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To improve silicon field emitters, an amorphous-carbon-nitride (*a*-CN) coating was applied by helical resonator plasma-enhanced chemical vapor deposition. By this process, *a*-CN was very uniformly coated on silicon tips without any damage. Microstructural and electrical investigation of the silicon and *a*-CN coated field emitters were performed. *a*-CN coating lowered turn-on voltage and increased emission current. Negative electron affinity of carbon nitride is suggested for enhancing emission current. © *1997 American Institute of Physics.* [S0003-6951(97)03629-2]

Field emitters have been discussed as a new electron source for flat panel display devices, electronic devices, and so on.[1,2] Among various types of emitters, the silicon emitter is the most widely used together with the Spindt-type emitter. This is due to its easiness in fabricating a sharp structure and compatibility with the conventional integrated circuit processes. However, silicon has some disadvantages, which result from its inherent properties. It is easily oxidized and vulnerable to the damage by ion bombardment during fabrication and/or operation, which can hurt the uniformity and the efficiency of electron emission.

To enhance the emission current and chemical stability of silicon field emitters, it has been coated by various materials such as metals,[3] carbides,[4] and nitrides.[5] But there has still been no superior material or technology discovered for field emitters. In addition, control of the uniformity and microstructure of the grown film is needed for field-emission device applications. Recently, diamond[6–8] and diamondlike carbon (DLC)[9,10] have attracted much attention due to their unique properties such as negative electron affinity,[11] high thermal conductivity, extreme hardness, and good chemical stability. Many researchers reported that diamond could emit electrons at very low electric fields. But the mechanism of electron emission from diamond is not clearly understood yet. Also, by typical plasma processes using hydrocarbon precursors, diamond grows only in a particle or facet shape, not in a uniform and smooth layer.

On the other hand, DLC can be deposited microscopically smooth, following the morphology of the emitter tips. One of the most important advantages of DLC application over diamond is lower deposition temperatures ranging from room temperature to 250 °C. However, the thermal stability of DLC is kept only up to 300 °C.

In this study, amorphous-carbon-nitride (*a*-CN) film by helical resonator plasma-enhanced chemical vapor deposition (HR-PECVD) was coated on the silicon tips and tested as a new field emitter. Carbon nitride is a material that, if it can be made to have the stoichiometry of β-C_3N_4, would have the same structure as β-Si_3N_4 and show properties comparable to those of diamond.[12] Especially, the optical band gap of carbon nitride is estimated to be as wide as diamond.[13] According to the theoretical calculation based on the bond length and the bond ionicity, carbon nitride is expected to have a larger bulk modulus (4.83 Mbar) than diamond (4.43 Mbar).[12] Since the hardness is proportional to the bulk modulus, the hardness of carbon nitride might be higher than that of diamond.

In our experiment, a carbon-nitride film with an amorphous structure was synthesized by HR-PECVD. Though having an amorphous structure, it shows high hardness and chemical inertness. Also, the thermal stability of *a*-CN is expected to be even better than that of DLC. In addition, by varying the deposition conditions, the optical band gap of *a*-CN film can be controlled within the range of 1.5–2.6 eV. Many physical properties of *a*-CN and DLC were compared in Table I.[14–16]

It is well known that the field emission depends highly upon the physical structure of the emitter material. Especially when coating the field emitter, the surface morphology of the emitter should maintain the sharpness of the initial tips. To maintain the sharpness, the coating material should not be too thick and the damage by ion bombardment during deposition should be minimized. In this view, HR-PECVD is considered as an appropriate method to coat the field emitters. In this process, an intense plasma can be sustained below 10 mTorr.[17] This process offers low-energy particles at low pressure and allows a uniform coating of *a*-CN without damaging the sharpness of the silicon tips. A schematic diagram of this system is shown in Fig. 1.

This system is composed of a reactor and a discharge source tube. A resonator source was fitted concentrically over the tube mounted on top of the reactor. Prior to the deposition, the entire system is evacuated by a turbomolecular pump. Plasma generating gases (nitrogen or argon) enter the top of the tube, pass through the discharge zone within the helical coil and the flow reactor. A reactive gas (meth-

TABLE I. Properties of *a*-CN and DLC (Refs. 14–16).

Properties	*a*-CN	DLC
Optical band gap (eV)	1.5–2.6	1.5–3.0
Electrical resistivity (Ω cm)	10^4–10^{11}	10^{10}–10^{13}
Thermal stability (°C)	600–900	400
Hardness (kg/mm^2)	5000	1000–3000
Refractive index	2.0–2.3	1.8–2.2
Friction coefficient	0.2–0.4	0.2–0.3

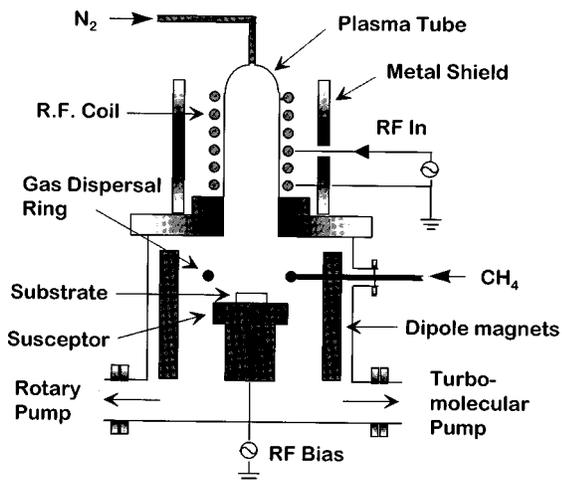[a)]Electronic mail: thinfilm@bubble.yonsei.ac.kr

FIG. 1. Schematic diagram of HR-PECVD system.

ane) enters through a dispersal ring and disperses above the substrate. In the reactor, dipolar permanent magnets were equipped in order to reduce a loss of electrons and ions to the chamber wall and to confine the plasma within the substrate area.

The helical resonator was designed for a quarter-wave resonant frequency of 13.56 MHz. It consists of an outer cylindrical metal shield and an inner helically shaped copper coil whose length is approximately 1/4 the wave length of the desired resonant frequency. One end of the coil is attached to the shield to fix the low potential end, while the opposite end of the coil is isolated from the shield and discharge tube. RF power is supplied directly at a point on the helical coil to match the transmission line and resonator impedances during the discharge operation.

The silicon tips on which a-CN was coated had been prepared from a vapor–liquid–solid process. Details of the fabrication process of the silicon tips are described elsewhere.[18] And the main deposition conditions for a-CN by HR-PECVD are summarized in Table II. For the evaluation of the material characteristics of the a-CN film, some samples were prepared on planar substrates of silicon or glass. Scanning electron microscopy (SEM) and Fourier transformation infrared spectroscopy (FT-IR) were used to examine the tip morphology and the structural quality of the films, respectively.
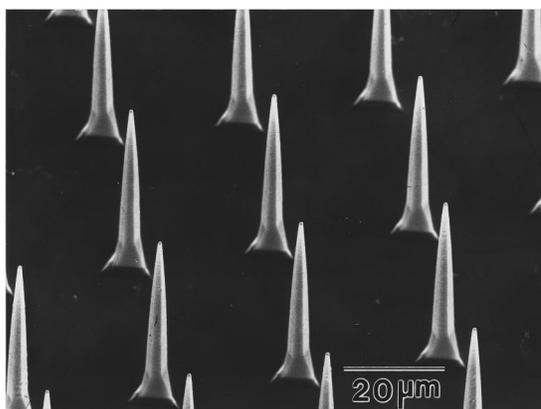
SEM micrographs of silicon field emitters before and after a-CN coating are shown in Fig. 2. The silicon tips are very sharp and uniformly arrayed. After coating, though, the apices of the tips became a little blunt. The total geometry did not change from the original shape. The films were

TABLE II. Deposition conditions of a-CN by HR-PECVD.

RF frequency	13.56 MHz
RF power	100 W
Base pressure	$<4\times10^{-6}$ Torr
Working pressure	9×10^{-4} Torr
CH_4 flow rate	3 sccm
N_2 flow rate	10 sccm
Deposition temperature	No intentional heating
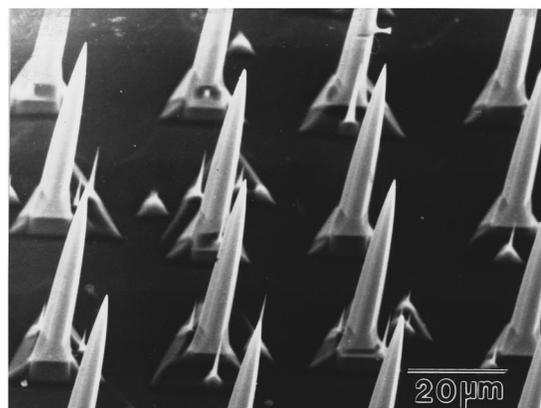
(a)

(b)

FIG. 2. SEM micrographs of silicon field emitters (a) before and (b) after a-CN coating.

coated very uniformly showing a smooth surface morphology.

Figure 3 shows a FT-IR spectrum of a-CN film deposited on the silicon wafer. The absorption peak at $2190 \ cm^{-1}$ is attributed to the stretching vibration of the triple bondings between carbon and nitrogen ($C\equiv N$,
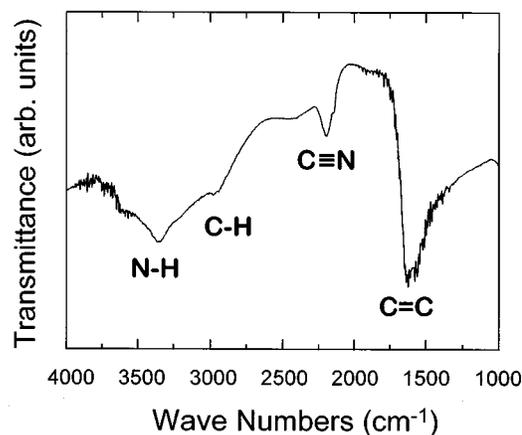

FIG. 3. FT-IR spectrum of a-CN film deposited on a silicon wafer. The absorption peaks corresponding to various stretching modes are shown: $1600 \ cm^{-1}$ ($C=C$), $2190 \ cm^{-1}$ ($C\equiv N$), $2900 \ cm^{-1}$ ($C-H$), and $3300 \ cm^{-1}$ ($N-H$).
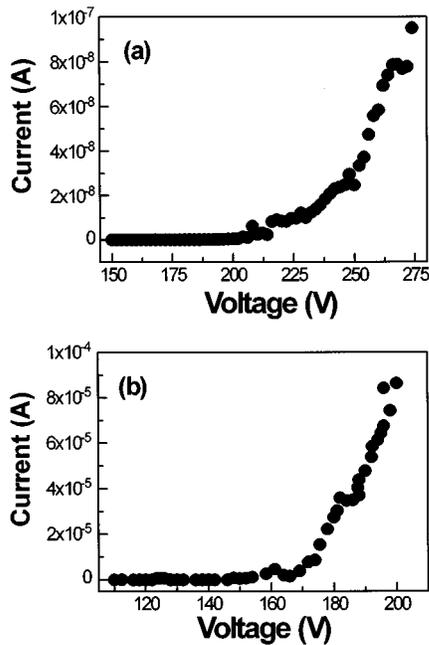
FIG. 4. Current–voltage characteristics of (a) as-grown and (b) a-CN coated silicon field emitters.

nitrile).[19,20] This result makes sure that the carbon and the nitrogen atoms are chemically bonded to each other. The existence of the chemical bonding of C≡N is also confirmed by Raman and x-ray photoelectron spectroscopy (not shown in this letter). The absorption peaks centered at about 3300 and 2900 cm^{-1} are due to the N–H and C–H stretching modes, respectively. These peaks indicate a large amount of bonded hydrogen in the film. The peak at about 1600 cm^{-1} is assigned to the sp^2 C=C stretching mode, and is normally IR forbidden. The appearance of this feature suggests that the incorporation of nitrogen into carbon breaks the symmetry of the sp^2 domains and makes this mode IR active.[20]

For the samples of as-grown silicon tips and a-CN coated silicon tips, the field-emission tests were performed with a diode structure in an ultra-high-vacuum chamber. The measurements were carried out at a pressure lower than 3×10^{-9} Torr. The tip heights of the various emitters used for the current–voltage measurements were 100 μm. The distance between the emitter and the anode was kept at 150 μm.

$I-V$ curves for the two kinds of field emitters are shown in Fig. 4. The turn-on voltage of the a-CN emitters decreased to 150 V from 230 V, that of the silicon emitters. Here, the turn-on voltage corresponds to the voltage at which the emission current is 10^{-8} Å. The emission current for the a-CN emitters is significantly higher than that for the silicon emitters. These enhancements of the silicon emitters by the a-CN coating are comparable to those by the diamond coating. That is, in another experiment of diamond coating on silicon tips, we obtained a turn-on voltage of 130 V and an emission current of order of 10^{-6} Å.[21]

One possible mechanism of the enhanced emission would be a negative electron affinity (NEA) of the a-CN films. So far, no study has reported whether a-CN exhibits NEA or not. But, many physical properties of a-CN, such as hardness, thermal conductivity, and optical band gap, are very similar to those of diamond or DLC. In addition, many nitrides like AlN[22] and BN[23] also show NEA characteristics. Therefore, it might be expected that carbon nitride also has NEA. In addition, the uniform and smooth coating of a-CN was helpful in increasing the emission current. A detailed investigation of these behaviors is still progressing and will be discussed in another article.

In summary, a-CN was first applied to field emitters. The fabrication process using HR-PECVD was successfully developed to coat a-CN on silicon tips without damaging the original sharpness. It has been found that carbon nitride grown by HR-PECVD has an amorphous structure and contained chemical bondings of C≡N. After the coating of a-CN, the turn-on voltage was lowered and the emission current increased significantly. As the mechanism for the enhanced field emission of a-CN coated silicon tips, NEA and a uniform coating of a-CN were suggested.

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