

Highly Thermo-stable and Oriented Catalytic Metal using Co/Ir/Ta Layer Stack for Graphene Growth

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Abstract

This paper demonstrates that a Co/Ir/Ta stacked layer functions as an excellent catalytic metal structure for low temperature graphene growth. Highly crystalline orientation with no agglomeration for graphene growth at 600°C was achieved even with 10nm Co on Ir/Ta and resulted in the growth of flat multi-layer graphene. Moreover, a trench pattern was utilized to enhance graphene nucleation. Continuous graphene was realized by using Co/Ir/Ta. This shows that it is feasible to fabricate graphene film with fewer defects. In conclusion, this proposed scheme is a strong candidate of graphene wiring process for LSI interconnects.

1. Introduction

Theoretical studies have indicated that it is possible for graphene interconnects to have a lower resistivity than Cu interconnects in the width less than 10nm [1]. It has been reported that an hcp(002)- or fcc(111)-oriented catalytic metal layer is an important factor in low-defect graphene growth at 900°C [2]. We have previously reported that oriented catalytic metal is also an important factor for graphene growth at 600°C [3], and use of a catalytic metal layer with a facet enables low temperature growth [4]. It suggests that graphene interconnects can be formed by using a trench pattern. However, it has been difficult because of catalytic metal agglomeration during graphene growth at 600°C.

In this work, we propose a highly thermo-stable catalytic metal structure by inserting higher melting point material between Co as a catalytic metal (1497°C) and Ta as an underlayer; for example, Ir (2447°C), Ru (2334°C). Ir and Ru are materials that they have an hcp and fcc structure, respectively, and that form a complete solid solution system when used along with Co. Such a structure can not only retains hcp(002)- or fcc(111)-oriented catalytic metal but also suppresses agglomeration by the diffused Ru or Ir.

2. Experimental

Structures of the catalytic metal were Co/TiN = 30/5 nm, Co/Ta = 30/5 nm, Co/Ru/Ta = 30/5 nm, Co/Ir/Ta = 30/5/5 nm, and Co/Ir/Ta = 10/5/5 nm on a SiO₂/Si substrate fabricated by PVD. Graphene was grown by thermal CVD and the growth temperature was controlled at 600°C.

The agglomeration of Co was evaluated by cross-sectional TEM and the surface roughness of Co was measured by AFM. The ratio of the G and D band intensity (G/D ratio) of the graphene was investigated by RAMAN spectroscopic analysis and Backscattered Electron (BSE) images of gra-

phene grains were observed on the surface by SEM after it was grown. The crystalline orientations of the catalytic layer and the inserting layer (Ru or Ir) were measured by XRD, and the amount of Ir and Ru in Co was measured by SIMS after annealing at 600°C for 10min in N₂/H₂, this temperature was equal to that of the graphene growth.

3. Results and Discussion

A. G/D ratio of graphene and Co orientation

The XRD spectra of the catalytic metal layers are shown in Fig. 1. It is clear that the Co of three samples was oriented to the hcp(002). Moreover, the peak intensity of the hcp(002) plane with Co/Ir/Ta and Co/Ru/Ta was significantly higher than that of Co/Ta. The dependence of the G/D ratio of graphene on the intensity of the hcp(002) plane is shown in Fig. 2. We found that the G/D ratio was in proportion to the intensity of Co hcp(002) in the case of Co/TiN, Co/Ta, and Co/Ru/Ta. It seems that the low-defect graphene was grown on the catalytic metal oriented to the hcp(002), possibly because the Co hcp(002) plane is similar to the graphene sheet. In the case of Co/Ir/Ta, the G/D ratio couldn't be evaluated because the intensities of both G and D bands were too weak, as described later.

B. Co agglomeration

Figure 3 shows TEM images of multi-layer graphene that was deposited on three types of catalytic metal layers; a) Co/Ta, b) Co/Ru/Ta, and d) Co/Ir/Ta. The Co agglomeration behavior is quite different among the samples. The Co roughness with Ru/Ta became smaller than that with Ta, and the flatness with Ir/Ta became excellent. On the other hand, the volume of multi-layer graphene apparently decreased as the Co roughness decreased. Figure 4 shows that the number of graphene layers is in proportion to the Co roughness. The amount of graphene was also small on the Co/Ir/Ta, because very smooth Co surface reduced the frequency of facets where graphene growth started. So, G and D bands weren't observed on the Raman spectrum.

Magnified TEM images at the Co surface in Figs. 3 (b) and (d) are shown in Figs. 3 (c) and (e). It seems that the graphene growth originated on the facet of the Co as a catalytic layer and then spread in parallel with the substrate. This suggests that the facet in the roughness of Co was the nucleus of the graphene growth and that highly oriented Co was a significant factor in controlling the surface growth of the graphene.

Thinner Co on Ir/Ta was evaluated to examine the thermo-

stability, as shown in Figs. 3 (f) and (g). No agglomeration was achieved even with 10nm Co on Ir/Ta.

C. Diffusion of Ir and Ru

Figure 5 shows the impurity in Co film after annealing at 600°C. Ir and Ru were diffused into Co, which indicates that Co agglomeration is suppressed by diffused high-melting point metal. The Co-Ir system had complete solubility in the solid state, thus enabling diffused Ir to displace Co. It then seems able to retain the Co orientation in spite of the Ir diffusion into Co and suppress agglomeration by diffused Ir in Co.

D. Graphene growth on a trench

Figure 6 shows the cross-sectional TEM images of graphene on Co/Ir/Ta at a trench. Graphene was grown from the bottom corner of the trench. Figure 7 shows BSE images of the graphene on : (a) for a blanket, (b) and (c) for a trench. Dark region in the BSE images is graphene. It is noted that the quite continuous graphene is observed along the trench step. The trench pattern itself enhanced graphene nucleation significantly. These results strongly support our conclusion that graphene interconnects can be formed on Co/Ir/Ta with a facet which was formed by the trench pattern.

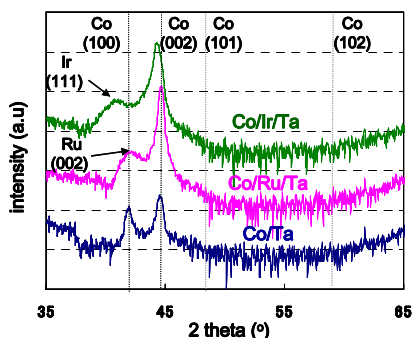


Fig. 1 XRD spectra of catalytic metal layers after annealing.

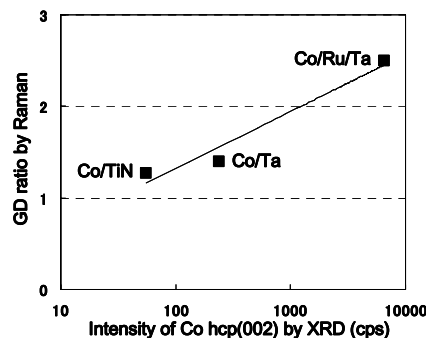


Fig. 2 Dependence of G/D ratio on the XRD intensity of Co hcp (002)

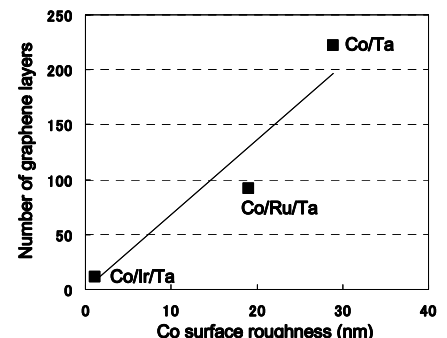


Fig. 4 Dependence of number of graphene layers on Co roughness

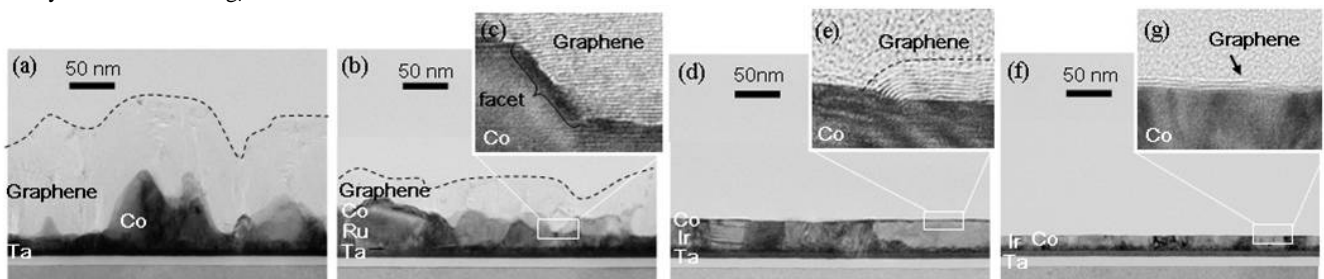


Fig. 3 TEM cross-sectional images of catalytic metal layer: (a) for Co/Ta = 30/5 nm, (b) for Co/Ru/Ta = 30/5/5 nm, (d) for Co/Ir/Ta = 30/5/5 nm, and (f) for Co/Ir/Ta = 10/5/5nm after graphene growth. (c), (e), and (g) show magnified TEM images at Co surface.

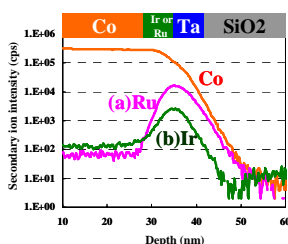


Fig. 5 In-depth SIMS analysis after annealing: (a) for Co/Ru/Ta, (b) for Co/Ir/Ta

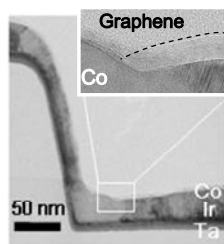


fig. 6 TEM cross-sectional image of graphene on Co/Ir/Ta at the trench.

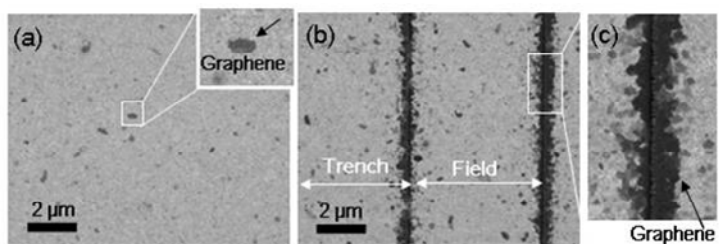


Fig. 7 Top-view BSE images of graphene on Co/Ir/Ta: (a) for a blanket and (b) for a trench after graphene growth. (c) shows magnified BSE images.

4. Conclusions

We proposed a highly thermo-stable and oriented catalytic metal layer of Co/Ir/Ta. Co(002) orientation was enhanced by an Ir/Ta underlayer. No agglomeration for graphene growth at 600°C was evident, even with 10nm Co on Ir/Ta by Ir diffusion, which resulted in the formation of flat multi-layer graphene. Moreover, continuous graphene was realized by using Co/Ir/Ta with a trench to enhance graphene nucleation.

We conclude that this scheme is a strong candidate for the fabrication of graphene interconnects in nano-scaled devices.

Acknowledgments

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Reference

- [1]A. Naeemi et al. IEEE EDL 28 (2007) 428
- [2]H. Ago et al., Carbon 50 (2011) 57-65
- [3]M. Wada et al., MRS Fall Meeting (2011), Session AA4.3
- [4]Y. Yamazaki et al., Appl, Phys, Express 5 (2012) 025101