structure appeared instead of the one peak observed at the starting point. A dead time of about 20 ns appeared between two peaks when the electron current decreased to zero [Fig. 2(d)]. A considerable degradation was observed for the emission charge, which characterizes a total emission capability of the cathode per current pulse. The emitted charge reduced by a factor of 3 during the test, from 3.1×10^{-7} C per pulse [Fig. 2(a)] to 0.9×10^{-7} C per pulse [Fig. 2(d)]. Figure 3 shows the dependence of the electron-emitted charge Q per pulse versus the number of shots. It should be noted that despite the rather low repetition rate ($f=100$ Hz) the electron current did not appear for each applied high-voltage pulse. While at the first stage of the test, the current pulses were detected in every shot, at the last stage, after 5×10^5 shots, about 20%–30% of the electron current pulses did not appear at all.

During the experiment gradually growing damage of the cathode surface was observed; from a small local damaged point on the emitting surface at the beginning of the test to severe damage, leading finally to total destruction of the cathode bulk. The final damage to the cathode is presented in Fig. 4. The damage at the front emitting side is seen in Fig. 4, small holes penetrated through the 1-mm-thick cathode. The surface damage development was correlated to the reduction in the measured electron current [Figs. 2(a)–2(d)].

IV. DISCUSSION

The studied ferroelectric cathodes[1–15] are related to different phase states (ferroelectric, antiferroelectric, relaxor, and paraelectric). The strong electron emission was excited in the two above-mentioned reversal and nonreversal modes as well as during electric field-induced phase transitions. Ferroelectric TGS crystals and ferroelectric ceramics PLZT 7/65/35 were studied in the reversal mode.[6,10] The fabricated strong emission cathode using the same 7/65/35 PLZT composition was also studied in the nonreversal mode.[10] The ceramics PLZT 12/65/35 are related to the paraelectric phase and do not possess spontaneous polarization at all. The studies of this ceramic cathode were undertaken in the nonreversal mode.[8] The nonreversal mode of the strong emission excitation was also used for PZT and $BaTiO_3$ ferroelectric ceramics.[14,15] Analysis of the published experimental results

showed that regardless of all the above-mentioned differences between the studied ferroelectric cathodes (composition, phase state, mode of the emission excitation) the following common features were observed: (a) strong electron emission, (b) light emission, and (c) ion emission. These experimentally observed effects allow us to come to the conclusion that the strong emission from the studied TGS crystals[6] and ferroelectric ceramics[4,5,10,14,15] is a plasma-assisted phenomenon.

The PZT ceramics studied in this article are related to the ferroelectric phase. However, application of repetitive unipolar high-voltage pulses to the samples eliminated any reversal of spontaneous polarization. The observed surface erosive damage and irreproducibility of the electron current and charge when the cathode was operated at high repetition rate indicate that the strong emission current is also extracted from the surface flashover.

The surface plasma in a vacuum may be generated in two ways. The first one is desorbtion and ionization of atoms and molecules of residual gases localized on the ferroelectric surface. The second way is sputtering off and evaporation of the surface atoms from the ferroelectric cathode and electrode. The repetition rate of the applied high-voltage pulses determines which of the processes takes place. It is known that in a vacuum of 10^{-5} Torr at ambient temperature, a monolayer of air will be adsorbed on the ceramic surface in 0.2 s.[20,21] Since the lowest repetition rate used was 100 Hz, the longest time period was 0.01 s. It means that for the studied ferroelectric PZT cathodes the plasma initiation occurred on account of the cathode material itself. The observed strong damage of the cathodes (Fig. 4) is a natural effect occurring as a result of the surface flashover plasma formation. Obviously, at the final stages of the cathode operation when the damage becomes critical, the irreproducibility of the electron-emission current from ferroelectric cathodes increases. The observed changes of the current shape [Figs. 2(a)–2(d)] and emitted charge (Fig. 3) per pulse is the experimental evidence that the studied PZT ferroelectric cathodes have limited reproducibility and lifetime when they are operated in the repetitive mode. The observed lifetime for cathodes based on PZT (APC 856) ceramics, operated with a repetition rate of 100–200 Hz, was $\sim 10^6$ shots of 0.2 μs current pulses.

Discussing factors influencing the lifetime of ferroelectric cathodes with high current density, two basic issues should be stressed. The first one is the trigger voltage applied to the ferroelectric cathode. It has been shown that the trigger voltage determines the surface plasma density.[4] One can assume that the higher the surface plasma density, the higher the cathode damage due to sputtering off and evaporation of the ceramic and electrode materials. According to the experimental conditions used for the studied PZT ceramic samples, the trigger voltage ($V_{tr} < 1$ kV) was close to the threshold voltage of the plasma formation and electron emission.[4,6,8,10] This implies that the measured lifetime is close to the maximal one, due to the surface plasma of lowest density in the given experimental conditions. The second issue is the extraction voltage influence. In this experiment the extraction voltage was <1 kV. Presumably, full separation of plasma charges due to sufficiently high extraction voltage should decrease the cathode lifetime.

The presented experimental data show that the lifetime of the strong ferroelectric PZT cathodes, operated at high frequency rates, is limited. An improvement of the emission current stability of the ferroelectric cathodes was reported recently[22] where a specific electrode, which consisted of a pattern of unconnected patches contained within a ring, caused a reproducible emission current over 100 shots.

Ferroelectric cathodes can be compared to velvet and carbon-fiber cathodes that also operate in pulse mode and have limited lifetimes of $\sim 10^4$ and $\sim 10^6$ pulses, correspondingly. A range of applications was proposed for ferroelectric cathodes with different electronic devices such as flat panel displays[23,24] and spark switches.[25,26] Specifically, the usage of a ferroelectric cathode as an electron source for microwave tubes was shown to be feasible.[27] A microwave tube employing a ferroelectric cathode will have the benefits of a high-current density, immediate operation (no activation process), easy treatment of the cathode, no heating and therefore simpler electron gun, and modest vacuum requirements that allow the use of materials that usually are not used in conventional microwave tubes. However, the severe lifetime limitation of the ferroelectric plasma cathodes operated at high-frequency rates, reported in this article, reduce their application in these long-term devices.

The simplicity of the ferroelectric cathodes construction and operation and their low cost open new possibilities for the microwave tube technology. In particular, disposable microwave tubes for short-term uses can be conceived (for instance, in missiles, projectiles, chaff decoys, etc.). Furthermore, the cathodes can be integrated with the microwave circuit on the same dielectric substrate forming miniature microwave tube systems. These examples, and others, stem from the unique features of the ferroelectric plasma cathodes, in our view they justify further research of these cathodes for novel microwave tubes.

[1] H. Gundel, H. Riege, E. J. N. Wilson, J. Handerek, and K. Zioutas, Nucl. Instrum. Methods Phys. Res. A **280**, 1 (1989).
[2] H. Riege, I. Boscolo, J. Handerek, and U. Herieb, J. Appl. Phys. **84**, 1602 (1998).
[3] B. Jiang, G. Kirkman, and N. Reinhardt, Appl. Phys. Lett. **66**, 1196 (1995).
[4] D. Shur, G. Rosenman, Ya. E. Krasik, and R. Advani, J. Phys. D **31**, 1375 (1998).
[5] G. Pleyber, K. Biedrzycki, and R. Le Bihan, Ferroelectrics **141**, 125 (1993).
[6] D. Shur, G. Rosenman, and Ya. Krasik, Appl. Phys. Lett. **70**, 574 (1997).
[7] W. Zhang and W. Huebner, J. Appl. Phys. **83**, 6034 (1998).
[8] D. Shur, G. Rosenman, Y. Krasik and V. Kugel, J. Appl. Phys. **79**, 3669 (1996).
[9] D. N. J. Shannon, P. W. Smith, P. J. Dobson, and M. J. Shaw, Appl. Phys. Lett. **70**, 1625 (1997).
[10] D. Shur and G. Rosenman, J. Phys. D **32**, L29 (1999).
[11] V. Pusckarev and G. A. Mesiatz, J. Appl. Phys. **78**, 5633 (1995).
[12] G. Benedek, I. Boscolo, J. Handerek, and H. Riege, J. Appl. Phys. **81**, 1396 (1997).
[13] D. Flechtner, C. Golokowski, J. D. Ivers, G. S. Kerslick, J. A. Nation, and L. Schahter, J. Appl. Phys. **83**, 955 (1998).
[14] A. Dunaevsky, Ya. E. Krasik, J. Felsteiner, and S. Dorfman, J. Appl. Phys. **85**, 8464 (1999).
[15] A. Dunaevsky, Ya. E. Krasik, J. Felsteiner, and S. Dorfman, J. Appl. Phys. **85**, 8474 (1999).

[16] G. Rosenman, V. Okhapkin, Yu. Chepelev, and V. Shur, JETP Lett. **39**, 477 (1984).
[17] G. Rosenman, O. Malyshkina, and Yu. Chepelev, Ferroelectrics **110**, 99 (1990).
[18] G. Rosenman, D. Shur, H. Knor, R. Cohen, and Y. Krasik, J. Appl. Phys. **82**, 772 (1997).
[19] American Piezo Ceramics, Data sheet, P.O. Box 180, Mackeyville, PA 17750.
[20] P. A. Redhead, J. P. Hobson, and E. V. Kornelsen, *The Physical Basis of Ultrahigh Vacuum* (Chapman and Hall, London, 1968). Chap. 2.
[21] J. F. O'Hanlon, *A User's Guide to Vacuum Technology* (Wiley, New York, 1989).
[22] I. Boscolo, A. Scurati, and M. Stellato, J. Appl. Phys. **85**, 8337 (1999).
[23] O. Auciello, M. A. Ray, D. Palmer, J. Duarte, G. E. McGuire, and D. Temple, Appl. Phys. Lett. **66**, 2183 (1995).
[24] G. Rosenman, D. Shur, and A. Skliar, J. Appl. Phys. **79**, 7401 (1996).
[25] H. Gundel, H. Riege, J. Handerek, and K. Zioutas, Appl. Phys. Lett. **54**, 2071 (1989).
[26] K. Bergmann, R. Lebert, J. Kiefer, and W. Neff, Appl. Phys. Lett. **71**, 1936 (1997).
[27] R. Drori, M. Einat, D. Shur, E. Jerby, G. Rosenman, R. Advani, R. J. Temkin, and C. Pralong, Appl. Phys. Lett. **74**, 335 (1999).