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Electron emission observations from as-grown and vacuum-coated chemical vapor deposited diamond

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A. Lamouri and Yaxin Wang
General Vacuum, Inc., Cleveland, Ohio 44105

G. T. Mearini, I. L. Krainsky, and J. A. Dayton, Jr.
NASA Lewis Research Center, Cleveland, Ohio 44135

W. Mueller
Research 2000, Inc., Westlake, Ohio 44145

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Field emission has been observed from chemical vapor deposited diamond grown on Mo and Si substrates. Emission was observed at fields as low as 20 kV/cm. The samples were tested in the as-grown form, and after coating with thin films of Au, CsI, and Ni. The emission current was typically maximum at the onset of the applied field, but was unstable, and decreased rapidly with time from the as-grown films. Thin Au layers, ~15 nm thick, vacuum deposited onto the diamond samples significantly improved the stability of the emission current at values approximately equal to those from uncoated samples at the onset of the applied field. Thin layers of CsI, ~5 nm thick, were also observed to improve the stability of the emission current but at values less than those from the uncoated samples at the onset of the applied field. While Au and CsI improved the stability of the emission, Ni was observed to have no effect. © *1996 American Vacuum Society.*

I. INTRODUCTION

Recently, there has been a growing interest to study the properties of chemical vapor deposited (CVD) diamond for possible application in many electronic devices. In part, this was motivated by the observation of high secondary electron yields and field emission at relatively low fields. Secondary electron emission yields of $\sigma = 12-50$ have recently been observed from CVD diamond.[1-4] These yields are 20 times greater than those from materials presently used in secondary electron emitter applications.[5] State of the art field emitters generally require applied fields above 5×10^7 V/cm.[6] Room temperature field emission has recently been observed by Shovlin and Kordesch at fields as low as 30 kV/cm.[7]

Unassisted field emission from CVD randomly oriented polycrystalline diamond films grown on Si and Mo has been demonstrated and observed at room temperature at fields as low as 20 kV/cm. The emission was observed from 1×1 cm^2 samples. The applied field for emission ranged from 20 to 160 kV/cm. The total current densities ranged from 1 μA to 0.1 mA/cm^2, averaged over the entire sample.

The mechanism responsible for the field emission from CVD diamond at such low fields is not understood at present and is possibly the result of the negative electron affinity of diamond, although Shovlin and Kordesch[7] speculate that the presence of an adlayer such as gold would quench the surface states responsible for this property of CVD diamond.

In this article we will present cold field emission data from CVD diamond on Si and Mo in the as-grown form and after being coated with thin layers of Au, CsI, and Ni.

II. EXPERIMENTAL SETUP

The CVD diamond films were made by depositing a 10–20 μm continuous film on 1×1 cm^2 Si or Mo substrates by thermal decomposition of 1% methane in hydrogen using a hot tungsten filament technique. The substrates were polished with 1/4 μm diamond paste and ultrasonically cleaned in alcohol before they were introduced into the deposition chamber. Au and Ni were evaporated on the diamond samples from Al_2O_3 crucibles and CsI was evaporated from a Ta boat in a diffusion pumped high vacuum chamber that was operated at 3×10^{-8} Torr. The thickness of the Au, Ni, and CsI layers was determined using a quartz crystal microbalance (QCM) which was calibrated with a thickness interferometer. Following the deposition, the substrates were removed from the deposition chamber and immediately introduced into the test chamber.

The field emission tests were performed in an ion pumped high vacuum chamber at a base pressure of 7×10^{-7} Torr. The measurements were carried out using an anode with a diameter (~5 mm) slightly smaller than the dimensions of the samples, which were approximately 1 cm^2. This anode was used in order to eliminate possible field emission currents emanating from the "sharp" edges of the cathode. The measurements were obtained by applying up to 16 kV across a 1 mm gap separating the anode and the emitting cathode as is shown in Fig. 1. The high voltage was applied to the anode and the emission current was measured at the cathode as a function of applied field. The field was varied by increasing the applied voltage or by varying the cathode-anode separation.

III. RESULTS AND SUMMARY

After the diamond samples were introduced into the measurement chamber, a gradually increasing field was applied

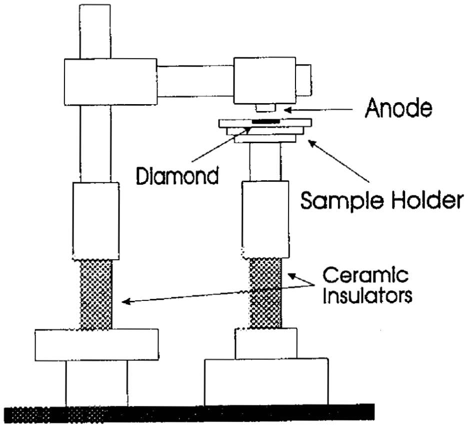

FIG. 1. Schematic diagram of field emission measurements setup.

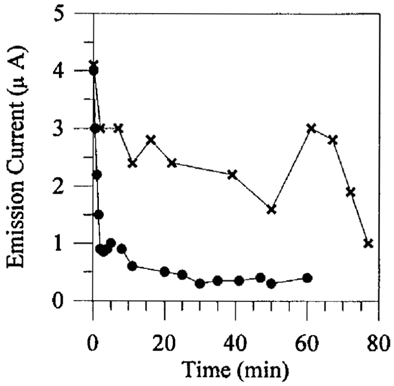

FIG. 3. Emission current at 80 kV/cm from diamond-coated Si before (dots) and after (crosses) coating with 10 nm of Au.

in order to induce emission. Typical "turn-on"fields for Si and Mo diamond-coated electrodes ranged from 20 to 50 kV/cm.

For the uncoated samples, the electron emission currents were typically maximum at the onset of the applied field, but were unstable, and decreased rapidly as a function of time. As a result, no meaningful I–V data could be recorded from the as-grown CVD diamond samples.

Relatively stable emission currents with values equal to or close to those from the uncoated samples at the onset of the applied field were observed when the diamond films were coated with thin layers of Au. In addition to a significant improvement in stability, a substantial enhancement of the field emission currents was observed when Au films approximately 15 nm thick were present on the diamond surface. As shown in Fig. 2, the emission currents from CVD diamond samples on Mo were relatively stable and increased with Au coverage between 0.5 and 15 nm. For coverages greater than 15 nm, the emission currents, although relatively stable, decreased rapidly as a function of Au coverage. No emission currents were observed from these films when coated with a thick layer (~130 nm) of Au.

The data presented in Fig. 2 were obtained from the same CVD sample, that was tested in the as-grown form and with incremental Au coverages. Samples that were tested only after they were coated did not have maximum emission current like those from the as-grown samples at the onset of the applied field. The emission currents from these samples were similar to those of Fig. 2 at comparable Au coverages.

Similar data were obtained for CVD diamond grown on Si substrate, except that the emission currents from diamond-coated Si were significantly less stable before they were coated with Au. As shown in Fig. 3, the emission current from the as-grown samples are very unstable and significantly lower than those from Mo-coated CVD diamond at the onset of applied fields.

Typical data recorded from CVD diamond samples on Si substrates coated with 10 nm of Au are plotted in Fig. 4. These data indicate that, within the experimental field range,

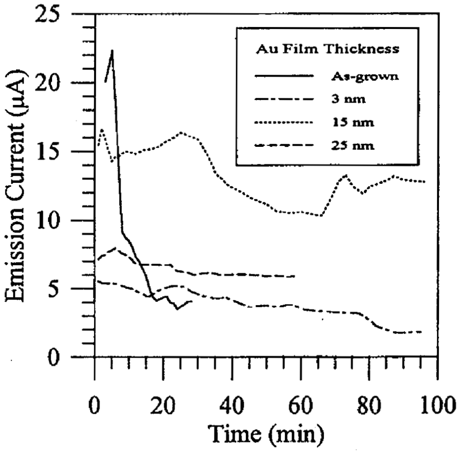

FIG. 2. Time dependence of emission current at 100 kV/cm from CVD diamond-coated Mo as a function of Au coverage.

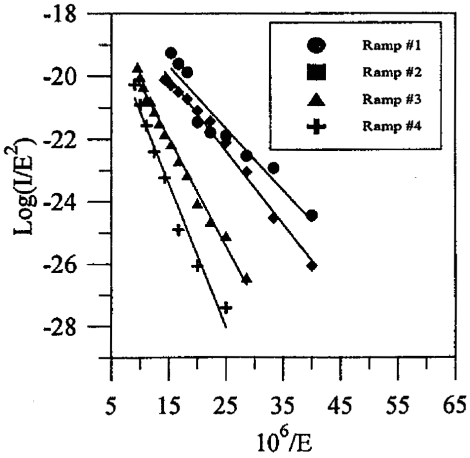

FIG. 4. Fowler–Nordheim plots of emission currents from CVD diamond on Mo coated with 10 nm of Au.

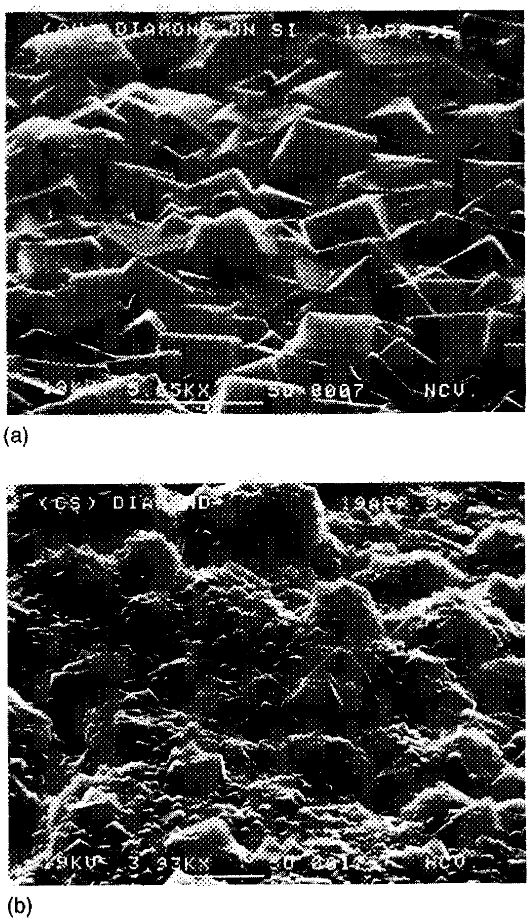

FIG. 5. SEM photographs showing the surface morphology of CVD diamond films grown on (a) Si and (b) Mo.

the I–V characteristics are well described by the Fowler–Nordheim regime. In addition, they show that even the Au-coated samples are unstable for high fields since stronger fields are required to obtain the same field emission currents from successive voltage ramps.

Scanning electron microscopy (SEM) analysis of the Si and Mo coated CVD diamond samples showed that the films had well-faceted structures. Typical SEM photographs from CVD diamond samples on Mo and Si substrates are shown in Figs. 5(a) and 5(b), respectively. Figures 5(a) and 5(b) show that the surface roughness of the Mo-coated CVD diamond is higher (low magnification SEM photographs show that the Si-coated diamond samples are flat over the entire surface area of the samples). It is possible that the surface roughness is at least partially responsible for the higher and more stable electron emission currents from the films grown on Mo.

Our data for Au-coated CVD diamond on Mo and Si are in good agreement with those of Shovlin and Kordesch.[7] In fact, they were only able to observe field emission current from their CVD diamond films after the samples were coated with 15 nm of Au, presumably due to the enhancement of emission current at this coverage.

Preliminary data from thin layers of CsI (0.1 and 5 nm), vacuum deposited onto the diamond samples, significantly

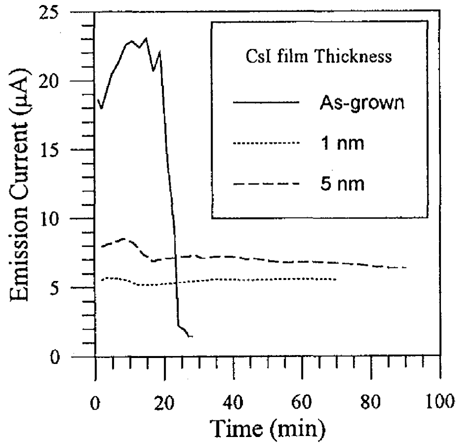

FIG. 6. Time dependence of emission current at 100 kV/cm from CVD diamond on Mo as a function of CsI coverage.

improved the stability of the emission current at values comparable to those from Au at the same coverage, as is shown in Fig. 6. These results are not surprising since CsI films 5–10 nm thick are known to stabilize and enhance secondary electron emission (SEE) from CVD diamond after they have been activated by electron bombardment.[4] Measurement for thicker CsI films on CVD diamond-coated Mo are currently underway and it is possible that more stable and enhanced emission currents will be obtained for coverage of ~10–20 nm.

The mechanism responsible for the stability of the emission currents induced by CsI and the stability and enhancement induced by Au is not understood at present. It is possible that hydrogen termination of the surface, believed to be responsible for stabilizing and enhancing SEE from CVD diamond,[1,2] is stabilized when Au or CsI is present on the surface. In fact, the instability of the coated samples for long exposures is believe to be the result of sputter erosion of hydrogen due to ions formed close to the cathode, presum-

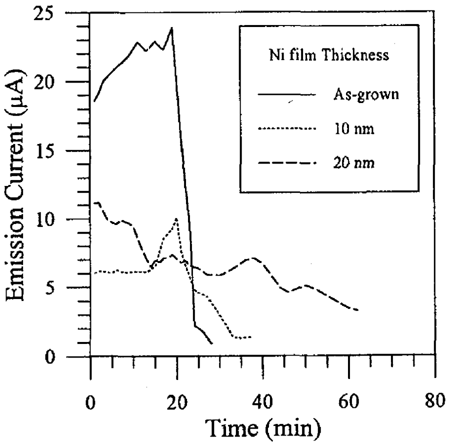

FIG. 7. Time dependence of emission current at 100 kV/cm from CVD diamond on Mo as a function of Ni coverage.

ably due to the relatively high pressures (mid 10^{-7} Torr) in our test chamber. In their measurements of secondary yields from CVD diamond, Mearini *et al.*[1,2] discovered that the total secondary yields are significantly reduced when the substrates are bombarded by high-energy hydrogen ions due to graphitization of the diamond surface.

We have also tested field emission from CVD diamond films on Mo coated with Ni. Unlike Au and CsI, Ni does not appear to have a stabilizing effect on the electron emission. As shown in Fig. 7, the emission current for Ni-coated CVD diamond were observed to decrease very rapidly as a function of time, although the maximum emission currents at the onset of the applied field were comparable to those from diamond samples coated with Au and CsI.

All of the field emission experiments presented here were repeated on bare Al, Cu, Ta, Mo, and Si substrates, and those substrates coated with Au, CsI, Ni, Ti, and BaF_2. No emission was observed from these materials with applied field up to 300 kV/cm, well beyond the fields at which stable emission was observed when diamond was included.

ACKNOWLEDGMENTS

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