# Effect of Annealing on Electrical Properties of Networked-Nanographite Wire Grown by Metal-Photoemission-assisted Plasma-enhanced CVD

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#### Abstract

The effect that annealing has on the electrical properties of networked-nanographite (NNG) wires has been investigated using a cross-sectional transmission electron microscope (TEM), Raman spectroscopy and resistivity measurement. Photoemission-assisted Plasma-enhanced CVD has been used as the growth method on dielectrics without catalysts. It was found that the resistivity of the NNG wire decreases as the annealing temperature increases. This result indicates that the quality of the NNG wires improves during the annealing process. Although we need to clarify the mechanism of this improvement, we propose that an NNG wire can be a candidate for a future interconnect material.

## 1. Introduction

With conventional Cu/low-k interconnects, the resistivity increases and the EM reliability deteriorates as the line width decreases. Carbon-based materials, such as carbon nanotubes (CNT) and graphene nanoribbons (GNR), have been studied as interconnect materials because of their lower resistivity[1] and intrinsically higher current carrying capacity[2] compared with Cu. Recently, we have proposed a photoemission-assisted plasma-enhanced CVD method as a way to fabricate multilayer graphene for interconnects [3]. We have succeeded in growing NNG films and fabricating NNG wires on dielectric layers without any metal catalysts [4]. In this study, we have investigated the way the resistivity of the NNG wire decreases and clarified issues in using it as a future interconnect material.

#### 2. Experimental

Figure 1 shows the metal-photoemission-assisted plasma CVD method as used on dielectric layers without any metal catalysts, with Ta metal for the retainer electrode. The UV light source is a Xe excimer lamp ( $\lambda$ =172nm), and the glow-discharge plasma is generated above the wafer and retainer electrodes. The NNG film was grown on a SiO<sub>2</sub>/Si substrate at a growth temperature of 600°C. The flow ratio of CH<sub>4</sub>/Ar was 1/10, and the total pressure was 100Pa. The discharge voltage and current were 270V and 1.5mA, respectively. The exciting laser wavelength was

514.5nm in the Raman measurements. The resistivity was measured by the four-probe method for NNG films and the four-terminal method for the NNG wires. The annealing of NNG films was performed with an IR furnace in a nitrogen atmosphere. The reliability tests of the NNG wires were performed in a vacuum chamber under a current density of  $5E5A/cm^2$  and non-current at an ambient temperature of  $350^{\circ}C$ . The length of the NNG wire was 2, 3 and 5µm with

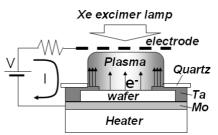


Fig. 1 Schematic illustration of metal-photoemission-assisted plasma-enhanced CVD system, using Ta metal for the retainer electrode

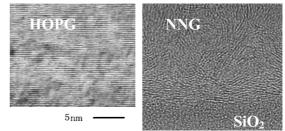
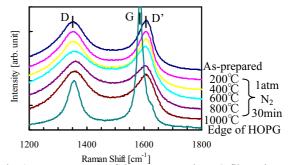
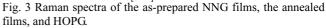


Fig. 2 Cross-sectional TEM images of HOPG and NNG on a  $\mathrm{SiO}_2$  dielectric





a constant width of  $5\mu m$  (TLM pattern). We calculated the sheet and contact resistance of the NNG wires from these measurements.

## 3. Results and Discussion

Figure 2 shows cross-sectional transmission electron microscope (TEM) images of HOPG and NNG on a  $SiO_2/Si$  substrate. From these images, we found that NNG film contains graphite with a nano-size networked domain.

Figure 3 shows the Raman spectrum of HOPG and NNG. The D band, G band and D' band can be observed at  $\sim$ 1350 cm<sup>-1</sup> and  $\sim$ 1580 cm<sup>-1</sup> and  $\sim$ 1605 cm<sup>-1</sup>, respectively. The G and D bands derive from the stretching vibration of the C=C sp<sup>2</sup> chemical bond and the radial breathing vibration in the aromatic rings, respectively. The D' band indicates defects such as the edge of the graphene sheets. Therefore, NNG film contains a small domain of graphene sheets with some defects. In order to increase the domain size and decrease the resistivity of NNG film, we tried an annealing process. As a result of the annealing, the intensity of the D' band decreased at an annealing temperature of over 800°C. This tendency suggests that the edge of graphene decreases and the domain size of NNG film becomes larger as the annealing temperature increases.

Figure 4 shows the change in resistivity of NNG films after the annealing process. The resistivity decrease as the annealing temperature increases. This result indicates that the quality of the NNG wires improves during the annealing process. We need to clarify this improvement mechanism to control the wire resistivity.

Figure 5 illustrates a schematic cross-section of the NNG wire and the Au /Ti electrodes used in the high temperature reliability test. Figure 6 shows the changes in sheet and contact resistance of the NNG wires after the reliability tests. The decrease in sheet resistance in the current test case was larger than that in the non-current test case. It is considered that the NNG wire annealed by self-heating at a high temperature of above 350°C in the current test case. In fact, the temperature of the NNG wire has been estimated to be about 400°C due to Joule heating. On the other hand, the contact resistance decreases to the same level in both test cases. As seen in figure 6, however, it is clear that the metal diffusion occurred in the contact interface only in the current test case. The NNG wire may need a barrier metal in the case of the metal electrodes for higher reliability.

## 4. Conclusions

We have investigated the annealing properties of networked-nanographite (NNG) wires as the first step for producing multilayer graphene interconnects. We used our original photoemission-assisted plasma-enhanced CVD method on dielectrics without metal catalyst films. Although we need to lower the resistivity by expanding the grain size, our CVD technology has potential in the development of future multilayer graphene interconnects, and is suited to the LSI fabrication processes.

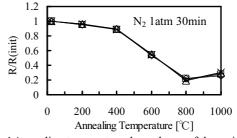


Fig. 4 Annealing temperature dependency of the resistivity.



Fig. 5 Schematic cross-section of the NNG wire

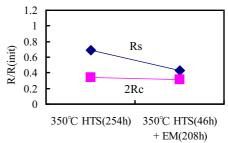
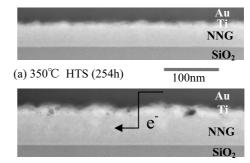


Fig. 6 Sheet and contact resistance change of the NNG wires after reliability tests. The values were measured at room temperature before and after the tests.



(b) 350°C HTS (46h) + 350°C EM (208h)

Fig. 7 Cross-sectional TEM images, (a) after high temperature storage test, (b) after electromigration test.

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