Journal of Ceramic Processing Research. Vol. 3, No. 3, pp. 228~230 (2002)

J O U R N A L O F
Ceramic
Processing Research

Surface treatment effects on the electron emission characteristics of ultra thin AlN coated molybdenum tips

D. Kang* and J.J. Cuomo
Materials Science and Engineering North Carolina State University, Raleigh, NC 27695 Box 7907

Even though surface treatment has proven useful for both metal and diamond field emitters, there is at this time no study of its effects on AlN emitters. In this study, a 7 nanometer film of AlN deposited on molybdenum emitter tip was treated with different gas plasmas (H_2, O_2, N_2). All surface treatments and measurements were carried out by using an *in-situ* technique inside the magnetron sputtering chamber. Changes in the measured I-V curves were not observed for the emitter treated with either hydrogen or nitrogen plasmas, but were observed for the oxygen plasma treatment and after the deposition of a very thin (<10A) aluminum film. The aluminum film deposition was very effective at enhancing emission from a Mo tip coated with AlN. This may be explained by lowering of the surface barrier due to the electronegativity difference at the surface.

Key words: AlN, Field emission, Surface treatment.

Introduction

Electron emission from Wide Band Gap (WBG) materials has been gaining interest due to their potentials for possible application in Flat Panel Displays (FED). Since WBG materials generally have high melting points, high thermal conductivity, low electron affinity, and are chemically inert, they have been considered as coating materials for gated and ungated metal tip arrays [1]. When coating sharp emitters, the major practical factors to be considered are the thickness [2-4], and surface condition of the coating layers [5, 6]. However, most of the previous studies [2, 4, 5, 6] were focused on diamond and carbon related materials. There are only a few [7-10] studies on AlN, but these show that AlN has properties similar to diamond. More importantly, there is no study on the effects of surface treatment on electron emission from ultra thin AlN coated Mo tips. In the present work, this is accomplished by using an *in-situ* I-V measurement technique that allows repeated deposition and measurement on the same tip without exposure to the atmosphere.

TIP Preparation, AlN Deposition and Experiments

Molybdenum field emitters were fabricated using an electrochemical polishing in KOH solution [2]. The typical radius of curvature of the tip was about 100 nm. Before AlN deposition the Mo tips were treated with an Argon plasma for two minutes to remove any possible surface contamination. An ultra thin AlN layer was deposited by reactive sputtering for 15 seconds at 200°C in a N_2-Ar atmosphere with the $N_2/(N_2+Ar)$ ratio of 0.75. The base pressure was 3.5×10^{-7} Torr. These conditions result in a coating layer approximately 7 nm thick, as measured by Transmission Electron Microscopy (TEM).

A schematic drawing of the I-V measurement set up for *in-situ* measurement and plasma treatment is shown in Fig. 1. Details of the system and procedures can be found in Reference 3. The AlN coated emitters were sequentially treated with hydrogen, oxygen, and again with hydrogen plasma within the deposition chamber. Following the plasma treatment, aluminum (10A) was deposited on the tip by sputtering an Al target with the magnetron for 6 seconds. The effects of nitrogen

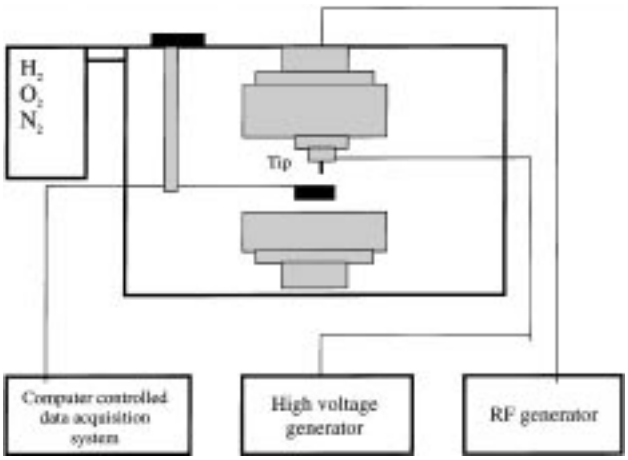

Fig. 1. Schematic drawing of *in situ* I-V measurement.

*Corresponding author:
Tel : 919-515-1973
Fax: 919-515-6538
E-mail: dkang@eos.ncsu.edu

Table 1. The experimental conditions of surface treatment

Gas	Pressure (Torr)	RF power (Watts)	Treatment time (mins)
Hydrogen	2×10^{-1}	39	2
Oxygen	2×10^{-1}	38	2
Nitrogen	2×10^{-1}	39	2
Aluminum	3×10^{-3} Torr (Argon)	DC modulated	6 seconds

plasma treatment were studied with using another Mo emitter coated with AlN under identical deposition conditions. The details of experimental conditions are shown in Table 1. After each treatment, I-V characteristics were measured immediately by a computer-controlled *in-situ* technique.

Results and Discussion

The coating thickness and morphology were measured by TEM as shown in Fig. 2. The thickness of the coating layer was about 7nm and it showed a very smooth and continuous surface. Because of this we believe that there is no change in emission characteristics by a roughened surface or by nano-protrusions. Figure 3. shows I-V characteristics of the emitter before and after surface treatment by different plasmas and aluminum depositions. Emission started at 620 V for the as-deposited tip with a cathode to anode distance of using a point to plane geometry.

Hydrogen plasma treatment, which has a big influence on diamond, did not significantly change the emission from the AlN coated Mo emitter. On the other hand, oxygen plasma treatment had strong adverse effects on emission, similar to the results found for diamond [6]. Nitrogen plasma treatment on another tip did not influence the emission characteristics (Fig. 4).

A surprising result is that an ultra thin layer of aluminum enhances emission in AlN coated metal tips. In addition, the aluminum deposition results in a great improvement in emission stability. Weide *et al.* [11] reported that a thin titanium layer changes the electron affinity of certain diamond surfaces from positive to negative, and consequently emission is enhanced. However, this is the first observation that an ultra thin aluminum film improves electron emission from AlN. It should also be noted that this thin aluminum layer, probably a few monolayers, might also have oxidized and produced a form of aluminum oxide, but this would be impossible to determine at this point in time.

Electronegativity, defined as the ability of an atom or molecule to attract an electron to itself, is a very useful term in predicting the surface dipole direction [8]. Table 2 shows electronegativity of some selected elements.

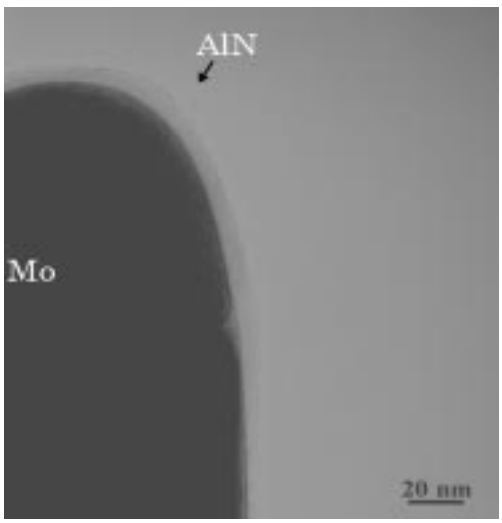

Fig. 2. TEM image of Mo tip coated with 7nm of aluminum nitride.

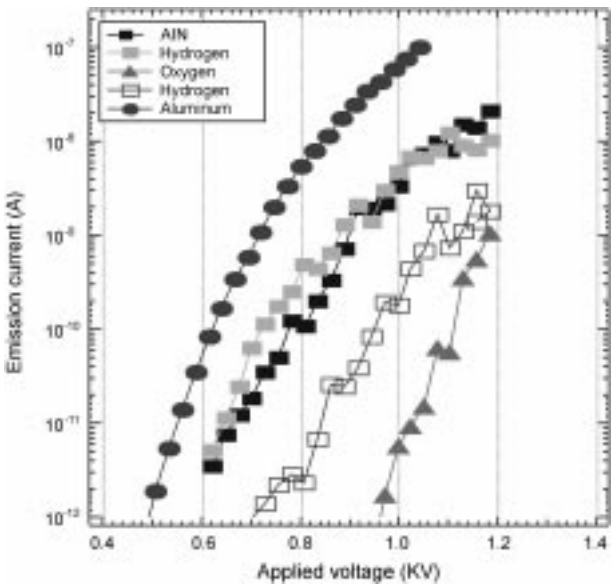

Fig. 3. I-V characteristics of AlN coated Mo tip as deposited(black squares), then treated in sequence by H_2 plasma, O_2 plasma, H_2 plasma again and finally aluminum.

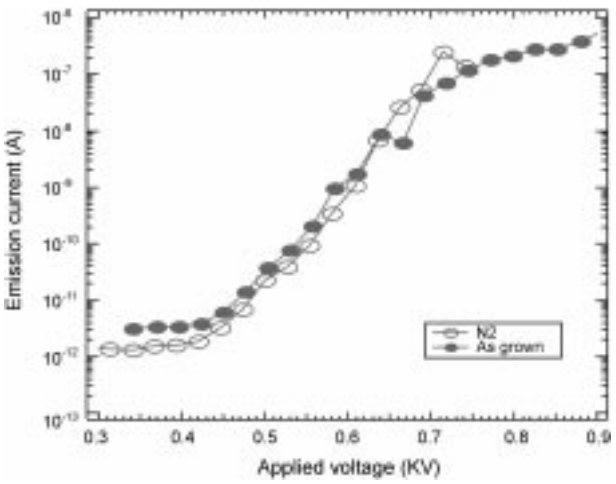

Fig. 4. I-V characteristics of AlN coated Mo tip treated by N_2 plasma.

Table 2. Electronegativities of selected elements

H	2.1	F	4.0
C	2.5	Li	1.0
N	3.0	Al	1.5
O	3.5	Si	1.8
Cs	0.7	Ti	1.5

Since the direction of the surface dipole influences the surface barrier with regard to electron emission, these values could explain electron emission characteristics as well. For example, in the case of oxygen plasma, the surface dipole direction is toward the bulk, due to the higher electronegativity of oxygen compared to both Al and N. Since the dipole field is added to the surface barrier, emission will drop off as in the case of diamond. The electron emission enhancement after the thin Al deposition may also be explained by this effect. Since aluminum has a lower electronegativity (1.5) compared to N (3.0), nitrogen atoms at the surface draw more electrons close to themselves, which results in the dipole direction being out of the bulk and subsequently subtracting from the surface barrier. This aluminum layer would be relatively stable if it terminated the surface of the bulk AlN. It would also be stable if it terminated any type of thin oxide layer on the surface. In either case, a surface dipole favorable to emission would result. Nitrogen plasma treatment also shows the expected I-V characteristics. The tendency of the surface to be nitrogen-terminated is implied by the fact additional nitrogen on the surface has no effect.

The case of hydrogen plasma treatment is different from what was expected. The electron plasma treatment has no effect, and the second treatment shows emission suppression, although this may be due to the incomplete removal of oxygen deposited by the previous plasma. The most likely explanation for this behavior is that unlike cubic silicon and diamond, hydrogen will not form a stable bond to the surface of hexagonal AlN. This is supported by the known fact that the incorporation of hydrogen in AlN films results in very high oxidation rates.

Conclusions

Plasma treatment is a very effective process in changing the electron emission characteristics of AlN coated Mo tips. Hydrogen plasma and nitrogen plasma treatments have little or no influence on emission, but oxygen plasma results in a significant decrease in electron emission. A very thin aluminum deposition results in a strong increase in electron emission. We propose that the effects of oxygen plasma and aluminum deposition are due to a change in the surface barrier by a strong surface dipole. Furthermore, the magnitude and direction of the dipole can be predicted by the difference in electronegativity between the underlying and terminating species.

References

1. V.V. Zhirnov, G.J. Wojak, W.B. Choi, J.J. Cuomo, and J.J. Hren, J. Vac. Sci. Technol. A(15), May/Jun 1997, p. 1733-1738.
2. V.V. Zhirnov, W.B. Choi, J.J. Cuomo, and J.J. Hren, Applied Surface Science 94/95 (1996) 123-128.
3. D.H. Kang, V.V. Victor, G.J. Wojack, E.D. Preable, W.B. Choi, J.J. Hren, and J.J. Cuomo, Journal of Vacuum Science and Technology B17[2] Mar/Apr (1999) 632-634.
4. L.K. Chea, X. Shi, B.K. Tay, S.R. Silva, and Z. Sun, Diamond Related Materials 7 (1998) 640-644.
5. N.A.N.A. Fox, S. Mary, T.Y. Davis, W.N. Wang, P.W. May, A. Bewick, J.W. Steeds, and J.E. Butler, Diamond Related Materials 6 (1997) 1135-1142.
6. T. Yamada, H. Ishihara, K. Okano, S. Koizumi, and J. Itoh, J. Vac. Sci. Technol. B 15[5], Sep/Oct (1997), 1678-1681.
7. G.J. Wojak, W.B. Choi, A.F. Myers, J.J. Cuomo, and J.J. Hren, International Vacuum Microelectronics Conference, St. Petersburg, Russia, July 1996 (unpublished).
8. R.J. Nemanich, M.C. Benjamin, S.P. Bozeman, M.D. Brenser, S.W. King, B.L. Ward, R.F. Davis, B. Chen, Z. Zhang, and J. Bernholc, Materials Research Society Symposium Proceeding Vol. 395, p. 777-788.
9. D.P. Malta, G.G. Fountain, J.B. Posthill, T.P. Humphreys, C. Pettenkofer, and R.J. Markunas, Materials Research Society Symposium Proceeding Vol. 468 (1997) p. 437-442.
10. B.V. Spitsyn, V.V. Zhirnov, A.N. Blaut-Bachev, L.V. Bormatova, A.F. Belyanin, P.V. Pashchenko, L.L. Bouilov, E.I. Givargizov, Diamond, and Related Materials 7 (1998) 692-694.
11. J. van der Weide and R.J. Nemanich, Journal of Vacuum Science and Technology B10(4), Jul/Aug (1992) 1940-1943.