Influence of Graphene on Morphologies of Substrate Copper Foils during CVD Process and Fabrication of High Conductivity Graphene-Copper Composite

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Abstract:

Copper is one of the most important electrical and electronic materials because of its outstanding electrical and thermal conductivities. Significant research efforts have been devoted to the improvement of copper conductivity, such as the preparation of ultra-pure copper or ultrapure oxygen-free copper, with limited results (only 3% improvement). Graphene has excellent conductivity and it is possible to get higher electrical conductivity than copper matrix by introducing graphene as a reinforcement into the copper matrix. In this study, Gr/Cu composite were obtained by hot-pressing several pieces of Gr/Cu/Gr sandwich heterostructures which were prepared by depositing monolayer graphene on the surface of copper foil with micron size thickness. Grain growth and preferential orientation transformation of Cu foil matrix due to graphene growth and the hot-pressing process and the introduction of the high conductivity Gr/Cu interface is the reason for the high conductivity of the layered composites.

The conductivity of the samples was measured by four-probe method. The samples were divided into monolithic samples (monolithic Gr/Cu/Gr heterostructure, original copper foil, annealed copper foil) and hot-pressed samples (Gr/Cu composite, original copper foil hot-pressed sample, annealed copper foil hot-pressed sample). The conductivity of the original copper foil was 54.9×10^6 S/m (94.7% IACS), and conductivity were increased to 57.9×10^6 S/m and 58×10^6 S/m after the annealing process and graphene CVD process, close to but not exceeding 100% IACS. The electrical conductivity of the Gr/Cu composite was improved to 67.2×10^6 S/m (115.7% IACS), which was higher than that of silver. For the comparative samples, however, the sintered samples

corresponding to the original copper foil and the annealed copper foil exhibited only a slight increase in the electrical conductivities of 2.8% IACS and 1% IACS, respectively.

The scattering of grain boundaries on the electron transport is the main factor affecting the conductivity of the metal, and the decrease of the grain boundary is beneficial to the enhancement of the conductivity. The EBSD data clearly reflect the evolution of the morphology of the original copper foil after annealing and graphene growth process. A significant increase in grain size occurs in the graphene CVD process, yet these strong morphological changes did not result in an additional increase in conductivity.

Although the grain growth and orientation change of Cu foil did not improve the conductivity of the Gr/Cu/Gr heterostructure, it is positive for the increase of the crystallinity of the copper matrix. X-ray diffraction shows that the intensity of Cu (111), the main peak of the Gr/ Cu composite, was enhanced after hot-pressing. This indicates that the preferential orientation and the increase of crystallinity may be responsible for the increase of the electrical conductivity of Gr/Cu composite. The two-dimensional graphene lattice (2.46 Å) has good structural consistency with the Cu (111) crystal face (2.56 Å). The interfacial energy reduction is the driving force, and graphene promotes preferred orientation during hot-pressing.

The interface between the reinforcement and the matrix has an important effect on the conductivity of the composite. For Gr/Cu composite, the polished Gr/Cu interfacial region was subjected to curren-mapping testing. At the graphene layer, the intensity of the current increases markedly, which is three orders of magnitude higher than that of the copper matrix.

The observed improvement of the electrical properties of Gr/Cu composites are primarily arising from a) the changes in Cu grain size and orientation caused by CVD of graphene, promoting the curing of grain boundaries and increasing of crystallinity during hot-pressing, and b) the ultrahigh interface conductivity of three order of magnitude higher than copper matrix.