Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp652-653

Heat-Resistant Co-W Catalytic Metals for Multilayer Graphene CVD

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1. Introduction

The reduction of Cu interconnect sizes in the future will lead to serious problems, including increased specific resistance and degraded reliability. Therefore, nanocarbon (NC) materials such as multilayer graphene (MLG) are considered to be superior to Cu because their resistance increase is suppressed and their thermal stability is high [1, 2]. To form MLG films for interconnect application, chemical vapor deposition (CVD) is the most suitable method. Since the use of a catalytic metal is essential for CVD growth, selection of the metal to be used is a critical issue.

In our previous work, we investigated MLG film growth on such metals as Co, Ni, W, Ti and Ru, which are widely used in LSI manufacturing [3]. We found that using Co and Ni achieved suitable growth and that higher temperature conditions improved film qualities such as crystallinity. However, within the temperature range between 600 and 700 ^{o}C, surface morphology of the catalytic metals degraded severely due to agglomeration during CVD. In order to avoid the agglomeration, it is important to improve the heat resistance of the catalytic metals.

In this study, we used a Co-W alloy as a heat-resistant catalytic metal, since this alloy's melting point can be raised as was shown in a Co-W phase diagram [4]. It should be noted that a Co-W alloy made by an electroless plating method has also been used as a cap metal in Cu interconnects. We made the first-ever attempt to achieve CVD growth of MLG films on a Co-W catalytic metal by varying the W composition. We found that using a Co-W alloy with optimized W composition improves MLG film crystallinity, meaning a higher peak intensity ratio, G/D, can be achieved.

2. Experimental

We used DC magnetron sputtering to deposit 100 nm-thick Co-W films with varying W composition on a SiO_2/Si substrate. The W composition was controlled by varying the W area ratio in the surface area of the target between 2.5 % and 37.5 %. The W composition in the deposited films was measured by XPS; the values obtained are summarized in Table 1. Then, an MLG film was deposited by thermal CVD using ethanol as the precursor with an Ar carrier gas [3]. The CVD temperature was between 640 and 790 ^{o}C. After the CVD, we used scanning electron microscopy (SEM) to observe the surface morphology of the sample. Raman spectroscopy was used for evaluating the MLG film crystallinity. Cross-sectional transmission electron microscopy (TEM) was used to observe the MLG film structures on the atomic scale.

3. Results and Discussion

Changes in Co-W heat resistance and MLG crystallinity with W composition

Figure 1 shows a comparison of cross-sectional SEM images for the surface morphology of the Co-W catalytic metal with varying W composition after CVD at 640 ^{o}C. As the figure shows, the surface roughness was suppressed and the total thickness decreased as the W composition increased.

Figure 2 shows a comparison of the Raman spectra for MLG films deposited at 640 ^{o}C on Co-W with varying W composition. The G and D peaks in the spectra lie at around 1560 and 1360 cm^{-1}, respectively. The peak intensity ratio, G/D, can be used as the index of MLG quality [5]. The G/D decreased as the W composition increased. The peak widths became wider in the samples with W composition of 9.1 % or more, indicating that the crystallinity was degraded by adding W.

The results make it clear that in the W compositions there is a trade-off between heat resistance and MLG quality. In the range of this study, 0.7 % W was the most suitable composition.

Improved MLG quality through high temperature CVD

In order to improve the MLG quality, CVD at higher temperatures was explored using Co-W with the optimum W composition, 0.7 %. As Fig. 3 shows, CVD performed at higher temperature improved the G/D ratio. At 735 ^{o}C the ratio was 5.9, higher than the 3.6 for pure Co obtained with CVD at 640 ^{o}C (not shown).

Figure 4 shows plane-view SEM images obtained with CVD at 735 ^{o}C for (a) Co-W (0.7 at.%) and (b) pure Co. Although severe agglomeration was observed for the pure Co, it was eliminated for the Co-W. The SEM contrast for the Co-W sample corresponds to the thickness variation of the MLG films, as shown in the TEM cross-section in Fig. 5. For Co-W (0.7 at.%) the MLG layer thickness was greater for CVD at 735 ^{o}C than at 640 ^{o}C; this is considered to be the reason for the higher G/D ratio obtained. It should be noted that two MLG growth modes can be observed in Fig. 5, growth from the catalyst facets and growth over the facets. The growth from the facets is consistent with the results reported by Yamazaki et.al [6]. For Co-W with a high W composition (9.1 %), the MLG grew in the shape of islands (not shown). We consider that this is because the

W inhibited the MLG growth and as a result the grain size became small.

4. Conclusion

We investigated Co-W alloys with varying W composition as heat-resistant catalytic metals for use in multilayer graphene (MLG) chemical vapor deposition (CVD). It was found that in the W compositions there is a trade-off between heat resistance and MLG quality. The W composition of 0.7 % was the most suitable for the MLG CVD in this study. Using the heat-resistant Co-W catalytic layer, we obtained improved MLG quality at higher CVD temperatures. Cross-sectional transmission electron microscopy (TEM) confirmed the MLG growth and two growth modes were observed, growth from the facets and growth over the facets. Although the variation in MLG film thickness may pose problems in future interconnect applications, Co-W alloys are a promising candidate for use as heat-resistant catalytic metals to achieve highly crystalline films in MLG CVD.

Acknowledgements

The authors thank Y. Awano of Keio University, H. Shibata of Toshiba Corporation, and NC interconnect group members of LEAP for their useful comments and suggestions, and N. Sumihiro and S. Kimura of LEAP for their encouragement. This work was performed as part of the Ultra-Low Voltage Device Project supported by the New Energy and Industrial Technology Development Organization (NEDO) and the Ministry of Economy, Trade and Industry (METI) of Japan.

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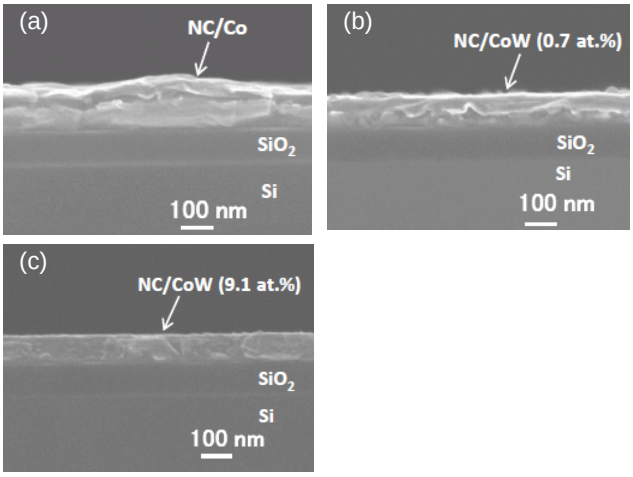

Fig. 1 Comparison of SEM cross-sections of MLG for (a) Co, (b) Co-W (0.7 %), and (c) Co-W (9.1 %) after CVD at 640 °C.

Table 1 W composition measured by XPS.

W area ratio (%)	W composition (at. %)
2.5	0.7
5.1	9.1
15.3	15.5
25.5	24.1
35.7	42.2

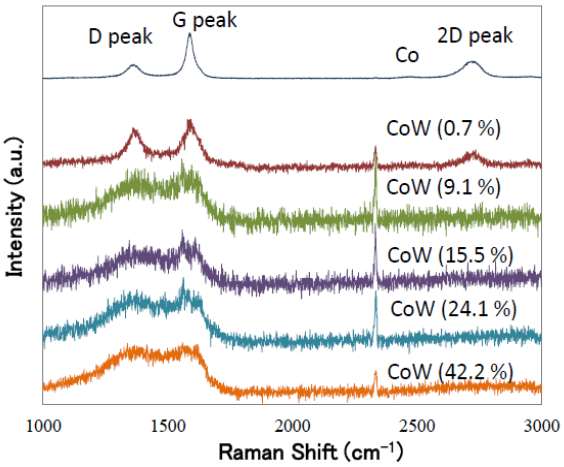

Fig. 2 Comparison of Raman spectra for MLG deposited on Co-W with varying W composition.

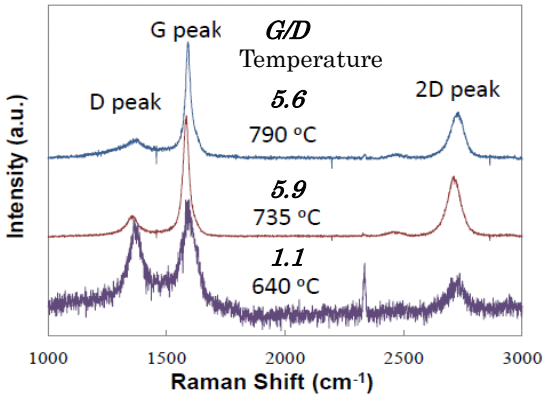

Fig. 3 Comparison of Raman spectra for MLG deposited on Co-W (0.7 %) at different CVD temperatures.

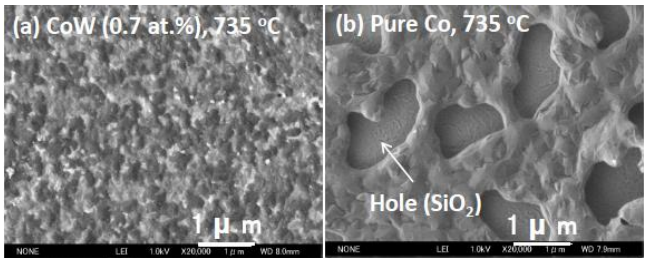

Fig. 4 Comparison of SEM plane-views for (a) Co-W (0.7 %) and (b) pure Co after CVD at high temperature (735 °C).

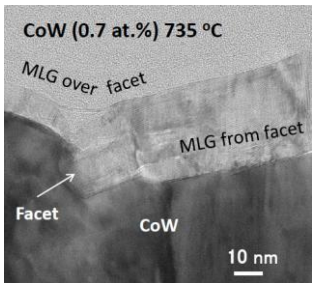

Fig. 5 TEM cross-section of MLG deposited on Co-W (0.7 %) at 735 °C.