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ABSTRACT

The field emission properties of the controlled emission edge of a vertically aligned graphene-based thin film are presented. A current and current density of above 7 mA and 200 A/cm², respectively, with uniform electron emission, are achieved. Uniform high current and current density emissions can be realized by the pre-mechanical shaping and post electrical conditioning of reduced graphene oxide (rGO) film emission, owing to the robustness, thinness (<1 μm), and well-defined uniform film thickness. Field emission luminance demonstrates uniform emission over the entire emission area with a high aspect ratio. Along with a high current emission, the rGO film exhibits excellent emission stability, long-term. This offers prospects for various applications in field emission displays, electron microscopy, and particularly for the realization of miniaturized terahertz vacuum electronic devices, which require electron sources with uniform high currents and current densities, such as long-lifetime cold cathodes.

1. Introduction

Electrons from a solid can be emitted into vacuum through quantum electron tunneling by applying substantial electric fields. Unlike conventional hot cathodes, electron emission from field emitters provides high-quality electron beams due to low thermal energy dispersion. In conventional electron devices such as X-ray sources, electron microscopes, or cathode ray tubes using thermionic emission, energy dispersion acts as noise and blurs the images; hence, field emission cathodes are attractive for obtaining clearer or higher magnification images [1–3]. Thermionic cathodes have been utilized in vacuum electronic devices to generate high-power electromagnetic waves; however, they are problematic in the high frequency range because they are bulky and cause the heating of the surrounding device.
housing [4], providing an emission current density that is insufficient for overcoming electron thermal random motion [5]. Therefore, cold cathode emitters that remain at room temperature (300 K) and provide a high current density at a low electric field are desirable and have been studied for various applications such as X-ray sources for medical imaging [6], high-resolution field emission electron microscopes [7], flat panel displays [8], and vacuum electronic devices [9] for border security or satellite communication. Field emission occurs in high electric fields at approximately 10–100 MV/cm, which is beyond the typical vacuum breakdown strength at approximately 100 kV/cm. In order to avoid breakdown and meet the above condition, field emitters are required to have highly sharp emission surfaces, of several to several tens of nanometers, for enhancing the electric field, with a high aspect ratio emission surface such as in a lightning rod [10].

In many of the applications mentioned above, the uniformity of the emitted electron beam is crucial for a stable and high performance. Thus, it is critical to control the sharp, high aspect ratio emission surface morphology imposed for large field enhancements. In the case of the field emission electron microscope, reactive ion etching (RIE) [11], electrical discharge machining [12], electrical aging [13], and focused ion beam (FIB) machining [14] have been used to uniformize the emission surface of a point emitter such as an LaB₆ single crystal or a carbon nanotube (CNT) tip. On the other hand, flat panel displays and X-ray sources use array [15–17], flake [18,19] or yarn emitters [8,20], formed by a collection of individual electron emission elements in order to obtain large emission areas and emission currents, respectively. These types of emitters are usually fabricated by microelectromechanical system technology for Si and metal-based emitters [17] and by chemical vapor deposition [21], printing methods [22], and electrophoretic deposition [18] for carbon-based emitters. Due to the limitations of the fabrication method, the individual field emission points are not equal, resulting in an uneven field emission surface. Nonuniform field emission points inevitably result in local high field emission, accompanied by the local evaporation of the emission element and therefore, electrical breakdown due to poor vacuum [23]. This not only causes non-uniform electron emission but is also a critical obstacle in determining the lifetime of field emission devices. In order to solve these issues, it is necessary to uniformize the individual field emission points and to treat the surface using methods such as plasma treatments [24,25], laser surface treatments [26], electrical discharging machining [27], and controlled electrical break treatments [28]. Although it is possible to obtain more stable and uniform field emissions using these methods, the random nature of the individual field emission points embedded in the fabrication method cannot be completely compensated. Therefore, most field emission cathodes have problems in that their stability and lifetime are significantly lower than those of the well-established thermionic cathodes. Recently, a field emission cathode using a graphene oxide film was developed using the modified Hummer method; it could be cut freely, mechanically, to form the desired field emission surface [29]. However, uniform control of the surface morphology has not yet been achieved in microscopic regions of the order of tens of nanometers from the surface, where field emission occurs.

Of late, graphene has generated significant interest because of its unique properties [30,31] and potential applications in nanoelectronics [31,32], supercapacitors [33], field effect transistors [34], and field emitters [19,35,36]. The advantages of graphene over the other field emitters such as CNT is that it has a greater emission area, rendering it an excellent field emitter following the Fowler–Nordheim (F–N) equation [37], as all the other field emitters. In this study, a novel graphene-based freestanding film, which is thinner and harder than
the previous graphene-based films, is fabricated using the modified Hummer method and a hydrothermal process with oxygen reduction by nitrogen annealing. Owing to the robustness of the film, it is possible to achieve precise mechanical cutting with a microtome; a uniform field emission surface was successfully obtained only through electrical conditioning using this knife-cut surface as the field emission surface. Electron microscopy images before and after conditioning show the existence of a well-defined uniform field emission surface with a roughness under several tens of nm and uniform electron beam emission was confirmed through field emission luminescence. In addition, due to the thinness and high aspect ratio of the film, the emission current density reaches up to 300 A/cm² and is not significantly reduced due to the screen effect of local electric field [38] between the individual emission points, which occurs in the conventional array, flake and paste-type graphene, or in the CNT field emission cathode. As this type of field emission device can increase the theoretically infinite length, it is possible to obtain a high current. In this study, we obtained an emission current of several mA, while maintaining the current density level in the order of hundreds of A/cm², using a film several mm in length. The graphene-based film field emitter presented in this paper can be adopted for various applications, particularly, for miniaturized terahertz vacuum electronic devices requiring uniform high current densities and currents.

2. Preparation of graphene-based films for field emitters

2.1. Film synthesis

Recent reports have shown that free-standing reduced graphene oxide (rGO) films can be fabricated by a chemical process using the modified Hummer method [39], followed by hydrothermal synthesis. These films are free-standing, highly flexible, easy to handle, and have a controllable thickness [40,41]. In this study, we have adopted the above-mentioned method for synthesizing the films. During the hydrothermal process, the oxygen functional groups in these films are reduced to partially recover the original graphene properties. It is advantageous for our application, which requires high electrical and thermal conductivities. The field emission scanning electron microscope (SUPRA, 55 VP) image in Figure 1(a) depicts a multilayered rGO film with a thickness of a few micrometers. Its high length-to-thickness aspect ratio enables a high enhancement factor, under an applied electric field. As shown in Figure 1(b), the fabricated rGO film is flexible and sufficiently robust for manual handling. For further reduction, the synthesized films are annealed in a furnace at a temperature of 800 °C, under a nitrogen environment. After the annealing process, the films are examined using energy-dispersive X-ray spectroscopy to confirm the reduction of their oxygen ratio. The wt% of carbon and oxygen before annealing were determined to be 69 and 24%, respectively, whereas, after annealing they became 79 and 12%, respectively. This implies that the broken sp² bonding, due to the oxygen in the graphene structure, are partially recovered after annealing [42].

2.2. Mechanical shaping

The prepared rGO film was cut by various methods such as the RIE, laser cutting, knife cutting, microtome, and FIB to produce a uniform field emission surface. Figure 2 depicts the tolerances of the graphene-film sections cut using various methods. Although the FIB method provides the highest uniformity, it is inefficient and time-consuming because graphene and
its relatives, such as the rGO film, are strong against ion collision [43], which is the mechanism of the FIB cutting method. As the prepared rGO film is free standing for the enhancement of the field emission performance, it is difficult to mask the film tightly against ion etching. Therefore, the RIE method, which cannot provide uniform etching, is not suitable because the uniformity of the cut edge is critical. The laser-cutting method is also not suitable for rendering a uniform emission edge because it easily forms debris, as shown in the inset of Figure 2 because it concentrates high-density energy on a local spot and burns the material. On the other hand, due to the excellent flexibility and stiffness of the rGO film, it can be handled manually, rendering it possible to be mechanically cut; this would not be possible with ordinary graphene-film surface treatment. It exhibits good surface uniformity, even with knife cutting and microtome. In order to apply the microtome, rectangularly preshaped rGO films, using the knife cutting method, are prepared and embedded in paraffin wax, for holding, during the microtome operation. After shaping using the microtome, the paraffin wax is removed using diluted xylene solution. The less-than-100-nm protrusions and
nonuniform portions remaining on the emission edge are uniformized through electrical aging by field emission.

3. Experimental results

The prepared rGO film was cut into a rectangular shape with an emission edge length of 3 mm and height of 5 mm. A well-shaped rGO film was sandwiched between the cathode block, made of stainless steel and screwed such that the height of the film protruding from the cathode surface was 0.5 mm (Figure 3(a)). For electrical aging and the field emission tests, an ultra-high vacuum chamber equipped with a rotary pump (Varian, SD-300), turbo pump (Varian, Turbo-V301), and an ion pump (Varian, Vacion plus 500) was used. A diode-type experimental setup was prepared by inserting a ceramic insulator spacer between the film-mounted cathode blocks and the molybdenum anode, and carefully placed in the prepared vacuum chamber. The thickness of the ceramic insulator was 1 mm and the height of the mounted film was maintained at 0.5 mm such that the distance from the field emission surface to the anode was maintained at 0.5 mm. The schematic and photographic image of the test setup, configured with a diode setup, are displayed in Figure 3(b) and (c), respectively.

Before the start of the experiment, a vacuum level of $10^{-7} - 10^{-8}$ Torr was created; this is retained during the experiment also. A dc voltage source (Glassman High Voltage Inc., EQ005R240C22) with the maximum output voltage of 5 kV and current of 250 mA was used; a current meter with a nano-ampere range (NI PXI-4071, 7 1/2-digit FlexDMM), connected to a computer, was used to measure the output current.

There was a high risk of sudden electrical breakdown due to the heavy degassing rate generated by the electrons striking the anode surface. To avoid this, during the early stage of the experiment, a low step up voltage was applied for a sufficient time. To create a uniform emitting surface by electrical treatment, a design process that stepped up the applied voltage with step of 100 V was implemented. As shown in Figure 4, as the number of voltage cycles increases, a lower voltage is required to achieve the same field emission current level.

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**Figure 3.** Schematic of the (a) rGO film mounting method (b) total test setup; (c) Experimental setup installed in a vacuum chamber. Inset shows the vertically aligned rGO film between the anode and cathode blocks.
in the low voltage regime (1.5–2.5 kV). This is a variation from the CNTs that emit electrons at much lower fields, before conditioning, as presented in literature [44]. Also from Figure 4, as the conditioning process continues, the emission current becomes increasingly stable. In order to avoid vacuum breakdown, we maintained the upper applied-voltage limit to 3.5 kV, during conditioning. As seen in Figure 4, the $I$–$V$ curves finally reach a narrow range with a stable emission current (the 4th and 5th curves). The surface emission current density was calculated by dividing the current obtained immediately after mounting and the saturated current after conditioning, by the emission area (Figure 5(a)). The error bar was calculated as the deviation of first and last three experimental values, before and after conditioning, respectively. The variation in the current density before conditioning is considerable; however, it is negligible, after conditioning. This indicates that the emission edges of the rGO film become gradually clean after a series of electrical aging, as shown in Figure 4. The $I$–$V$ characteristics, in stable operation, demonstrate that the emission current reaches up to approximately 7 mA, at an applied DC voltage of 3.5 kV. The calculated maximum current density was approximately 200 A/cm$^2$, (Figure 4(b)), which is one of the highest for a free standing rGO film in stable condition, till date. Figure 5(b) shows the F–N plot, used to examine the field emission property of the cathode from the $I$–$V$ curve; after conditioning, the gradient of the F–N plot recovered its linearity. This implies that the emission current fully originated from field-induced quantum tunneling [10].

To characterize the emission uniformity, field emission luminescence was performed using a phosphor screen on a conductive ITO glass, used as the anode. To avoid burning the phosphor elements on the ITO glass, the applied potential was retained below 2.5 kV to emit a lower current. The emission current was less than 1.25 mA, when the photograph of the ITO glass surface was taken. Before conditioning, it can be observed that the beam was broad and nonuniform, with extremely bright spots expected to be caused by a nonuniform surface with protrusions (Figure 6(a)). On the other hand, a clear and uniform sheet-like beam mark was obtained after electric conditioning, as in Figure 6(b). The width of the beam striking mark is well matched with that of the rGO emitter.
Figure 7 shows the time trace of the current density at a fixed applied voltage of 3 kV for the vertically aligned rGO film, after the conditioning process. We determined the occurrence of stable electron emission for more than 40 days, under continuous operating conditions, due to the uniform emission surface obtained by electrical treatment, after mechanical shaping. Despite being operated at a higher current density of approximately 100 A/cm², compared to the other graphene-based field emitters, it shows a remarkable stability with fluctuations less than 5% of the emission current, during the entire stability test period. We believe that the excellent field emission properties of the rGO film edge emitter results from
the higher electrical and thermal conductivities of the film, and the uniform emission surface, by emission surface conditioning. We also believe that the high aspect ratio and the vertically aligned thin geometry increase the emission area and enhance the electric field applied to the emission surface, resulting in high current density and high current electron emission.

4. Conclusion

In conclusion, a vertically aligned freestanding graphene-based film field emitter was synthesized by annealing in nitrogen environment, after application of the modified Hummer method followed by a hydrothermal process. The field emission performance of the synthesized film was experimentally examined, using a diode configuration. Owing to its high aspect ratio with a thin film geometry, a significant current of more than 7 mA was obtained from a single field emitter by increasing the length of the emission edge, without current density loss (approximately 200 A/cm²). The synthesized rGO films exhibited high robustness, sufficient for mechanical shaping, which is essential for obtaining uniform emission surfaces by removing the remaining small protrusions through field-induced electrical material evaporation. A controlled electrical aging process was performed to uniformize the emission edges of the rGO films, resulting in a uniform emission current and a highly stable emission for a duration longer than 40 days, under a continuous operation condition with a negligible current degradation, less than 5% of the average emission current, during the life-time test. The high current and high current density, along with the uniform and stable field emission properties of the rGO films, are attributed to its excellent electrical, thermal, and mechanical properties, and the high aspect ratio with a vertically aligned thin geometry; this resulted in a mechanically shapeable large emission edge with a high uniformity, without losses in the substantial electric field on the emission surface. This may pave the way for future devices, particularly, for miniaturized terahertz vacuum electronic devices that require high current, high current density, uniform, and long-term stable cold cathodes, compared to the existing ones.
Disclosure statement

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