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Twin-formation suppression in fcc epitaxial metal films for graphene growth by spinel ($MgAl_2O_4$) substrates

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1. Introduction

Graphene synthesis on metal catalyst is one of the easiest ways to grow graphene films [1]. Quality of the graphene films depends on crystal quality of the catalysts. The orientation of graphene on a metal crystal depends on the orientation of the metal crystal. Therefore, single crystalline is preferable for catalyst metal. However, it is not easy to obtain large single crystals of metals. This limits the size of the graphene on them. Making use of metal films on amorphous layer such as SiO_2 enables large graphene growth [2][3]. But the metal films are poly crystalline. Graphene films on such substrates are also poly crystalline.

Epitaxial metal films grown on single crystal substrates possibly overcome these problems [4]. Large substrates are available in the case of dielectric crystals, such as sapphire. There is a possibility to grow single crystal layer of metals on them. However, making use of single crystal substrates does not guarantee single crystal epitaxial growth on them. In the case of combination of c-face sapphire and face-centered cubic (fcc) type metals, such as Ni and Cu, twins are formed in the metal layer. The authors found that the twin boundary causes excessive carbon segregation and degrades uniformity of graphene layers as shown in Fig.1 [5][6]. Making use of hexagonal close-packed (hcp) type metal, such as Ru, is one of the solutions for this problem [5][6]. But most of hcp metals belong to noble metal and are not compatible with standard semiconductor processes. MgO substrate can suppress twin formation of fcc metals on it [7]. But MgO is a hygroscopic material and the surface is not stable. It must be handled with care.

We report the result with stable crystal; spinel ($MgAl_2O_4$) as substrates. $MgAl_2O_4$ is non-hygroscopic material in cubic isometric crystal system. Oxygen atoms in the lattice are in closed-packed system similar with fcc crystal as shown in Fig.2. We found that it can suppress twin formation and single fcc crystal can be grown on it.

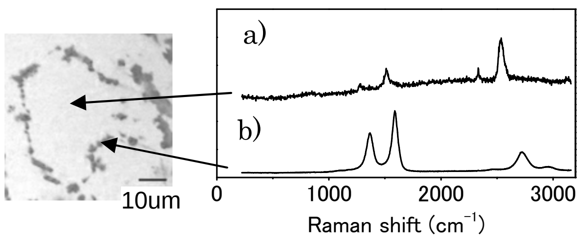

Fig. 1 Microscope image and Raman spectra of graphene on Ni/sapphire sample: a) on flat area, b) on twin boundary.

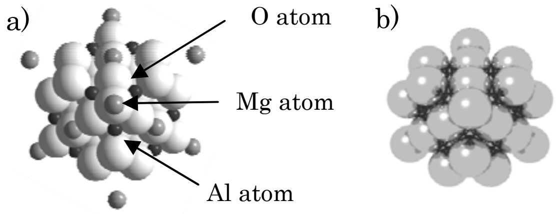

Fig. 2 Illustrations of crystals viewed from [111] direction.
a) spinel ($MgAl_2O_4$), b) fcc metal

2. Experiments

$MgAl_2O_4$ (111) crystal and c-face sapphire crystal were used as substrates and compared. From 200nm to 2μm thick Ni and Cu films were sputtered on the substrates and annealed in a furnace for solid phase epitaxy (SPE) at from 800 to 1050 degree C for more than 10 minutes. Crystals of the metal films were characterized by X-ray diffraction (XRD) and Nomarski microscopy.

3. Results and discussion

X-ray diffraction 2theta-theta profiles of metals after SPE are shown in Fig.3. In both substrates, strong diffractions from (111) plane and (222) plane are seen and no other diffractions from other planes are detected. In each case metal crystal epitaxially grows on the substrate.

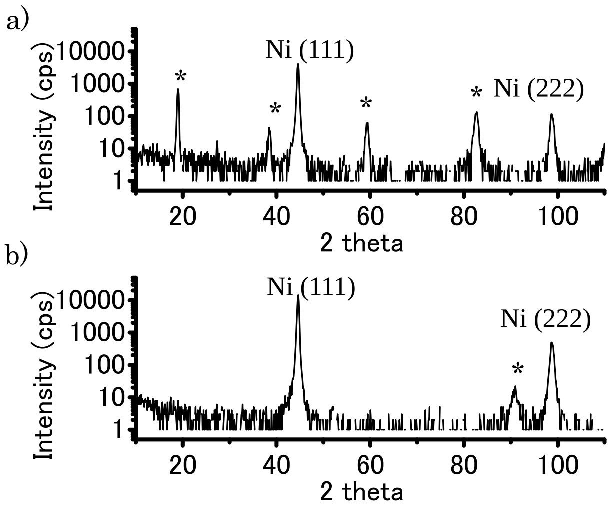

Fig. 3 XRD profiles of a) Ni/$MgAl_2O_4$ sample, b) Ni/c-sapphire sample: c) Cu/$MgAl_2O_4$ sample, d) Cu/c-sapphire sample.
*: diffractions from substrates.

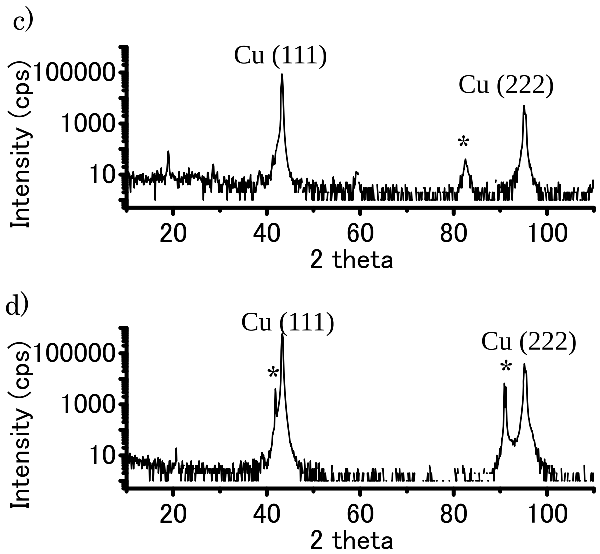

Fig. 3 (continued)

The difference between the two substrates are obvious in pole figures of X-ray diffraction from {200} planes of metals as shown in Fig.4. Single crystal of fcc metal has only three {200} poles in a half sphere. Metal films on sapphire substrates have six poles. It means that there are twins in the metal films. In contrast, metal films on $MgAl_2O_4$ substrates have only three poles. The directions of the {200} planes of metals are coincident with the directions of {200} planes of $MgAl_2O_4$ substrates. It was found that $MgAl_2O_4$ substrate can suppress twin formation both in Ni and in Cu epitaxial films on it.

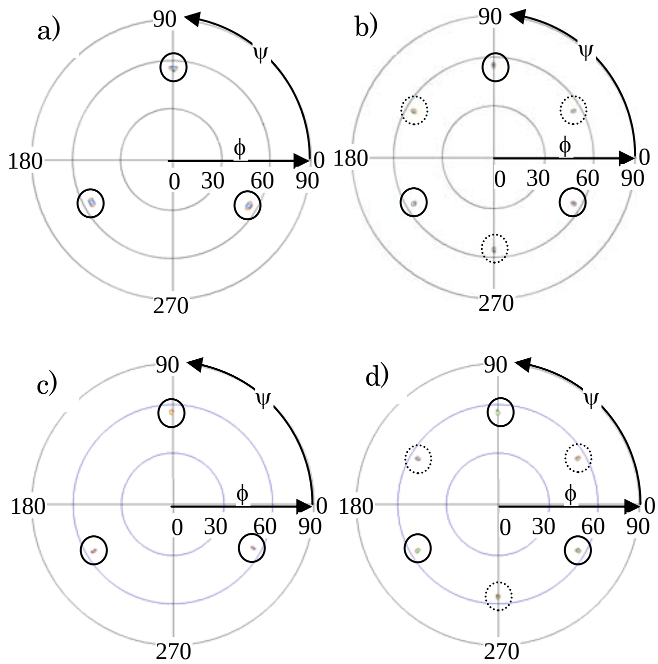

Fig. 4 Pole figures of diffraction from {200} planes of metals: a) Ni/$MgAl_2O_4$ sample, b) Ni/c-sapphire sample, c) Cu/$MgAl_2O_4$ sample, d) Cu/c-sapphire sample.

Nomarski microscope images are shown in Fig.5. Polygonal patterns caused by twin boundaries are seen on metals on sapphire substrates. In contrast, $MgAl_2O_4$ substrate samples have no such a pattern and have much smoother surfaces.

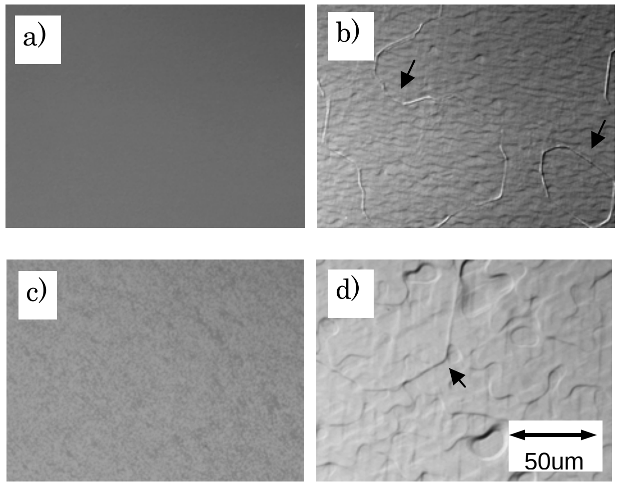

Fig. 5 Nomarski microscope images of metal/substrate samples: a) Ni/$MgAl_2O_4$ sample, b) Ni/c-sapphire sample, c) Cu/$MgAl_2O_4$ sample, d) Cu/c-sapphire sample. Twin boundaries are indicated by arrows.

4. Conclusions

We found that single crystal films of fcc metals, including Ni and Cu can be epitaxially grown on spinel ($MgAl_2O_4$) substrates. The metal catalyst films on them are free from twin boundary problem. Epitaxial fcc metal films on spinel ($MgAl_2O_4$) substrates provide large and high quality metal crystal surface for graphene growth.

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