Effect of gases on the field emission properties of ultrananocrystalline diamond-coated silicon field emitter arrays

M. Hajra and C. E. Hunt[a)]
Department of Electrical and Computer Engineering, University of California, Davis, California 95616

M. Ding
Beijing Vacuum Electronics Research Institute, Beijing, China

O. Auciello, J. Carlisle, and D. M. Gruen
Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 20 February 2003; accepted 2 June 2003)

We performed studies of electron emission from ultrananocrystalline diamond (UNCD)-coated, ungated silicon field emitters as a function of *in situ* exposure to various gases during current versus voltage and current versus time measurements. The emitter arrays were fabricated by a subtractive tip fabrication process and coated with UNCD films using microwave plasma chemical vapor deposition with a CH_4/Ar plasma chemistry. The emission characteristics of the coated tip arrays were studied in the diode configuration; using a 2 mm diameter anode with rounded edges to suppress arcing. Significant enhancement of the electron emission was observed, increasing from 35% to 100%, after the emitting surface was exposed to H_2 at pressures in the 10^{-5} and 10^{-4} Torr range. Upon termination of the H_2 exposure, the current decreased to the initial value of 2 μA. The emission current subsequently remained stable at 2 μA upon continued evacuation down to the base pressure below 10^{-9} Torr. The emission current variation is repeatable with ensuing hydrogen exposure, indicating that the enhancement is due to the hydrogen exposure. Negligible emission current variations are observed at pressures less than 10^{-5} Torr. Exposure to either Ar or N_2 resulted in a reduction of the emission current for ambients of up to 10^{-5} Torr. This effect is reversible. The effect of the investigated gases on the emission characteristics of UNCD-coated Si tip arrays is attributed to a modification of the effective work function at the localized sites from where electrons are being emitted. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1594268]

I. INTRODUCTION

A very high electric field must be used to achieve field emission (FE) from the surface of a material. To enhance the electric field near the surface, the material may be sharpened into a microtip. Materials used for microtips should be able to endure extremely high electrical stresses for fabrication of high aspect ratio features, and have a good thermal conductivity. As a result, Si[1] and refractory metals, such as Mo,[2] are typically used for fabrication of microtips. In practical vacuum microelectronics, or a FE display device, the electron emitters usually operate in the presence of residual gases. Adsorbates can form on the emitting surface during operation and change the surface barrier. Suppression of the emission current and poorer device performance are then usually observed as the vacuum pressure increases.[3] In addition, the electric field near the microtip is high enough to capture ionized residual gases and the resultant ion bombardment of the microtip eventually results in its failure.[4] However, control of the background gas species and/or surface treatment of the emitter can offer the possibility of operational enhancement.

Silicon FEAs coated with ultrananocrystalline diamond (UNCD) have been reported to emit electrons at fields as low as 2.6 V/μm.[5] A low field is advantageous in reducing ion formation and damage from ion bombardment. In addition, diamond is very inert, exhibiting the lowest physical sputtering yield characteristic of carbon, and has a high thermal conductivity. Diamond coating of Si FEAs[6] and individual Mo microtips,[7] and diamondlike-carbon coating of Mo FEAs[8] have recently been reported to enhance the FE current. Here, we report the effects of Ar, N_2, and H_2 gases on the FE properties of UNCD-coated Si microtips.

II. EXPERIMENT

The device configuration considered for the surface coating of the emitter array with UNCD is a "bed of nails," which is an array of ungated single crystal Si emitters placed in an area of 4 mm^2 with a tip-to-tip spacing of 6 μm. The emitters were formed from p-type (1–10 Ω cm) Si (100) substrates by the subtractive tip fabrication process[9] as seen in Fig. 1. First, 1000 Å of Cr was deposited on 2000 Å of thermally grown SiO_2 on a Si substrate. Then, 3.0 μm disks were patterned in this layered structure using photolithography. Using the chromium and the SiO_2 cap as a mask, the outline of the emitter tip was formed by means of isotropic plasma etching with SF_6 gas. The tips were then oxidation sharpened, as we have previously described elsewhere.[10] The caps were subsequently removed by wet etching. The final

a)Electronic mail: hunt@ucdavis.edu

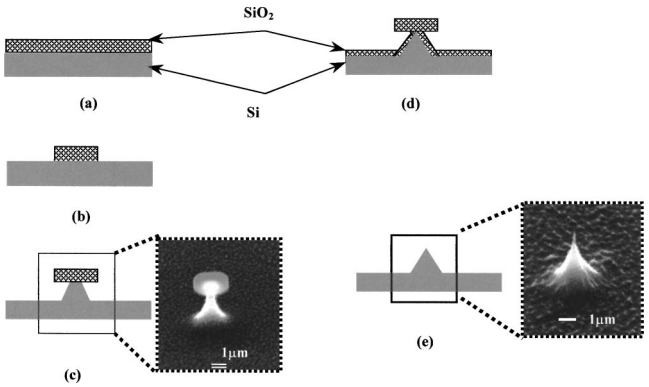

FIG. 1. Subtractive tip fabrication process: (a) thermal oxidation of silicon, (b) patterning of SiO_2, (c) isotropic plasma etching of silicon, (d) oxidation sharpening of silicon, and (e) removal of SiO_2 in buffer etch oxide.

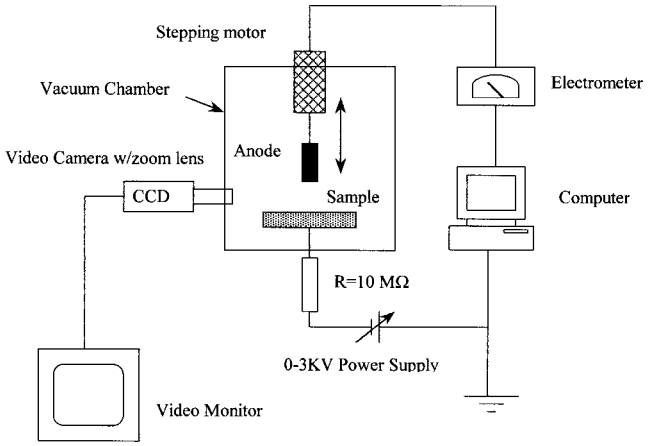

FIG. 3. Block diagram of the FE measurement system.

silicon emission tip is shown in Fig. 1(e). The typical tip radius of curvature, estimated using scanning electron microscopy (SEM), averages 15 nm.

The Si tips were then cleaned in 20% HF for 30 s to remove the native oxide and other surface contaminants. Then the tips were seeded for 3 min in a 5 nm diamond powder suspension in ethanol, using the electrophoresis method.[11,12] Following the seeding procedure, the tip emitters were immediately loaded into a microwave plasma enhanced chemical vapor deposition reactor (ASTeX-PD-17) for diamond deposition. A mixture of CH_4 and Ar gases were admitted to the deposition chamber through mass flow controllers. The total pressure in the chamber was kept constant at 100 Torr, while the flow rates were 1 and 99 sccm for CH_4 and Ar, respectively. The microwave-input power was 800 W, and the substrate temperature was 800 °C. It has been previously demonstrated[11–14] that these conditions lead to the growth of phase-pure diamond films with equiaxed 2–5 nm grains. The deposition was carried out for 20 min to obtain a diamond film thickness of about 100 nm. FE studies done previously show a substantial reduction in emission turn-on voltage for UNCD diamond-coated tip emitters and a large enhancement in emission current for films within the thickness range of 0.1 μm to 2.4 μm.[5] Figure 2 shows the SEM images of the uncoated and UNCD-coated silicon FEA. The emitters are uniformly and conformally coated with the UNCD film.

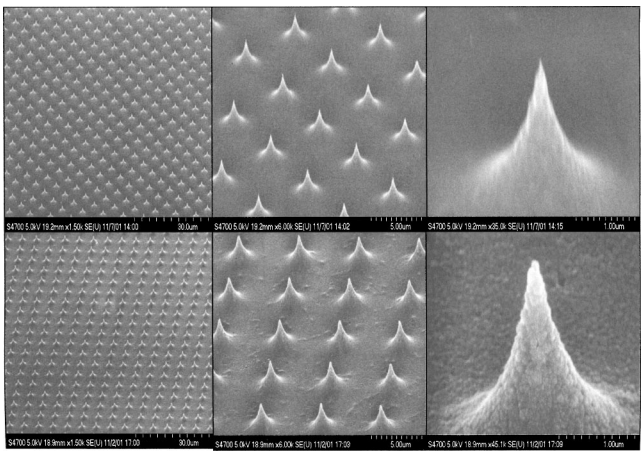

FIG. 2. SEM images of the as-etched, uncoated silicon FEA (upper row) and UNCD-coated silicon FEA (lower row).

The FE characteristics in various gaseous environments were investigated using a computer-controlled current–voltage ($I-V$) testing system, as seen in Fig. 3. The emission current was measured using an anode, 2 mm in diameter, with rounded edges to suppress potential arcing. The anode–cathode spacing was determined by using a high-magnification charge coupled device camera with a scale. The vacuum system reaches a base pressure in the high 10^{-10} Torr region. The FE characteristics from the UNCD-coated silicon FEA were studied using *in situ* exposure to various gas species during operation.

III. RESULTS AND DISCUSSION

In practical applications, the pressure in the system in which the FE cathodes operate can be considerably high (it can reach up to 10^{-6}–10^{-4} Torr), and the ambient may contain chemically active and inert gases, such as N_2, Ar, and H_2. It is important therefore to study the performance of FEAs at elevated pressures and in the presence of these gases. In this work, we investigated the effects of Ar, N_2, and H_2 residual gases on the FE properties of UNCD-coated Si FEAs, to quantify the effect of exposure in different ambient pressures and composition. The special case of reactive O_2 exposure has been investigated and is reported elsewhere.[15] The FE measurement technique employed to control, as well as to investigate, the electron emission process, used the setup depicted in Fig. 3. The anode–cathode distance was kept at 150 μm throughout the experiment. The electron emission current was collected at the anode and measured by an electrometer. The gas species were introduced into the chamber (base pressure below 10^{-9} Torr) while the emitters were kept at a constant emission current level of 2 μA.

As N_2 was first introduced into the system, a continuous decrease in the emission current was measured as the gas pressure increased. A similar trend was found, by other investigators, measuring electron emission in the presence of N_2 from Mo wires coated with diamond.[16] The behavior of

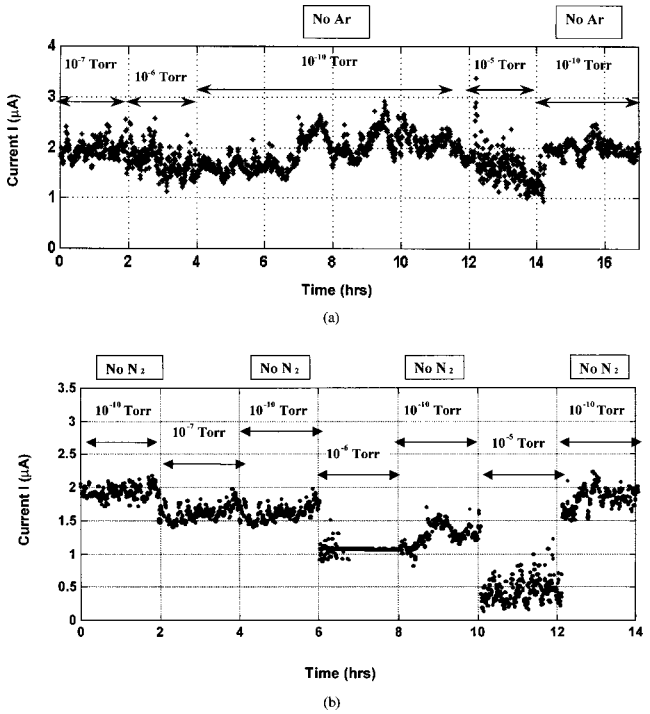

FIG. 4. (a) Plot of the emission current level from a UNCD-coated silicon emitter array in Ar atmosphere at three different pressures: 1×10^{-7}, 1×10^{-6}, and 1×10^{-5} Torr. (b) Plot of the emission current from UNCD-coated silicon emitter array in N_2 atmosphere at three different pressures: 1×10^{-7}, 1×10^{-6}, and 1×10^{-5} Torr. The chamber was allowed to stabilize for 2 h before recording data in the gas ambients.

the emission current when Ar was introduced into the system also shows a decrease in the emission current as the gas pressure increases. Figures 4(a) and 4(b) illustrate the emission current behavior from the UNCD surface in the presence of Ar and N_2, respectively. The emission data was collected over a period of 5 h for every pressure range from 10^{-10} to 10^{-5} Torr. In the first 2 h of the experiment, the pressure was allowed to stabilize to the set value. Subsequently, the emission data for the next 2 h of operation were plotted and analyzed. The data recorded in Fig. 4 show the emission current levels at various pressures during these last 2 h of operation. Exposure to Ar and N_2 resulted in a reduction of the emission current by factors of 2 and 4 for an ambient of up to 10^{-5} Torr, respectively. This effect was reversible as the emission current attained its original value of 2 μA after the gas was pumped out and the background pressure in the chamber reached the original base value of 8×10^{-10} Torr.

We believe one explanation for the effect of Ar and N_2 gas exposure on the emission current is that upon introduction of the gases into the chamber, localized microplasmas are formed in front of the tips resulting in bombardment of the UNCD surface by Ar^+ or N^+ ions. This bombardment can lead to ion-induced desorption of hydrogen species on the surface of UNCD, which provides a localized low surface barrier for electron emission. The desorption of the hydrogen species can lead to the electron emission reduction. Upon evacuating Ar/N_2 gas from the chamber, hydrogen from the ambient is readsorbed on the surface of UNCD creating sites for electron emission and resulting in the emission current recovery. Work involving surface analysis for hydrogen using a direct recoil spectroscopy technique developed at Argonne National Laboratory[17] can provide direct evidence for the hydrogen effect proposed herein, and it will be performed in the near future.

Very different behavior was found when high-purity (99.999%) H_2 was introduced into the system. The emission current remained essentially unchanged when exposing the emitter array to up to 10^{-5} Torr of H_2. Significant enhancement of the electron emission was observed after the emitting surface was exposed to H_2 at pressures in the 10^{-5} and 10^{-4} Torr range. The initial current of about 2 μA increased by a factor of anywhere from 2.7 to 4, followed by a subsequent current decrease to the initial value as the H_2 was being pumped out. The emission current then remained stable at 2 μA upon evacuating the hydrogen and returning to the base pressure. The repeatability of the emission current behavior as a function of hydrogen exposure indicates that the effect is due to hydrogen exposure. Figure 5(a) illustrates the emission current behavior from the UNCD surface in the presence of H_2. Figure 5(a) is a plot of the emission current levels at various pressures. When H_2 was pumped away and the vacuum returned to the background pressure, the emission current decreased to its original value as seen in Figs. 5(b) and 5(c).

Figures 6(a) and 6(b) show the $I-V$ characteristics and the corresponding Fowler–Nordheim (F–N) plots of the UNCD-coated silicon FEA for different pressures of H_2. After each exposure, the vacuum system was evacuated to 10^{-9} Torr and FE $I-V$ curves were measured, as shown in Fig. 6(a). It is seen from Fig. 6(a) that, for the longer exposure to H_2, there is a significant reduction in the turn-on voltage and an increase in the emission current. In Fig. 6(b), the FE data are plotted $\ln(I/V^2)$ versus $1/V$ to allow comparison with the straight-line behavior predicted by the F–N equation. The F–N plot shows that there is virtually no change in the slope of the straight lines as the exposure increases, and the lines can be considered parallel. Therefore, we conclude that there is no change in the work function or the field-enhancement factor, but the emission uniformity across the array increases. These improvements in the emission across the silicon FEA can be attributed to the increase in the number of emitters contributing to the emission process.

This current behavior suggests a particular effect of hydrogen to the UNCD-emitting surface. Since the current change only occurs at certain pressures, we propose that after H_2 was introduced into the system, a part of it was dissociated or ionized by the electron beam. Polarized hydrogen atoms and ions were attracted back to the diamond-emitting surface and formed a stable dipole layer. Such a layer reduces the surface barrier, which can be attributed to the modification of the effective work function at the localized sites from where electrons are being emitted. The layer can also possibly initiate a negative electron affinity (NEA) property on a diamond surface. More detailed experimentation is needed to verify such a NEA property of the UNCD surface after the exposure to H_2 ambient. The aforementioned effects

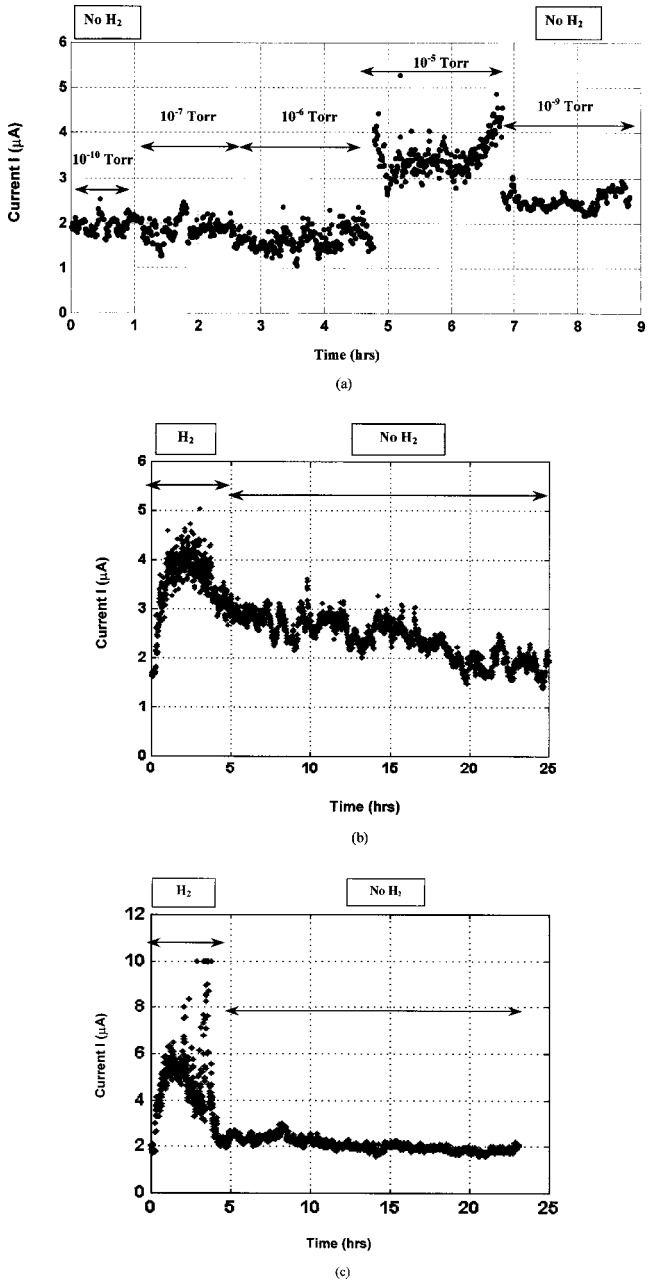

FIG. 5. (a) Plot of the emission current levels from UNCD-coated silicon emitter array in H_2 atmosphere at three different pressures: 1×10^{-7}, 1×10^{-6}, and 1×10^{-5} Torr. Plot of the emission current from UNCD-coated silicon emitter array in H_2 atmosphere at pressures: (b) 1×10^{-5} and (c) 1×10^{-4} Torr.

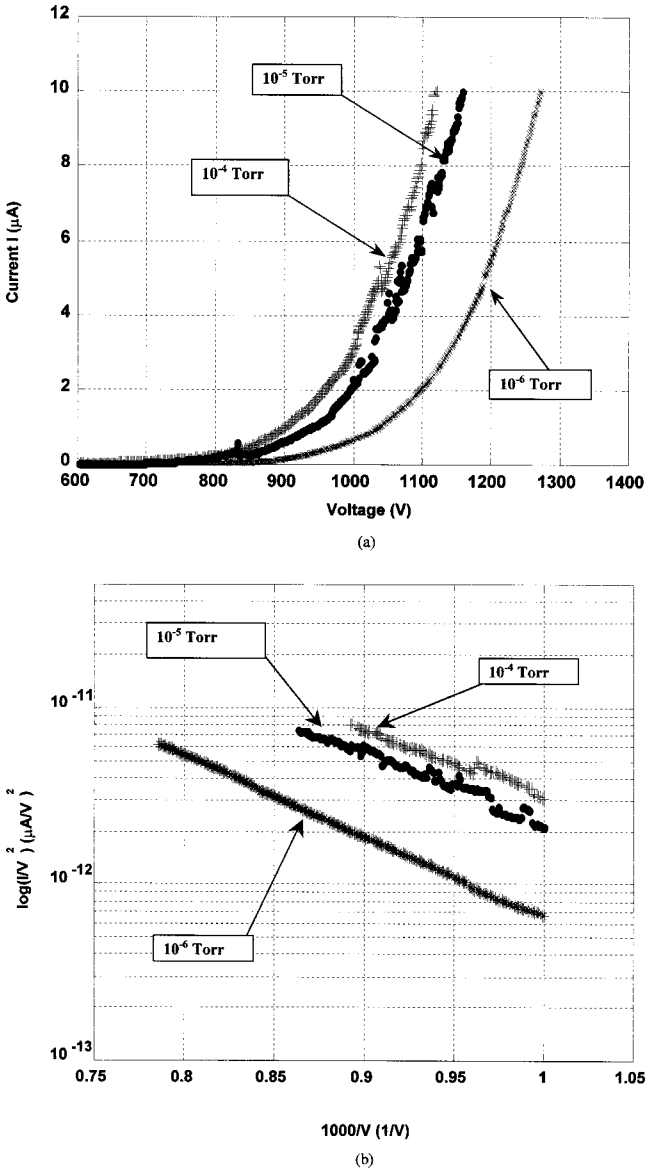

FIG. 6. (a) $I-V$ characteristics. (b) F–N characteristics of UNCD-coated silicon emitter array in H_2 atmosphere at pressures 1×10^{-4}, 1×10^{-5}, and 1×10^{-6} Torr.

result in an increase in the number of emitters contributing to the emission process, improving the emission characteristics of the silicon FEA.

IV. CONCLUSION

We report that the FE properties of the UNCD-coated silicon FEA are enhanced with exposure to hydrogen. There is a significant reduction in the turn-on voltage and an increase in the emission current due to the modification of the effective work function at the localized emission sites. This effect increases the emission uniformity over the array by increasing the number of emitters contributing to the total emission current. Exposure to Ar and N_2 results in a reduction of the emission current for an ambient of up to 10^{-5} Torr. This effect was reversible as the emission current was restored to its original value after Ar and N_2 was pumped out and the background pressure in the chamber reached its original value of 8×10^{-10} Torr. This study demonstrates the high-pressure operation of UNCD-coated field emitters, which we believe are valuable to practical applications.

[1] R. N. Thomas and H. C. Nathanson, Appl. Phys. Lett. **21**, 384 (1972).
[2] C. A. Spindt, J. Appl. Phys. **39**, 3504 (1968).
[3] M. Aslam, P. Klimecky, G. P. Myers, H. H. Busta, B. J. Zimmerman, B. E. Artz, L. W. Cathey, and R. E. Elder, J. Vac. Sci. Technol. B **11**, 422 (1993).
[4] I. Bordie and C. A. Spindt, Adv. Electron. Electron Phys. **83**, 1 (1992).
[5] A. R. Krauss, O. Auciello, M. Q. Ding, D. M. Gruen, Y. Huang, V. V. Zhirnov, E. I. Givargizov, A. Breskin, R. Chechen, E. Shefer, V. Konov, S.

Pimenov, A. Karabutov, A. Rakhimov, and N. Suetin, J. Appl. Phys. **89**, 2958 (2001).
[6] W. B. Choi, J. J. Cuomo, V. V. Zhirnov, A. F. Myers, and J. J. Hern, Appl. Phys. Lett. **68**, 720 (1996).
[7] F. Y. Chuang, C. Y. Sun, H. F. Cheng, C. M. Huang, and I. N. Lin, Appl. Phys. Lett. **68**, 1666 (1996).
[8] J. H. Jung, B. K. Ju, Y. H. Lee, J. Jang, and M. H. Oh, IEEE Electron Device Lett. **18**, 197 (1997).
[9] J. Trujillo, Ph.D. dissertation, University of California-Davis 2000.
[10] R. B. Marcus, T. S. Ravi, T. Gmitter, K. Chin, D. Liu, W. J. Orvis, D. R. Ciarlo, C. E. Hunt, and J. Trujillo, Appl. Phys. Lett. **56**, 236 (1990).
[11] A. R. Krauss, D. M. Gruen, D. Zhou, T. G. McClauley, L. C. Qin, T. D. Corrigan, O. Auciello, and R. H. Chang, Mater. Res. Soc. Symp. Proc. **495**, 299 (1998).
[12] T. G. McCauley, T. D. Corrigan, A. R. Krauss, O. Auciello, D. Zhou, D. M. Gruen, D. Temple, R. P. H. Chang, S. English, and R. J. Nemanich, Mater. Res. Soc. Symp. Proc. **498**, 227 (1997).
[13] D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, J. Appl. Phys. **75**, 1758 (1994).
[14] R. Csencsits, C. D. Zuiker, D. M. Gruen, and A. R. Krauss, Solid State Phenom. **51**, 261 (1996).
[15] M. Ding, M. Hajra, C. E. Hunt, O. Auciello, J. Carlisle, and D. M. Gruen (unpublished).
[16] S. C. Lim, R. E. Stallcup II, I. A. Akwani, and J. M. Perez, Appl. Phys. Lett. **75**, 1179 (1999).
[17] A. R. Krauss, O. Auciello, and J. A. Schultz, Mater. Res. Bull. **20**, 18 (1995).