Field emission characterization of silicon tip arrays coated with GaN and diamond nanoparticle clusters

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Wide band-gap materials show promise for applications in coating of field emission tips. Recently nanocrystalline hexagonal GaN crystallites as small as 12 nm average diameter have been formed using reactive laser ablation of gallium metal in nitrogenating ambient [T. J. Goodwin *et al.*, Appl. Phys. Lett. **70**, 3122 (1997)]. In this article we investigated the performance of ungated emitters with and without surface coating. Silicon tip arrays are coated by dielectrophoresis of gallium nitride nanoparticles or nanocrystalline diamond clusters from an ethanol suspension. The emitters were evaluated and compared before and after the surface treatment using SEM image and $I-V$ measurements in the diode configuration. The results suggest that the emitters benefit from coating the surface with nanocrystalline diamond clusters in terms of reduction in the turn on voltage by 100 V and increase uniformity in emission during low voltage operation. The long-term emission stability for both types of the coated cathodes was studied over a period of 90 h. The emitters coated with GaN nanoparticle clusters show a significant improvement in the current fluctuation from 150% (for untreated cathodes) to 50%. © *2003 American Vacuum Society.*
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I. INTRODUCTION

The presence of adsorbed species on the surface of the field-emitter tip can remarkably influence the behavior of electron emission based devices. The presence of the surface contaminants leads to unstable cathode operation. Therefore, the desirable cathode surface is one that is chemically inert. For high current emission, a cathode with a low work function is desired. Investigation of overcoating metal emitter tips (Mo) with Cs whose work function is ~1.8 eV has been conducted.[2] Low work function results is a chemically active surface; they rapidly degrade in their emission characteristics because of the increasing work function caused by the formation of chemical compounds such as oxides or hydrides on the emitter–tip surfaces. Hence potentially chemically inert emitter–tip overcoatings with wide-band-gap materials are preferred for a field emission system.

Cathodes coated with diamond,[3–5] have been evaluated by many researchers in recent years. The results reported show lowering of the effective work function and also increase in the emission current stability. The semiconductor III–V nitrides (GaN, AlN, InN) and their solid solutions also show great promise for applications in coating of field emission tips since their wide-band-gap encompasses a broad range of energies (up to 6.2 eV). These semiconductors have high chemical inertness and radiation resistance.[6]

Recently, nanocrystalline GaN clusters were successfully synthesized by using reactive laser ablation of gallium metal in a nitrogenating ambient.[1] The method uses a pulsed Nd: YAG (266 nm) laser beam focused on the target through UV grade quartz windows. Products of the synthesis are deposited on the selected target. As a result, hexagonal GaN crystallites as small as 12 nm mean diameter (with log-normal size distribution) have been formed.

These nanoparticles can be deposited on silicon and other substrates using dielectrophoresis.[7] In this article we investigate the performance of ungated emitter arrays when coated by dielectrophoresis of gallium nitride (GaN) nanoparticles (NP) and nanocrystalline diamond clusters.

II. FABRICATION

The device configuration considered for the surface treatment of the emitters is the ''bed of nails'' which is an array of ungated single crystal Si emitters placed in an area of 4 cm^2 with a tip-to-tip spacing of 6 μm. The emitters were formed from p-type (1–10 Ω cm) Si(100) substrate by the subtractive tip fabrication process as seen in Fig. 1. First, thermally grown oxide of 2000 Å thick, covered with 1000 Å thick chromium layer on the Si was patterned into a 3.0-μm-diameter disk. Using the chromium and the SiO_2 cap as a mask, the outline of the emitter tip was formed by means of reactive ion etching with SF_6. The tips were then sharpened using the method of oxidation sharpening as we have previously described elsewhere.[8] Tip caps were subsequently removed by wet etching of the silicon dioxide. The final silicon

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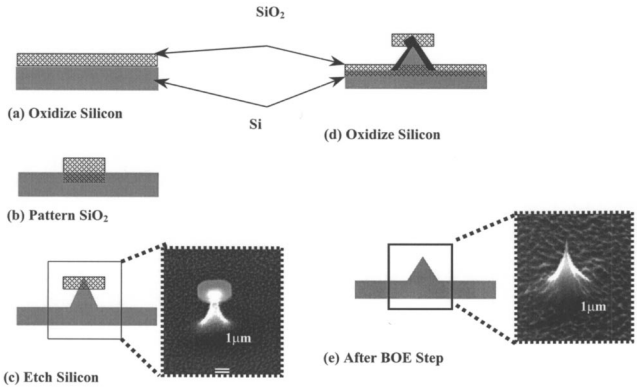

FIG. 1. Subtractive tip fabrication process.

emission tip is shown in Fig. 1(e). The typical tip curvature radius is estimated using SEM microscopy, to be on the order of 15 nm.

The emitters are coated using dielectrophoresis of GaN nanoparticles or nanocrystalline diamond from an ethanol suspension.[6] This technique allows us to coat the emitter with nanoparticle clusters on the tip surface as seen in Fig. 2. The advantage of this process was that the deposition was carried out in room temperature.

In this work, first results on emission from silicon emitters coated with nano-GaN particle clusters are reported. We studied and compared the field emission characteristics and emission stability before and after the emitter surface is coated with GaN nanoparticles or nanocrystalline diamond clusters.

III. RESULTS AND DISCUSSION

We tested the emission properties of the cathodes in a diode configuration. The packaging of the cathodes containing the array of ungated Si tips for testing in a high vacuum environment is done by placing quartz spacers, 70 μm thick between the cathode and the phosphor screen, which acts as an anode, as seen in Fig. 3.

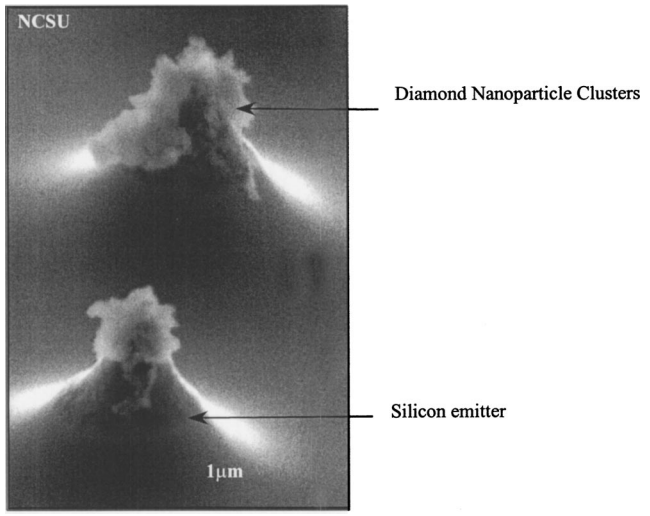

FIG. 2. SEM of the silicon emitter coated with nanoparticle diamond clusters.

The whole assembly is then held together on both sides by a spring clip. This arrangement helps us to remove the sample after the measurements, maintain the same measuring setup before and after the surface treatment and also allows us to compare the emission characteristic before and after treatment of the arrays. A medium voltage green-color phosphor (Osram Sylvania 9620) was deposited on patterned ITO glass by electrophoresis. The phosphor screen helps us to visually investigate the distribution of the emitting tips.

Field emission properties of the untreated and treated cathodes were measured in a vacuum chamber under a residual gas pressure of 10^{-8} Torr. The Hewlett–Packard 4142B modular dc source/monitor was used to acquire the emission data. A positive potential (to 1000 V) was applied to the anode, and the cathode had a negative bias. The field emission properties of the untreated and treated cathodes were measured after the tips were conditioned for 300 h under a constant dc bias. The conditioning of the emitters is also known as the forming process. The forming process is associated with the removal of the native oxide, burn off the

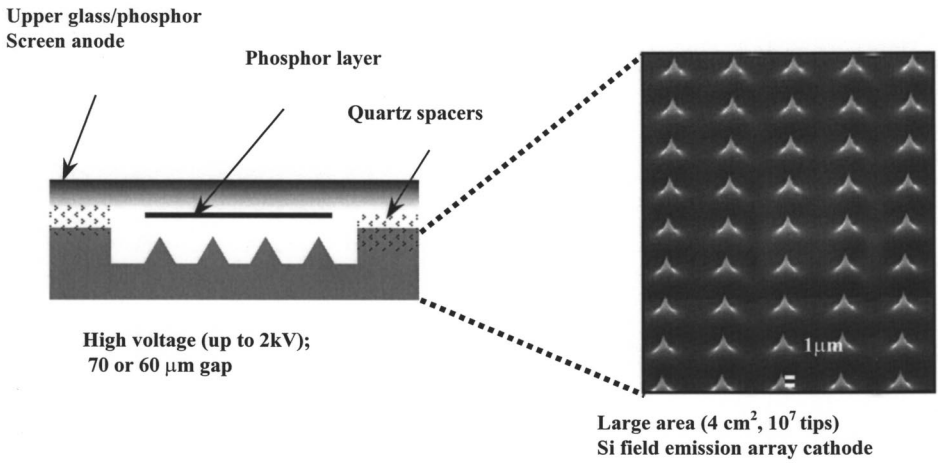

FIG. 3. Test structure: diode design for Si-tip array testing.

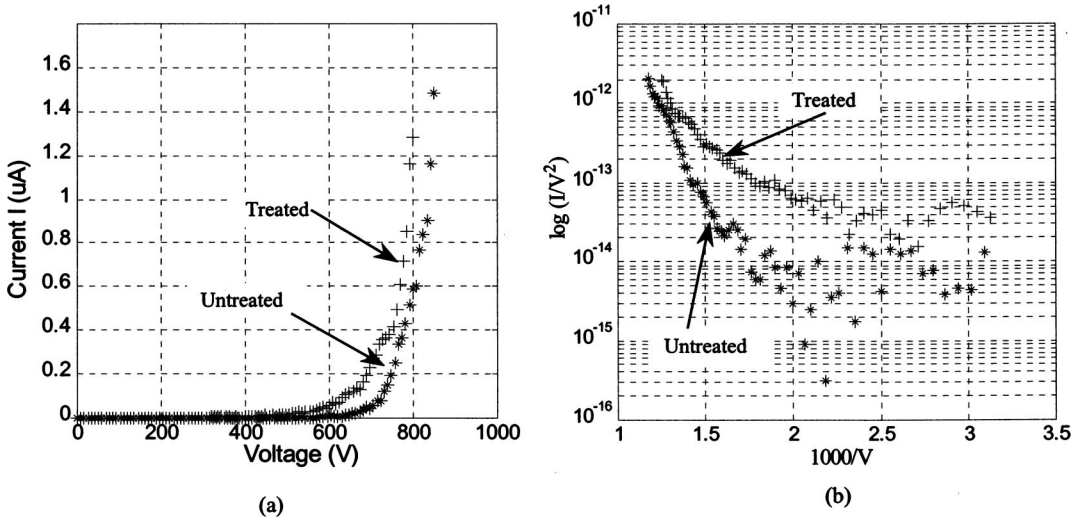

FIG. 4. (a) *I–V* characteristic and (b) the FN characteristic of the untreated and treated emitter array (coated with nanocrystalline diamond clusters).

fine protrusions (artifacts of the etching process) on the surface of the emitters and possible surface impurities, which helps to achieve stable and reproducible emission current showing linear Fowler–Nordheim characteristics.

Initially, ten samples have been coated to optimize the deposition parameters. After the deposition parameter was determined, five more samples were coated with nanocrystalline diamond. It has to be noted that all five diamond-coated samples showed the same trend on reduction of the turn on voltage and similar behavior of the emission characteristics, as described below. Unfortunately, the reproducibility for the GaN method was not easily confirmed due to extremely low yield of the nanocrystalline material synthesis and the lack of material available for coating. Only two samples with GaN had sufficient coating quality which made them suitable for further investigation.

A. Current–voltage characteristics

The *I–V* characteristics, as seen in Fig. 4(a), correspond to the two curves measured before and after the surface of the emitter was coated with nanocrystalline diamond (particle size about 5–10 nm) clusters. It is seen from the graph that there is a reduction in the turn on voltage by 100 V and there is an increase in the maximum extracted emission current at the applied voltage of 800 V by a factor of 2. The turn-on voltage is defined as the applied voltage required attaining 0.1 μA current. Figure 4(b) is a Fowler–Nordheim plot of these data. It is seen from the graph that the emission characteristics show a straight-line behavior in both the coated and the uncoated case, this confirms the occurrence of FN tunneling current. The slope of the FN curve decreased from 4 A/V for untreated emitters to 2 A/V after coating the emitter with diamond nanoparticle clusters. In order to explain the observed electron-emitting properties of the nanoparticle diamond clusters, we can infer that the increase in the emission current, decrease in the turn-on field and improvement in the emission uniformity during the low voltage operation is due to the increase in the emission sites and/or decrease in the effective work function. As nanoparticle diamond is a shock wave synthesized carbon cluster, it changes the morphology of the emitter surface and introduces nanoprotrusions that act as emission sites, thus increasing the number of emission sites emitting. The results do not show significant enhancement in the emission properties; this is due to the nonuniform deposition of diamond nanoparticle clusters. With the dielectrophoresis deposition method, for an array of microtips, many of the tips will have no diamond coating at all, while the size and location of the diamond clusters varies from tip to tip as seen from Fig. 2.

The *I–V* characteristics as seen in Fig. 5(a) correspond to the two curves measured before and after the surface of the emitter was coated with GaN nanoparticles (particles size about 2–20 nm). It is seen from the two curves that there is an increase in the turn on voltage and there is considerable degradation in the emission current. This result can be attributed to the nonuniform assembly of the nanoparticles on the emitter tip surface. The resulting assembly of nanoparticles predictably depends upon the applied voltage, suspension concentration, pulse duration, and tip geometry. Figure 5(b) is a Fowler–Nordheim (FN) plot. Again, both the treated and untreated case have straight FN behavior. This result can be attributed to the nonuniform assembly of the nanoparticles on the emitter tip surface.

B. Long-term emission stability

Long-term stability is the temporal dependence of the average emission current. The cathodes coated with GaN nanoparticles and nanocrystalline diamond clusters were operated over a period of 300 h. The long-term emission stability was studied over a period of 90 h. The current versus time characteristics as seen in Figs. 6(a) and 6(b) show the signature of the emission current during the course of this experiment. It has to be noted that both GaN coated samples exhibited similar reduction of the current fluctuations.

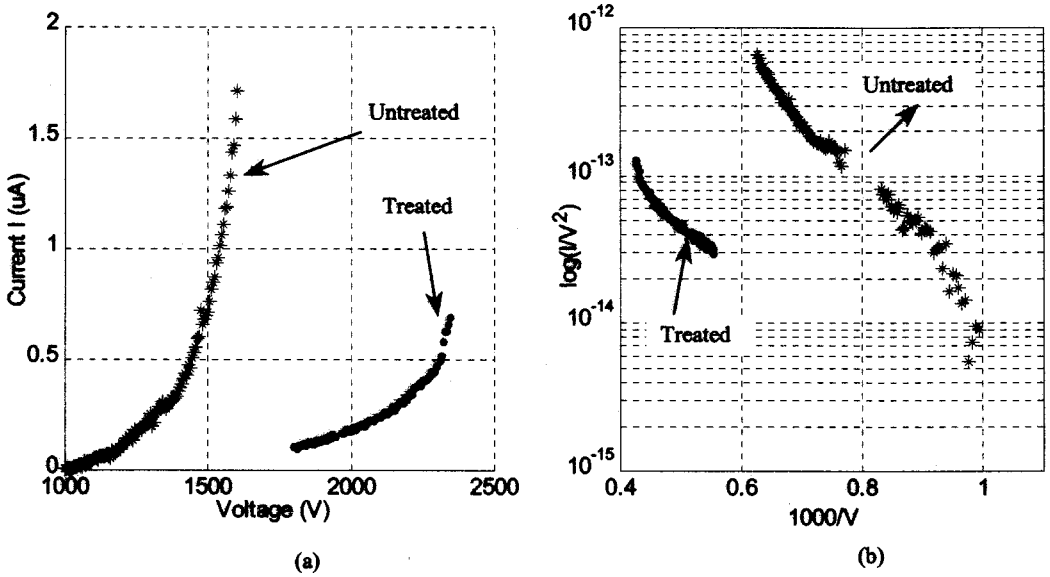

FIG. 5. (a) I–V characteristic and (b) the FN characteristic of the untreated and treated emitter array [coated with nanoparticle (NP) GaN clusters].

It is seen from Fig. 6(a) that in the case of the emitter surface coated with GaN nanoparticle cluster, the current significantly decreases after the appearance of an initial short pulse and remains constant over the rest of the operation cycle. Such a short pulse with height about 8 μA indicates the appearance of gas discharge of the tested FEA which resulted in a remarkable decrease of the emission current. The cathode still works at a lower emission level of about 0.5 μA. The other short pulses that appear do not show significant altering in the emission current level, which means the discharge energy is under the destruction limit. One possible mechanism concerning with gas discharge has to be related to field enhanced operation of contamination in combination with the gas ionization. Except for the few initial bursts, the current is stable, indicating a clean surface, at least for the duration of the measurement.

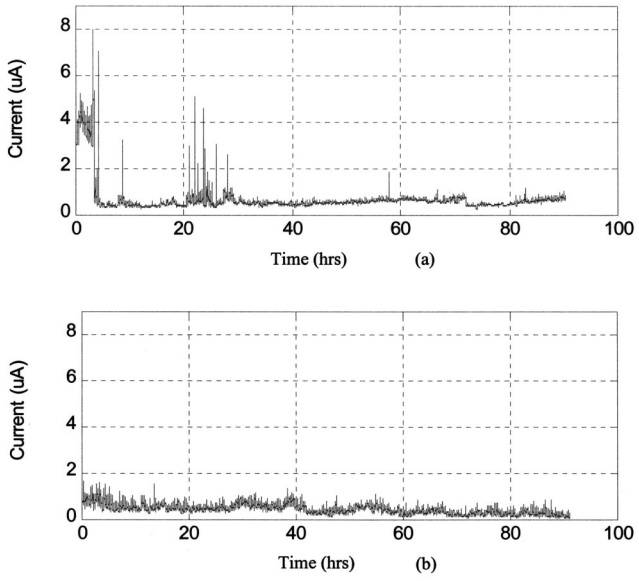

FIG. 6. I–t characteristics observed over an operating period of 90 h for the emitter array treated with (a) GaN nanoparticle clusters (b) with nanocrystalline diamond clusters.

It is seen from Fig. 6(b) that in case of the emitter surface coated with diamond nanoparticle clusters, the current is relatively stable over the operating cycle. The signature of the emission current consists of gentle change of the average emission current, which is probably caused by local work function changes due to the contaminants in the active surface. Hence it is necessary to treat the emitter surface with plasma (of inert, hydrogen, or forming gases) in the UHV environment to remove the contaminants after processing. This helps to obtain a stable and reproducible emission.

For both the cathodes the long-term stability during the last 13 h of operation was measured. Emission current fluctuations were determined as $S=(I_{\max}-I_{\min})/I_{\text{av}}$, where $I_{\max}$, $I_{\min}$ and I_{av} are correspondingly maximum, minimum, and average currents measured at fixed voltage. The duration at which $I_{\max}$, $I_{\min}$, and I_{av} are calculated is 1 h. Dependencies $I_{\text{av}}(t)$ and $S(t)$ for both the cathodes are shown in Figs. 7 and 8.

It is seen from Fig. 7(a) that in case of emitters coated with GaN nanoparticle clusters, except for the one initial burst, the current is stable, indicating a chemically inert surface. Figure 7(b) shows that the average current of 0.63 μA varies ± 0.05 μA during the operating cycle. Figure 7(c) shows the current fluctuation within 50% and a sharp transition in the region where a current burst occurs during the measurement.

It is seen from Figs. 8(a) and 8(b) that in case of emitters coated with diamond nanoparticle clusters, the current is stable and the average current of 0.72 μA varies ± 0.12 μA during the operating cycle. Figure 8(a) shows that the current fluctuation is around 100%.

Both the coated cathodes show an improvement in the long-term stability when compared to the untreated emitters

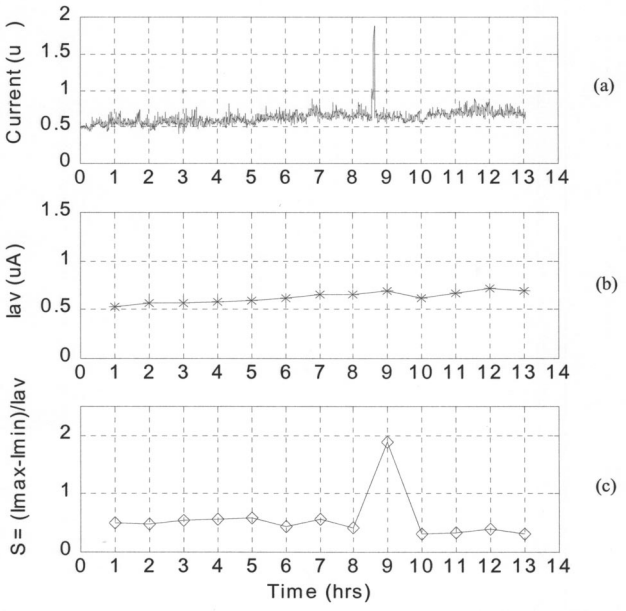

FIG. 7. (a) Current vs time, (b) average current vs time, (c) current fluctuation vs time of an array of silicon emitter coated with GaN nanoparticle clusters.

as seen in Fig. 9. The current versus time characteristics as seen in Fig. 9 shows the emission current stability of (a) an untreated, (b) coated with GaN nanoparticles, and (c) coated with nanocrystalline diamond emitter array over an operating cycle of 13 h. In case of untreated silicon as seen in Fig. 9(a),

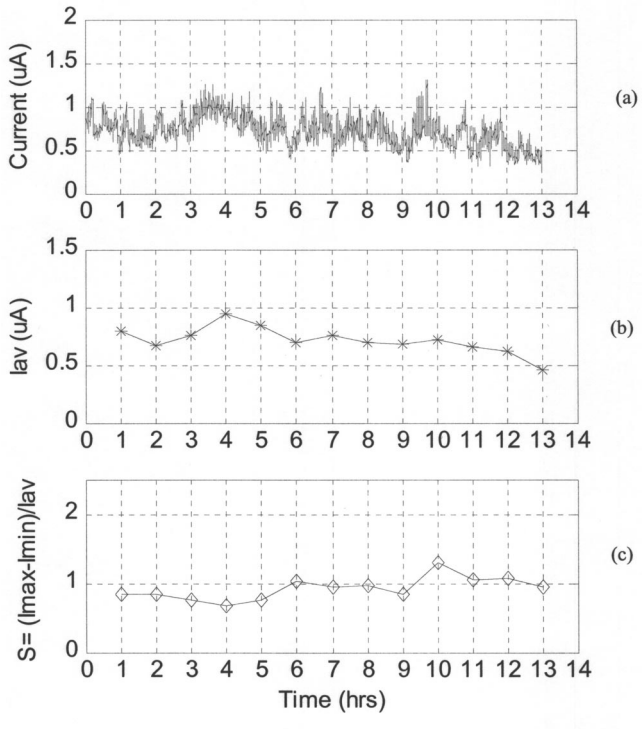

FIG. 8. (a) Current vs time, (b) average current vs time, (c) current fluctuation vs time of an array of silicon emitter coated with nanocrystalline diamond clusters.

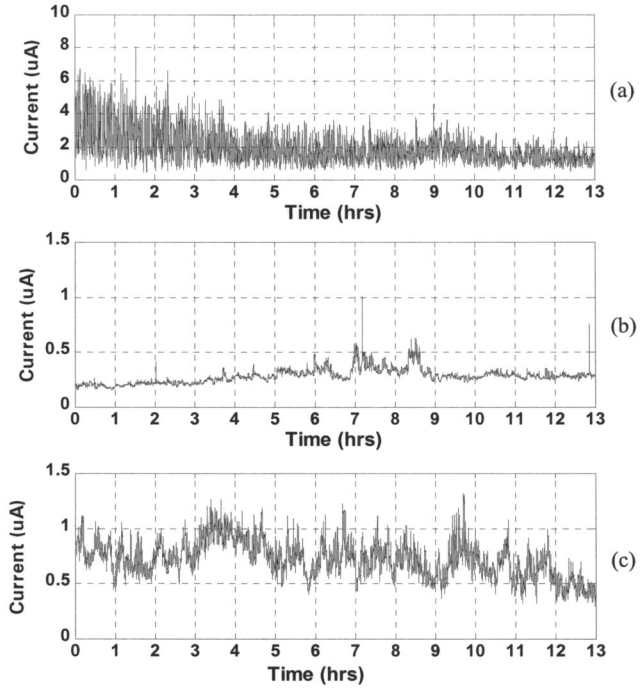

FIG. 9. Current vs time characteristics of an array of silicon emitter: (a) untreated; (b) coated with GaN nanoparticle clusters; (c) coated with nanocrystalline diamond clusters.

the standard deviation of current fluctuation was about 49% of the average current value (1.91 μA). The emitter surface coated with GaN nanoparticles and nanocrystalline diamond as seen in Figs. 9(b) and 9(c) show a significant improvement in the current stability. The standard deviation of current fluctuation was about 24% of the average current value 0.28 and 0.72 μA, respectively. The improvement in the current stability is mainly due to the chemically inert intrinsic behavior of diamond and gallium nitride. It acts as a protective layer for the tip from ion bombardment.

IV. CONCLUSION

In this article we studied the behavior of the cathodes coated with GaN nanoparticle and nanoparticle diamond clusters over an operating cycle of 90 h. Comparative studies show that the emitters coated with GaN nanoparticle and diamond nanoparticle clusters show a significant improvement in the current fluctuation over the uncoated emitters. Both the coated cathodes show stable operation during the course of the experiment. Hence, gallium nitride can be a promising candidate for coating materials, as it is a wide-gap semiconductor with a work function lower than diamond, chemically inert, capable of *n* or *p*-type doping unlike diamond (which cannot be doped *n* type). The degradation in the emission current after coating with GaN nanoparticle clusters appears to be due to the nonuniform assembly of the nanoparticles on the emitter surface. The assembly of nanoparticles predictably depends mainly upon suspension concentration and also upon other factors like applied voltage, pulse duration and tip geometry. To understand the emission

properties of the cathodes coated with GaN nanoparticle clusters in detail, further experiments with optimized deposition conditions have to be carried out.

As seen from the results of nonconformal nanoparticle diamond clusters, there is a degree of stabilization of the emission current and reduction of the threshold field, but they are subjected to the thermal runaway due to the poor thermal conductivity of Si. For an array of microtips, many of the tips will have no diamond coating at all, while the size and location of the diamond ''blob'' varies from tip to tip. It is desirable from both an experimental and device point of view to produce conformal, smooth diamond coatings with uniform, controllable thickness, capable of yielding low threshold fields, high electron emission currents with good reproducibility, lateral uniformity, and temporal stability. All the above properties are achieved by coating the silicon field emitter array with UNCD films using MPECVD in combination with a dielectrophoretic seeding process. A detailed experiment is being carried out to study the properties of UNCD diamond.

ACKNOWLEDGMENTS

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