Investigation of carbon-cap formation by thermal CVD using ethanol for ruthenium and molybdenum

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Graphene-capped copper (Cu) interconnects are attracting attention as a candidate for the next generation of low-resistance nano-interconnects.[1] It has also been reported that covering the surface of ruthenium (Ru) with graphene reduces resistance. [2] Molybdenum (Mo), like Ru, is a candidate as an MOL metal, but suppression of surface oxidation is an issue. [3] We previously reported that surface oxidation can be suppressed by depositing a carbon (C) cap on a nickel surface by thermal CVD at a low temperature of 350°C. [4] The objective of this study is to examine whether the thermal CVD could be applied to Ru and Mo.

A 30 nm thick film of Ru and Mo was deposited by sputtering on a Si substrate (8 inch) with a 100 nm thick thermal oxide film. For Ru sputtering, tantalum (Ta) with a thickness of 3 nm was deposited prior to Ru sputtering as an adhesion layer. The substrate cut into 1 cm squares was placed inside the quartz tube of the CVD apparatus reported previously, [4] heated in an electric furnace to the set temperature between 300 and 700 ℃ in an Ar atmosphere at normal pressure, and when the set temperature was reached, ethanol bubbled with Ar was supplied for 10 minutes. The CVD conditions are the same as those previously used for Ni. [4] For comparison, samples annealed without flowing ethanol were also prepared. For evaluation, C deposition was investigated using Raman spectroscopy, and sheet resistance before and after CVD or annealing was measured using a four-point probe method. SEM, XPS, and XRD were used for analysis.

Fig. 1(a) and (b) show the Raman spectra after CVD on Ru and Mo, respectively. No carbon deposition was observed on Ru at any temperatures. On the other hand, G and D band features were observed on Mo, indicating amorphous C deposition. No obvious dependence on temperature was observed. Fig.2 (a) and (b) show the resistivity changes of Ru before and after CVD and annealing, respectively. Although the initial resistivity varied probably due to the variations in film thickness, the resistivity of Ru decreases after CVD or annealing. According to SEM observation and XRD, the reason for the decrease in resistance is considered to be grain growth. It is noted that the reduction ratio of resistivity was greater with CVD than with annealing at 500℃. The reason is thought to be that surface oxidation of Ru was suppressed in the case of CVD, as shown in Fig. 3, which shows a comparison of the composition depth profiles by XPS. In the annealing in this experiment, it is considered that surface oxidation of Ru occurred due to residual oxygen, but it is possible that either the residual oxygen was removed or the oxidized Ru was reduced by flowing ethanol gas. In contrast to Ru as shown in Fig. 4(a) and (b), no decrease in resistance was observed for Mo after CVD or annealing, but rather the resistance increased at 700°C. As a result of XRD analysis in Fig. 5, molybdenum carbide peaks were observed in the sample after CVD at 700°C, and molybdenum oxide peaks were observed in the annealed sample. From this result, it is considered that a low temperature at which carbide is not formed is desirable when depositing a carbon cap on Mo.

In this study, we investigated the possibility of C cap formation by thermal CVD using ethanol on Ru and Mo, which are candidate metals to replace Cu or W. In Ru, surface oxidation was suppressed under an argon atmosphere with ethanol flowing, and resistivity was reduced due to grain growth, but no C deposition was observed. On the other hand, with Mo, C deposition was observed even at low temperatures, but no reduction in resistivity was observed. Further studies will be necessary to explore the possibilities of using CVD conditions, such as increasing the flow rate and plasma CVD.

References

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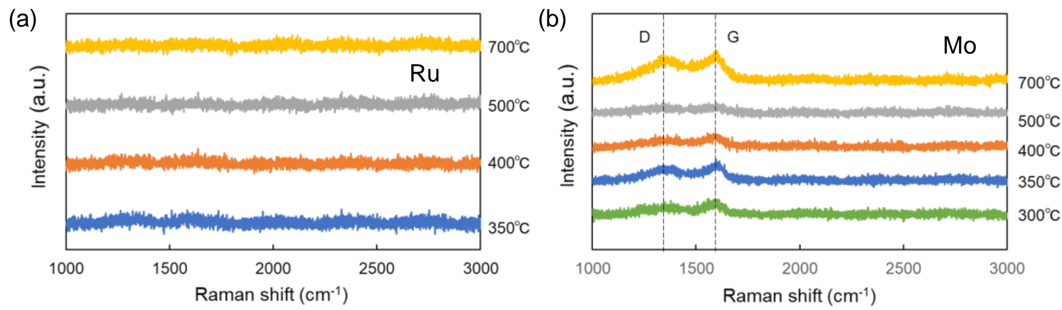

Fig. 1. Raman spectra after CVD between 300℃ and 700℃ on (a) Ru and (b) Mo.

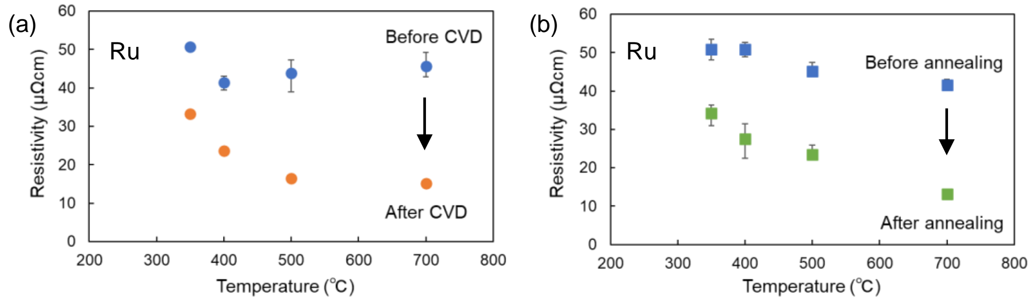

Fig. 2. Resistivity changes of Ru before and after (a) CVD and (b) annealing. Variations in resistivity before CVD or annealing may be due to variations in film thickness.

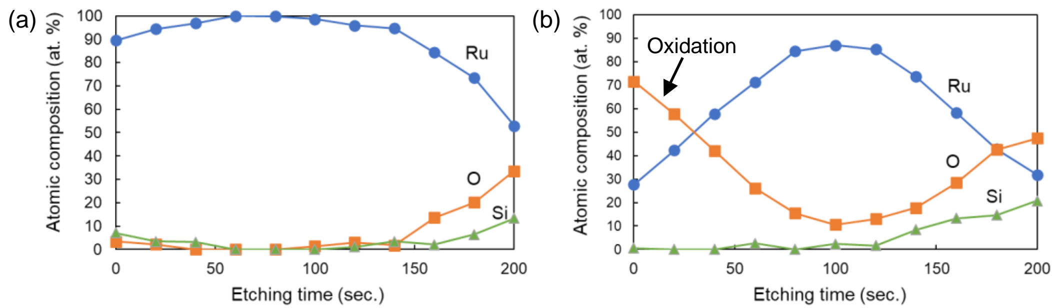

Fig. 3. Composition depth profiles of Ru films by XPS (a) after CVD and (b) after annealing at 500℃.

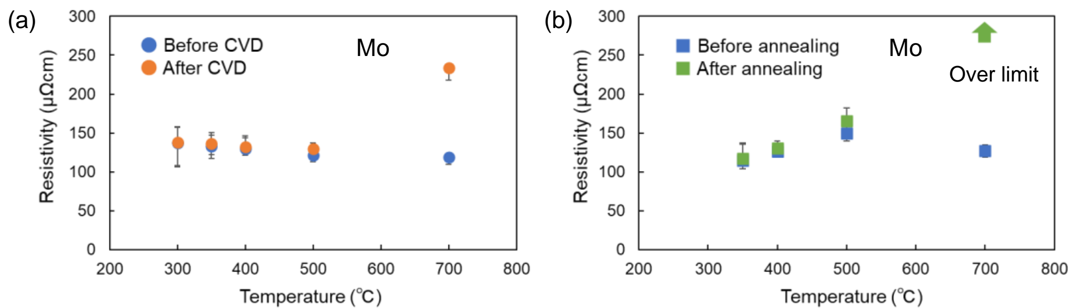

Fig. 4. Resistivity changes of Mo before and after (a) CVD and (b) annealing. Variations in resistivity before treatment may be due to variations in film thickness.

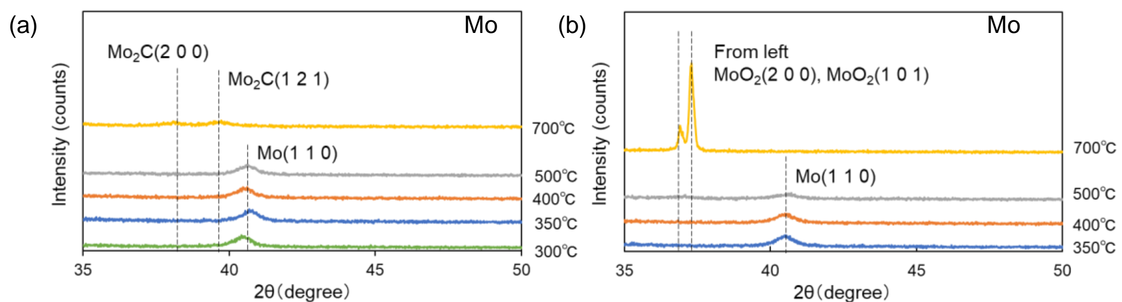

Fig. 5. XRD patterns of Mo films (a) after CVD and (b) annealing at temperatures between 300℃ and 700℃.