

## Field electron emission from nanostructured heterogeneous $\text{HfN}_x\text{O}_y$ films

M. Y. Liao<sup>a)</sup>

*Ion Beam Engineering Experimental Laboratory, Graduate School of Engineering, Kyoto University, Yoshida-homachi, Sakyo-ku, Kyoto 606-8501, Japan*

Y. Gotoh, H. Tsuji, and J. Ishikawa

*Department of Electronic Science and Engineering, Kyoto University, Yoshida-homachi, Sakyo-ku, Kyoto 606-8501, Japan*

(Received 21 April 2003; accepted 27 June 2003)

Nanostructured heterogeneous  $\text{HfN}_x\text{O}_y$  films comprising of nanoscale conductive hafnium nitride grains embedded in a matrix of dielectric oxide or oxynitride were deposited on silicon substrate by magnetron sputtering at room temperature. Electron emission with low threshold field  $25 \text{ V}/\mu\text{m}$  and good current stability were reported. The field emission characteristics depend on the concentration of hafnium nitride phase, revealing the nature of heterogeneous structure. Field enhancement in  $\text{HfN}_x\text{O}_y$  film was explained in terms of the interaction between the conductive grains separated by dielectric layers under external electric field. The experiment is expected to open a group of nanostructured heterogeneous material consisting of stable conductive nitride and insulating oxide for field emitter, and also provide an insight into the emission mechanism of carbon films. © 2003 American Institute of Physics. [DOI: 10.1063/1.1604944]

Cold cathode material with high power efficiency and stable structure is crucially important in display technology as well as vacuum microelectronics. Since the fabrication of Spindt type arrays requires complex techniques, there is growing interest in planar field emitter. Among the investigated materials, diamond and diamond-like carbon (DLC) films have been extensively concerned.<sup>1-5</sup> The fact that physical constituent, i.e., conductive  $sp^2$  phase embedded in a background of dielectric  $sp^3$  carbon, and the distribution of the two phases in DLC films determine the field emission,<sup>2-5</sup> leads to a hypothesis that electrically nanostructured heterogeneous (ENH) materials would exhibit low threshold field emission if properly prepared. An ENH material can be pictured basically as conductive nanoscale inclusions embedded in a dielectric matrix.<sup>6,7</sup> However, since the early work,<sup>8</sup> too few experiments have been made on this class of material except carbon. This is not enough either for understanding the arguable mechanism of field emission from ENH materials (including carbon) or their technological applications.

In this letter, we demonstrate the potential of heterogeneous  $\text{HfN}_x\text{O}_y$  film as an alternative cold cathode for its low threshold field emission and good current stability. The purpose of the present work is two-fold. One is to understand the emission mechanism of ENH materials. The other is to develop suitable candidate as cold cathode. The choice of  $\text{HfN}_x\text{O}_y$  as the target is because of the intrinsic properties of HfN and  $\text{HfO}_2$ . For example, HfN has a low electron affinity and resistivity ( $35 \mu\Omega \text{ cm}$ ),<sup>9</sup> while  $\text{HfO}_2$  is well known as a dielectric material.<sup>10</sup> Both of them have good mechanical properties and chemical stability. In addition,  $\text{HfN}_x\text{O}_y$  film can be prepared at room temperature, favorable to panel field emission display technology. This material should offer the advantage over conductive oxides for its low electric field

emission and no loss of the good stability that conductive oxides possess.<sup>11</sup>

$\text{HfN}_x\text{O}_y$  films were prepared using the way based on our previous systematic study about HfN films by sputtering a HfN compound target. The detailed process will be described elsewhere. Briefly, depositions of heterogeneous  $\text{HfN}_x\text{O}_y$  films were performed on heavily boron doped Si (100) substrates using a rf-sputtering apparatus in an argon gas atmosphere mixed with 1% oxygen. Two films examined were deposited at total working pressures of 4.0 and 6.0 Pa with a rf power of 30 W at room substrate temperature, which were denoted as samples A and B, respectively. The film thickness is about 300 nm.

The composition of the film was estimated by Rutherford backscattering spectroscopy using  $\text{He}^{2+}$  beam with an energy of 2.0 MeV. Only hafnium, nitrogen, and oxygen were detected in the whole film. The ratios of oxygen to nitrogen are about 1:2 and 2:1 in samples A and B, respectively. X-ray diffraction measurement shows that HfN grains in  $\text{HfN}_x\text{O}_y$  are in nanosize (5 nm) for sample A, and sample B is almost amorphous. Both of the films have poor conductivity ( $>20 \text{ M}\Omega$ ).

The chemical bonding states of the films after removing the surface layer were characterized by x-ray photoelectron spectroscopy with monochromated Al  $K\alpha$  (1486.6 eV) radiation. Figure 1 shows the spectra of one of the  $\text{HfN}_x\text{O}_y$  films compared with a stoichiometric HfN film. As illustrated in Fig. 1(a), Hf 4f spectra from the  $\text{HfN}_x\text{O}_y$  film include at least four features, 15.4 and 16.9 eV, and 17.7 and 19.0 eV, which were obtained by a simple deconvolution of the curve. The former two are related to Hf 4f bonding to nitrogen, while the latter are associated with hafnium oxide<sup>10,12</sup> or oxynitride. A comparison of the N 1s spectra from HfN with  $\text{HfN}_x\text{O}_y$  in Fig. 1(b) indicates that there is indeed some transitional structure such as oxynitride beside nitride and oxide. The results give the fact that the structure of the present

<sup>a)</sup>Electronic mail: liaomy@nishiki.kuee.kyoto-u.ac.jp

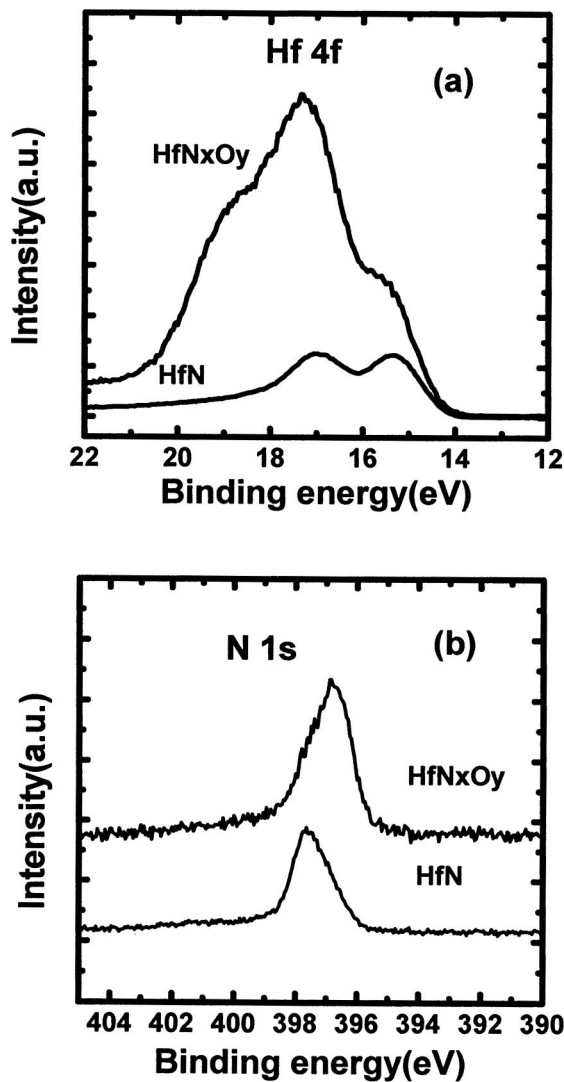


FIG. 1. X-ray photoelectron spectra of Hf 4f (a) and N 1s (b) from a HfN<sub>x</sub>O<sub>y</sub> film compared with HfN.

HfN<sub>x</sub>O<sub>y</sub> film is complex, namely, conductive HfN grains embedded in a dielectric matrix.

Field emission measurements were carried out in an UHV system (base pressure  $2 \times 10^{-9}$  Torr) using a sphere-to-plane geometry with a 2 mm gold-ball collector. The collector was mounted on a linear piezoelectric device, which can control the collector position with respect to the emitter surface. The sample holder can also move mechanically along the lateral directions,<sup>13</sup> allowing investigation of the emission at various regions on the emitter. Prior to the measurements, the samples were aged for about 10 h at various currents to achieve reproducible emission. The current-voltage measurements were carried out at relatively low fields to avoid destruction to the film, and recorded in an X-Y recorder.

Figure 2(a) presents the current-voltage characteristics measured at a collector-emitter distance  $d_{EC}$  of 4.5  $\mu\text{m}$ . The threshold voltage, defined at 1 nA was about 240 V for sample A and 500 V for sample B. The corresponding Fowler-Nordheim (FN) plots  $1000/V$  vs  $\ln(I/V^2)$  were also given in Fig. 2(b). The linear dependence of the plots indicates that the emission is subjected to a tunneling mechanism. To obtain the threshold electric field, the variation of

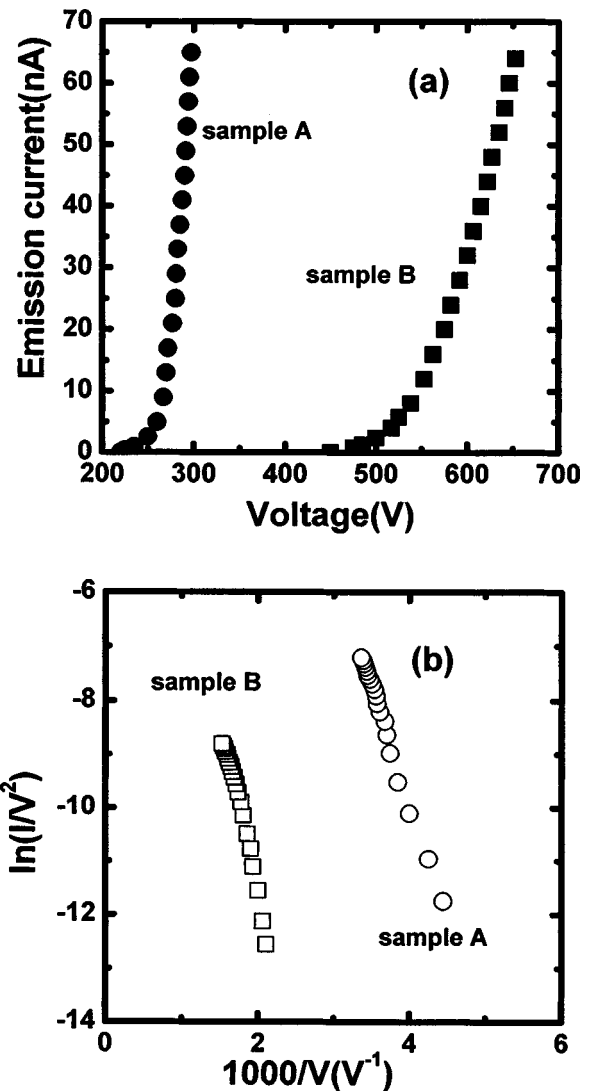


FIG. 2. Current-voltage characteristics of samples A and B (a), and corresponding FN plots (b).

anode voltage versus collector-emitter distance  $d_{EC}$  was examined at a constant current 1 nA, as shown in Fig. 3. Above 3  $\mu\text{m}$ , the applied voltage increases linearly with  $d_{EC}$ , demonstrating that the electric field between the collector and film surface can be modeled using a parallel plate configuration. The extracted threshold field, corresponding to the slope of the upper part in such plot, is about 25 V/ $\mu\text{m}$  for sample A, and 70 V/ $\mu\text{m}$  for sample B. The large electric field needed at smaller  $d_{EC}$  might result from the difference of emissive sites or the change of field distribution, which should be disclosed further by emission pattern. The maximum current achieved before breakdown is about 25  $\mu\text{A}$  for sample A. The emission performance of HfN<sub>x</sub>O<sub>y</sub> films is as good as those of wide-band gap semiconductors such as some diamond-like carbon<sup>14</sup> and aluminum nitride.<sup>15</sup>

According to the tunneling theory, the slope of Fowler-Nordheim plot is  $-bs\Phi^{3/2}/\beta$  and intercept  $\ln[Aa\beta^2/\Phi]$ , which are related to voltage-to-barrier-field conversion factor  $\beta$  (cm<sup>-1</sup>) and effective emission area  $A$  (cm<sup>2</sup>), respectively. Here  $a(=1.54 \times 10^{-6} \text{ A V}^{-2} \text{ eV})$ ,  $b(=6.83 \times 10^7 \text{ V cm}^{-1})$  are constants. The slope correction factor  $s$  can be assumed to 1 for a planar emitter here.  $\Phi$  (eV) is work function. As revealed in Fig. 2(b), only slight difference was

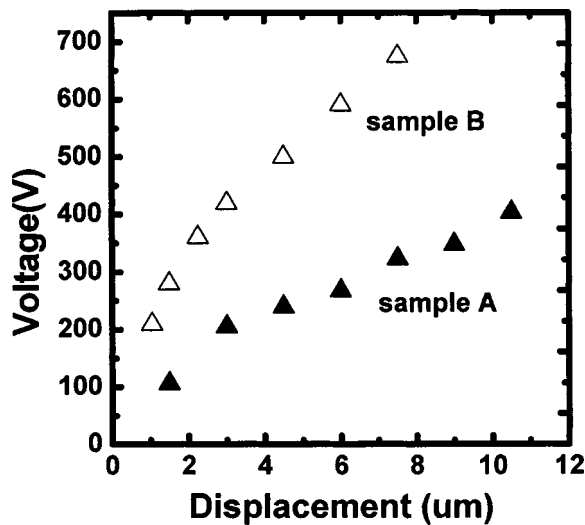


FIG. 3. Anode voltage variation as collector-emitter distance at an emission current of 1 nA.

found in the slopes between samples A and B. This implies that the local field enhancement is similar for these two samples, if  $\Phi$  is assumed the same. However, the intercept indicates that sample A has a larger effective emission area or more emissive sites than B, probably associated with the difference in conductive HfN grains concentration between the two samples. The earlier analysis can be considered as a hint of the heterogeneous nature of the  $\text{HfN}_x\text{O}_y$  films.

Taking  $\Phi$  as 5 eV, which was roughly measured by Kelvin probe in the air, the conversion factor  $\beta$  was evaluated about 23 000, corresponding to a value of field enhancement factor  $\gamma (= \beta d_{\text{EC}})$  100. That no features were observed on the films by scanning electron microscopy precludes the surface geometrical effect as a main factor for so large enhancement. The detailed reason for field enhancement is not very clear at this stage. Our explanation is that conductive HfN grains form channel from substrate to the front surface, leading to local field enhancement. Provided a channel like a chain, which is composed of HfN grains connected by dielectric layers, field enhancement will occur between separated HfN grains within the film due to the interface mismatch of HfN with dielectric layers.<sup>14,16</sup> The internal interparticle effect will improve the conductivity of the path from substrate to the topmost conductive particle. This enables us to evaluate the notional maximum  $\gamma$  using the surface-particle field-enhancement formula  $\gamma = 0.7 h/r$ , where  $h$  is film thickness and  $r$  is particle radius.<sup>6,7</sup> Using the film thickness 300 nm and the crystal size of HfN about 5 nm, we got a  $\gamma$  value of 84, comparable with the experimental one. Obviously, the enhancement factor will be affected by the size and density of conductive HfN grains, and the matrix dielectric constant. There likely exists an optimum value of conductive phase cluster size to achieve the highest enhancement factor as occurs in DLC films.<sup>3</sup> Theoretically, the interaction among HfN grains in  $\text{HfN}_x\text{O}_y$  film under an external field belongs to a many-body problem. Further experiments and numerical calculation should be performed to support the suggestion.

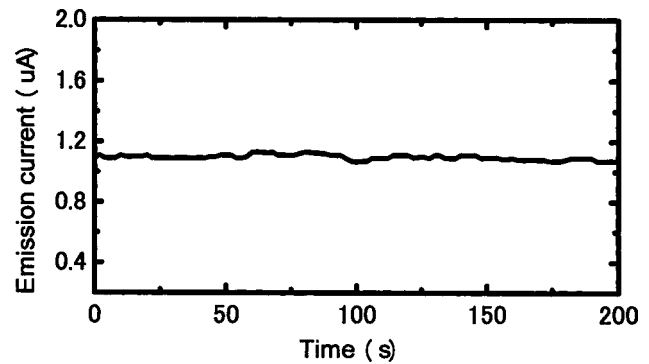


FIG. 4. Emission current stability of sample A at a fixed anode voltage.

Emission stability was examined at a certain applied anode voltage, as illustrated in Fig. 4. The current fluctuation is below 5%. No clear degradation was observed when the sample was left at 1  $\mu\text{A}$  level for 12 h at a fixed applied voltage. The low noise shows that  $\text{HfN}_x\text{O}_y$  has a stable surface structure and little atoms arrangements or evaporation take place during emission.

In summary, we have reported the field emission from nanostructured heterogeneous  $\text{HfN}_x\text{O}_y$  films, which consist of conductive HfN nanoscale crystals and a dielectric matrix. Low threshold electric field and stable emission was found on this kind of film. Field enhancement is induced by the heterogeneous nature in the films. The present work indicates that this material is possible as a cathode in display technology and vacuum microelectronics devices.

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology through a Grant in Aid No. 12135204.

- <sup>1</sup>M. W. Geis, N. N. Efremow, K. E. Krohn, J. C. Twichell, T. M. Lyszczarz, R. Kalish, J. A. Greer, and M. D. Tabat, *Nature (London)* **393**, 431 (1998).
- <sup>2</sup>V. P. Mammana, T. E. A. Santos, A. P. Mammana, V. Baranauskas, H. J. Ceragioli, and A. C. Peterlevitz, *Appl. Phys. Lett.* **81**, 3470 (2002).
- <sup>3</sup>A. Ilie, A. C. Ferrari, T. Yagi, and J. Robertson, *Appl. Phys. Lett.* **76**, 2627 (2000).
- <sup>4</sup>N. A. Fox, W. N. Wang, T. J. Davis, J. W. Steeds, and P. W. May, *Appl. Phys. Lett.* **71**, 2337 (1997).
- <sup>5</sup>J. D. Carey, R. D. Forrest, R. U. Akahan, and S. R. P. Silva, *Appl. Phys. Lett.* **77**, 2006 (2000).
- <sup>6</sup>R. G. Forbes, *Ultramicroscopy* **89**, 7 (2001).
- <sup>7</sup>R. G. Forbes, *Solid-State Electron.* **45**, 779 (2001).
- <sup>8</sup>S. Bajic, M. S. Mousa, and R. V. Latham, *J. Phys. (Paris)* **50**, C879 (1989).
- <sup>9</sup>H. O. Pierson, *Hand Book of Refractory Carbide and Nitride* (Noyes, Park Ridge, NJ, 1996).
- <sup>10</sup>P. D. Kirsch, C. S. Kang, J. Lozano, J. C. Lee, and J. G. Ekerdt, *J. Appl. Phys.* **91**, 4353 (2002).
- <sup>11</sup>B. R. Chalamala, R. H. Reuss, K. A. Dean, E. Sosa, and D. E. Golden, *J. Appl. Phys.* **91**, 6141 (2002).
- <sup>12</sup>S. Kang, H. J. Cho, K. Onishi, R. Nieh, R. Choi, S. Gopalan, S. Krishnan, J. H. Han, and J. C. Lee, *Appl. Phys. Lett.* **81**, 2593 (2002).
- <sup>13</sup>Y. Gotoh, T. Kondo, M. Nagao, H. Tsuji, J. Ishikawa, K. Hayashi, and K. Kobashi, *J. Vac. Sci. Technol. B* **18**, 1081 (2000).
- <sup>14</sup>J. D. Carey, R. D. Forrest, and S. R. P. Silva, *Appl. Phys. Lett.* **78**, 2339 (2001).
- <sup>15</sup>A. T. Sower, J. A. Christman, M. D. Bremser, B. L. Ward, R. F. Davis, and R. J. Nemanich, *Appl. Phys. Lett.* **71**, 2289 (1997).
- <sup>16</sup>Z. Wang, Z. Peng, K. Lu, and W. Wen, *Appl. Phys. Lett.* **82**, 1796 (2003).