Stabilized field emission behavior of diamond-like carbon-coated Si tips

Sang-Hyuk Ahn a,b, Kwang-Ryeol Lee a,*, Kwang Yong Eun a, Dongryul Jeon b

a Thin Film Technology Research Center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 110-650, South Korea

b Department of Physics, Myongji University, Yongin, Kyunggi-do 449-728, South Korea

Abstract

Micromachined Si tips have been considered as a strong candidate for cold cathode materials. However, as-prepared Si tips showed unstable emission behavior, presumably due to native oxide, chemical reaction with residual gases or changes in tip geometry during operation. In order to stabilize the emission behavior, diamond-like carbon (DLC) films were deposited on the Si tips by DC magnetron sputtering of high purity graphite. We focused on the stability of the emission behavior by repeating the I–V measurement with anode voltages ranging from 100 to 2500 V. With increasing number of I–V measurements, the onset electric field decreased in both as-prepared and DLC-coated Si tips. However, the emission current of as-prepared Si tips decreased with increasing number of I–V measurements and eventually could not be observed after 10 measurements. On the other hand, DLC-coated tips exhibited improved emission behavior by repeating the I–V measurement. These results showed that the DLC coating can prevent the Si tips from oxidation or from being contaminated, which stabilized the field emission behavior. Furthermore, the DLC coating seems to reduce the effect of the changes in tip apex morphology by reducing the sharpness of the tip apex. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diamond-like carbon; Field emission; Si-tip; Sputtering

1. Introduction

Because of advanced semiconductor microfabrication technology, Si has become a popular selection for field emitter cathode material in fabricating vacuum micro-electronic devices. However, compared with refractory metals such as Mo or W, Si has limited properties for use as a field emitter tip. As-prepared Si tips generally showed unstable emission behavior, presumably due to native oxide [1], chemical reactions with residual gases [2], adsorbed impurities, arcing between the tip and gate electrode and changes in tip geometry [3]. In order to stabilize and enhance the emission behavior, surface treatment, such as etching the native oxide layer or coating the Si tips by diamond or diamond-like carbon (DLC), has been intensely investigated [1,4-10].

Diamond-coated field emitters have shown a great improvement in the emission performance, such as low onset voltage, high current density and better stability [4-6]. However, the chemical-vapor deposition process commonly used for diamond film deposition requires very high substrate temperatures (>800°C) and is not compatible with the semiconductor process. DLC films that can be coated at low substrate temperature were thus considered as the coating materials for the tip emitters. Myers and coworkers investigated the effect of DLC coating by the filtered cathodic arc process on the emission behavior of Si and Mo tips [11,12]. They observed that the field emission from the Si tip was not improved by the DLC coating where the film contained 90% sp3 bond [11]. However, the DLC films of 50% sp3 bond enhanced the field emission from Mo tips [12]. Based on the microstructure observed by TEM of the coated Mo tip, they suggested that an optimum content of sp3 bond is required to render an electrically conducting path through the film [12]. Ko et al. [10] and Jung et al. [7] also reported the improved emission behavior from a DLC-coated Si knife edge and Mo tips respectively.

The present paper reports the experimental results on the field emission behavior of DLC-coated Si tips by DC magnetron sputtering. We focused on the stability...
of the field emission when repeating the current–voltage \((I–V)\) measurements. Enhanced emission behavior was observed when the Si tip was coated by the DLC film. DLC-coated tips exhibited increased emission current as the \(I–V\) measurement was repeated, whereas the emission current of as-prepared Si tips decreased. However, the fluctuation of the emission current in the DLC-coated Si tips appeared to be larger than in uncoated Si tips.

2. Experimental

An array of Si tips was fabricated on n-type Si wafer. Conventional dry etching and an oxidation sharpening process were employed, as shown in the schematic of the fabrication process (Fig. 1) [13]. We could obtain sharp Si tips with a radius of curvature in the order of 1 nm. The surface of the tip appeared very smooth. We investigated the field emission behavior of as-prepared, sputter cleaned and DLC-coated tips. The surface treatment of the tip was performed in a hybrid reactor, which is composed of a 13.56 MHz r.f. cathode and DC magnetron sputter gun. Details of the reactor were described elsewhere [14]. The array was placed on the cathode and sputter cleaned by using an r.f. glow discharge of Ar. During the cleaning process, the Ar pressure and the self-bias voltage were kept at 0.53 Pa and \(-400\) V respectively. The sputter cleaning time was varied from 10 to 30 min.

DLC films were deposited by DC magnetron sputtering of high purity graphite. Prior to deposition, the Si tip was sputter cleaned by Ar glow discharge for 15 min. This process was essential to improve the adhesion of the DLC films. The films were then deposited at a constant DC current density of 15 mA/cm\(^2\). The sputtering pressure was varied from 1.33 to 4 Pa in order to control the structure of the DLC films. The deposition rate decreased slightly from 2.0 to 1.6 nm/min with increasing sputtering pressure. The structure and properties of DLC were reported elsewhere [15]. The structure of the DLC films was intimately related with the sputtering pressure, as confirmed by the evolution of the \(\pi\) plasmon loss peak in electron energy loss spectroscopy and the G-peak shift in Raman spectra [15]. As the sputtering pressure increased from 1.33 to 4 Pa, the film appeared to contain a higher graphitic component. This behavior is due to the reduced mean free path at the higher sputtering pressure, which results in a lower kinetic energy of the sputtered carbon atoms. The \(I–V\) characteristics were observed in a vacuum chamber kept at \(4 \times 10^{-5}\) Pa. A steel ball of diameter 6 mm was used for the anode. The distance between the anode and the specimen was 50 \(\mu\)m, as measured by the specimen manipulator of 1 \(\mu\)m resolution. We focused on the stability of the emission behavior by repeating the \(I–V\) measurement with anode voltages ranging from 100 to 2500 V. Fluctuation of the emission current was also measured at 2400 V for 30 min.

![Si tip fabrication process](image1)

**Fig. 1.** Schematic of the Si tip fabrication process.

![Emission behavior of as-prepared Si tips](image2)

**Fig. 2.** Emission behavior of as-prepared Si tips: (a) \(I–V\) characteristics for various numbers of measurement; (b) dependence of onset voltage and emission current at 2400 V on the number of the \(I–V\) measurements.
3. Results and discussion

$I-V$ curves of as-prepared Si tips [Fig. 2(a)] show typical dependence of the emission behavior of Si tips on the number of measurements [1,16]. The emission was first enhanced by repeating the $I-V$ measurement. However, after the third measurement, the emission behavior rapidly degraded with the measurements, and the emission eventually disappeared after 10 measurements. Fig. 2(b) shows the changes of onset voltage and the emission current at 2400 V. The onset voltage was defined as the anode voltage where the emission current was larger than 1 nA. Although the onset voltage was almost constant at 1000 ± 100 V after two measurements, the emission current drastically decreased from 9.6 mA in three measurements to 0.26 µA in eight measurements. This result implies that the number of tips emitting electrons decreased with repeated $I-V$ measurements. Chemical reaction with residual gases in the chamber, which is mainly H$_2$O, seems to passivate the Si tips [2].

The Ar sputter cleaning significantly changed the tip morphology. Fig. 3 shows a series of scanning electron microscope (SEM) microstructures of the tips for various sputter cleaning times. Ar-ion bombardment for 10 min increased the aspect ratio and sharpness of the tips, as can be seen in Fig. 3(a) and (b). This is due to the angular dependence of the sputter etching rate. However, overbombardment damaged the tip apex and resulted in dull tips [see Fig. 3(c) and (d)]. Ar bombardment also increased the roughness of the tip surface. Although the morphology was significantly changed by the Ar sputter cleaning, field emission exhibited a similar dependence on the number of $I-V$ measurements to that of the as-prepared Si tips. The emission current firstly increased and then decreased as the $I-V$ measurement was repeated. The tips were all passivated after eight or nine measurements.

However, the emission current and onset voltage were strongly dependent on the sputter cleaning time. Fig. 4 shows the $I-V$ curves after five measurements for various Ar sputter cleaning times. Relatively large scattering in

![Fig. 3. SEM microstructures of the Ar sputter-cleaned tips for various sputter cleaning times of (a) 0 min, (b) 10 min, (c) 15 min, (d) 30 min.](image)

![Fig. 4. $I-V$ characteristics of Ar-sputtered Si tips for various sputter cleaning times.](image)
The $I-V$ curve was commonly observed in the sputter-cleaned samples. High-energy ion bombardment can induce an amorphous surface layer on the tip, which is known to exhibit the fluctuating emission behavior [2]. Hence, the present observation seems to be due to the surface amorphization by Ar-ion bombardment. As the sputter cleaning time increased from 10 to 30 min, the onset voltage changed from 1800 to 1250 V. Considering that the longer Ar-ion bombardment resulted in dull tips (Fig. 3), this result would seem to show that, in the present experimental condition, the emission behavior is significantly dependent on the surface condition, such as the amorphization or roughness change, rather than the morphology of the tip apex.

Fig. 5 shows the typical SEM microstructures of the DLC-coated tips. The DLC films were deposited at a sputtering pressure of 1.33 Pa. As the film thickness changed from 20 nm to 60 nm, the morphology of the tip apex cleaned samples. High-energy ion bombardment can induce an amorphous surface layer on the tip, which is known to exhibit the fluctuating emission behavior [2]. Hence, the present observation seems to be due to the surface amorphization by Ar-ion bombardment. As the sputter cleaning time increased from 10 to 30 min, the onset voltage changed from 1800 to 1250 V. Considering that the longer Ar-ion bombardment resulted in dull tips (Fig. 3), this result would seem to show that, in the present experimental condition, the emission behavior is significantly dependent on the surface condition, such as the amorphization or roughness change, rather than the morphology of the tip apex.

Fig. 6 shows the $I-V$ curves after four measurements of the DLC-coated samples on the number of $I-V$ measurements. The thickness of the DLC film is 60 nm.
[Fig. 2(b)], the onset voltage decreased from 1800 to 1200 V after five measurements. Furthermore, the emission current increased with increasing number of $I-V$ measurements. This result clearly shows that the passivation of the Si tips can be much suppressed by the DLC coating. Surface stability, chemical inertness and low sputter yield of the DLC film seem to play a positive role in the field emission stability.

Fluctuations of the emission current measured in as-prepared, Ar-cleaned and DLC-coated tips are summarized in Fig. 8. The fluctuation was defined by $(I-I_{ave})/I_{ave}$, where $I$ is the emission current and $I_{ave}$ the average emission current during the measurement. The fluctuation measurement was performed after 10 measurements. Although the DLC coating reduced the current fluctuation observed in Ar-sputtered tips [Fig. 8(a) and (c)], the emission current from the DLC-coated tip showed a larger fluctuation than that of the as-prepared Si tip [Fig. 8(b)]. As previously discussed, the larger fluctuation of the emission current could be due to both the amorphization of the Si tip surface during the Ar sputtering and/or the amorphous structure of the DLC films. Fig. 8(a) and (c) shows that the effect of the amorphized Si layer on the current fluctuation was suppressed by the DLC coating. In order to control the fluctuation, therefore, it would be more effective to optimize the thickness and structure of the DLC films. More investigations are in progress to reduce the current fluctuation by modifying the film structures.

4. Conclusions

In the present work, we investigated the stability of Si tips by repeating $I-V$ measurements. DLC coating on the Si tips by DC magnetron sputtering can increase the stability of the emission behavior, even if the fluctuation of the emission current is increased by the amorphous DLC layer and/or amorphous Si layer due to Ar-ion bombardment. These results showed that the DLC coating can prevent the Si tips from oxidation or contamination, which stabilizes the field emission behavior. Furthermore, the DLC coating seems to reduce the effect of the changes in tip apex morphology by reducing the sharpness of the tip apex. The present results imply that a DLC protective layer can be used for stabilized cold cathode tips in vacuum microelectronics or field emission displays. However, the fluctuating emission current should be controlled by optimizing the Ar sputter-cleaning process and modifying the structure of the DLC films.

Acknowledgements

This work was financially supported by the Ministry of Science and Technology of Korea. Partial support
from the Korea Science and Engineering Foundation through the Center for Interface Science and Engineering of Materials at Korea Advanced Institute of Science and Technology is gratefully acknowledged.

References