Role of Graphene in Reducing Fatigue Damage in Cu/Gr Nanolayered Composite

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ABSTRACT: Nanoscale metal/graphene nanolayered composite is known to have ultrahigh strength as the graphene effectively blocks dislocations from penetrating through the metal/graphene interface. The same graphene interface, which has a strong sp2 bonding, can simultaneously serve as an effective interface for deflecting the fatigue cracks that are generated under cyclic bendings. In this study, Cu/Gr composite with repeat layer spacing of 100 nm was tested for bending fatigue at 1.6% and 3.1% strain up to 1,000,000 cycles that showed for the first time a 5−6 times enhancement in fatigue resistance compared to the conventional Cu thin film. Fatigue cracks that are generated within the Cu layer were stopped by the graphene interface, which are evidenced by cross-sectional scanning electron microscopy and transmission electron microscopy images. Molecular dynamics simulations for uniaxial tension of Cu/Gr showed limited accumulation of dislocations at the film/substrate interface, which makes the fatigue crack formation and propagation through thickness of the film difficult in this materials system.

KEYWORDS: Cu, graphene, nanolayered composite, crack, fatigue, bending

With recent developments in flexible and stretchable electronics, advanced materials design that can prevent mechanical failure is critical in ensuring the device reliability. The simplest solution for achieving the required flexibility and stretchability is to make use of all flexible materials; organic light emitting diodes (OLEDs) that are composed of flexible cathode and anode fabricated on a polymer substrate are good examples of all flexible materials design.1−4 In many cases, however, such all flexible, stretchable materials systems may come at the cost of the device performance; poor thermal and chemical stability of the organic materials used in organic field-effect transistors (FETs) is known to cause significant degradation, which is a major limitation that needs to be overcome in comparison to its rigid, inorganic material-based counterpart.5−7 One solution for optimizing the device performance and reliability would be to utilize the highest performance yet rigid materials for the key device components and to connect them using flexible, stretchable interconnects.8−10 For example, a complementary metal-oxide-semiconductor (CMOS) inverter interconnected with serpentine structured metal electrodes was shown to be highly reliable and can withstand an extreme stretchability of ~140% without any observable degradation of the electrical performance.11,12 Here, the ability of the metal interconnects to withstand repeated, extreme mechanical strains without fatigue failures is, therefore, the key to achieving high reliability.

Metal interconnects used for the flexible electronics applications require robust mechanical properties, and the Institute for Interconnecting and Packaging Electronic Circuits (IPC) standards require the flexible circuit in a mobile phone to undergo more than 1,000,000 sliding and folding motions to test for operational reliability.13 Such repeated motions can cause a fatigue damage via crack formation and propagation in the metal electrode, thereby degrading the electrical properties.14,15 Even with a small applied strain below the yield point of the metal thin film electrode, dislocations can accumulate on the film/substrate interfaces after a large number of strain cycles; the piled-up dislocations can then cause voids and extrusions, which in turn can cause cracks to be initiated at these regions with high stress.

Supporting Information

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For the case of metal thin film or patterned line interconnects, any initiated cracks will quickly propagate through thickness of the metal film to cause failure or degradation of the conductivity of the electrode. Therefore, suppressing the crack initiation and propagation is critical for the development of a reliable metal conductor for the flexible electronics applications.

Instead of using the traditional metal only interconnects, one can think of using metal/graphene nanolayered composite that can suppress the crack propagation for enhanced resistance to...

**Figure 1.** Illustration of wet transfer method for the fabrication of Cu/Gr composites. Wafer-scale graphene layer was first grown on Cu foil by CVD, and PMMA was used as a support layer to transfer graphene on 100 nm thick Cu-deposited PI substrate. This process was repeated to fabricate multilayered Cu/Gr composites.

**Figure 2.** Cross section SEM images of (a) Cu electrode and (b) Cu/Gr composites both with total thickness of 400 nm. Cross section TEM images of Cu and Cu/Gr at low magnification (c,d) and a high-magnification showing the Cu/Gr interface (e,f).
fatigue-induced damage. Graphene is known to significantly enhance the strength of the metal when fabricated in the form of a metal/graphene nanolayered composite due to its 2D geometry and outstanding mechanical properties with strength and Young’s modulus of 130 GPa and 1TPa, respectively. By inserting the graphene layers between the metal thin films, the strength of the metal/graphene composites can be remarkably enhanced. Cu/Gr and Ni/Gr nanolayered composites with the layer spacing of 70 and 100 nm, respectively, showed ultrahigh strength of 1.5 and 4.0 GPa under compression, which are 31% and 52% of the respective metal’s theoretical strength given by $\mu/10$. Inclusion of high density of interfaces in the form of nanocrystalline or nanotwinned Cu, or metal only nanolayered composite such as Cu/Ni or Cu/Nb can also contribute to an increase in the initial strength by limiting dislocation motion, but the degree of strengthening is not as pronounced as the Cu/Gr nanolayered system, as explained in the Supporting Information. Graphene with its strong sp2 bonding is expected to be superior in blocking and deflecting dislocations as well as the fatigue-induced cracks generated within the metal layer. In addition, graphene is a good conductor with electron mobility of $\sim$15,000 cm$^2$/V·s and sheet resistance of $\sim$350 Ohm/sq, which makes it an excellent candidate for reinforcing the metal interconnects in the form of metal/graphene nanolayered composite. Therefore, the effect of graphene inclusion in the form of Cu/Gr nanolayers on the fatigue-induced damage was explored for the first time for potentially replacing the traditional metal interconnects.

Large-scale Cu/Gr nanolayered composites were fabricated on polyimide substrate for bending fatigue tests via repeated Cu thin film depositions and wet-transfers of graphene, as shown in the schematic in Figure 1. Previously known chemical vapor deposition (CVD) method was used to grow the wafer-scale graphene (100 $\times$ 200 mm$^2$), which was then transferred using a PMMA support layer onto a sputter deposited Cu thin film on polyimide substrate. The PMMA support layer was then removed using acetone, and the process of Cu deposition and graphene transfer was repeated with a layer spacing of 100 nm to a total thickness of 400 nm. For comparison, Cu-only thin film with the same total thickness of 400 nm was also fabricated by depositing 100 nm Cu layer four times. The detailed procedure of the sample fabrication process can be found in the Supporting Information. Cross-section scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images taken at the interfaces of Cu/Gr composite clearly confirm that the graphene layers were inserted in between the Cu layers and that the Cu grains are discontinuous across the graphene interface (Figure 2). Although there is a (111) texture in the Cu layers (Supporting Information), the in-plane orientations are not matched with the grains of underlying Cu layer. Cu/Gr interface is known to have van der Waals interaction, as revealed in several density functional theory (DFT) calculations for different metal/graphene interfaces. Cu only film showed a columnar grain structure that is interrupted at each 100 nm of deposition, as expected. Nanotwins were often observed for both Cu/Gr and Cu only samples, as shown in Figure 2e, f.

In order to investigate the effects of the graphene inclusion on the robustness of the Cu/Gr nanolayered composite electrode during bending fatigue, repeated tensile bending strain was imposed while monitoring the electrical resistance of the specimen in situ. Fatigue-induced crack generation and propagation is expected to cause increase in the resistance and hence, by monitoring the fractional resistance change ($R - R_0$) of the specimen can be measured. Lower fractional resistance indicates enhanced resistance to fatigue failure or enhanced fatigue resistance. Initial sheet resistances of Cu and Cu/Gr electrode were measured to be 1.53 and 1.74 ohm/sq, respectively, and thus it can be inferred
that the inserted graphene layer acts as a sufficient conductor that does not increase the overall resistance significantly.

At 1.6% bending strain condition, the fractional resistance of Cu thin film electrode was increased by 150% at 100,000 cycles and 32.5% at 1,000,000 cycles as shown in Figure 3a. For the case of Cu/Gr composite, the fractional resistance increase was initially greater than that of Cu electrode presumably due to the presence of defects and impurities introduced during the wet transfer process but showed a remarkable enhancement beyond 12,000 cycles; fractional resistance increase of Cu/Gr was 5 times smaller than that of Cu electrode at 1,000,000 cycles, as shown in Figure 3b. In addition, the fractional resistance increase in the Cu/Gr composite reached a plateau, whereas the resistance of Cu electrode kept increasing rapidly even at 1,000,000 cycles. At a larger bending strain of 3.1%, resistances of both the Cu electrode and Cu/Gr composite increased more rapidly but a similar trend was observed. Cu/Gr composite showed 6 times smaller increase in fractional resistance compared to that of Cu electrode at 1,000,000 cycles under bending strain at 3.1%, as shown in the Figure 3c.

The increase in the fractional resistance of the metal thin films under bending fatigue is known to be caused by the interruption of current flow associated with formation of voids and cracks due to buildup of dislocations at the film/substrate interface. In the work by Kim et al., introduction of nanoholes has the effect of annihilating dislocations at the free surfaces of the nanoholes to reduce the overall dislocation density piled-up at the film/substrate interface. Instead of patterning the Cu thin film into nanohole arrays, which can be problematic in fabricating thin line electrodes as the width of the line approaches the nanohole dimension, simple insertion of a graphene layer in between the unpatterned Cu layers has proven to be efficient in reducing the fatigue-induced damage. The fractional resistance increase in Cu/Gr with 100 nmrepeat layer spacing was reduced by a factor of 5–6 in comparison to that of the Cu thin film with same total thickness. The cause of the dramatic enhancement in the fatigue resistance of Cu/Gr composite electrode is proposed to be not only the high intrinsic strength of the composite but also the ability of the graphene interface to deflect crack propagations and to block dislocations from piling-up all at the film/substrate interface as discussed in detail below.

To analyze the crack evolution in Cu thin film electrodes and Cu/Gr composites, plan view and cross-sectional SEM images of both samples before and after 1,000,000 bending cycles at 1.6% were analyzed as shown in Figure 4. Cu and Cu/Gr electrodes both indicate that cracks were formed on the top surface after bending fatigue cycling. Interestingly, the density of cracks formed in the Cu/Gr electrode was smaller than that in the Cu thin film electrode, and the Cu/Gr electrode showed shorter cracks and deflections in crack path. Cross sectional SEM images indicate that the cracks traveled through the entire thickness in the Cu thin film electrode. However, the cracks were discontinuous in the Cu/Gr composite electrode as a result of the ability of the graphene to limit crack propagation on to the next layer, as shown in Figure 4c,d. Discontinuous cracks in the Cu/Gr composite would then leave a continuous electrical pathway to cause enhanced retention of the conductivity during the bending fatigue cycles. The annular dark-field scanning transmission electron microscope (ADF-STEM) and TEM images of the Cu/Gr electrode further confirmed that the crack was deflected at the Cu/Gr interface and could not penetrate through it (Figure 4e). The columnar Cu grains in each layer often have nanotwinned microstructure within the grain (Figure 2e,f and Figure S2), and such additional nanotwinned interface is expected to have an effect in the crack initiation and propagation preferentially occurring along the grain boundaries.

Fatigue-induced cracks are expected to start from the topmost layer since it is subjected to the largest tensile bending strain. These cracks can easily propagate through the entire thickness of Cu only electrode but are deflected in the Cu/Gr interface due to the high strength and modulus of the graphene. Strong sp2 bonding with strength and modulus of 130 GPa and 1 TPa, respectively, makes graphene an extremely stiff and hard interface to cut across. Thus the cracks that are generated in one of the Cu layers of the Cu/Gr nanolayered composite would therefore be blocked or deflected at the interface, which hinders further crack propagation on to the next layer. The deflected cracks then do not have enough driving force to propagate under the condition.
of the tensile in-plane strain imposed via bending and thus will be arrested.

Second reason for hindrance of crack propagation is the smaller crack size that can be fitted into the Cu/Gr nanolayers than into the Cu thin film. Because one can think of the Cu/Gr nanolayers as Cu thin film being divided into four thinner layers with spacing of 100 nm that are separated by graphene, the crack sizes that can form within each Cu layers of the Cu/Gr composite is much smaller than those in Cu thin film electrode with equal total thickness (4 times the 100 nm thickness). According to the Griffith criterion, stress needed to propagate a crack of radius $a$ is given by $\sigma = \left(\frac{2E}{\pi a}\right)^{1/2}$, where $E$, $\gamma_S$, and $\gamma_P$ are the modulus, surface energy, and plastic work per unit area of the created surface, respectively. Thus, it is harder for the cracks in Cu/Gr composite to propagate than those in Cu electrode because the maximum crack size in Cu/Gr is limited to the repeat layer spacing of Cu (100 nm), which is smaller than the total thickness of the Cu only electrode without graphene (400 nm).

Aside from the ability of the graphene interface to hinder crack propagations, the ability in blocking dislocations from propagating across the interface that results in reduction in the density of dislocations piled-up at film/substrate interface can also contribute to enhanced fatigue resistance. In order to gain insights to the interaction of dislocations at the graphene interface, MD simulations of tensile straining of Cu and Cu/Gr composites were performed. In the MD simulation setup, a Cu thin film and a Cu/Gr sandwich structure was subject to the fixed boundary condition at the free surface in [111]$_{\text{Cu}}$-direction (Figure S5 and Figure S4). A vertical crack was introduced at the free surface in [111]$_{\text{Cu}}$-direction for each model, where the crack tips were propagated upon tensile strain (Figure S5 and Figure S4). In the case of the Cu thin film, the dislocation initiated from the crack tip was able to propagate through the entire thickness of Cu block, which reached to the other end of the Cu layer without any interference and piled-up at film/substrate interface (Figure S5a and Supporting Movie 1). On the other hand, the initiated dislocation in the Cu/Gr sandwich structure was blocked by the graphene layer (Figure S5c), and the deflection of the dislocation occurred as the strain increased further (Figure S5d, Supporting Movie 2). The difficulty of dislocation propagation in the Cu/Gr sandwich structure caused higher ultimate tensile strength compared to that of the Cu block, as shown in Figure S5e. Therefore, the same graphene interface that blocks dislocations to increase the strength of the composite was shown to have a pronounced effect on blocking the crack propagation in the Cu/Gr nanolayers to result in the experimentally observed 5–6 times increase in the robustness against fatigue-induced damage in comparison to Cu thin film.

The details of the MD simulation can be found in Supporting Information.

In summary, the robustness of Cu/Gr composite with 100 nm repeat layer spacing against fatigue-induced damage was explored for the first time that showed a remarkable 5–6 times enhancement in Cu/Gr compared to the conventional Cu only electrode when subjected to bending fatigue of 1,000,000 cycles at 1.6% and 3.1% strain. The enhancement in fatigue resistance was shown to be due to the ability of the graphene to block and deflect crack propagations; strong sp2 bonding of graphene as well as the limited crack size in Cu with smaller layer spacing both contribute to the reduced crack propagations in the Cu/Gr nanolayers. In addition, the ability of each Cu/Gr interface to block dislocations, as revealed by the MD simulations, can suppress the fatigue crack formation mechanism found in Cu only thin film, in which heavy build-up of dislocations occur at the Cu film/substrate interface. It is noteworthy that this remarkable enhancement in resistance to fatigue-induced damage in Cu/Gr, which in turn sustains the conductivity of the electrode for longer fatigue cycles, makes this Cu/Gr composite system well-suited for future flexible and stretchable interconnect applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b01431.

Details of the fabrication process of Cu/Gr nanolayered composites and XRD analyses of Cu and Cu/Gr composites. Comparison of Cu/Gr to other interface engineered materials and additional TEM analysis of Cu/Gr nanolayers after bending cycles. Details of the MD simulation and the tensile deformation movies of the Cu composites (AVI) Details of the MD simulation and the tensile deformation movies of the Cu/Gr composites (AVI)
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Notes
The authors declare no competing financial interest.

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