Investigation of Nano-Carbon Cap Formation on Ruthenium by Low Temperature Thermal CVD

Yumehito Temmyo, Shotaro Ushitora, Kazuyoshi Ueno*

Graduate School of Engineering and Science, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto, Tokyo, 135-8548, Japan

Graphene-capped copper (Cu) interconnects have attracted attention as a candidate for next-generation low-resistance nano-interconnects. [1] It has also been reported that coating ruthenium (Ru) surfaces with graphene reduces the resistance. [2] We previously attempted to form graphene caps on 30 nm Ru films by thermal CVD, but no carbon deposition was observed. [3] The purpose of this study is to apply thermal CVD to Ru to deposit nano-carbon (NC) caps and investigate their potential as NC / Ru low-resistance nano-interconnects.

Ru films of 10, 20, 30, and 50 nm thickness were sputter-deposited on a 100 nm thick thermally oxidized Si substrate (8 inches). Tantalum (Ta) of 3 nm thickness was deposited as an adhesive layer before Ru sputtering. 1 cm square substrates were placed in the quartz tube of the previously described CVD system [3] and heated in an electric furnace to a set temperature of 400 °C in an Ar atmosphere at normal pressure, and once the set temperature was reached, ethanol bubbled with Ar was supplied for 20 minutes, and the CVD was performed under the conditions shown in Table 1. For comparison, samples annealed without ethanol flow and samples annealed under a vacuum condition (1.24×10^{-2} Pa) were prepared. For evaluation, Raman spectroscopy was used to examine NC deposition, and a four-point probe method was used to measure sheet resistance before and after CVD or annealing. XPS were used for analysis.

Fig. 1 shows Raman spectra after CVD at Ru 30 nm with varying precursor supply rate; no carbon deposition was observed at 100 sccm and 300 sccm, while G- and D-band features were observed above 500 sccm, indicating NC film deposition. On the other hand, no clear precursor supply rate dependence was observed from 500 sccm to 1000 sccm. Since no clear 2D-bands were observed, the deposited films are considered as less crystalline and closer to amorphous carbon. Fig. 2 shows the Raman spectra after CVD with Ru film thickness varied from 10 nm to 50 nm, and no NC deposition was observed on 10 nm- and 20 nm-thick Ru. On the other hand, the intensity of the G- and D-bands increased at 50 nm. This indicates that the activity of Ru as a catalyst increases with increasing film thickness. Fig. 3 shows the resistivity for each Ru film thickness before and after CVD; reduction in resistivity was observed for the samples after CVD and annealing, which is considered due to Ru grain growth. No reduction in resistivity was observed with the carbon film deposition. Fig. 5 shows XPS spectra of Ru after CVD or annealing. The surface spectrum after annealing in Ar atmosphere was shifted toward RuO_2 compared to that after CVD, suggesting surface oxidation. In this experiment, the surface oxidation of Ru may have been caused by residual oxygen during annealing, but it is also possible that the oxidized Ru was reduced by the ethanol gas flow. It has been reported that Ru surface oxidation affects the electrical and chemical properties of the interface with the NC film [4], and since it is considered important to remove the oxide film at the interface, it is necessary to establish a CVD process to remove the oxide film on the Ru surface in the future.

In this study, we investigated the possibility of NC-cap formation by thermal CVD on Ru for nano-interconnect application. By increasing the precursor supply, NC caps were successfully deposited on 30 nm Ru, but no NC was deposited on Ru thinner than 30 nm. In addition, no reduction in resistivity with NC-caps was observed probably due to the oxidation of interface between the NC-cap and Ru. Further process improvement to remove Ru-oxide at the interface of NC and Ru will be necessary in the future.

References

1. L. Li, Z. Zhu, A. Yoon, H.-S. P. Wong, IEEE Electron Device Lett. **40**, 815 (2019).
2. S. Achra, *et al.*, Carbon **183**, 999 (2021).
3. T. Fukuda, Y. Temmyo, and K. Ueno, 2024 MAM (Milan, 2024)
4. S. Achra, *et al.*, Applied Surface Science **538**, 148046 (2021).

** corresponding author e-mail: ueno@shibaura-it.ac.jp*

Table 1. CVD conditions.

CVD (Annealing) Temperature (℃)	400
Precursor flow-rate (sccm)	100 , 300 , 500 , 700 , 1000
Ethanol supply-time (min.)	20

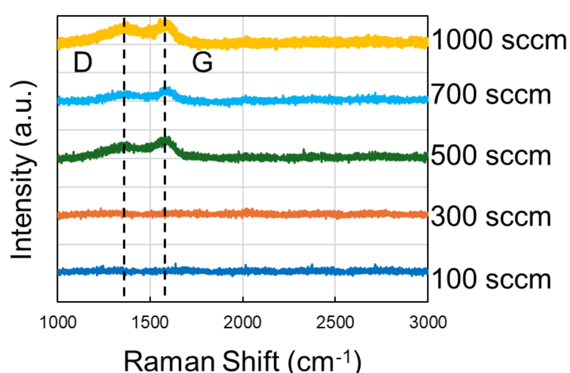

Fig. 1. Raman spectra after CVD between 100 sccm and 1000 sccm on 30 nm-thick Ru.

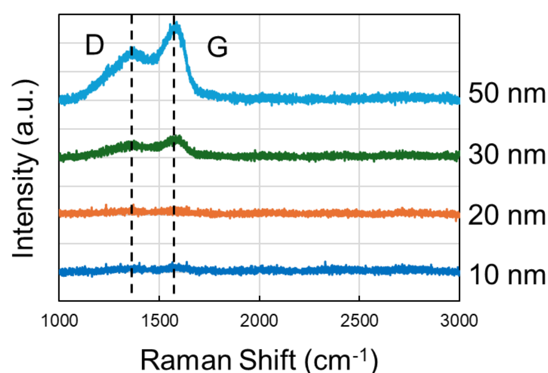

Fig. 2. Raman spectra after CVD between 10 nm- and 50 nm-thick Ru.

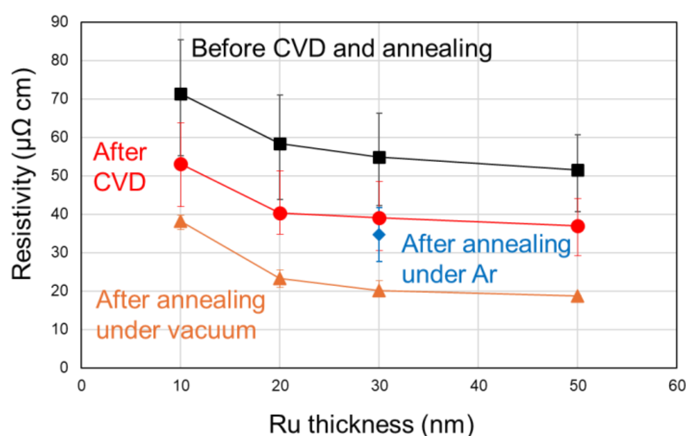

Fig. 3. Resistivity changes of Ru before and after CVD or annealing. Variations in resistivity before CVD or annealing may be due to variations in film thickness. Resistivity is calculated by the total thickness of the Ru and Ta layers.

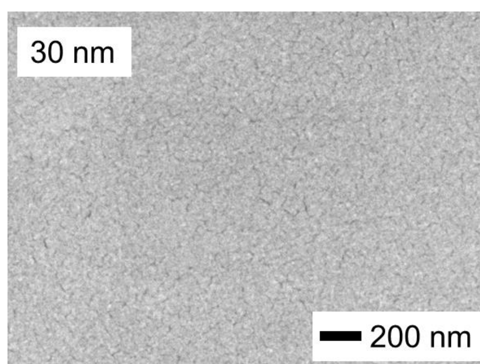

Fig.4. Surface SEM image of NC/Ru of 30 nm-thick Ru after CVD. There is no CNT-like formation on the surface, and NC is considered to be uniformly formed.

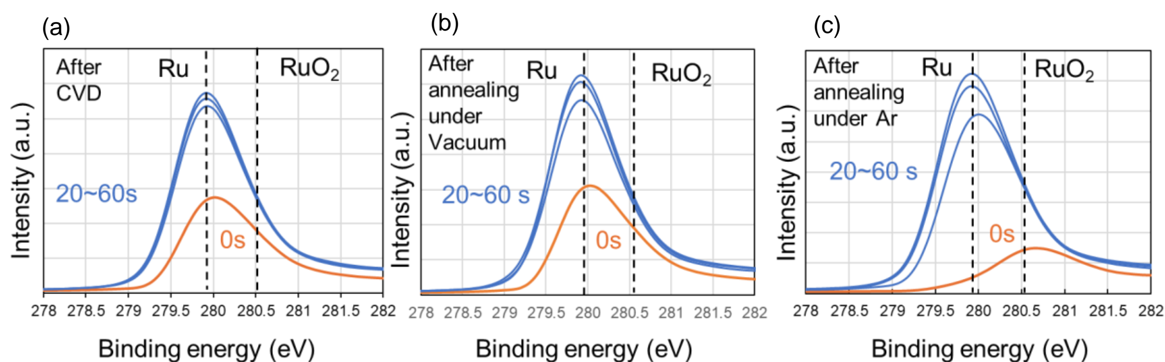

Fig. 4. XPS spectra after (a) CVD, (b) annealing under vacuum, and (c) after annealing under Ar atmosphere.