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FIELD-EMITTER ARRAYS FOR RF VACUUM MICROELECTRONICS

C.A. Spindt, Program Director
A. Rosengreen, Senior Research Engineer
P.R. Schwoebel, Research Engineer
Physical Electronics Laboratory

SRI Project 2743

Prepared for:

Defense Advanced Research Projects Agency
Defense Sciences Office
Virginia Square Plaza
3701 North Fairfax Drive
Arlington, VA 22203-1714

Attn: Dr. Bertram H. Hui

ARPA Order No. 8162

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Approved:

Ivor Brodie, Director
Physical Electronics Laboratory

Donald L. Nielson, Vice President
Computing and Engineering Sciences Division

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C.A. Spindt, A. Rosengreen, and P.R. Schwoebel

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SRI International has completed the fifth quarter of a program to develop field-emitter arrays for vacuum microelectronics. The goals of the effort are 5 mA at 5 A/cm2 for at least 2 hours, and demonstrated modulation of the emission at 1 GHz.

Low-capacitance cathodes were fabricated that produced 10 mA emission with an applied voltage of 130V, using a chemical vapor deposition process to produce SiO2 layers. One year of continuous 1000-tip cathode operation was achieved for a low-frequency emission test, significantly exceeding the program current density goal. Fabrication and assembly were completed for an apparatus required for microwave testing.

In the program to optimize performance of field-emitter arrays, a series of plasma-cleaning experiments, involving hydrogen glow discharge, was performed.

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EXECUTIVE SUMMARY

SRI International has completed the fifth quarter of Phase I of a research and development program on the SRI Spindt-type field-emitter-array cathode with a view toward eventual applications in microwave amplifiers. Goals for this first phase have been set at 5 mA total emission, with a current density of 5 A/cm^2 for at least 2 hours and demonstrated modulation of the emission current at a frequency of 1 GHz. Our approach has been to identify methods of adapting and modifying the basic cathode structure of microwave operation and to experimentally investigate means of implementing those methods.

During the quarter we have accomplished the following, as documented in detail in this technical report:

- Continued research on basic cathode technology as defined by the goals of the DARPA program and related NRL project (Section 1)
- Fabricated low-capacitance cathodes that produced 10 mA emission with an applied voltage of 130 V, using our chemical vapor deposition process to produce SiO_2 dielectric layers (Section 2)
- Achieved one year of continuous 1000-tip cathode operation for a low-frequency emission test, significantly exceeding the program current density goal (Section 3)
- Completed fabrication and assembly of the apparatus required for microwave testing (Section 4)
- Performed a series of plasma-cleaning experiments, involving hydrogen glow discharge, directed toward optimized performance of field-emitter arrays (Section 5)
- Planned activities for the period of 1 January through 31 March 1993 (Section 6)

CONTENTS

ILLUSTRATIONS

1. INTRODUCTION

SRI International is participating in an effort of the Defense Advanced Research Projects Agency (DARPA) and the Naval Research Laboratory (NRL) to perform research and development on the SRI Spindt-type field-emitter-array cathode with a view toward eventual applications in microwave amplifiers. The current DARPA program is the vehicle for advancing the basic cathode technology for microwave applications (e.g., reducing intrinsic capacitance and driving voltage requirements), and continues the original program plan to establish the characteristics of the cathode in its preprogram state of development, identify methods of adapting and modifying the structure for microwave operation, and experimentally investigate means of implementing those methods. For the NRL program, which began earlier than the DARPA project, SRI has shifted emphasis to the support of NRL's in-house vacuum microelectronics program by providing NRL with state-of-the-art Spindt-type cathodes and consultation on setting up and using cathodes.

At the beginning of the program, two areas of development required immediate attention. The first was a materials and processing issue related to providing and maintaining a suitable vacuum environment for the cathodes. The second related to the cathode's inherent high capacitance and means for reducing that capacitance to a level that is consistent with the microwave applications envisioned for the cathode.

Our approach has been to research these two issues in parallel, using an easy-to-build, low-frequency-triode configuration fabricated on a TO-5 header as a test vehicle for materials and processing studies, and at the same time designing and researching fabrication techniques for building high-frequency-cathode structures on dielectric substrates (e.g., quartz or glass). Specific tasks that are being addressed on these related programs are:

1. Fabrication of a supply of state-of-the-art cathodes for use in establishing cathode characteristics, and for developing structures, circuits, and procedures for testing the cathodes as triodes
2. Development of a close-spaced anode test configuration that can be used to investigate triode characteristics at low frequency (kHz to MHz) in order to study the known problems with cathode survival under close-spaced anode conditions
3. Development of a circuit for driving the cathodes and demonstrating gain, frequency response, and peak emission levels
4. Studies of advanced cathode structures (geometry, fabrication technology, and processing) for high-frequency operation
5. Investigations (with NRL) of cathode mounting and connecting procedures using practices that are consistent with the microwave goals of the effort

2. LOW-CAPACITANCE CATHODE FABRICATION

During the three-month hiatus on the NRL program, low-capacitance (LC) cathode fabrication development continued on the related DARPA program. Our chemical vapor deposition (PECVD) process produced usable SiO_2 dielectric layers. We fabricated LC cathodes that produced 10 mA emission with an applied voltage of 130 V. Figure 1 is an oscillograph of the current/voltage trace for one of a group of cathodes (102L-E10-26B) that performed well. At the peak current of 10 mA, the current density is 400 A/cm^2, and the transconductance is about 400 μS.

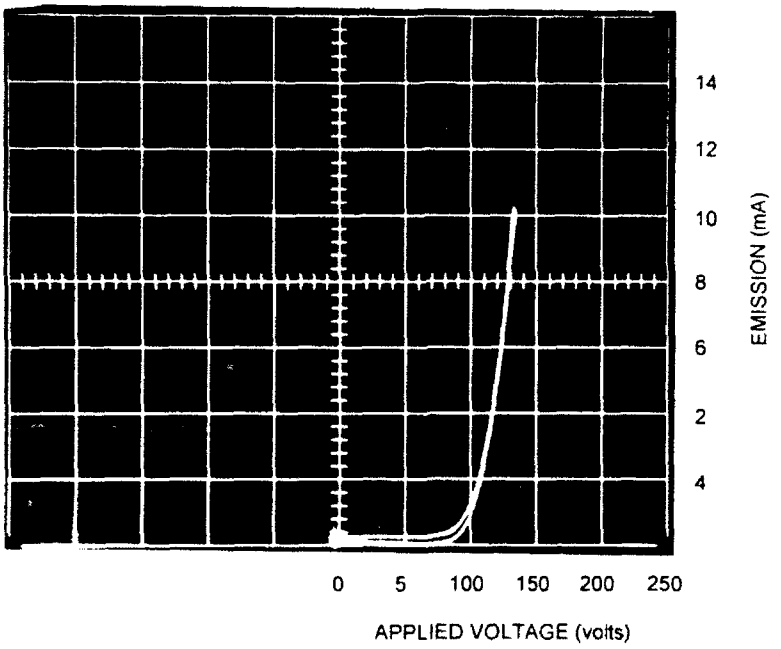

Figure 1. Current/voltage oscillograph of cathode 102L-E10-26B. The cathode consists of a 1.25-mm-long line of 625 tips with 2-μm spacing. The width of the overlapping electrodes is 4 μm. At peak emission, the current density is 400 A/cm^2, and the transconductance is 400 μS.

Several fabrication parameters are still not fully under control; however, we now have shown that it is possible to fabricate 1.25-mm-long single rows of emitter tips on 2-μm centers, centered on a 4-μm-wide active area. Figure 2 is a scanning electron micrograph (SEM) of a portion of one of the better cathodes of this kind that we have fabricated.

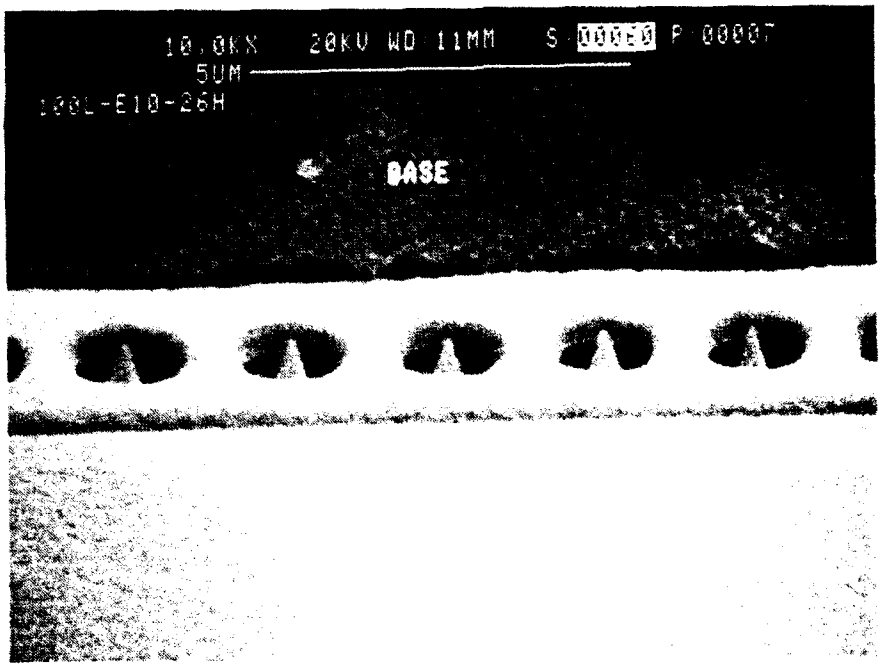

Figure 2. Scanning electron micrograph of a portion of a 1.25-mm-long line of 625 emitter tips spaced on 2-μm· centers. The width of the overlapping electrode area is 4 μm.

2.1 PHOTORESIST MATERIALS

Although we achieved positive results when we used the photoresists, developers, and strippers that we usually use in our cathode work, we experienced difficulties with the photoresist materials modified by manufacturers responding to environmental considerations The new products tend to behave differently from those we are used to working with.

Historically, we have used solvent-based AZ 1350 and 1375 photoresists (manufactured and distributed by Hoechst Celanese in Sunnyvale, California), 351 developer, and solvents (e.g., acetone) to strip the resist. Solvents were used because we found that the vendor's strippers (R 10 and ETM 130) corroded our molybdenum films.

Now the AZ 1350 and 1375 photoresists have been discontinued, and a new solvent-based resist (HPR 506, manufactured and distributed by OCG of Santa Clara, California) has been substituted. Unfortunately, when this resist is used with the recommended developer (HPR 428) and stripper (2001), it leaves a residue on the molybdenum that has been impossible to remove by any means other than sputter cleaning. We have experienced similar difficulties with Dynachem's EPA-194 AWEZ. Although sputter cleaning works well for some processes, we cannot sputter clean the cathodes after the cones have been formed, because molybdenum is sputtered from the sides of the cones onto the SiO_2 sidewall in the holes, shorting out the base and gate electrodes.

We consulted the vendor, who reports numerous complaints about residue from these new products. As a result, a new solvent-based resist (AZ 1529) is being made available. The

AZ 1529 resist is designed to be compatible with the R 10 or 2001 stripper, which has been used in the part of the process where we have experienced the difficulty. However, in separate experiments, we have found that the 2001 does not stain the molybdenum if the temperature is kept below 90 °C. It may also be possible to use solvents to strip AZ 1529. Or, we might be able to expose the remaining AZ 1529 after etching and use the developer to remove the resist, since the resist is positive. However, this can be done only if the resist has not been hard baked after development.

If these residue difficulties can be remedied by the new resists, the fabrication of LC cathodes should become fairly routine. The only remaining risky step would then be the actual cone formation process. The LC cathode structure on glass substrates has discontinuities or steps in the surface of the structure due to the patterning of the base electrode. These steps are the source of stress risers in the relatively thick films that are deposited during cone formation. These stresses often become sufficiently large to cause cracking of the thick films and the underlying substrate. This usually ruins the cathode since the emitter cones are at most 5 μm from the edge of the base electrode, and the breakup of the film and substrate usually includes the emitter area. When working with molybdenum, we are always working on the edge of this problem and must exercise extreme care with our control of the ratio of the rate of deposition between the molybdenum and closure films so as to minimize the stresses. These stresses can be greatly reduced by using other materials, such as niobium; eventually, other options will be investigated.

At the end of the quarter, we had been successful in removing residue from the base film with sputter cleaning. However, sputtering of the gate had not been successful because of contamination of the silicon dioxide sidewalls of the holes. Cathodes have been fabricated but have not tested well, presumably because of the residue from the resist.

2.2 VENDOR PROCESSING

Now that the PECVD system is on line, the only process dependent on outside vendors is precise positioning of the line of gate holes on the substrate by a high-resolution optical stepper.

3. LOW-FREQUENCY EMISSION TESTS

An ongoing life test with 1000-tip cathode 53i+300-7Q had been operating at 15 mA with a half-wave 60-Hz driving voltage for one year (8760 hours) as of 10 November 1992. The cathode has 1000 emitter tips covering an area of 6.55×10^{-4} cm^2 and, therefore, the current density is 23 A/cm^2 and the average emitter-tip current is 15 mA/tip. This is not extraordinary tip loading; however, the cathode is set up with a close-spaced nickel collector biased to +180 V. Under these conditions, the collector gets very warm. An attempt to increase the emission to 20 mA resulted in overheating the structure so that the gate contact warped and moved away from the cathode, thereby interrupting emission. After being off for a few moments, the gate reestablished contact, and emission was continued at 15 mA.

The emission has been very consistent over long periods of time. Figure 3 shows current/voltage oscillographs taken after operation at 15 mA for 1 hour, 3888 hours, 5736 hours, and 8448 hours, showing no discernible trend toward change.

Unfortunately, three days after reaching the one-year mark at 15 mA, the cathode was shorted by a mistake in wiring during the installation of another tube in the same rack. (The accident occurred, appropriately, on Friday the 13th of November.) However, the 23 A/cm^2 maintained for longer than a year far exceeds the program goal of 5 A/cm^2 for 2 hours.

4. HIGH-FREQUENCY TESTS

Final fabrication and assembly of the apparatus required for microwave testing was completed. Figure 4 is a photograph of the cathode mounting structure, microstrip lines, and SMA connectors assembled for the microwave tests.

First tests with the high-frequency test apparatus were initiated early in October. Trials with the Hewlett-Packard (HP) 8510 network analyzer were difficult because of the need for pulse driving the cathode to avoid overheating the anode structure. We found that it is necessary to protect the network analyzer with blocking switches so that transients do not damage the analyzer during the rapid rise and fall of the cathode driving pulse. During the time needed to modify the apparatus, a cathode was set up with RF coupling tees, and the emission was modulated by applying RF to the gate electrode with a high-frequency signal generator (8620A sweep oscillator with an 86220A RF plug-in) while the cathode was driven with our standard 60-Hz half-wave voltage pulse. The input and output signals were monitored with a high-frequency oscilloscope (Tektronix 7104 with 7429 plug-in).

This RF modulation set-up worked well for demonstrating modulation of the cathode emission. Figure 5 shows a schematic of the circuit and the waveforms used for pulsing the cathode emission at 60 Hz and modulating the gate emission at 220 MHz.

Figure 6 is an oscillograph of the anode-current envelope obtained with the circuit shown in Figure 5 when the gate is modulated with a triode set up for a 1.01-GHz signal while the cathode is driven with our standard 60-Hz half-wave driving voltage. This result demonstrates that it is indeed possible to modulate the cathode emission at a 1-GHz rate, meeting one of the goals established for the DARPA Initiative on Vacuum Microelectronics.

Difficulties with the HP Network Analyzer are still under investigation, and an HP representative has been asked to check the apparatus.

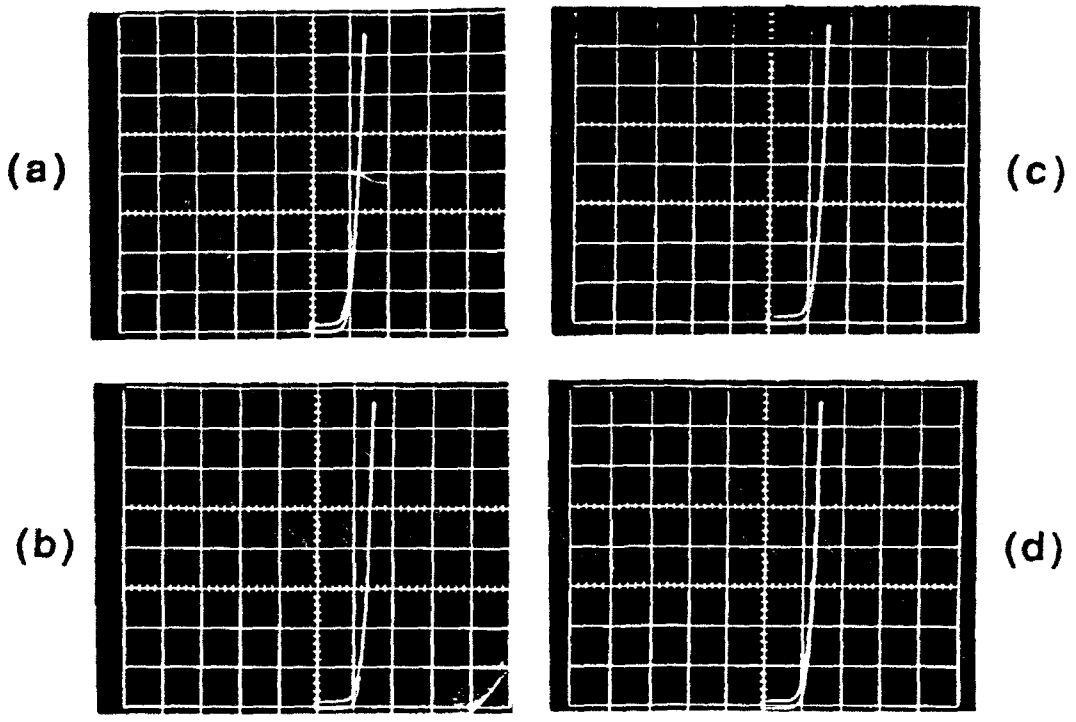

Figure 3. Current/voltage characteristics for 1000-tip array 53i-300-7Q after operation at 5 mA peak emission (23 A/cm^2) with a 60-Hz half-wave driving voltage for 1 hour (a), 3888 hours (b), 5736 hours (c), and 8448 hours (d)

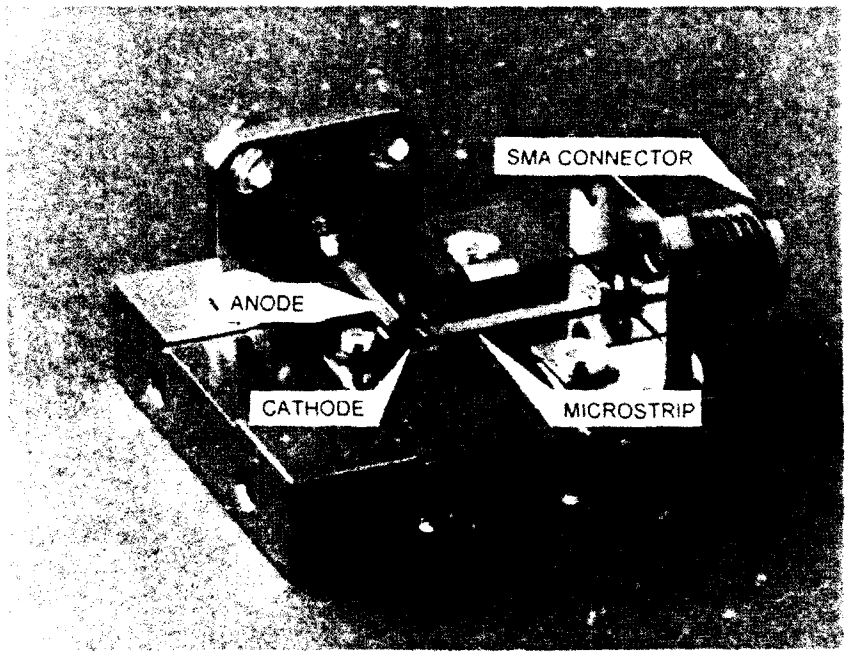

Figure 4. Microwave test fixture with SMA connectors, microstrip lines, and LC cathode mounting

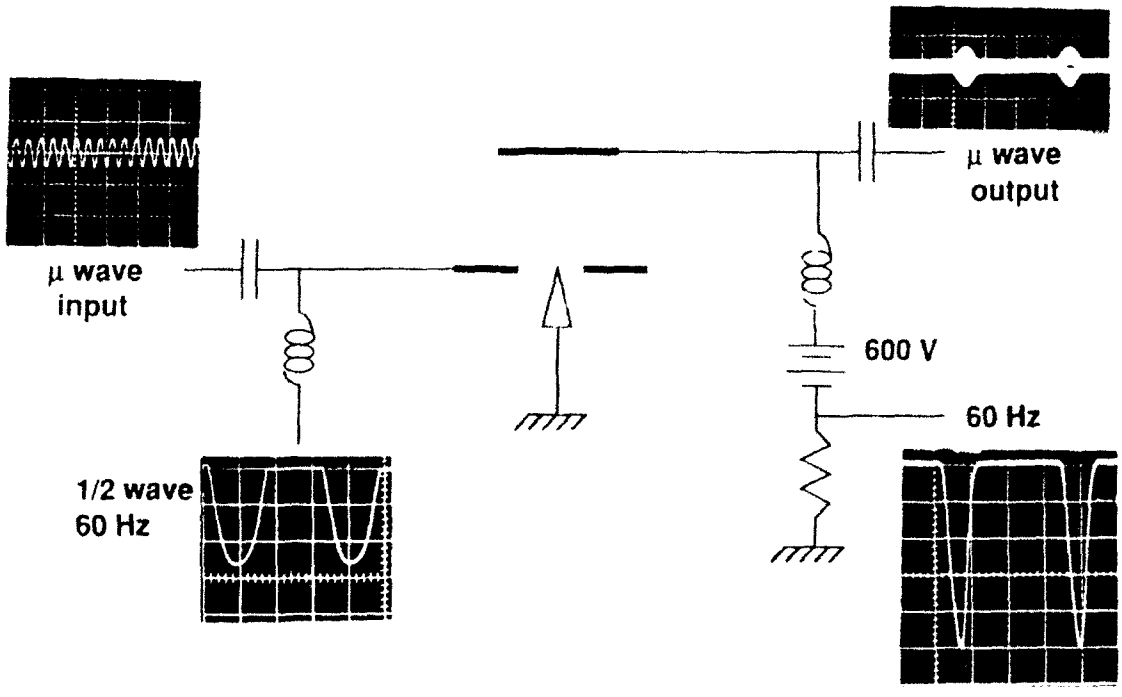

Figure 5. Schematic of the circuit and waveforms for demonstrating microwave modulation of the emitter array

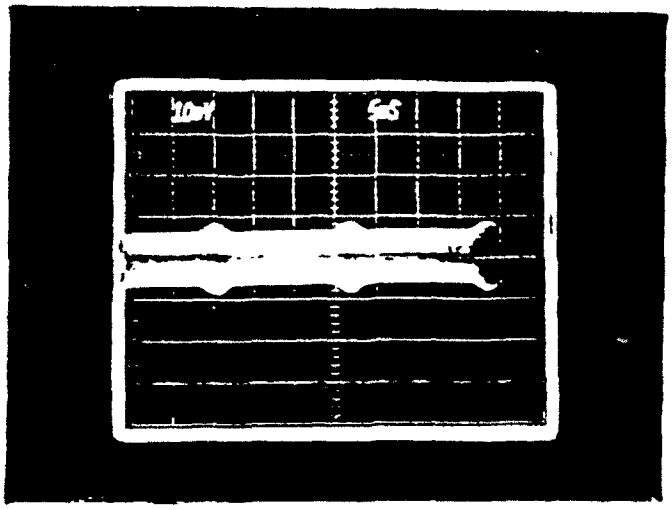

Figure 6. Emission current envelope for 1.01-GHz modulation of the emitter gate while pulsing the cathode on with a 60-Hz half-wave driving voltage as shown in Figure 5

5. FIELD-EMISSION MICROSCOPE STUDIES TO OPTIMIZE THE PERFORMANCE OF FIELD-EMITTER ARRAYS

Our last report gave a detailed outline of a series of experiments directed towards optimizing field-emitter array performance by increasing the rate and reliability of array turn-on, reducing the operating voltage, and maximizing the electron emission uniformity. Our first series of experiments has involved the *in situ* glow discharge cleaning of emitter arrays. We will see that the results of our glow discharge 'processing' experiments show that this procedure is a successful step towards the goal of emitter array performance optimization. A copy of a paper discussing in detail the results summarized here has been submitted for publication and is appended to this report.

Our work with hydrogen plasma processing thus far has demonstrated its importance to field-emitter array performance optimization through operating voltage reduction and improved electron emission uniformity. In addition, preliminary indications are that initial immediate array turn-on to high-current operation with good stability is possible. We conclude that this plasma-cleaning procedure has the potential to greatly simplify the implementation of microfabricated field-emitter arrays into technologically important devices.

5.1 BACKGROUND

It is well known that exposing emitter arrays to the ambient atmosphere and the processes involved in microfabrication leads to carbonaceous surface contamination and oxide formation. The presence of such contamination on the array surface increases the average surface work function and may lead to erratic emission turn-on voltages and current stability.

Typical surface cleaning procedures often involve high-temperature flashing or annealing (T greater than ~0.5 T_m) in vacuum or a gaseous environment. This is often combined with sputtering by inert gas ion bombardment.[1] Unfortunately, the inherent construction of field-emitter arrays precludes the use of such procedures. The combination of the material properties in the emitter arrays does not allow for effective surface cleaning by heating to temperatures greater than ~900 K without destruction of the array. In addition, ion bombardment sputter cleaning can result in the deposition of material on the SiO_2 walls, between the array's electrodes, thereby leading to electrical leakage. To circumvent these problems we have investigated the use of glow discharge cleaning techniques.

Glow discharges have been used in the cleaning of substrates prior to thin-film deposition for many years.[2] In addition, glow discharges have recently been applied to the cleaning of large vacuum chambers, such as those used for accelerators and fusion reactors, where conventional baking procedures are difficult to implement[3]. In the course of the vacuum chamber cleaning studies, some understanding of the initial and post-plasma-treated surface conditions, and the effectiveness of various gases for contaminant removal, have been achieved. Hydrogen plasmas were found to be effective in reducing oxides and removing carbonaceous contamination.[3]

5.2 EXPERIMENT PROCEDURE

The chamber is an all-metal ultra-high-vacuum (UHV) field electron/ion emission microscope having a base pressure of ~5×10^{-11} torr at room temperature following an ~20-hour bake-out at 250 °C. Hydrogen (99.99995%) was admitted into the chamber from a 1-liter glass flask.

The field emitters were of the type developed at SRI: metal-insulator-metal, employing molybdenum for the emitter tips and anode, and SiO_2 as the insulating film. In these experiments, microfabricated single tips and 100-tip arrays were utilized. All experiments were performed at room temperature, and the emitters were subjected to no heating besides that involved in the vacuum system bake-out.

Hydrogen glow discharges were operated with direct current, the discharge electrodes being the negatively biased field-emitter array (array electrodes connected together) and a counterelectrode that could be positioned 1 cm in front of the array.

A typical result for hydrogen glow discharge treatment of a 100-tip array is shown in Figure 7. Following installation and system bake-out, the array was operated at 1 μA of emission current until the emission current stabilized ($\Delta I < 1.0\%$). This typically required several hours. Following this, the current/voltage characteristic was determined. Line A in Figure 7 shows this characteristic as a Fowler-Nordheim (FN) plot.

After collection of this initial current/voltage data, the system was back-filled with hydrogen gas, and the dc glow discharge was initiated for various time periods. Conditions of the hydrogen glow discharges were maintained at: pressure, P ~5×10^{-1} torr hydrogen; applied voltage, V ~300 V; and current density, J = 0.1 to 1.0 mA/cm^2. Following plasma treatment, the system was again evacuated to UHV conditions and current/voltage characteristics redetermined.

For the 100-tip emitter array that initially yielded the current/voltage characteristic in Line A of Figure 7, a hydrogen plasma treatment for 2.5 minutes (dose of ~1×10^{18} ions/cm^2)

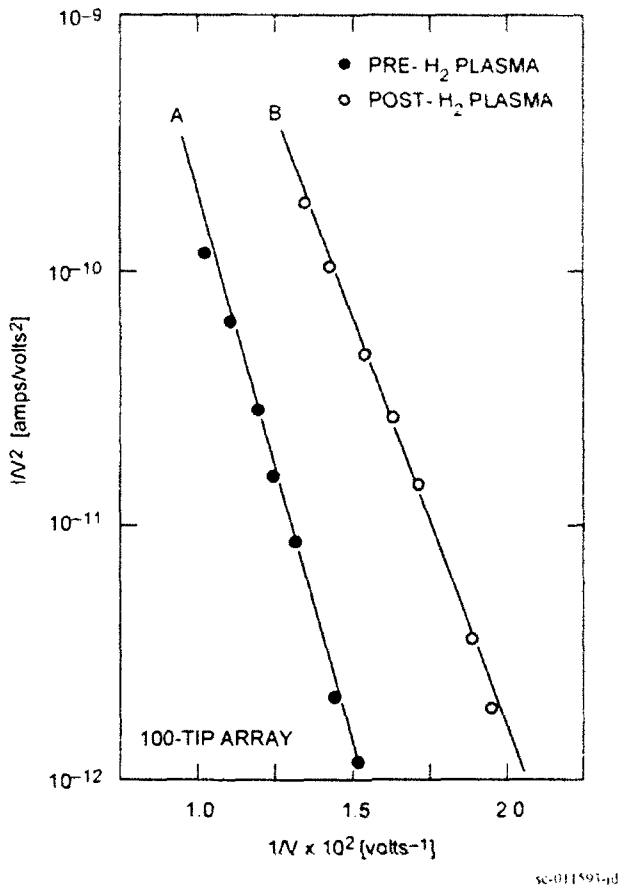

Figure 7. Effect of hydrogen plasma treatment on a 100-tip array. Line A: FN data prior to hydrogen plasma treatment. Line B: FN data following hydrogen plasma treatment (dose ~1 x 10^{18} ions/cm^2). The work function was 1.1 eV.

resulted in the current/voltage characteristic shown in Line B. This characteristic remained unchanged for continuous operation of the array for periods as long as ~100 hours, at which point experiments were terminated.

We have consistently observed a definite point in the dose, ranging from 10^{18} to 10^{19} ions/cm^2, above which no further changes in the current/voltage characteristic are observed. This result indicates that the cleaning action of the hydrogen plasma reached completion. This dose range has been observed to be that required to clean the surfaces of stainless-steel vacuum systems with hydrogen plasmas.[3]

Standard analysis of the FN data in Figure 7 yields information about the *relative changes* in the emitting area and work function.[4] In general, the change in emitting area was relatively small, typically increasing by less than a factor of 2 following hydrogen plasma treatment. In addition, as the sputtering yield of molybdenum by hydrogen[5] is only on the order of 10^{-4} atoms/ion at 300 V (assuming a clean surface), doses on the order of 10^{19} ions/cm^2 result

in the removal of approximately one monolayer of molybdenum from the emitter surface. Therefore, since the emitter tip shape change due to sputtering is small, it is reasonable to neglect a change in the proportionality factor, β between the magnitude of the applied electric field, E, and voltage, V ($E = \beta V$). Changes in the current/voltage characteristic induced by the plasma treatment are then primarily the result of changes in the work function.

These work function changes can be calculated from

$$\phi_1 = (S_1/S_2)^{2/3}\phi_2$$

where ϕ_1 and ϕ_2 are taken as the emitter work functions prior to and following hydrogen plasma treatment, respectively, and S_1 and S_2 are the corresponding slopes of the FN plots. As there is a dose beyond which further hydrogen treatment does not result in any improvement in the current/voltage characteristic, we assume that the emitters are 'clean' at this point and take ϕ_2 to be 4.9 eV, the work function of hydrogen-covered molybdenum.[6] Applying this reasoning to the results shown in Figure 7, we find that the hydrogen plasma treatment resulted in a work function decrease of 1.1 eV. Work function decreases of ~1 eV were typical, but decreases ranging from ~0.5 to 1.5 eV have been observed. Some variability is to be expected, as this merely reflects differing degrees and types of initial surface contamination.

In conjunction with current/voltage data, changes in the spatial distribution of the field electron emission distribution were investigated. Figures 8a and 8b are micrographs of the field-emission pattern prior to and following hydrogen plasma treatment, respectively, and correspond to the current/voltage characteristics in Figure 7. We observe that the uniformity of the electron emission is noticeably improved by the hydrogen plasma treatment. This result was typical for the arrays.

The effect of hydrogen plasma treatment on *single* microfabricated field-emitter tips was also investigated. The results were similar to those for the arrays: work function decreases ranged from ~ 0.4 to 1.5 eV, and the emission uniformity increased.

The increase in the emission uniformity of single tips after plasma treatment is clearly a contributing factor to the increase in uniformity observed with emitter arrays. We also note that the spread in work function changes observed with single emitter tips, as a result of the plasma treatment, persisted even between tips microfabricated in parallel and stored together until used. This indicates that the contaminants must be distributed *anisotropically* across the multitip field-emitter arrays. It can thus be concluded that the increase in the uniformity of the spatial distribution of electron emission observed with the emitter arrays following plasma treatment must also be, in part, due to the participation of more emitter tips in the electron emission process.

We have also conducted studies of recleaning arrays that have been exposed to dry nitrogen (99.99%) by venting the vacuum system to atmospheric pressure for time periods of ~10 to 60 minutes. Often the post-venting current/voltage characteristics fell somewhere in between those of the pre- and post-hydrogen treatment. In all cases, with hydrogen plasma treatment to a dose of $\sim 2 \times 10^{18}$ ions/cm^2, the pre-venting (i.e., the initial post-hydrogen treatment) current/voltage characteristic was recovered.

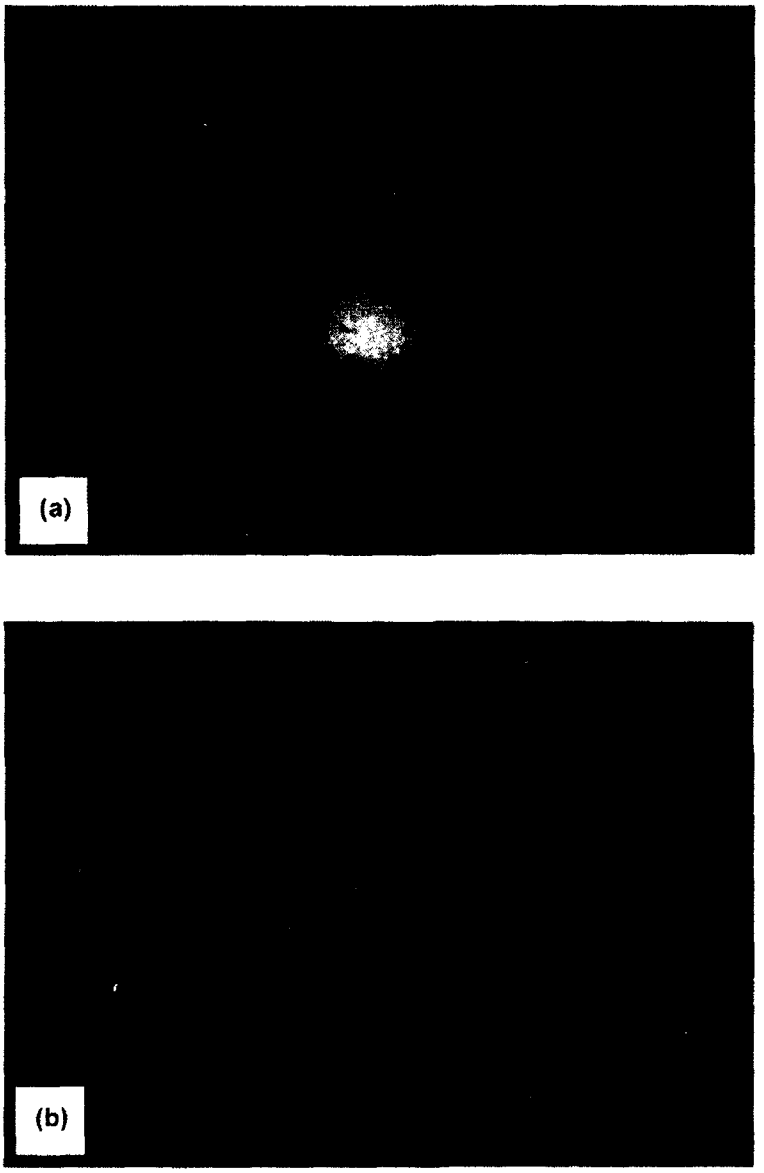

Figure 8. Field electron micrographs of 100-tip array whose current/voltage characteristics appear in Figure 7. (a) Electron micrograph of the array prior to hydrogen plasma treatment (V = 115 V, I = 10 μA). (b) Electron micrograph of the array following hydrogen plasma treatment (V = 91V, I = 10 μA).

In addition, we note that preliminary investigations involving the sequential use of hydrogen and He/O_2 plasma-cleaning procedures have been conducted. The results indicate that the He/O_2 plasma treatment causes not only oxidation, but also emitter blunting due to sputtering. No improvement over the current/voltage characteristics achieved following the initial hydrogen plasma treatment was observed.

5.3 CURRENT EXPERIMENTS

A very important aspect of field-emitter array technology involves streamlining the steps necessary to achieve stable current operation at the application-dependent power level. To date, emitter turn-on to an operational level of ~1 μA/tip requires high-temperature vacuum system bake-out (~700 K) and gradual increases in operating current over a time period of ~40 hours. This treatment is required so that the initial desorption of contaminants from the emitter tips is gradual, thereby avoiding sudden, large increases in emission current and array destruction. Clearly it would be advantageous to avoid prolonged procedures to achieve stable operation, and tube construction techniques would be less limited if high-temperature baking was not required.

We have initiated experiments to test whether hydrogen plasma treatment can serve as a substitute for the present processing procedures used to achieve emitter array current stability. To date we have observed that following system bake-out to ~250 °C and hydrogen plasma treatment, 1 μA/tip of current can be drawn from the array immediately at turn-on and that current stability is on the order of a few percent. No array failures have been observed as yet (five arrays tested) and we are presently in the process of increasing the initial current per tip extracted, and accumulating more statistics. These preliminary results look very promising.

6. WORK PLANNED

Efforts will be directed toward fabrication of a supply of cathodes for testing at NRL and SRI, and characterization of the cathodes with the HP 8510 network analyzer.

The glow discharge processing experiments will be continued to further bracket optimum procedures and complete the high current turn-on investigations. In addition, we plan to revisit the use of He, CH_4, and He/O_2 plasmas. As these experiments are being conducted we will be preparing experiments to investigate thermal-field forming (e.g., emitter tip remolding) effects to reduce operating voltage, and directly investigate the emission uniformity of the arrays and adapt our processing techniques to maximize the uniformity if necessary.

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Field-Emitter Array Performance Enhancement Using Hydrogen Glow Discharges

P. R. Schwoebel and C. A. Spindt

Physical Electronics Laboratory, SRI International, Menlo Park, California 94025

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ABSTRACT

The changes in the current-voltage characteristics and electron emission spatial distribution of microfabricated field emitters following exposure to hydrogen low-pressure glow discharges have been investigated. The hydrogen discharge was found to result in a permanent work function decrease typically between 0.5 and 1.5 eV following a dose of 10^{18} to 10^{19} ions/cm^2. The net result is a reduction in the operating voltage and an improvement in the spatial uniformity of the electron emission.

INTRODUCTION

The use of microfabricated field-emitter arrays in technologically important areas, such as microwave tubes and flat-panel displays, has motivated research into optimizing field-emitter array performance and into shortening the time required from initial turn-on to stable operation at the levels required by the device in which it is being used.[1] A fundamental issue involved in improving the reproducibility/reliability of the electron emission is controlling the physical and chemical state of the field-emitter surfaces.

It is well known that exposing emitter arrays to the ambient atmosphere and the processes involved in microfabrication leads to carbonaceous surface contamination and oxide formation.[2] The presence of such contamination on the array surface increases the average surface work function and may lead to erratic emission turn-on voltages and current stability.

Typical surface cleaning procedures for conventional field-emission tips usually involve high-temperature flashing or annealing (T greater than ~0.5 T_m) in vacuum or a gaseous environment. This is often combined with sputtering by inert gas ion bombardment.[2] Unfortunately, the inherent construction of micro-field-emitter arrays precludes the use of such procedures (see Figure 1). The combination of the material properties in the emitter arrays does not allow for effective surface cleaning by heating to temperatures greater than ~900 K without destruction of the array. In addition, ion bombardment sputter cleaning can result in the deposition of material on the SiO_2 walls, between the array's anode and cathode, and thereby lead to electrical leakage.

Our current method of achieving emitter array stability consists of vacuum baking (~400 °C) combined with a seasoning process in which the array is operated for extended periods (~100 hours) at relatively high electron current per tip loading levels (tens of microamperes per

tip). Although the emission characteristics are improved, this procedure does not result in the total removal of surface contaminants since the average fields at the emitter tip apices are less than those required for field evaporation for tightly bonded adsorbed atoms.[3] Also for technological applications it is clear that it would be convenient to avoid prolonged procedures to achieve stable operation, and that tube construction techniques would be less limited if high-temperature baking was not required.

In this paper, we report the use of low-pressure hydrogen glow discharge techniques for the purpose of cleaning the tips in a controlled way. Preliminary results from this laboratory have been published previously.[4]

Glow discharges have been used in the cleaning of substrates prior to thin-film deposition for many years.[5] In addition, glow discharges have recently been applied to the cleaning of large vacuum chambers, such as those used for accelerators and fusion reactors, where conventional baking procedures are difficult to implement.[6] In the course of the vacuum chamber cleaning studies some understanding of the initial and post-plasma-treated surface conditions, and the effectiveness of various gases for contaminant removal, has been achieved. Hydrogen plasmas were found to be effective in reducing oxides and removing carbonaceous contamination.[6]

EXPERIMENT

The chamber is an all-metal ultra-high vacuum (UHV) field electron/ion emission microscope having a base pressure of ~5×10^{-11} Torr at room temperature following an ~20-hour bake-out at 250 °C. Hydrogen (99.99995%) was admitted into the chamber from a 1-liter glass flask.

The field emitters were of the type developed at SRI: metal-insulator-metal, employing molybdenum for the emitter tips and anode, and SiO_2 as the insulating film[1] (see Figure 1). In

these experiments microfabricated single tips and 100-tip arrays were utilized. All experiments were performed at room temperature and the emitters were subjected to no heating besides that involved in the vacuum system bake-out.

Hydrogen glow discharges were operated with the discharge electrodes being the field-emitter array (array electrodes together) and a counterelectrode that could be positioned 1 cm in front of the array. In direct current discharges, the power supply was operated in the current regulating mode, whereas for alternating current discharges a 20-kΩ current-limiting resistor was placed in series with the power supply.

RESULTS/DISCUSSION

A significant difference in the resulting I-V characteristics of the emitter arrays was not observed when alternating current (60 cycle) as opposed to direct current hydrogen discharges were used. Glow discharges were therefore conducted with current-regulated dc power, as this facilitated control of the ion dose delivered to the emitter array.

A typical result for hydrogen glow discharge treatment of a 100-tip array is shown in Figure 2. Following installation and system bake-out, the array was operated at 1 μA of emission current until the emission current stabilized ($\Delta I < 1.0\%$). This typically required several hours. Following this, the I-V characteristic was determined. Line A in Figure 2 shows the I-V characteristic as a Fowler-Nordheim (FN) plot.

After collecting this initial I-V data the system was back-filled with hydrogen gas and the dc glow discharge initiated for various time periods. Conditions of the hydrogen glow discharges were maintained at: pressure, $P \sim 5 \times 10^{-1}$ Torr hydrogen; applied voltage, V ~300 V; and current density, J = 0.1 to 1.0 mA/cm^2. Following plasma treatment, the system was again evacuated to UHV conditions and I-V characteristics redetermined.

For the 100-tip emitter array that initially yielded the I-V characteristic in Line A of Figure 2, a hydrogen plasma treatment for 2.5 minutes (dose of ~1×10^{18} ions/cm^2) resulted in the I-V characteristic shown in Line B. This I-V characteristic remained unchanged for continuous operation of the array for periods as long as ~100 hours, at which point experiments were terminated.

We have consistently observed a definite point in the dose, ranging from 10^{18} to 10^{19} ions/cm^2, above which no further changes in the I-V characteristic are observed. This result indicates that the cleaning action of the hydrogen plasma reached completion. This dose range has been observed to be that required to clean the surfaces of stainless-steel vacuum systems with hydrogen plasmas.[6]

Standard analysis of the FN data in Figure 2 yields information about the *relative changes* in the emitting area and work function.[7] In general the change in emitting area was relatively small, typically increasing by less than a factor of 2 following hydrogen plasma treatment. In addition, as the sputtering yield of molybdenum by hydrogen[8] is only on the order of 10^{-4} atoms/ion at 300 V (assuming a clean surface), doses on the order of 10^{19} ions/cm^2 result in the removal of approximately one monolayer of molybdenum from the emitter surface. Therefore, since the emitter tip shape change due to sputtering is small, it is reasonable to neglect a change in the proportionality factor, β, between the magnitude of the applied electric field, E, and voltage, V ($E = \beta V$). Changes in the I-V characteristic induced by the plasma treatment are then primarily the result of changes in the work function.

These work function changes can be calculated from

$$\phi_1 = (S_1/S_2)^{2/3}\phi_2,$$

where ϕ_1 and ϕ_2 are taken as the emitter work functions prior to and following hydrogen plasma treatment, respectively, and S_1 and S_2 are the corresponding slopes of the FN plots. As there is a dose beyond which further hydrogen treatment does not result in any improvement in the I-V

characteristic, we assume that the emitters are 'clean' at this point and take ϕ_2 to be 4.9 eV, the work function of hydrogen-covered molybdenum.[9] Applying this reasoning to the results shown in Figure 2, we find that the hydrogen plasma treatment resulted in a work function decrease of 1.1 eV. Work function decreases of ~1 eV were typical but decreases ranging from ~0.5 to 1.5 eV have been observed. Some variability is to be expected as this merely reflects differing degrees and types of initial surface contamination.

In conjunction with I-V data, changes in the spatial distribution of the field electron emission distribution were investigated. Figures 3a and 3b are micrographs of the field emission pattern prior to and following hydrogen plasma treatment, respectively, and correspond to the I-V characteristics in Figure 2. We observe that the uniformity of the electron emission is noticeably improved by the hydrogen plasma treatment. This result was typical for the arrays.

The explanation for the increase in the emission uniformity becomes more evident with the investigation of the effects of hydrogen plasma treatment on single emitter tips. Line A_1 in Figure 4 is the I-V characteristic of a microfabricated single tip acquired prior to hydrogen glow discharge treatment. Line B_1 is the I-V characteristic following hydrogen plasma treatment to a dose of $\sim 2 \times 10^{18}$ ions/cm^2. Lines A_2 and B_2 show the results of an identical experiment performed on a different single tip. Analysis similar to that above yields a work function decrease of 1.5 eV for tip 1 and a decrease of 1.1 eV for tip 2. As with the arrays, work function decreases with single tips are observed to range from ~0.5 to 1.5 eV.

Emission micrographs for the single emitter tips were also studied, an example of which is shown in Figure 4. The micrographs in Figures 5a and 5b correspond to the pre- and post-hydrogen treatment I-V characteristics, respectively, for tip 1 in Figure 4. It was common with single tips to observe slight increases in the emission area and uniformity (averaged over the area encompassing the emitting regions) following plasma treatment.

The increase in the emission uniformity of single tips after plasma treatment is clearly a contributing factor to the increase in uniformity observed with emitter arrays. We also note that the spread in work function changes observed with single emitter tips, as a result of the plasma treatment, persisted even between tips microfabricated in parallel and stored together until used. This indicates that the contaminants must be distributed *anisotropically* across the multi-tip field emitter arrays. It can then be concluded that the increase in the uniformity of the spatial distribution of electron emission observed with the emitter arrays following plasma treatment must also be, in part, due to the participation of more emitter tips in the electron emission process.

We have also conducted studies of recleaning tips that have been exposed to dry nitrogen (99.99%) by venting the vacuum system to atmospheric pressure for time periods of ~10 to 60 minutes. Often the post-venting I-V characteristics fell somewhere in between those of the pre- and post-hydrogen treatment. In all cases, with hydrogen plasma treatment to a dose of ~2 × 10^{18} ions/cm^2, the pre-venting (i.e., the initial post-hydrogen treatment) I-V characteristic was recovered.

Lastly, we note that preliminary investigations involving the sequential use of hydrogen and He/O_2 plasma cleaning procedures have been conducted. The results indicate that the He/O_2 plasma treatment causes not only oxidation, but also emitter blunting due to sputtering. No improvement over the I-V characteristics achieved following the initial hydrogen plasma treatment were observed.

CONCLUSION

Hydrogen plasma treatments with doses on the order of 10^{18} to 10^{19} ions/cm^2 result in a work function decrease of ~1 eV for both microfabricated single tips and arrays, presumably due

to the removal of carbonaceous contamination and the reduction of surface oxide compounds. The net result is a reduction in the operating voltage and an increase in the spatial uniformity of the electron emission.

Hydrogen plasma treatment should improve the performance of a host of different types of field-emitter arrays since in most cases effective conventional surface cleaning procedures cannot be employed. For example, emitter arrays based on silicon tips should also show improved performance following hydrogen plasma treatment by the *in situ* reduction of the oxide layer present and the removal of carbonaceous contamination.

We expect that this plasma cleaning procedure will also allow for the rapid achievement of emission current stability. Combined with the observed increases in emission uniformity, hydrogen plasma treatment would greatly simplify the implementation of microfabricated field-emitter arrays into technologically important devices such as flat-panel displays.

An important difference between the preliminary results reported earlier[4] about a volt was that a gradual increase in work function was observed after the cleaning process, returning to its original value in about 100 hours. We attribute this to the relatively poor base pressure and composition of the residual gas of the vacuum system used in these experiments. This suggests that all parts used in tubes using these field-emission cathodes should be fired in hydrogen to ensure that this is the major component of the residual gas whatever the base pressure.

ACKNOWLEDGMENTS

Discussions with I. Brodie and C. E. Holland were helpful during the course of this research. The authors would also like to thank D. English, R. L. Stroppini, and J. A. Drennon of SRI's central model shop for their invaluable help in equipment construction, and D. A. Thibert, S. L. Shepherd, and S. Chhokar of the vacuum microelectronics group for emitter fabrication. This research was supported by the Defense Advanced Research Projects Agency under Contract MDA972-91-C-0029.

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FIGURE CAPTIONS

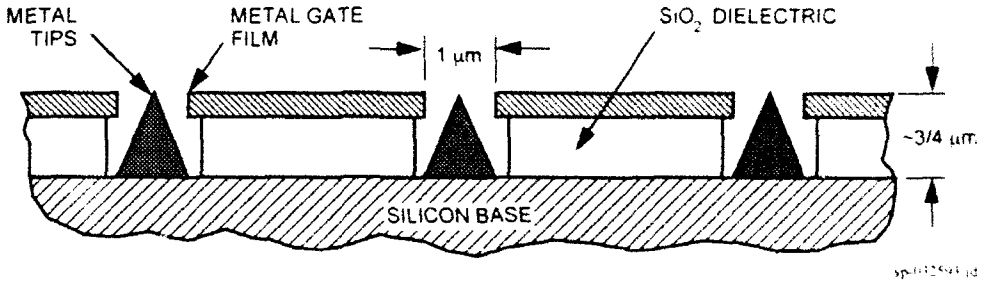
Figure 1. A schematic of the field-emitter array. The substrate is a single-crystal silicon wafer. The field-emitter cathodes and anode film are vapor-deposited molybdenum, and the insulating layer is thermally grown SiO_2.

Figure 2. The effect of hydrogen plasma treatment on a 100-tip array. Line A: FN data prior to hydrogen plasma treatment. Line B: FN data following hydrogen plasma treatment (dose ~1×10^{18} ions/cm^2). The work function decrease was 1.1 eV.

Figure 3. Field electron micrographs of the array whose I-V characteristics appear in Figure 2. 3a: Electron micrograph of the array prior to hydrogen plasma treatment (V = 115 V, I = 10 μA). 3b: Electron micrograph of the array following hydrogen plasma treatment (V = 91 V, I = 10 μa).

Figure 4. The effect of hydrogen plasma treatment on two different single tips. Line A_1: FN data of tip 1 prior to hydrogen plasma treatment. Line B_1: FN data of tip 1 after hydrogen plasma treatment (dose ~2×10^{18} ions/cm^2). The work function decrease for tip 1 was 1.5 eV. Line A_2: FN data of tip 2 prior to hydrogen plasma treatment. Line B_2: FN data of tip 2 following hydrogen plasma treatment (dose ~ 2×10^{18} ions/cm^2). The work function decrease for tip 2 was 1.1 eV.

Figure 5. Field electron micrographs of tip 1 whose I-V characteristics appear in Figure 4. Figure 5a: Prior to hydrogen plasma treatment (V = 168 V, I = 1 μA). 5b: Following plasma treatment (V = 126 V, I = 1 μA).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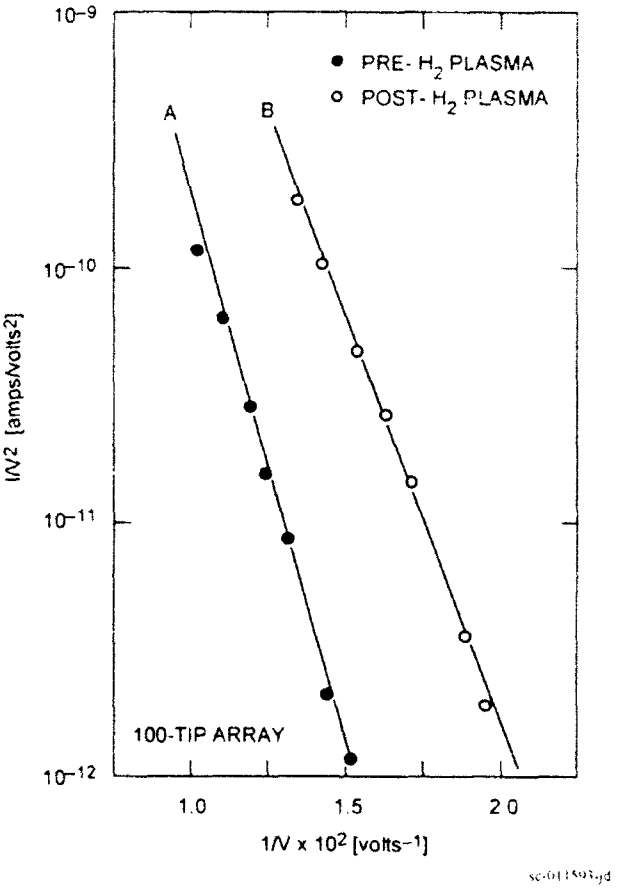
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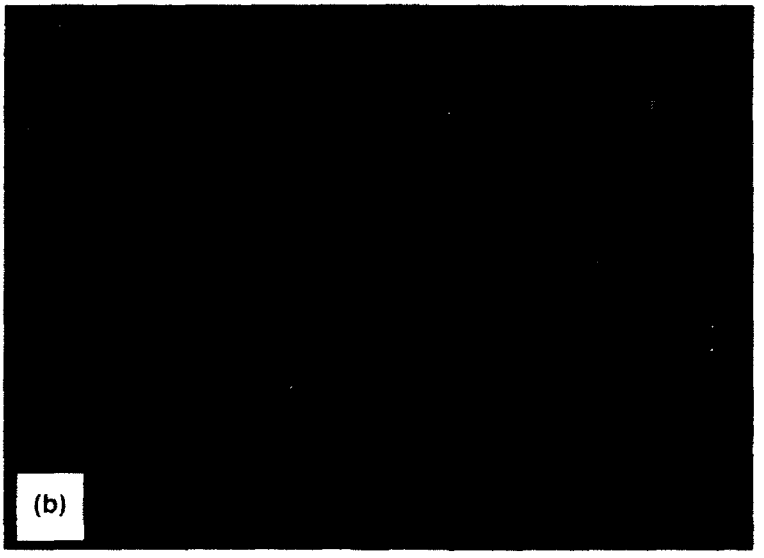
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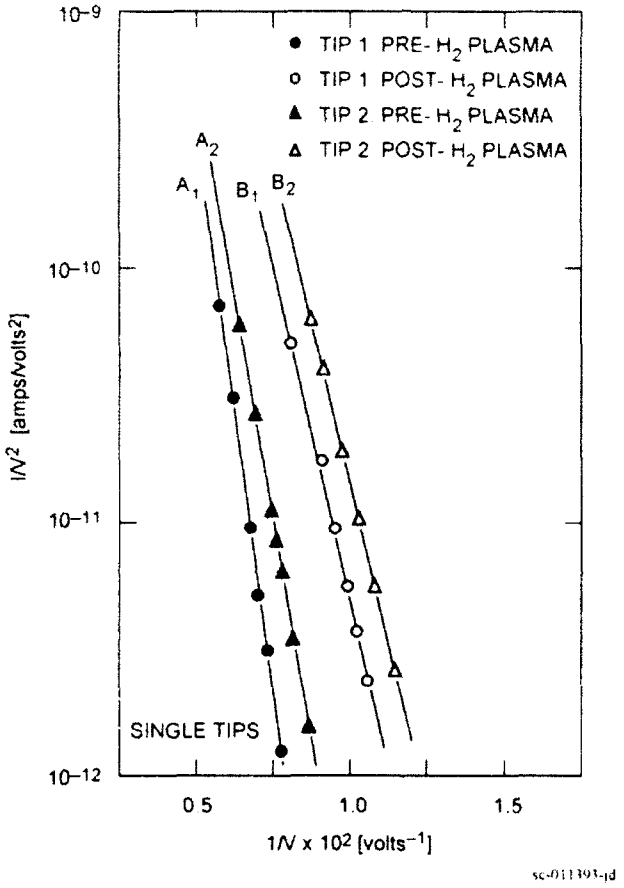
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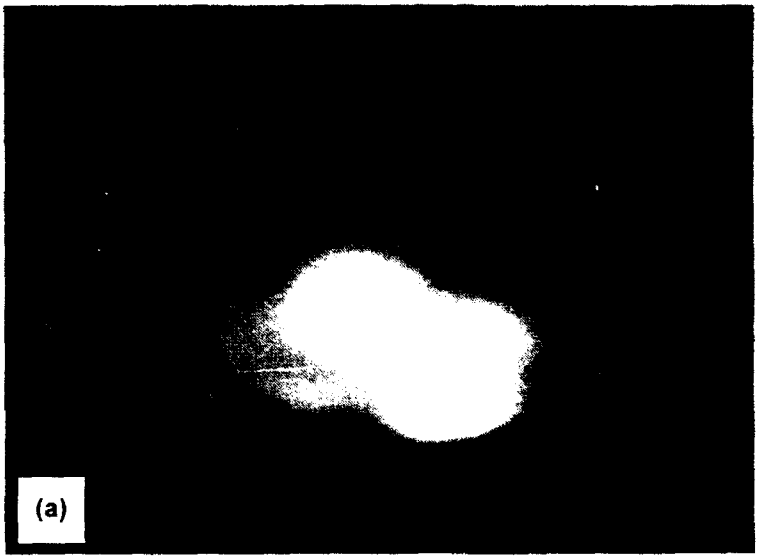
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SUPPLEMENTARY

INFORMATION

5 April 1993

Dr. Bertram H. Hui
Defense Advanced Research Projects Agency
Defense Sciences Office
Virginia Square Plaza
3701 North Fairfax Drive
Arlington, Virginia 22203-1714

Reference: Contract No. MDA972-91-C-0029
ARPA Order No. 8162
(SRI Project No. ECU-2743)

Subject: Quarterly Technical Report No. 5 addendum

Dear Dr. Hui:

In regards to subject report, enclosed is a new Figure 5 to replace the existing version. The 1/2 wave (60 Hz) photograph was inadvertently flipped upside down.

I apologize for any inconvenience this error may have caused. If you have any questions, please contact me at (415) 859-3432.

Sincerely,

Lenny Kissell
Specialist, Publications Coordinator

Enclosure

cc: Mr. Donald Sharkus/CMO (1 copy)
Mr. Myles Jones, ACO/DCMAO-SF (1 copy)
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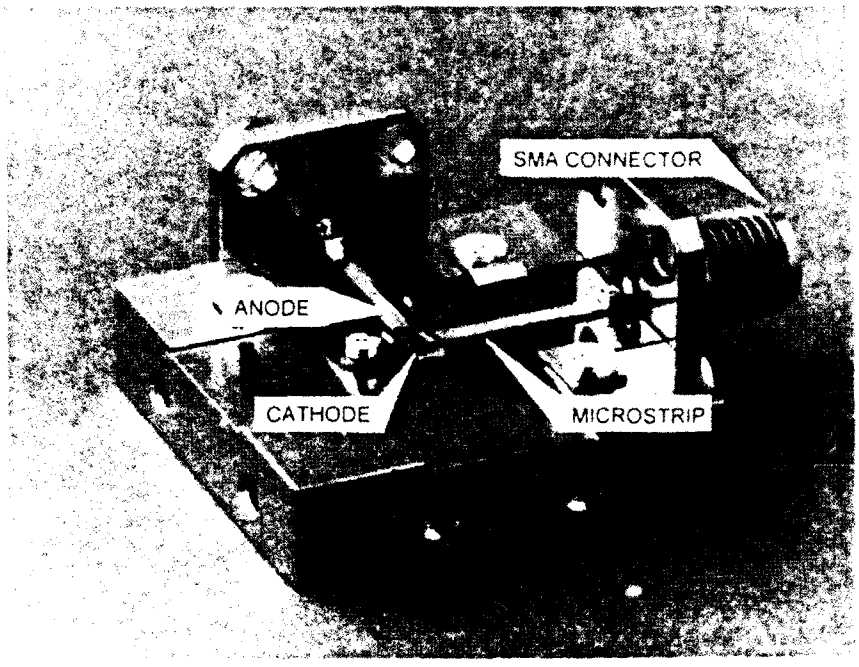

Figure 4. Microwave test fixture with SMA connectors, microstrip lines, and LC cathode mounting

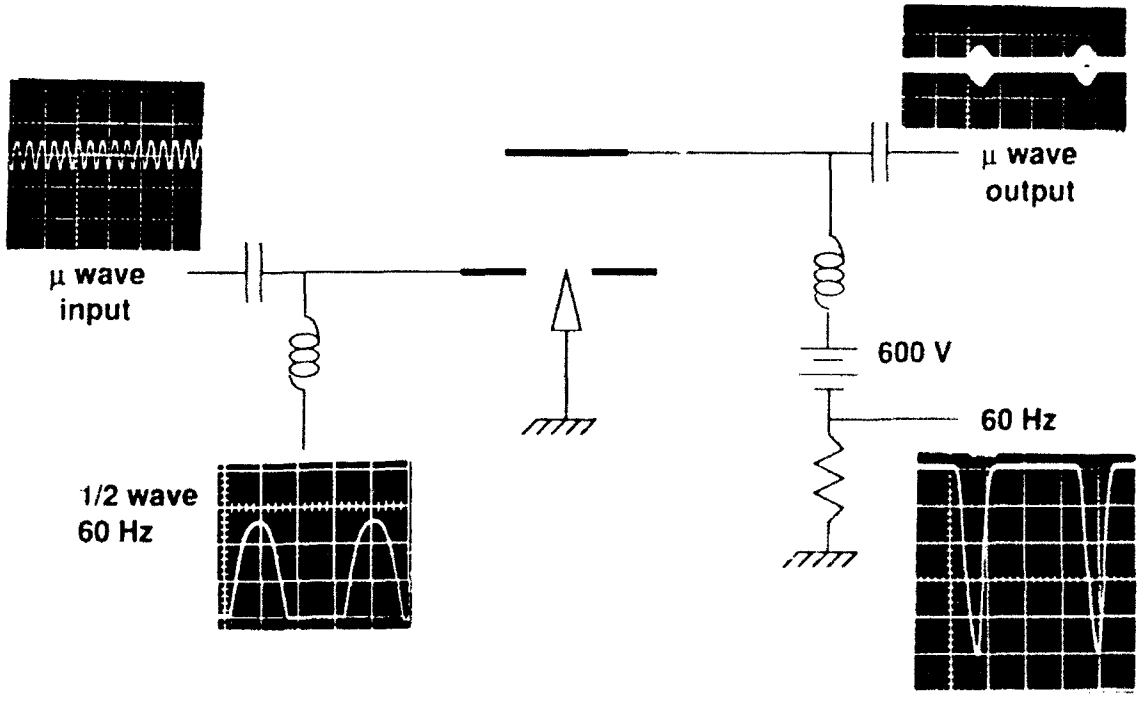

Figure 5. Schematic of the circuit and waveforms for demonstrating microwave modulation of the emitter array