Nanocarbon application including interconnects and thermal interface materials

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Abstract

Nanocarbon materials such as graphene and carbon nanotubes are promising electronic materials for future LSIs due to their excellent physical properties.

Here, we fabricated sub-10-nm-wide intercalated multi-layer graphene (MLG) interconnects and demonstrated a resistivity lower than that of copper (Cu) with similar dimensions. The MLG was synthesized by thermal chemical vapor deposition (CVD) on an epitaxial cobalt film, resulting in quality and electrical properties as good as those of a graphite crystal. After intercalation with FeCl₃ molecules, the interconnects were narrowed down to a width of 8 nm by electron beam lithography. The 8-nm-wide intercalated MLG interconnects exhibited a resistivity of 3.2 $\mu\Omega$ cm, which is lower than the predicted resistivity of Cu interconnects with the similar dimensions.

We also fabricated carbon nanotube thermal interface materials (CNT-TIMs) and compared their thermal resistance with that of indium film, which is generally utilized as a TIM. The CNTs were also synthesized by the thermal CVD method. After growth, the densification of CNTs was performed by lateral compression. As a result, the density of the CNTs became three times higher than that before densification without causing damage, leading to a thermal resistance as low as that of indium films.

Our results show that nanocarbon materials are really promising for future electronic materials

1. Introduction

Nanocarbon materials including graphene [1, 2] and carbon nanotubes [3, 4] are really attractive as future electronic materials due to their excellent physical properties. Therefore, many kind of studies regarding nanocarbon materials have been performed for a few decades. In this presentation, we focus on MLG wiring and carbon nanotube thermal interface materials (CNT-TIM), although we also carry out research regarding graphene channels and CNT interconnects [5, 6]

2. Experiment

The synthesis of MLG on a Co epitaxial film was conducted by the thermal CVD method in a low pressure chamber. As the source gases of graphene synthesis, CH₄ diluted by Ar and H₂ was used. The substrate temperature of CVD was approximately 1000°C. The fabrication process of graphene interconnects is shown elsewhere [7, 8].

CNTs were also synthesized with the thermal CVD method in a vacuum chamber. Iron and aluminum films were used as a catalyst, which were deposited on a SiO_2/Si substrate by a conventional sputtering method. As the carbon

source, a mixture of C_2H_2 and Ar gases was introduced into the CVD chamber. Hydrogen was also added during the growth, and the total pressure was 8 kPa. The substrate temperature was approximately 640°C during the CVD process. After synthesis, a rubber sheet was attached to CNTs while it was kept pulled and removed from the SiO₂/Si substrate. After removal, the rubber sheet with CNTs was snapped back when pulling stopped, which led to densification of CNTs. The experimental details were described elsewhere [9].

3. Intercalated multi-layer graphene

Four terminal I-V measurements were conducted for a MLG interconnect with a length of 6 μ m and a width of 4 μ m before and after FeCl₃ intercalation. The resistivity before intercalation was calculated to be 78.3 μ Ωcm. The thickness of the MLG interconnect was estimated to be approximately 10 layers, that is, ~3.4 nm, by light transmittance in the optical microscope image [10]. The intercalation process generally increases the thickness of MLG interconnects, which can be estimated from the stage number of intercalated MLG and the original thickness. For a MLG interconnect with stage 2 after intercalation, the resistivity was estimated to be 3.2 μ Ωcm with an increased thickness of ~6.4 nm. This resistivity is about the same order as that of bulk Cu.



Fig. 1 Schematic diagram of an intercalated MLG interconnect with four-terminal electrodes. A SEM image of ultra-narrow MLG interconnect with HSQ is shown in the inset.

After intercalation, ultra-narrow MLG interconnects with a length of 200 nm and a width of 8 nm were fabricated by electron beam lithography. Figure 1 shows a schematic diagram of an intercalated MLG interconnect with four-terminal electrodes. A scanning electron microscope (SEM) image of ultra-narrow MLG interconnect with hydrogen silsesquioxane (HSQ) is shown in the inset. The 8-nm-wide HSQ layer on the MLG interconnect is clearly observed. Transmission electron microscope (TEM) analyses also indicate that the MLG in this case had a width of 8 nm or narrower. The original thickness of MLG before intercalation was estimated to be approximately 10 layers by light transmittance. From the original thickness and Raman spectra, the thickness of 8-nmwide MLG was estimated to be 6.4 nm. The resistivity of 8nm-wide MLG is then estimated to be 3.2 $\mu\Omega$ cm, which is much smaller than the predicted resistivity of Cu interconnects with similar dimensions, and even close to that of bulk Cu [11].

4. Carbon nanotube thermal interface materials

Figure 2 shows SEM images of synthesized CNTs, in which vertically aligned CNT bundles on a substrate can be clearly observed. The height of CNTs was around 140 μ m. Analyzing the SEM images, the packing ratio of CNTs was estimated to be approximately 2-3 %. Figure 3 shows the TEM images of a typical CNT shown in fig.2, in which the average diameter of CNTs was estimated to be approximately 8 nm.



Fig. 2 SEM images of vertically-aligned CNTs bundle synthesized on a SiO₂/Si substrate with a thermal CVD method [9].



Fig. 3 TEM images of typical CNTs shown in fig. 2.

A packing ratio of as-grown CNTs is in general several percent, which is not enough to connect thermally between a heat spreader and a processor chip. Therefore, we proposed a new method to improve the density of CNTs to be used for TIMs. By compressing CNTs using the elasticity of the rubber, the density of the CNTs became three times higher than that before densification without causing damage. The thermal resistance of the CNT-TIM was found to be as low as that of indium film by using a temperature gradient method.

4. Conclusions

We demonstrated the sub-10-nm-wide intercalated multi-layer graphene interconnects whose resistivity was lower than that of copper with similar dimensions, and carbon nanotube thermal interface materials whose thermal resistance was as low as that of indium film. There results indicate that nanocarbon materials such as graphene and carbon nanotubes are really promising for future electronic materials

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References

- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
- [2] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, Nano Lett. 8, 902 (2008).
- [3] S. Iijima, Nature 354, 56 (1991).
- [4] Z. Yao, C. L. Kan, and C. Dekker, Phy. Rev. Lett. 84, 2941 (2000).
- [5] D. Kondo, S. Sato, K. Yagi, N. Harada, M. Sato, M. Nihei, and N. Yokoyama, Appl. Phys. Express 3, 025102 (2010).
- [6] M. Nihei, M. Horibe, A. Kawabata, and Y. Awano, Jpn. J. Appl. Phys. 43, 1856 (2004).
- [7] D. Kondo, H. Nakano, B. Zhou, I. Kubota, K. Hayashi, K. Yagi, M. Takahashi, M. Sato, S. Sato, and N. Yokoyama, Proc. IEEE Int. Interconnect Technology Conference, 2013, p. 1.
- [8] D. Kondo, H. Nakano, B. Zhou, A. I, K. Hayashi, M. Takahashi, S. Sato, and N. Yokoyama, Proc. IEEE Int. Interconnect Technology Conference, 2014, p. 189.
- [9] S. Hirose, M. Norimatsu, K. Suzuki, Y. Yagishita, Y. Suwa, T. Kurosawa, K. Kawamura, Y. Mizuno, D. Kondo, and T. Iwai, Ext. Abstr. Solid-State Devices and Materials, 2015, p. 454.
- [10] P. Blakea, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim, Appl. Phys. Lett. **91**, 063124 (2007).
- [11] A. Naeemi and J. D. Meindl, IEEE Trans. Electron Devices 56, 1822 (2009).