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Field Emission Properties of 10-nm Pillars of Organics Fabricated by Pt particles and Plasma Etching

Toshiya Suzuki[1], Keigo Takeda[1,4], Hiroki Kondo[1], Kenji Ishikawa[1], Yuichi Setsuhara[2,4], Masaharu Shiratani[3,4], Makoto Sekine[1,4], Masaru Hori[1,4]

[1] Nagoya Univ.
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
Phone: +81-052-789-3461 E-mail: suzuki.toshiya@b.mbox.nagoya-u.ac.jp
[2] Osaka Univ.
1-1 Yamadaoka, Suita, Osaka 565-0871 Japan
[3] Kyushu Univ.
6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan
[4] JST-CREST

1. Introduction

As entering an era of technologies of 10-nm half-pitch and beyond, more precise control of size and shape in plasma processes has been extremely difficult because fluctuations in the control at sub nm-scale become an essential factor and they would determine the device performance.

To realize high-aspect-ratio and nm-scale etch of organic materials is challenging due to their weakness in mechanical strength. Recently, we have succeeded in fabricating the 10-nm-scale pillars of organic low dielectric (Low-k) film organics by using top-down etching method. As etched mask, we introduced to use platinum nanoparticles deposited by supercritical fluid chemical vapor deposition [1]. During the etching, the sputtered Pt atoms are re-deposited onto the sidewalls of the nanofabricated structures. Then, they inhibit lateral etch and played a characteristic role for forming the nanopillar of mechanically-weak organics. On the other hand, it is suggested that nitrogen radicals would effectively change electronic properties of the etched materials during the nitrogen-containing plasma treatment. In actual, the nitrogen modification has been reported in the areas of graphene by irradiating with N^+ ion beam [2]. However, the electronic properties of the nanopillars formed by this process are not clarified yet.

In this study, the electron field emission (FE) properties of the nanopillars were studied with respect to their physical geometry and chemical bonding configurations of the plasma-modified surface. The effects of various plasma treatments on FE properties of carbon material such as the CNTs have been reported in the previous many papers [3]. However, the effects of the structural changes of nanopillars on field emission properties after the plasma treatment have never been reported.

2. Experiments

The 10-nm organic nanopillars were fabricated by applying two techniques as shown in Figure 1. The one was the 10-nm-sized Pt particles deposited on the bare organic films by employing the supercritical fluid chemical vapor deposition. Size of the particles could be changed by controlling the substrate temperature during deposition. The other was that the precise etch of organic material was conducted by controlling reactive species in plasmas of H_2-N_2 mixture and the Pt particles used as a mask for etch. We used a 100-MHz capacitively coupled plasma (CCP) equipment with a H_2-N_2 gas mixture at a total pressure of 2.0 Pa. For organic materials, we prepared films of SiLK™ (Dow chemicals) with thickness of 200 nm deposited on silicon substrate. A sequence of deposition of the Pt mask and then etching of the organic film was succeeded in form nanopillars with a mean diameter of about 10 nm and height of 200 nm.

Next field emissions (FE) properties were measured in a vacuum chamber at a pressure of ~ 10^{-3} Pa. A spherical stainless-steel anode (radius of 2 mm) was set with a distance of 200 μm above the sample surface. A negative voltage was applied between the anode and the sample not exceeding of 6 kV. Currents of the FE from the samples were changing with increasing in measuring times. So we neglected unstable currents observed at the first two runs and averaging over several runs after the third one. Sweep range was from 0 to 1 kV.

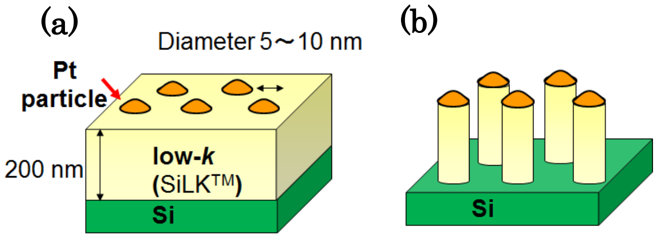

Fig.1 (a) Illustration of Pt particle deposited on organic low-*k* film (b) Illustration of organic nanopillar after etching treatment

3. Results and discussion

Figure 2 shows the Pt particle's diameter depending on the substrate temperature during super critical fluid chemical vapor deposition. The diameter increased with increasing substrate temperature [3]. In this experiment we applied substrate temperature as 190 deg. C to make nanopillar stand after etching treatment.

Figure 3(a) shows the scanning electron microscope (SEM) image of Pt core deposited on organic low-*k* film. 5 to 8-nm-diameter Pt particle can be confirmed. Figure 3 (b) shows the SEM image after etching treatment. Etching shape has high dependency on radical density and substrate temperature. After the etching with hydrogen (H)/N density ratio of 60/40 at 60 deg. C for 2 min, the organic low-*k* film was etched over to the bottom, and 10-nm-wide organic low-*k* nanopillars were formed. Its lateral etching was less than 1nm and aspect ratio was 18.7.

At the FE measurements, electron emission current was observed from the organic nanopillars sample. The threshold value was 8.0 V/μm. Relationship between emission current density (J) [mA/cm^2] and electric field (E) [V/μm] in FE property is written with Fowler-Nordheim equation;

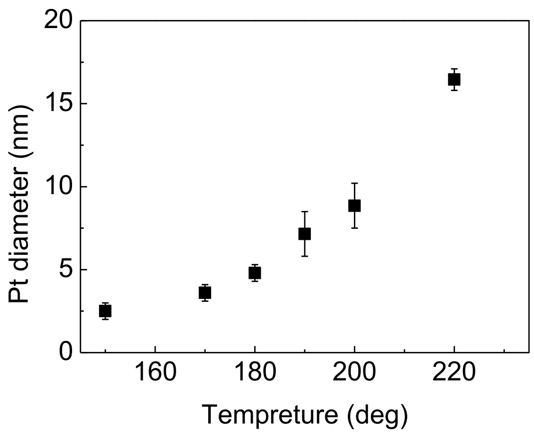

Fig.2 the Pt particle's diameter depending on the substrate temperature during super critical fluid chemical vapor deposition

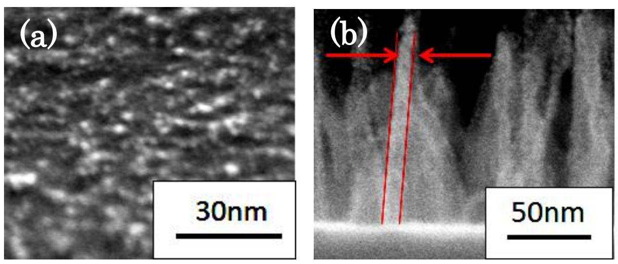

Fig.3 (a) SEM image of Pt particle deposited on organic low-*k* film
(b) SEM image after etching treatment. Etching shape has high dependency on radical density and substrate temperature

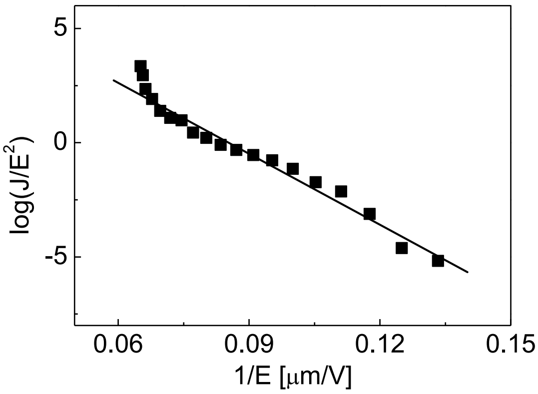

Fig.4 Measurement result plotted with J/E as horizontal axis and ln(V/E^2) as vertical axes

$$J = BE^2 \exp(-\frac{A}{E}) \qquad (1)$$

in this equation A and B are constant numbers defined as $A = 68.3\Phi^{3/2}/\beta$ and $\ln B = 1.54 \times 10^{-4}\beta^2 S/\Phi$;electron emission square (S), electric field multiplication coefficient (β) and work function (Φ).

Figure 4 shows the measurement result plotted with J/E as horizontal axis and ln(V/E^2) as vertical axes. From this figure it can be considered that the nanopillar has FE properties because the sample has a minus gradient with a straight line. From this result, Φ can be calculated to 1.13 eV based on the gradient value of the plot (81.9) if we define β as 1. However, this value is much smaller compared with work function values of Pt (5.3 eV) or graphite (4.8-5.05 eV). Therefore, electric field multiplication coefficient is assumed to be around from 8 to 12 based on the equations.

In this experiment field emission properties were measured from the material which used to be organic low-*k* film before etching. This result implies that organic low-*k* material's structure was changed into conductor material. Graphitic or nitride surface was formed by irradiation of hydrogen or nitrogen radical, respectively.

4. Conclusions

In this study, 10 nm-sized Pt particles were deposited on the organic low-*k* film by super critical fluid chemical vapor deposition, and after that the 10-nm-diameter organic nanopillars were fabricated by etching with Pt particles as a metal mask. In the end, Field emission of the nanopillar was analyzed. As a result, we could detect field emission from the nanopillar, which indicate that organic low-*k* material's structure was changed into conducting material.

References

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