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Electron emission from boron nitride coated Si field emitters

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Electron emission characteristics of sulfur (S)-doped boron nitride (BN) films synthesized by plasma-assisted chemical vapor deposition (PACVD) are investigated. The BN film consists of hexagonal grains of 3 nm in size. The energy gap is estimated to be as wide as 6.0 eV from ultraviolet-visible optical transmission measurement. The electrical resistivity is reduced to 4.9 $\times 10^2$ Ω cm. Si tip field emitters coated with the BN film are fabricated. The electron emission occurs at an electric field as low as 6 V/μm, while a high electric field of 20 V/μm is needed to emit electrons from the Si tip array without BN coating. It is deduced that the tunneling barrier height of 0.1 eV exists at the surface of the BN film. © *1997 American Institute of Physics.* [S0003-6951(97)00944-3]

Much attention has been paid to diamond base field emitters as an electron source with a highly reliable performance because diamond has superior properties such as negative electron affinity (NEA), chemical inertness, and mechanical hardness. Development of field emitters is desired for vacuum microelectronic devices and field emission flat panel displays. Electron emission from diamond films is observed at considerably low electric field.[1,2] Moreover, it was found that the operation electric field was reduced effectively for Si and Mo field emitters coated with diamond.[3–5] However, formation of thin diamond films with a smooth and uniform surface is needed to fabricate diamond-coated field emitters. Furthermore, it is not easy to grow *n*-type diamond films with a high electron concentration. Recently NEA has been observed for not only diamond but also AlN by ultraviolet (UV) photoelectron spectroscopy (UPS) study.[6] Moreover, the field emission characteristic of the boron nitride (BN) film synthesized by laser ablation suggested strongly that NEA appeared at the surface of the BN film.[7] Chemical and mechanical properties of BN are expected to be superior to those of Si and metals used so far for the study on field emitters.

Synthesis of BN films has been carried out by various methods.[8–13] BN is well known as a material which has various phases such as hexagonal, cubic, and so on with growth methods and conditions. We characterized BN films synthesized by plasma-assisted chemical vapor deposition and found that the electron emission occurred from sulfur (S)-doped BN films at a low electric field.[14]

In this letter, fabrication of the Si tip field emitters coated with S-doped BN film is attempted. A significant improvement of the emission characteristic is demonstrated for the BN-coated Si tip array.

Deposition of BN films was attempted on *n*-Si flat substrates and *n*-Si substrates with Si tip array. The array with 1600 tips was formed in the area of $0.4\times 0.4\ \mathrm{mm}^2$ with a separation of 10 μm using wet etching and thermal oxidation processes. BN films were synthesized by PACVD under application of dc negative-bias (V_{DC}) to the substrate. The schematic diagram of the experimental apparatus is shown in Fig. 1. BCl_3 and N_2 were utilized as source gases to avoid hazardous and toxic materials such as B_2H_6. The substrate was placed on a stainless holder, and was heated by an external furnace. The temperature was monitored with a thermocouple installed in the stainless holder. The reactor was evacuated to the base pressure of 1×10^{-3} Torr by a rotary pump. The substrate temperature and the total gas pressure were fixed at 650°C and 1 Torr, respectively. Prior to depositing BN films, the substrate was treated with H_2 plasma for 3 min in the reactor to clean the surface. A mixture gas of BCl_3 and H_2 was introduced near the substrate without mixing with N_2 plasma. The N/B flow rate ratio (N/B_{flow}) was regulated at 2.5 under the condition that BCl_3 was fixed at 0.8 sccm. N_2 plasma was produced 15 cm away from the substrate by supplying rf power (13.56 MHz) to the turn coil which was installed around the reactor. The rf power was fixed at 40 W. BCl_3 mixed with H_2 was decomposed near the substrate by heating due to the external furnace. N ions produced in the N_2 plasma were accelerated onto the substrate by application of the dc negative bias. The present experiment was carried out at the applied bias of 200 V. Sulfur (S) was doped as a donor impurity. Solid S was heated and transported with N_2 gas into the reactor as shown in Fig. 1. The growth rate was estimated to be 100 nm/h on the flat Si substrate under these conditions.

The field emission characteristic was measured at room temperature for BN films deposited on Si flat substrates and Si tip arrays. The film thickness was 300 nm. A Si wafer of 3 mm^2 in area was utilized as an anode electrode. The anode was set 125 μm away from the sample surface using two

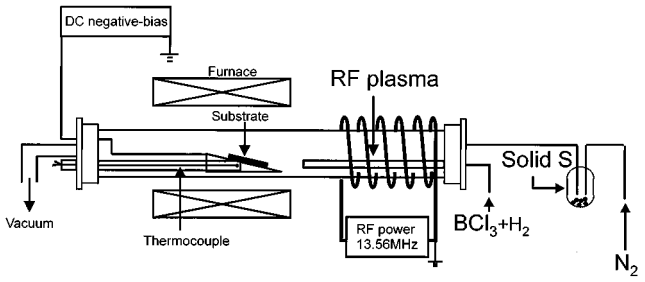

FIG. 1. Apparatus for plasma assisted chemical vapor deposition.

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TABLE I. Properties of BN film.

Structure	hexagonal nanocrystalline film	
Grain size	3 nm	
Band gap	6.0 eV	
Electrical resistivity	undoped BN	2×10^{11} Ω cm
	S-doped BN	4.9×10^{2} Ω cm

pieces of glass fiber as a spacer. Ohmic contacts on Si substrates were provided with Ag epoxy. A resistor of 5 MΩ was connected to the cathode electrode to protect the measurement equipment. The field emission measurements were carried out at a pressure of 5×10^{-7} Torr.

Optical and electrical characterization of the BN films was performed by transmission electron microscopic (TEM) observation, transmission electron diffraction (TED), Fourier transform infrared absorption (FTIR), ultraviolet-visible optical transmission and current–voltage ($I-V$) measurements.[14] Properties of BN films are summarized in Table I. TEM observation was carried out for a BN film as thin as 100 nm. It was confirmed that BN films consisted of small grains, the size of which is about 3 nm. Moreover, a significant ring pattern was observed for the same sample by TED measurement. The FTIR spectrum consisted of two absorption bands at 800 and 1380 cm^{-1}, which suggest the existence of the hexagonal phase of BN.[13] The energy gap of the BN film was evaluated to be 6.0 eV from the absorption spectrum measured in the UV-visible region. The electrical resistivity estimated from the $I-V$ characteristic was 2×10^{11} Ωcm for the undoped BN film. On the other hand, the electrical resistivity was reduced to 4.9×10^{2} Ωcm by doping with S.

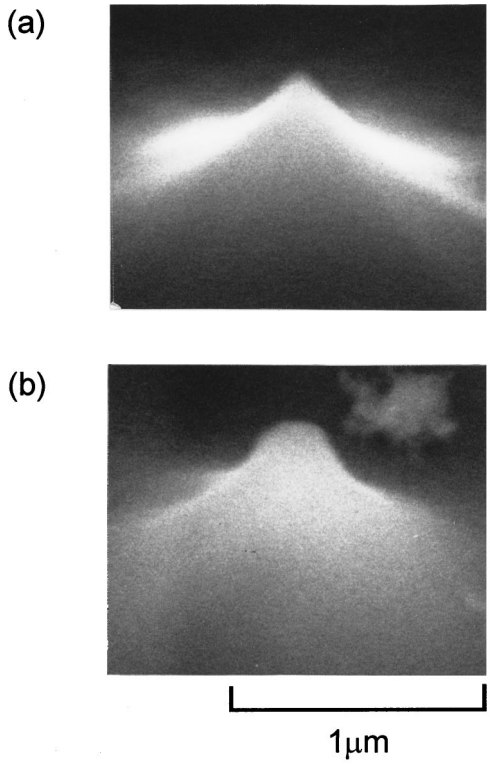

FIG. 2. SEM photographs of (a) Si tip and (b) BN-coated Si tip.

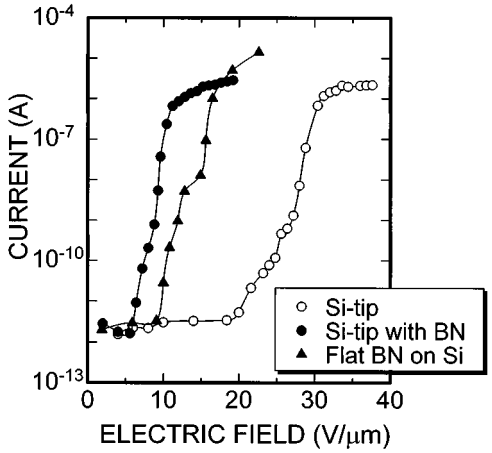

FIG. 3. Emission current vs electric field characteristics of Si tip array, BN-coated Si tip array, and flat BN film, which are indicated by open and solid circles and solid triangles, respectively.

Figure 2 shows scanning electron microscope (SEM) micrographs of Si tips before and after BN coating. It is observed that the Si cone is formed and its height is 1 μm. The curvature of the Si tip is 0.04 μm in radius. In contrast to this, a significant variation in the tip shape is observed after depositing BN film. The curvature of the tip is increased to 0.16 μm. This is due to depositing a BN film as thick as 0.3 μm on the flat surface of Si in the present experiment. It was confirmed that no remarkable change in the shape of the Si tip occurred due to etching with Cl atoms during deposition of the BN film.

The emission characteristics are measured at room temperature for Si tip arrays with and without coating with S-doped BN films. The emission characteristic of the S-doped BN film deposited on the flat substrate is also measured for comparison. Figure 3 shows the electron emission current as a function of the electric field which is estimated from the applied voltage and the separation (125 μm) between the anode and the sample surface. A measurement limit of the emission current was 1×10^{-12} A in the present apparatus. The emission current is detected at the electric fields higher than 9 V/μm for the flat BN film. This value of the electric field is designated as a threshold electric field in this letter. The field emission characteristic of the flat BN film corresponds to that of the diamond film terminated with hydrogen, the surface of which has negative electron affinity.[15] The threshold electric field is 20 V/μm for Si tip array without a BN film. On the other hand, the threshold electric field of the BN-coated sample is as low as 6 V/μm. A significant reduction in the threshold electric field can be achieved by coating with a BN film. Moreover, it is lower than that of the flat BN film sample. This is due to concentration of the electric field at the surface of the BN film deposited onto Si tips. It is expected that the threshold electric field can be further reduced by forming a BN-coated Si field emitter with a sharp tip.

Figure 4 depicts the Fowler–Nordheim (FN) plot for three samples shown in Fig. 3. The straight line suggests the emission of electrons tunneling through the potential barrier. When assuming that the electric field is uniform at the surface of the flat BN film, an enhancement factor (β) is 1. The

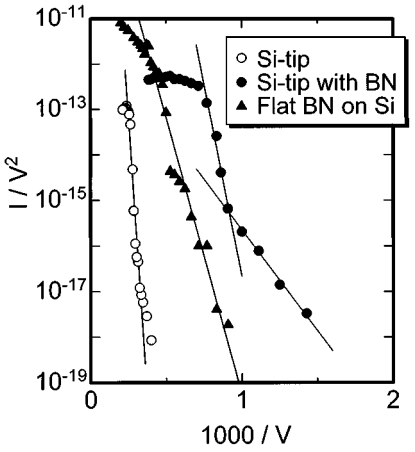

FIG. 4. FN plots for the samples shown in Fig. 3.

tunneling barrier height of the BN film is estimated to be 0.1 eV from the slope of the straight line. In the case of the Si tip array without BN coating, the enhancement factor is estimated to be 5.2×10^3 assuming the tunneling barrier height of Si to be 4.2 eV.[5] The value of the enhancement factor is different from that (1.8×10^5) calculated[16] using the curvature of the Si tip measured on the SEM photograph shown in Fig. 2. This is possible because surface oxidation and contamination cause an increase of the effective tunneling barrier height of the Si tip. In contrast to these two samples, it is found that the FN plot of the BN-coated Si tip array has two slopes of straight lines. The enhancement factor is estimated to be 2.2×10^2 in the low electric field region using 0.1 eV as a tunneling barrier height at the BN surface. On the other hand, the enhancement factor is calculated to be 8.4×10^2 using the curvature (0.16 μm) obtained from the SEM micrograph of the BN-coated Si tip. This value is quite close to that estimated from the FN plot. It is suggested that electrons are emitted from BN to vacuum tunneling through the potential barrier at the surface of the BN film. In the case that the tunneling barrier height was estimated assuming that the tunneling potential barrier exists at the interface between the BN film and the Si substrate, no coincidence was found between the barrier heights of the flat BN film and BN-coated Si tip. This means that a small positive electron affinity appears at the surface of the present BN films.

The steep slope of the FN plot in the high electric field region may be due to the electron emission from the different area. The enhancement factor is estimated to be 56 from the steep slope using the tunneling barrier height of 0.1 eV. A reduction of the enhancement factor means that the emission characteristic becomes similar to that at the flat BN surface. Therefore, it may be considered that electron emission occurs at the foot of Si tips.

In summary, Si tip field emitters are coated with S-doped BN film by plasma-assisted chemical vapor deposition. The electron emission occurs at the electric field as low as 6 V/μm for BN-coated Si tip array. It is demonstrated that BN coating is effective in improving characteristics of Si tip field emitters. Moreover, the present experimental results suggest that a tunneling barrier height as low as 0.1 eV exists at the surface of the BN film.

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