

Scanning Microscopy

Volume 1 | Number 3

Article 5

4-22-1987

Carbide Field Emitters

Hiroshi Adachi

Muroran Institute of Technology

Follow this and additional works at: <https://digitalcommons.usu.edu/microscopy>



Part of the [Life Sciences Commons](#)

Recommended Citation

Adachi, Hiroshi (1987) "Carbide Field Emitters," *Scanning Microscopy*: Vol. 1 : No. 3 , Article 5.

Available at: <https://digitalcommons.usu.edu/microscopy/vol1/iss3/5>

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.



CARBIDE FIELD EMITTERS

Hiroshi Adachi

Department of Applied Materials Science
Muroran Institute of Technology
27-1 Mizumoto, Muroran, Japan
Phone no: 0143-44-4181

(Received for publication February 17, 1987, and in revised form April 22, 1987)

Abstract

It has been reported that field emission current from a carbide single crystal is much more stable than a tungsten field emitter. Recent progress in the development of stable carbide field emitters is reviewed.

Existence of an optimum flashing temperature is pointed out and a recently developed stabilizing technique of the carbide field emitter is introduced. It is also pointed out that the quality of the vacuum is still important for stable operation of a carbide field emitter.

Key Words: Electron gun, Cathode, TiC, TaC, Tungsten field emitter, Field emission, Cold field emission, High brightness, Point cathode, Carbide of transition metals, Stable field emitter.

Introduction

The brightness of a field emitter is much greater than that of thermionic emitters, so that high resolution electron microscopes should favor field emitters [5,6,7,26,51]. The only drawback of a field emitter is high level current fluctuations. Stabilization of the field emission current is difficult, so that it prevents the wide application of the field emitters.

So far two approaches have been taken to realize stable field emitters [2]. One is to develop thermal field emission cathodes and the other is to find better materials for field emitters. Carbides of transition metals have been shown to be excellent for field emitters. Recent progress in the development of carbide field emitters is reviewed in this paper with emphasis on TiC emitters. Although ZrO/W(100)[33,47,49,53] and TiO/W(100) [20] thermal field emission cathodes are practical stable high brightness electron sources, the review of these cathodes is outside the scope of this paper.

The materials for field emitters should be [2]: 1) of low work function; 2) of high melting point; 3) of low vapour pressure at high temperatures; 4) of low electrical resistivity; 5) chemically stable; 6) highly resistant to ion bombardment; 7) mechanically hard, and 8) able to be made into a fine sharp needle easily.

It is very difficult to compare various materials point by point. The low work function and the high melting point are the same requirements as for thermionic cathodes. A figure of merit has been defined based on the Richardson Dushman equation, and many materials are evaluated through this figure of merit [2,59,60]. Carbides of transition metals have very large values for the figure of merit, so that they are good materials for thermionic cathodes and have been examined by several researchers [18,21,25,30,46,54]. These are also of rather low work

function, of very high melting points, and very hard. The stability of ZrC against ion bombardment exceeds that of tungsten by four orders of magnitude [9]. The electrical resistivity is very low, just one order higher than that of metals. These features are desirable for field emitter materials.

Current fluctuations of field emission cathodes are mainly caused by interactions between the cathode surface and residual gas molecules. Thus low residual gas pressure is an essential factor for stable operation.

Current Fluctuation

Figure 1(a) is a typical current fluctuation of a TiC(100) single crystal field emitter, measured in a vacuum of 2×10^{-10} Torr at room temperature. The TiC field emitter has the following features [1,10,11,41]: 1) The current fluctuations are fundamentally step and spike like; 2) No flicker noise ($1/f$ dependent noise) is included, and 3) Little decay of the DC current level over long time periods. Almost the same behavior is observed for TaC [57], ZrC [10], SiC [27], and carbon [12,14,19,28].

The current fluctuations in a tungsten field emitter are caused mainly by the migration of adsorbed gas molecules on the cathode surface [2,50,55]. However, fluctuation of 0.3% has been still observed, even if it is operated in an extremely good vacuum condition of 10^{-12} Torr [39,40]. This current fluctuation does not come from the adsorbate but it is due to the migration of tungsten atoms at the cathode surface.

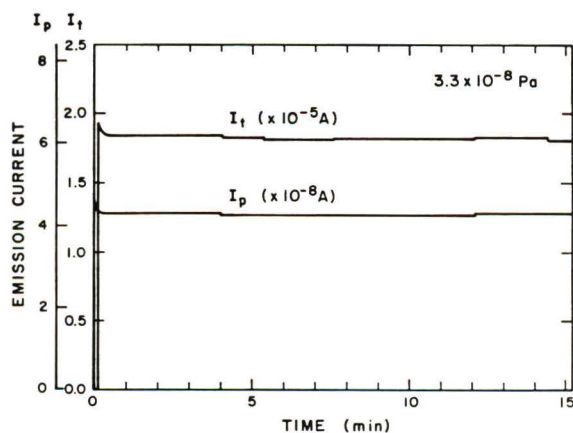


Figure 1. Typical step and spike like current fluctuations in the field emission from a TiC(100) single crystal at a relatively high emission current. I_p is the probe current measured through a $1\text{mm}\phi$ probe hole on the anode placed at 15 mm from the emitter tip. I_t is the total emission current.

Step and spike fluctuations in the current of figure 1 are also caused by residual gas molecules. The number of fluctuations observed in a period of 20 minutes is plotted against the product of the emission current and the residual gas pressure in figure 2 [3,11]. The experimental dots are on a line at 45 degrees to the axis. The proportionality to the emission current is due to stimulated desorption of gas molecules at the anode surface [44,50]. Thus the quality of the vacuum is an essential factor for stable operation, but the requirement is not so severe as for tungsten field emitters.

The reason may be related to the magnitude of the adatom dipole moment, e.g., the change in the TiC(100) work function by exposure to oxygen has been reported to be very small as shown in figure 3 [34,38,58]. This is in contrast with tungsten, whose work function increases dramatically. An oxygen exposure of 100L will result in a 1.6eV increase. When the surface of TiC is contaminated with tungsten, the change in the work function due to oxygen exposure is about 1.3 eV [35]. The lack of flicker ($1/f$ -type) noise may be due to no formation of a mobile physisorbed precursor to chemisorption [16,17].

When the emission current level is low, stable field emission can be observed for several tens of minutes even in relatively high vacuum level of 10^{-10} Torr, as shown in figure 4, where typical field emission current from a W(310) emitter is shown for a comparison [3]. In the case

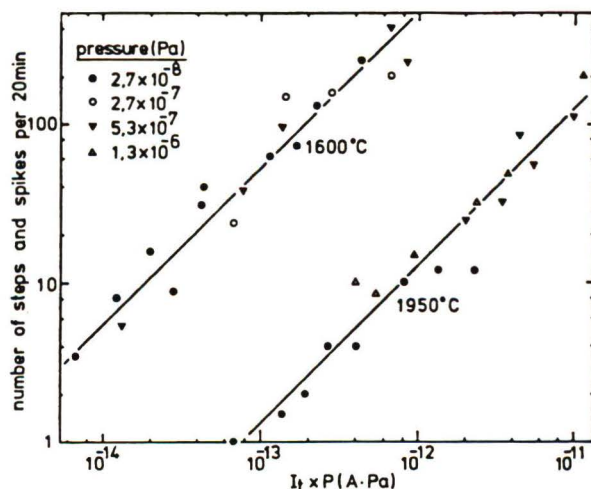


Figure 2. Number of steps and spikes per 20 minutes which appeared in the emission current from TiC as a function of the product of the total emission current and the vacuum pressure. The upper and lower lines respectively correspond to the flashing temperatures of 1600°C and 1950°C.

of tungsten field emitters, heating of molybdenum anode by 2000°C prior to the operation has been reported to cause a dramatic decrease in the current fluctuation [29,39]. This is also true for a carbide field emitter at a high emission current level [22]. Therefore avoidance of adsorbed gas molecules at the anode surface is essential for stable operation also for the TiC field emitters.

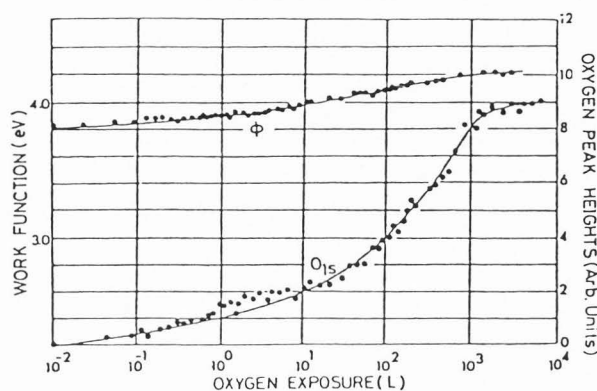


Figure 3. Change in the work function of a TiC(100) single crystal surface measured by using UPS (ultraviolet photoelectron spectroscopy) and the oxygen XPS (x-ray photo electron spectroscopy) peak heights as a function of oxygen exposure.

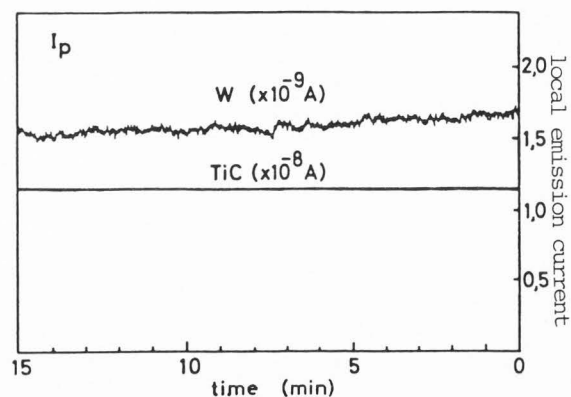


Figure 4. Typical traces on a strip recorder of the emission current from TiC(100) and W(310) oriented needles after continuous operation for five hours. Only the local current, which was collected through a 1mmφ probe hole on the anode plate, is shown. The total emission current was 2μA for TiC and 1μA for W. Pressure was 10⁻¹⁰ Torr.

Optimum flashing condition of the TiC field emitter

So far the mechanism of the step and spike like current fluctuation has not necessarily been understood completely, but it is very certain that the fluctuations are caused by the residual gas molecules in the vacuum. [3,11,56]

The current fluctuation is largely affected by the flashing condition as shown in figure 2. The flashing means a brief heating of the cathode tip just before the operation of a field emitter, and is essential for stable operation. Typically this process is done to remove the adsorbed gas molecules and for producing a round shape for the cathode apex. However, the apex of a TiC field emitter does not seem to be round after flashing.

The emission patterns of TiC field emitters change with the flashing temperature. Five distinct emission patterns are observed for TiC(100) as shown in figure 5 [3,11]. Lower flashing temperature than 1500°C does not give a symmetrical pattern. Flashing in two temperature regions 1500-1700°C and 1900-2100°C give symmetrical emission patterns, which present the four fold symmetry of the emitter crystal orientation, but the size of the pattern for the high flashing temperature is smaller than that for the low flashing temperature. The emission pattern for a flashing temperature between 1700-1900°C degrades in symmetry. Higher flashing temperature than 2100°C presents no symmetrical pattern.

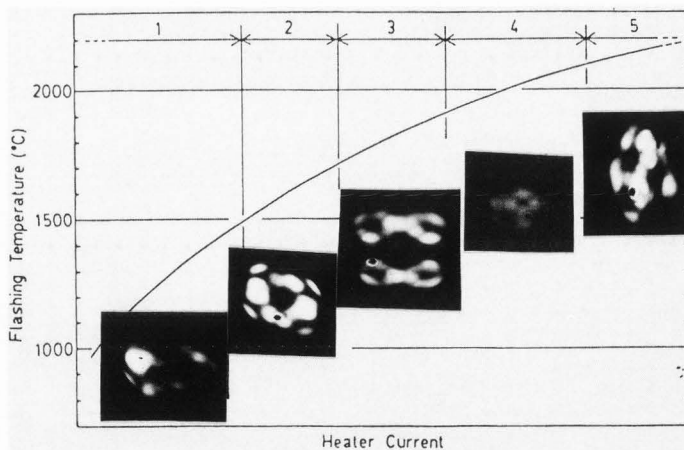


Figure 5. Five typical emission patterns for the TiC(100) single crystal tip as they appeared just after flashing. The patterns were observed at room temperature and five regions of the flashing temperature are distinguishable.

Five distinct emission patterns are observed also for a TiC(111) at almost the same flashing temperature regions as those for the TiC(100). Contrary to the case of TiC(100) emitters, the symmetric emission pattern for a high flashing temperature is larger than that for a low flashing temperature. These changes in the emission patterns occur due to the geometrical change of the cathode apex as stated below.

The stable field emission current is observed between 1900-2100°C, independent of the crystal orientation. Once a field emission tip experienced a high flashing temperature, the emission pattern does not change back to the pattern for a low flashing temperature, as long as vacuum is maintained.

This optimum temperature for stable field emission is somewhat higher than that reported by Oshima et al. [41]. They showed that the optimum temperature is between 1700°C and 1900°C. This difference in the optimum flashing temperatures may be due to the difference in the flashing processes. The flashing process of Oshima et al. is the following: namely, flashing of several seconds was repeated with an interval of a few minutes for a full day or longer. The flashing process of Fujii et al. is the following: namely, after the vacuum reached better than 10^{-10} Torr flashing of 5-15 sec was done. Successive flashing was done after the vacuum recovered better than 10^{-10} Torr, and repeated until the base pressure did not increase higher than 10^{-10} Torr [11]. The emitter tips of these two experiments were cut from the same mother crystal.

The applied voltage required to obtain a given emission current depends on the flashing temperature. Figure 6 shows the result of Oshima et al.'s measurements for a TiC(100) field emitter, where the applied voltage required to obtain 25 nA is plotted against the flashing temperature [41]. There are three distinct flashing temperature regions. Flashing at a temperature between 1400-1700°C required a low applied voltage. Once the field emission tip has experienced a flashing at the high temperature, the required applied voltage did not change back to the voltage for the low flashing temperature, as long as the field emission tip was kept in the vacuum [41].

The emission patterns for flashing temperatures between 1200-1450°C have no symmetry. A flashing temperature higher than 1450°C gives a symmetrical pattern. These features are also true for (111) and (110) oriented TiC crystals. A higher flashing temperature than 1700°C gives a stable field emission. Heating a TiC single crystal in a good vacuum to a

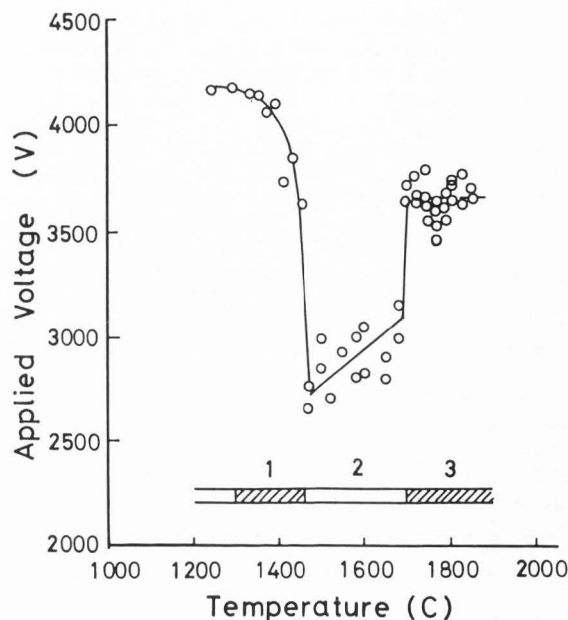


Figure 6. The applied voltages required for a field emission of $25\mu\text{A}$ from a TiC(100) tip are plotted against the flashing temperatures.

temperature higher than 1500°C means that a clean surface can be obtained, so that this stable field emission current is attributed to the clean emitter surface [41].

Heating a single crystal in a vacuum also changes its surface composition. The flashed TiC (100) surface consists of Ti and C atoms in an equal composition, but the outermost layer of the flashed TiC(111) surface consists of Ti atoms only and no carbon atoms are present [4,36,37,61]. Differences in the surface composition for different crystal orientations causes different faceting rates. As a result the cathode apex radius and shape change due to the flashing [1,11,15,41].

Geometrical change of the cathode apex

The changes in the emission patterns are caused by geometrical changes of the emitter apex. Fowler-Nordheim plots of the total emission current for TiC(111) and TiC(100) emitters are shown in figures 7 (a) and (b) [11]. The field emission current obeys the approximate Fowler-Nordheim equation [2]

$$J = 1.4 \times 10^{-6} F^2 / \phi \exp(-4.44 \times 10^7 \phi^{3/2} / F)$$

The slope of the Fowler-Nordheim plot is given by $(\phi^{3/2} / 25r)$, where ϕ is the work function and r is the effective radius of the cathode apex. A low flashing temperature gives a steeper slope than the high flashing temperature for the TiC(100)

emitter. On the contrary a high flashing temperature gives a steeper slope than a low flashing temperature for the TiC(111) emitter [11].

These changes in the Fowler Nordheim plot occur due to geometrical change of the cathode apex, rather than change in

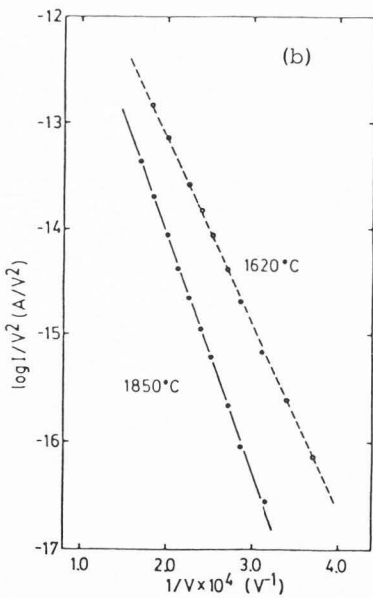
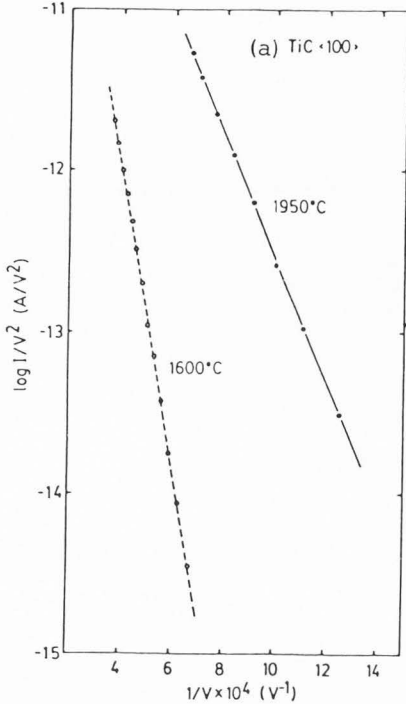


Figure 7. Fowler Nordheim plots of the field emission current from (a)TiC(100) and (b) TiC(111) tips. Temperatures indicated are the flashing temperatures. For each emitter, the lower temperature flashing was done prior to the higher temperature flashing.

the work function. According to the FIM (field ion microscopy) investigation of TiC single crystals, both (111) and (100) facets are developed by heating, and (110) facet is hardly developed [15]. The bright spots in the emission pattern correspond to the <110> directions. This fact can be understood by considering that (111) facets develop much faster than (100) facets. As a result sharp protrusions are developed to the <110> directions and the field emission occurs mainly at these protrusions [11].

Heating a TiC(110) crystal needle in a vacuum gives a sharp protrusion at the apex. A typical emission pattern is shown in figure 8(a) and the inferred apex shape is shown in figure 8(c) [36].

Stabilization by surface treatments

TiC field emitters are stabilized by a surface treatment. The process consists of three stages [23]. The first stage is flash heating at a temperature between 1500°C and 1600°C in a good vacuum condition to get a clean surface. The second stage is heating in a gas atmosphere at 1100°C for a given time t. Pressure P of the gas is about 10⁻⁶ Torr. The exposure is given by the product Pt in a unit of L (=10⁻⁶ Torr. sec). Ethylene, oxygen and hydrosulfide are used for the treatment. Sequential treatment of two or three kinds of gases sometimes gives better results [23,24]. The third stage is field emission of electrons at 10 μA total emission current in a good vacuum condition for a period of 30 minutes.

Figure 8 (b) is a typical emission

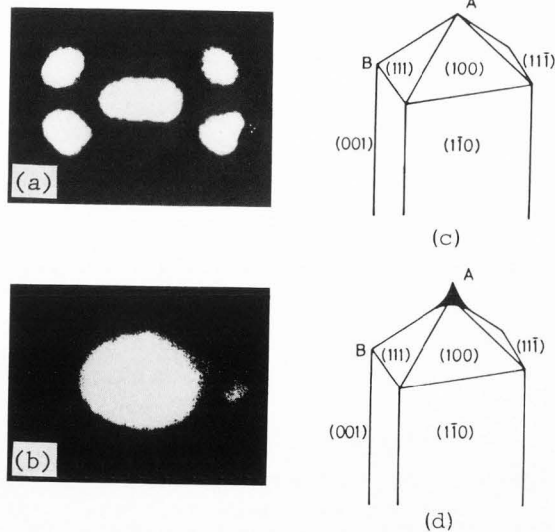


Figure 8. Field emission patterns and proposed tip shapes of the TiC(110) tip. (a) and (c) are for the clean, and (b) and (d) are for the oxygen processed tips.

pattern from a TiC(110) crystal treated by 8L oxygen exposure. Only one bright center spot can be seen and all other sub-spots are suppressed by the treatment. This indicates that the field emission occurs only at the very apex of the field emitter [23].

The applied voltage required to obtain 5nA emission is plotted against oxygen exposure in figure 9, (a) before and (b) after the third stage, i.e., 10 μ A emission for 30 minutes. An obvious difference due to the third stage begins at 1L exposure and remarkable differences are seen at more than 100L exposures. Thus the third stage is essential for the stabilization [23,24].

The work function of TiC increases by exposing it to oxygen, so that the applied voltage required to get a given current increases with oxygen exposure as seen on the curve (a). The adsorbed oxygen molecules are not desorbed by the third stage of treatment and the bright circular spot in the emission pattern can be seen only after the third stage, so that the dramatic decrease of the applied voltage as seen in curve (b) is due to the growing of a sharp protrusion at the apex [23].

The Fowler-Nordheim plot of the surface treated emitter is shown in figure

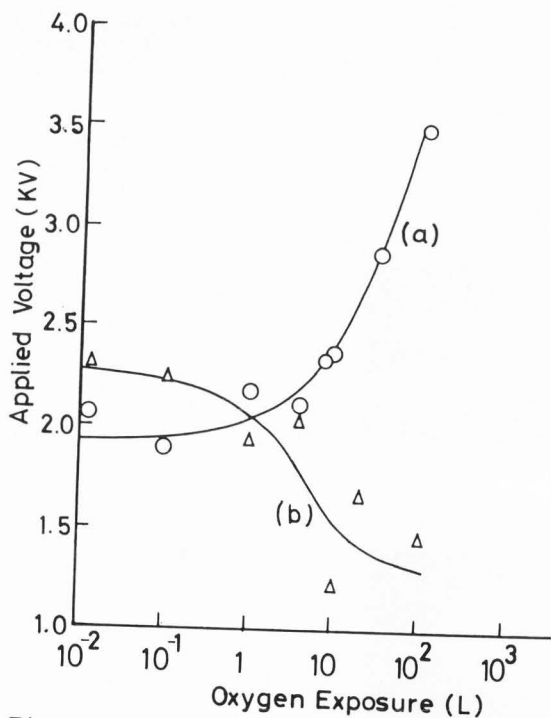


Figure 9. Oxygen exposure dependence of the applied voltage of the TiC(110) tip under the constant field emission current of 5nA. (a) Change in the applied voltage before emission of 10 μ A. (b) Change in the applied voltage after 30 minute emission of 10 μ A.

10. The slope becomes small and the emission increased after the treatment. The average apex radius is reduced by a factor of 0.5.

The maximum current for which no current fluctuation is observed for 20 minutes is plotted against the residual gas pressure in figure 11. The maximum current largely depends on the condition of the surface treatment. The successive treatment of 300L ethylene and 20L oxygen gives the most stable state. Very stable electron emission of 5 μ A is obtained at 10⁻¹⁰Torr.

Flashing at a higher temperature than 1200°C destroys the stable state. The applied voltage required for a certain emission current is steeply increased at 1200°C flashing. This steep change might be caused by evaporation of the material, which plays an important role for the stable field emission, but so far the evaporated material has not been identified [23].

Fabrication method

Carbides of transition metals generally have extremely high melting points, so that it is very difficult to grow a single crystal. The phases exist over broad composition ranges and appreciable vacancy concentrations (up to 50 at %) can exist on the carbon atom lattice sites with lesser concentrations on the metal-atom lattice sites [48,52]. The TiC single crystals for the stable field emitters have almost the stoichiometric composition. The composition ratio of carbon atoms to titanium atoms was about 0.97 [11,41].

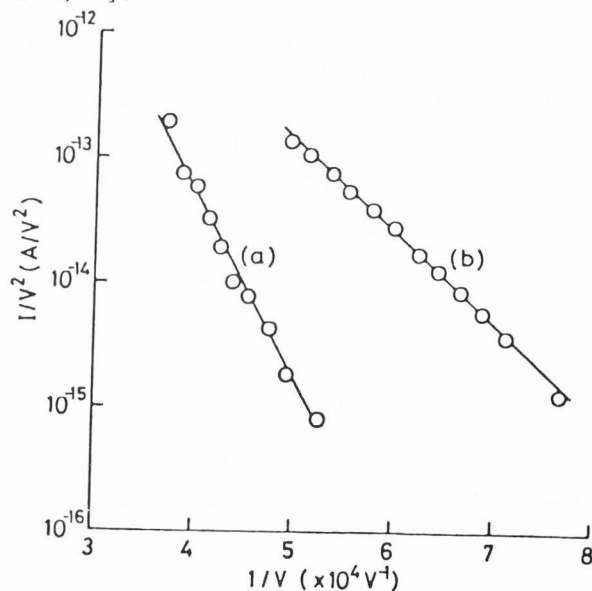


Figure 10. Fowler-Nordheim plots of TiC(110) tip. (a) is for clean and (b) is for oxygen processed tips.

Carbide Field Emitters

Carbide single crystals can be grown by a floating zone method with radio frequency induction heating [42]. Difficulties are mainly caused by evaporation of carbon atoms during crystal growth, so that it is necessary to compensate for the carbon deficiency while processing [43]. TiC single crystals grown by a floating zone method but without carbon compensation gave unstable field emission current [45].

Futamoto et al used carbide whiskers grown by chemical vapour deposition and reported that the emission current was not stable. Very high levels of step and spike like current fluctuations were found. The composition ratio of carbon to Ti was about 0.78. Stable FIM images could not be observed from non stoichiometric TiC, so that the surface of non-stoichiometric crystal might not be stable [13,15].

It is also reported that transition metals can be easily carburized when heated in hydrocarbon gas atmosphere [8]. Ono made a TaC cathode by heating a Ta needle in ethylene diluted by Ar and H₂ [32]. Hanawa obtained a TiC single crystal by heating a Ti needle in benzene mixed with hydrochloride. Neither emitter could show stable field emission, and the emission current included many steps and

spikes. No chemical analyses were done for these cathodes so that it is not known whether the cathodes had the stoichiometric composition. Most likely the high level of carbon deficiency might be included. FIM (field ion microscopy) work on carburized TaC showed that even extensive non-stoichiometry does not significantly degrade image quality, in contrast with the case of TiC whose image degrades with the carbon deficiency [31]. The interesting point is that the apexes of both carbide needles were single crystals of (100) orientation to the axis, although the starting materials were thin polycrystalline metal wires. In an ordinary case, the axis of an etched metal wire is (110) orientation, if the natural crystal phase of the metal is body centered cubic.

No surface treatment was done for the carburized TaC and TiC field emitters. The stabilization technique of the TiC field emitters by surface treatment was only recently developed, so that there may be some possibility to stabilize these emitters by applying the surface treatment.

Conclusion

Field emission currents from transition metal carbides are more stable than tungsten field emitters. The current fluctuations of carbide field emitters are also caused by interactions of the emitter surface with the residual gas molecules, so that quality of the vacuum is still essential for the stable operation.

The characteristics of the current fluctuation from a carbide field emitters are completely different from the current fluctuation of a tungsten field emitter. Current fluctuations of the carbide field emitters are fundamentally steps and spikes, and no flicker noise is included. This is due to the fact that adsorbed gas molecules hardly diffuse on the cathode surface and the change in the work function caused from the adsorption of gas molecules is small.

Recently, techniques for stabilization of TiC field emitters by surface treatment are established, although the stabilizing mechanisms have not necessarily been understood. This technique seems to have potential for stabilizing other kinds of carbide emitters. Further experimental confirmation of this technique is expected.

Acknowledgements

The author thanks Dr. Y. Ishizawa of National Institute for Research in Inorganic Materials for giving much information, and Prof K. Suzuki of Muroran Institute of Technology for his stimulating discussion.

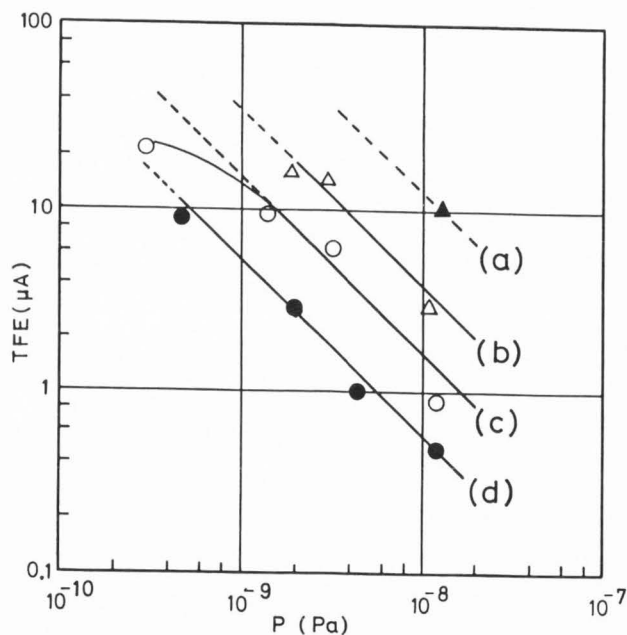


Figure 11. The maximum total field emission (TFE) current for which no current fluctuation is observed during a period of 20 minutes as a function of the residual gas pressure for the surface-processed TiC(110) tips. The surface treatments are (a) C₂H₄ (500L, 1100°C) + O₂ (10L, 1100°C), (b) C₂H₄ (100L, 1100°C) + O₂ (20L, 1100°C), (c) O₂ (20L, 1100°C) and (d) H₂S (10L, 1100°C).

References

- 1) Adachi H, Fujii K, Zaima S, Shibata Y, Otani S. (1984) Flashing Temperature Dependence of Field Electron Emission from TiC Single Crystals. (in Japanese). *Shinku* 27; 658-666.
- 2) Adachi H. (1985) Approach to a Stable Field Emission Source. *Scanning Electron Microsc.* 1985;II:473-487.
- 3) Adachi H, Fujii K, Zaima S, Shibata Y, Oshima C, Otani S, Ishizawa Y. (1983) Stable Carbide Field Emitter. *Appl. Phys. Lett.* 43 ; 702-703.
- 4) Bradshaw AM, van der Veen JF, Himpfel FJ, Eastman DE. (1980) Electronic Properties of the Clean and Hydrogen Covered TiC(111) Ti Terminated Polar Surface. *Solid State Comm.* 37; 37-40.
- 5) Crewe AV, Wall J, Welter LM. (1968) A High Resolution Scanning Transmission Electron Microscopy. *J. Appl. Phys.* 39; 5861-5868.
- 6) Crewe AV, Eggenberger DN, Wall J, Welter LM. (1968) Electron Gun Using a Field Emission Source. *Rv. Sci. Instrum.* 39, 576-583.
- 7) Crewe AV, Isaacson M, Johnson D. (1969) A Simple Scanning Electron Microscope. *Rev. Sci. Instrum.* 40; 241-246.
- 8) Eckstein BH, Forman R. (1961) Preparation of Tantalum Carbide. *J. Appl. Phys.* 33; 82-87.
- 9) Elinson MI, Kudintseva GA. (1962) Field Emission Cathodes of High Melting Metal Compounds. *Radio Engineering Electron Physics* 7; 1417-1423.
- 10) Fujii K, Zaima S, Adachi H, Otani S, Oshima C, Ishizawa Y, Shibata Y. (1983) Basic Field Emission Properties of TiC and ZrC Single Crystals. (in Japanese.) *Shinku* 26; 251-258.
- 11) Fujii K, Zaima S, Shibata Y, Adachi H, Otani S. (1985) Field Electron Emission Properties of TiC Single Crystals. *J. Appl. Phys.* 57; 1723-1728.
- 12) Futamoto M, Hosoki S, Kawabe U. (1979) Field Ion and Electron Microscopies of Carbon Tips. *Surface Science* 86; 718-722.
- 13) Futamoto M, Yuito I, Kawabe U. (1980) Field Ion and Field Emission Microscopy of Titanium Carbide. *Proc. 27th Field Emission Symposium (Tokyo)*; 363-367. (Maruzen Co.)
- 14) Futamoto M, Hosoki S, Yamamoto S, Kawabe U. (1980) Field Ion and Electron Microscopy Study of Carbon Field Emitters. (in Japanese.) *Shinku* 23; 430-437.
- 15) Futamoto M, Yuito I, Kawabe U, Nishikawa O, Tsunashima Y, Hara Y. (1982) Study on Titanium Carbide Field Emitters by Field-ion Microscopy, Field-electron Emission Microscopy, Auger Electron Spectroscopy and Atom-probe Field Ion Microscopy. *Surface Science* 120; 90-102.
- 16) Gasser RPH, Gowan PM, Newman DG. (1968) The Chemisorption of Carbon Monoxide on Tantalum Mono Carbide. *Surface Science* 11; 317-326.
- 17) Gasser RPH, Gowan PM, Newman DG. (1969) The Chemisorption of Hydrogen on Tantalum Monocarbide. *Surface Science* 14; 7-12.
- 18) Hojo H, Nakayama K. (1976) Coated Emitters of Transition Metal Carbides for Vacuum Measurement. (in Japanese.) *Shinku* 19; 312-317.
- 19) Hosoki S, Yamamoto S, Futamoto M, Fukuhara S. (1979) Field Emission Characteristics of Carbon Tips. *Surface Science* 86; 723-733.
- 20) Hosoki S, Takata K, Kaga H. (1986) Ti/W(100) Field Emission Source. *Proc. 11th Cong. on Electron Microscopy, Kyoto*; 219-222. (Maruzen Co.)
- 21) Ingold JH. (1963) Thermionic Properties of Some Refractory Metal Carbides. *J. Appl. Phys.* 34; 2033-2039.
- 22) Ishizawa Y, Aoki S, Oshima C, Otani S. (1986) Design and Operation of Extremely High Vacuum field Emission Electron Gun. (in Japanese.) *Shinku* 29; 544-548.
- 23) Ishizawa Y, Aoki S, Oshima C, Otani S. (1986) Field Emission Properties of Surface Processed TiC<110> Field Emitter. (in Japanese.) *Shinku* 29; 578-584.
- 24) Ishizawa Y. (1986) Carbide Field Emission Source. *Proc. 11th Int. Cong. on Electron Microscopy, Kyoto*; 223-226. (Maruzen Co.)
- 25) Kan KhS, Kul'var'skaya BS. (1978) Titanium Carbide Cathode with Improved Emission. *Sov. Phys. Tech. Phys.* 23; 460-462.
- 26) Komoda T, Todokoro H, Nomura S. (1977) Single Atom Image Observation by means of Scanning Transmission Electron Microscope. *Hitachi Review* 26; 151-156.
- 27) Kudo J, Nakamura S. (1975) SiC Whisker as a Field Emitter. *Jpn. J. Appl. Phys.* 14; 151-152.

Carbide Field Emitters

28) Lea C. (1973) Field Emission from Carbon Fibres. *J. Phys. D: Appl. Phys.* **6**; 1105-1114.

29) Martin EE, Trolan JK, Dyke WP. (1960) Stable High Density Field Emission Cold Cathode. *J. Appl. Phys.* **31**; 782-785.

30) Matskevech TL, Vil'k YuN. (1978) Thermionic-Emission and Adsorption Properties of a Eutectic Alloy of Zirconium Carbide and Tungsten. *Sov. Phys. Tech. Phys.* **23**; 1218-1221.

31) Meakin JD. (1968) Field Ion Microscopy of Refractory Metal Carbides. *Phil. Mag.* **17**; 865-869.

32) Ono M, Hojo H, Shimizu H, Murakami H. (1980) Tantalum Carbide Cathode for Field Emission Guns. 27th Int. Field Emission Symposium, Tokyo. Eds. Yashiro Y, Igata N. (Univ. of Tokyo); 353-362.

33) Orloff J. (1986) Development of the ZrO/W(100) Thermal Field Cathode. 11th Cong. on Electron Microscopy, Kyoto; pp. 211-214. (Maruzen Co.)

34) Oshima C, Tanaka T, Aono M, Nishitani R, Kawai S, Yajima F. (1979) Small Changes in Work function of the TiC(001) surface with Chemisorption of O₂ and H₂O. *Appl. Phys. Lett.* **35**; 822-823.

35) Oshima C, Zaima S, Tanaka T, Aono M, Shibata Y. (1980) The Work Function Change of the Tungsten-contaminated TiC(001) Surface With Oxygen Chemisorption. 27th Int. Field Emission Symposium, Tokyo. (Univ. of Tokyo) Eds. Yashiro Y, Igata N. 368-372.

36) Oshima C. (1981) Surface Properties of Transition Metal Carbides. (in Japanese.) *Oyo Buturi* **50**; 515-522.

37) Oshima C, Aono M, Zaima S, Shibata Y, Kawai S. (1981) The Surface Properties of TiC(001) and TiC(111) Surfaces. *J. Less-Common Metals.* **82**; 69-74.

38) Oshima C, Aono M, Tanaka T, Kawai S, Zaima S, Shibata Y. (1981) Clean TiC(001) Surface and Oxygen Chemisorption Studied by Work Function Measurement, Angle-Resolved X-Ray Photoelectron Spectroscopy, Ultra-Violet Photo-Electron Spectroscopy and Ion Scattering Spectroscopy. *Surface Science* **102**; 312-330.

39) Oshima C, Souda R, Aono M, Ishizawa Y. (1983) On the Field Emission Microscope with a Base Pressure of 10⁻¹⁰ Pa. (in Japanese.) *Shinku* **26**; 726-730.

40) Oshima C, Souda R, Aono M, Ishizawa Y. (1983) Stable Field Electron Emission

from a Tungsten Tip under the Ultrahigh Vacuum of 10⁻¹⁰ Pa. *Appl. Phys. Lett.* **43**; 611-612.

41) Oshima C, Souda R, Otani S, Ishizawa Y. (1984) Stable TiC Field Emitter. (in Japanese.) *Oyo Buturi* **53**; 206-211.

42) Otani S, Tanaka T, Hara A. (1981) Preparation of ZrC_x Single Crystals with Constant Compositions by Floating Zone Technique. *J. Crystal Growth.* **51**; 164-170.

43) Otani S, Honma S, Tanaka T, Ishizawa Y. (1983) Preparation of TiC_x Single crystals with Maximum Carbon Content by a Floating Zone Technique. *J. Cryst. Growth.* **61**; 1-7.

44) Saitou N. (1977) Trajectory Analysis of Ions Formed in the Field Emitter--- Inter Electrode Region. *Surface Science* **66**; 346-356.

45) Senzaki K, Kumashiro Y. (1974) Field Emission Studies of TiC Single Crystal. *Jpn. J. Appl. Phys. Suppl.* **2**; 287-292.

46) Shimizu H, Hojo H. (1977) Transition Metal Carbide Emitters. (in Japanese.) *Shinku* **20**; 17-24.

47) Shimizu R. (1986) Work Function Measurement of ZrO/W(100) Field Emitter. *Proc. 11th Int. Cong. on Electron Microscopy, Kyoto*; 215-218. (Maruzen Co.)

48) Stroms EK. (1967) *The Refractory Carbides.* Academic Press. N. Y.

49) Swanson LW and Martin NA. (1975) Field Electron Cathode Stability Studies Zirconium/Tungsten Thermal Field Cathode. *J. Appl. Phys.* **46**; 2029-2050.

50) Todokoro H, Saitou N, Yamamoto S. (1982) Role of Ion Bombardment in Field Emission Current Instability. *Jpn. J. Appl. Phys.* **21**; 1513-1516.

51) Tonomura A, Matsuda T, Endo J, Todokoro H, Komoda T. (1979) Development of a Field Emission Electron Microscope. *J. Electron Microsc.* **28**; 1-11.

52) Toth LE. (1971) *Transition Metal Carbides and Nitrides:* Academic Press.

53) Tuggle D, Swanson LW, Orloff J. (1979) Application of a Thermal Field Emission Source for High Resolution, High Current E-beam Microprobes. *J. Vac. Sci. Technol.* **16**; 1699-1703.

54) Yada K. (1986) Researches of Cathode Materials for Thermionic Emission. *Proc. 11th Int. Cong. on Electron Microscopy, Kyoto.* pp. 227-230. (Maruzen Co.)

55) Yamamoto S. (1977) Noise in Field Emission Electron Source. (in Japanese.) Oyo Buturi. 46; 1230-1233.

56) Yamamoto S, Hosoki S, Fukuhara S, Futamoto M. (1979) Stability of Carbon Field Emission Current. Surface Science 86; 734-742.

57) Zaima S, Saito K, Adachi H, Shibata Y, Hojo H, Ono M. (1980) Field Emission from TaC. Proc. 27th Field Emission Symposium, Tokyo. pp. 348-352. (Univ. of Tokyo).

58) Zaima S, Oshima C, Otani S, Aono M, Adachi H, Shibata Y. (1981) Change in Work function of TiC_x single Crystal with oxygen Chemisorption. 28th Field Emission Symposium, Oregon. (Eds.) Swanson LW, Bell AE. (Oregon Graduate Center.) 156-159.

59) Zaima S, Adachi H, Shibata Y. (1981) On the Evaluation of Cathode Materials-----Figure of Merit. (in Japanese.) Shinku 24; 660-666.

60) Zaima S, Adachi H, Shibata Y. (1984) Promising Cathode Materials for High Brightness Electron Beams. J. Vac. Sci. Technol. B2; 73-78.

61) Zaima S, Shibata Y, Adachi H, Oshima C, Otani S, Aono M, Ishizawa Y. (1985) Atomic Chemical Composition and Reactivity of the TiC(111) Surface. Surface Science 157; 380-392.

Discussion with Reviewers

J. Orloff: What is the advantage of carbide field emitters when they are applied to SEMs.

Author: In an ordinary case, the resolution of a SEM is the higher for the higher accelerating voltage. This is due to the fact that a high accelerating voltage gives quite parallel electron beam, which can give very fine focus. Recently, demands for low voltage SEMs with high resolution are increased, but the low accelerating voltage contradicts to high resolution. To overcome this difficulty, an electron source which can emit high density electrons from a very narrow area, i.e., a high brightness electron source is required. A field emission cathode is very bright, so that high resolution SEMs favor field emitters. The only drawback of a conventional tungsten field emitter is high level current fluctuations. Carbide field emitters are much more stable than tungsten field emitters.

M. Gesley: What crystal plane is being monitored by the probe current?

Author: The probe current was measured through a 1mm ϕ probe hole on the anode plate placed at 15 mm from the emitter tip. The emission pattern was four fold symmetry for the TiC(100) emitter. The probe current was measured by placing the probe hole at one of the bright spots, which do not correspond to facet planes but to protrusions surrounded by (100) and (111) facets on the emitter apex.

M. Gesley: The rms noise power for W(310) is about 70 times greater than for W(100), therefore on the basis of comparing noise power alone a qualification should be made regarding orientation.

Author: W(310) field emission cathodes are commonly adopted by high resolution SEMs, thus the typical current fluctuation from a W(310) field emission cathode is shown in figure 4 for comparison. It is true that the rms noise power for W(310) is much greater than for W(100), but the work function for W(100) is larger than that for W(310). Therefore more intense current can be obtained from a W(310) than W(100) emitter under the same operating condition. In the case of TiC field emitter, electron emission mainly occurs at protrusions on the cathode apex, so that it is very difficult to discuss the field emission characteristics of each crystal plane.

M. Gesley: Can a reference be given where the spectral density function of a carbide emitter has actually been measured? Has the absence of flicker 1/f noise been based on the type of measurements shown in figure 1? What is the minimum relative noise power detectable in this work? Is it possible the presence of 1/f-type noise has been missed due to detector sensitivity, dominance of spike noise, or absence of a power spectrum measurement?

Author: So far no reference has been published. The experimental result shown in figure 1 was a trace on a strip chart recorder, so that current fluctuations of high frequencies are missed. Very short current pulses of several micro seconds are detected by a high sensitive oscilloscope, but no random current fluctuation (1/f-type noise) is detected. Thus the behaviour of current fluctuation of a TiC field emitter is completely different from that of a tungsten field emitter.

M. Gesley: Given that heating a single crystal in a vacuum also modifies surface composition, is it not possible that this causes a change in the relative work functions of the various planes which results in variations in the emission patterns and abrupt changes in the applied voltage necessary to draw a given emission current? Is it not easier to explain the

Carbide Field Emitters

reduction in number of current spikes by flashing at 1950°C and the abrupt voltage change in figure 6 on a compositional change rather than a reduction in the TiC(100) radius?

Author: No systematic measurement of the work function change of the facet planes due to the flashing was done. The work function should be changed due to the change of the surface composition. However, in the case of TiC field emitters, electron emission does not occur over the facet planes, but occurs at protrusions surrounded by the facets [11]. The current fluctuations are possibly affected by the surface composition of the facets, but no explicit experimental evidence exist. The work function for the protrusion cannot be discussed by using the Fowler Nordheim equation, because only the average radius of the emitter apex is effective for the Fowler Nordheim equation and the effective radius of the protrusion itself cannot be deduced.

S. Yamamoto: What is the physical difference between the step and spike current fluctuations?

Author: The detailed mechanism of the current fluctuations has not necessarily been understood. It is inferred that the spikes of very short time occur due to collisions of residual gas molecules and/or ions, and the steps are due to absorption and desorption of residual gas molecules.

S. Yamamoto: If the apex of the TiC field emitter is metallic, flicker noise due to migration of adsorbed gas molecules should exist. What happens at the apex of a TiC field emitter when it is stabilized?

Author: It is true that field emission current from metallic field emitters always include flicker noise. It is inferred that the apex of the stabilized field emitter is covered by a material, but so far the kind of material has not been identified.

S. Yamamoto: In the case of carbon field emitters, shape of the apex was changed due to residual gas ion bombardment. The deformed apex could not be changed back to the initial round shape by flashing. How about for the case of TiC field emitters?

Author: The shape of a TiC field emitter also changes due to ion bombardment of the residual gas. The deformed apex cannot be changed back to smooth by flashing.