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Research Article

Nanomechanical and Macrotribological Properties of CVD-Grown Graphene as a Middle Layer between Metal Pt Cylinders and SiO_2/Si Substrate

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The CVD-grown graphene as a middle layer was introduced between Pt cylinders and SiO_2/Si to extend the application of graphene for improving the wear performance of microelectromechanical systems. Periodic arrays of Pt cylinders were prepared on the graphene/SiO_2/Si (Pt/graphene) and SiO_2/Si substrate (Pt/SiO_2) using the magnetron sputtering technique. To characterize Pt/graphene and Pt/SiO_2, nanoindentation and macrotribological tests were performed. The results showed that the friction coefficient was lower and the wear lifetime of Pt/graphene was longer than those of Pt/SiO_2. Graphene, as a middle layer, was not only observed to have significant influence on the mechanical properties (i.e., microhardness and elastic modulus), but also found to improve the adhesive strength between SiO_2/Si and Pt cylinders.

1. Introduction

The two-dimensional graphene is a solid lubricant which stacks in a lamellar structure with low shear strength similar to graphite; and also being the thinnest lubricant it remains chemically stable even under extreme environmental conditions [1]. Owing to these characteristics, graphene exhibits superior frictional properties both at atomic and at molecular scales [2, 3].

It is well established fact that graphene offers excellent tribological performance at nano/micro level [4, 5]. Nowadays, a great deal of effort is being spent to investigate its macrotribological behavior. Recent studies have shown that graphene grown by chemical vapor deposition (CVD) and the assembled reduced graphene oxide (RGO) developed by the oxidation reduction method [6, 7] have potential to be employed as a lubricant in order to protect the substrate surface under severe loading conditions. In another study by the authors [8], it has been demonstrated that the array of Pt cylinders on CVD-grown graphene further improves its macrotribological properties. Because CVD-grown graphene is always transferred onto the SiO_2/Si surfaces, the mechanical properties of graphene as a middle layer between Pt and SiO_2 film on macrotribological properties of SiO_2/Si substrate were not clarified.

The Si and SiO_2 surfaces have found various important applications in microelectromechanical systems. The Pt cylinders can be deposited on these surfaces to improve their tribological properties and affect the surface energy of the surface. However, Pt exhibits poor adhesion to these surfaces. This issue can be resolved using middle layers (typical thickness of 10–20 nm) such as titanium (Ti) at the interface between SiO_2/Si substrates and Pt [9]. Alternatively, graphene can also be used as a middle layer. In fact, the carbon vacancies on a graphene sheet enhance the Pt–graphene interaction [10]. Okazaki-Maeda et al. [11] have calculated the interactions between Pt and a graphene sheet by first-principles. They have proposed that the interface becomes stable as the number of Pt atoms increases, a form of three-dimensional (3D) planar configurations. Their results also indicate that the interconnected flexible network of graphene has a certain cohesive energy with SiO_2/Si substrate due to the existence of the oxygen defects in a SiO_2 surface.

The above discussion follows that introduction of graphene as a middle layer can improve bonding between Pt and SiO_2/Si substrate, and as a result the macrotribological properties of SiO_2/Si substrate can be improved. The current work is an attempt in this direction. The nanomechanical properties and macrotribological behavior of Pt/SiO_2 and Pt/graphene were investigated carefully. Additionally, the interaction effects between graphene and Pt cylinders were also discussed by nanoindentation tests and the contact angle analysis. The surface morphologies and composition at the center of the wear track of Pt/SiO_2 and Pt/graphene were analyzed by scanning electron microscopy (SEM) and Raman spectra.

2. Experimental and Methods

2.1. Preparation of Graphene and Metal Pt Cylinder-Array Structures. Graphene was prepared on Cu foils (20 × 20 × 0.025 mm) by CVD in a 5-inch quartz tube. H_2 (10 sccm) gas was made to flow for 30 min so as to clean and reduce the Cu foils. To generate a carbon source at 1000°C, CH_4 (65 sccm) was made to flow for 15 min to provide the carbon source. After growing graphene on Cu foils, polymethylmethacrylate (PMMA) was used as a supporting layer to protect the synthesized graphene during the etching process. The Cu catalyst was removed by 0.5 mol/L ferrous trichloride solution, followed by rinsing with deionized water. Then graphene was transferred to the SiO_2/Si substrate (graphene/SiO_2/Si) following the method reported in [8].

After the graphene is transferred onto the Si/SiO_2 substrate, a metal shadow mask with cylinder-array holes was laid on the top of Pt/SiO_2 and Pt/graphene. This was done employing magnetron sputtering following the method reported in the literature [8]. The periodic arrays of Pt cylinders were separately fabricated on the SiO_2/Si substrate and graphene/SiO_2/Si, as depicted in Figure 1. Figure 1 shows the surface morphologies of a triangular array of Pt cylinders on (a) SiO_2/Si substrate and (b) graphene/SiO_2/Si.

2.2. Nanoindentation and Surface Characteristics. The nanoindentation experiments on Pt/graphene and Pt/SiO_2 were carried out with the continuous stiffness measurement (CSM), which was configured with a Berkovich (3-sided pyramid) diamond tip. The test was measured at a loading rate of 4–40 mN/min. The load range was 2~20 mN, and the holding time was 10 s. The nanoindentation experiments for both Pt/graphene and Pt/SiO_2 were carried out randomly on the surface of Pt cylinders for five times and then both the average microhardness and elastic modulus were obtained.

The water contact angle (WCA) of graphene and SiO_2/Si was measured to determine surface energy measurements using a contact angle meter (DSA100, Kruss, Germany). In order to provide statistical means, at least four measurements on each sample were carried out and an average of these values was used.

The surface adhesive forces between graphene and SiO_2/Si substrate were measured using a friction force microscope (FFM). Square pyramidal silicon nitride (Si_3N_4) tips (tip radius ~50 nm) were used on a cantilever with a stiffness of 2 N/m. The pull-off force was considered to be the adhesive force. The adhesive force test on each sample was conducted for ten times to obtain an average adhesive force.

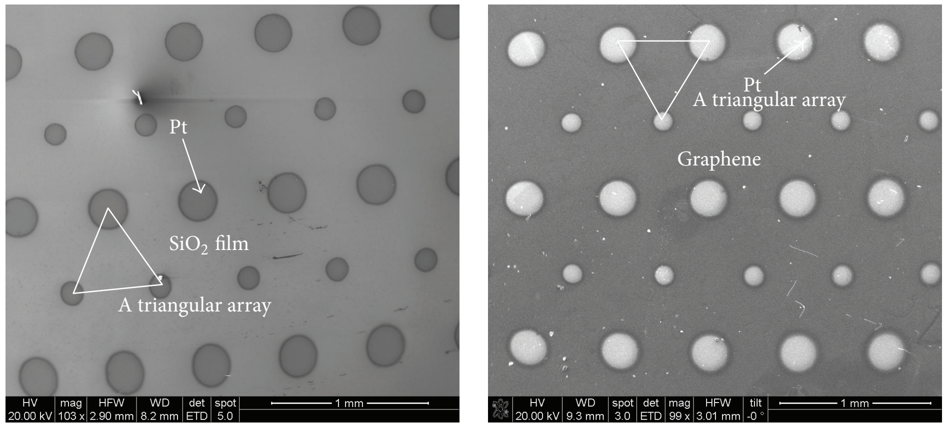
2.3. Macrotribological Tests and Surface Characteristics. Macrotribological tests were run employing a UMT-2MT tribometer (CETR) in a ball-on-plate contact configuration under the testing conditions of 0.1 N normal force and 1 Hz frequency. GCr15 steel balls (diameter, 6 mm, and mean roughness, 0.02 μm) were used as the stationary upper counter-bodies, and Pt/SiO_2 and Pt/graphene were mounted onto the flat base and driven to reciprocating motion at a distance of 0.5 cm. The friction coefficients versus time curves were generated automatically. All experiments were performed under ambient conditions of 25°C and 26% relative humidity.

The wear morphologies of Pt/graphene and Pt/SiO_2 were characterized by SEM (JEOL JSM-6300). Raman spectra (Labram HR800 Jobin Yvon) of the samples were measured using 514 nm laser excitation. The measurements for each sample were carried out for three times from three different locations so as to obtain average data.

3. Results and Discussions

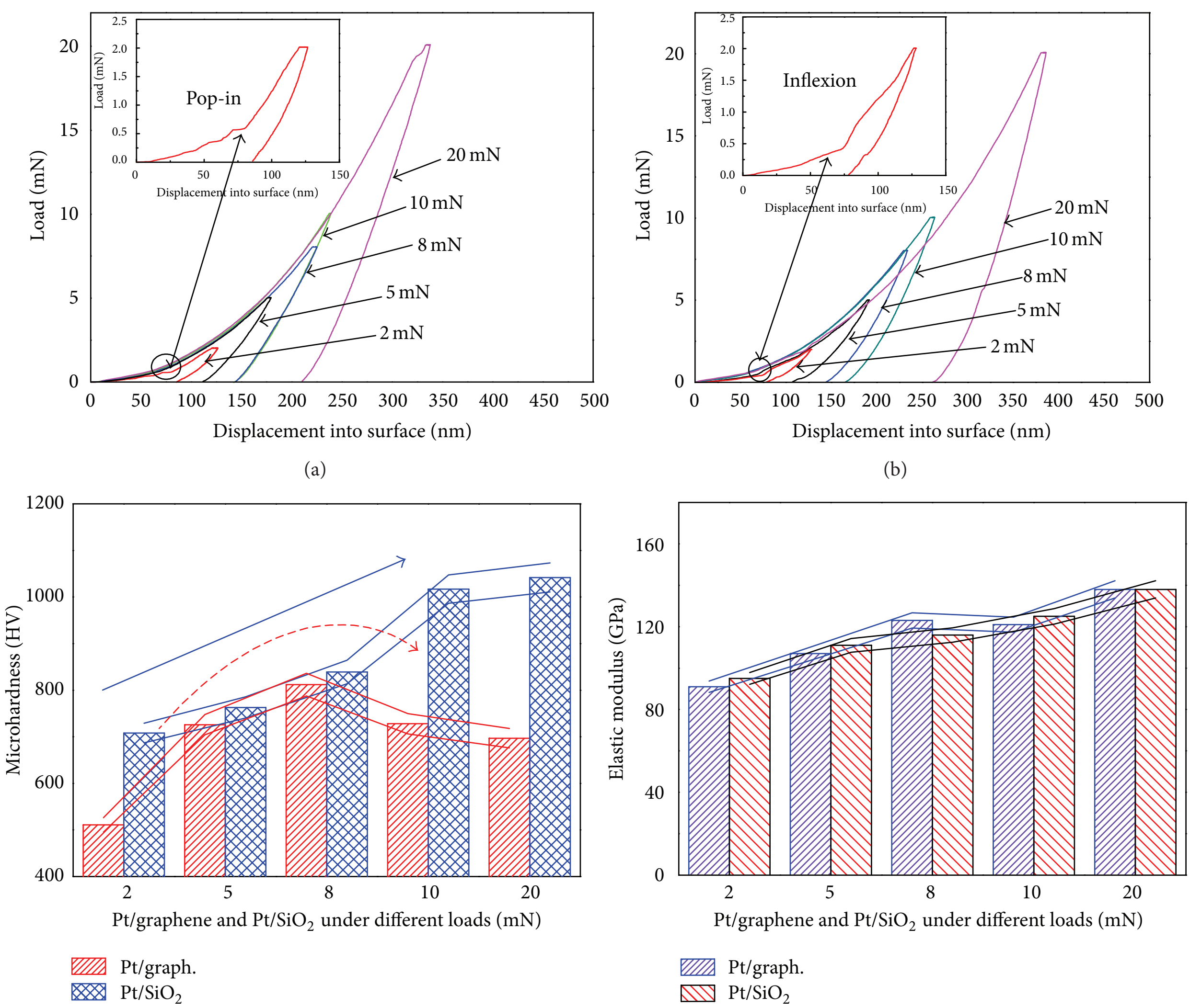
3.1. Nanoindentation of the Pt Cylinder-Array Structure. The effect of graphene as a middle layer on interface between Pt and SiO_2/Si was evaluated by analyzing the indentation load-depth curve. Figures 2(a) and 2(b) illustrate the load-displacement curves for Pt/SiO_2 and Pt/graphene under different loads. As can be seen from Figure 2(a), there is a sudden breakdown (or pop-in) in the displacement curve of Pt/SiO_2 corresponding to 2 mN load 70 nm depth. This indicates that the fracture at the Pt/SiO_2 surface can take place, due to a burst of strain accompanied by the transition from purely elastic behavior to plastic behavior [12]. Contrarily, the pop-in effect is not present on the Pt/graphene curve, except a slight inflexion around the depth of 70 nm as illustrated in Figure 2(b). This follows that the mechanical damage at the Pt/graphene interface is lighter than that at the Pt/SiO_2 interface. Furthermore, as obvious from the load-displacement curves, Pt/graphene experiences higher indentation depth than the SiO_2/Si does which reflects the effect of graphene film on Pt cylinders. Because the thickness of the Pt cylinder is approximately 100 nm, the pop-in displacement (70 nm) is more than 10–20% of a thin-film thickness. As reported in the literature [13], the results are obviously affected by the SiO_2 or graphene.

For the present systems, like a soft film (Pt) on a hard substrate (i.e., graphene/SiO_2/Si and SiO_2/Si), the interaction at the film-substrate interface can be analyzed by the depth sensing nanoindentation measurements [14]. Figure 2(c)



(a) (b)

FIGURE 1: Surface morphologies of a triangular array of Pt cylinders on (a) SiO_2/Si substrate and (b) graphene/SiO_2/Si.



(a) (b) (c) (d)

FIGURE 2: The loading-unloading curves of (a) Pt/SiO_2 and (b) Pt/graphene, respectively. (c) The microhardness and (d) elastic modulus with variations in the loads.

shows the microhardness curves for the Pt/graphene and Pt/SiO_2 under different loads. This is to notice that the microhardness of the Pt/graphene increases with increasing load till the load of 8 mN; however, afterwards the microhardness gradually drops with the increase in the load. Because the indentation depth is found to be less than 230 nm, ranging from the thickness of the Pt cylinder (100 nm) to SiO_2 film (300 nm), effect of graphene on the support of Pt cylinder begins playing a role under the load of 8 mN, shown in the triangle of Figure 2(c). Recent research also confirms the finding that the graphene layer can carry higher loads than the Pt(111) surface at similar penetration depths [15]. On the contrary, the microhardness of the Pt/SiO_2 increases with the increase of the load and finally reaches a nearly constant value when a load of 10 mN or higher is applied. It can be observed from Figure 2(c) that the hardness gradually increases with increase in load and till a load of 10 mN which afterwards becomes almost constant. Moreover, the indentation depth is in the range of the thickness of 250–300 nm, which corresponds to the thickness of SiO_2 film on Si substrate. Thus, to some extent, the microhardness of Pt/SiO_2 may be affected by SiO_2 film with the thickness of 300 nm. According to the above analysis, these findings reveal that even a thin layer of graphene (less than 1 nm) can act as an effective support material which can be attributed to its high compressive strength.

The elastic moduli of the Pt/graphene and Pt/SiO_2 are shown in Figure 2(d). The elastic modulus of both Pt/SiO_2 and Pt/graphene gradually increases as the load increases. However, Pt/graphene exhibits higher elastic modulus than Pt/SiO_2 does until the load of 8 mN. Here, the loading displacement is less than 220 nm. The results show that the interface between Pt and graphene and graphene and SiO_2 film will affect the change in the elastic modulus of Pt/graphene and could be attributed to the effect of graphene due to its high strength and large elastic modulus [16]. This is to observe that the elastic modulus of Pt/SiO_2 rapidly increases when loaded under 20 mN and approaches that of Pt/graphene.

From the above findings, it follows that graphene as a middle layer between Pt and SiO_2 film can have an important influence on the microhardness and the elastic modulus. When the indenter comes into contact with graphene, the carbon network of graphene provides a thin support layer for Pt cylinders until the frame is broken. Therefore, the present nanoindentation provides a potential approach for evaluating the effect of graphene as a middle layer on interface between Pt and SiO_2 film.

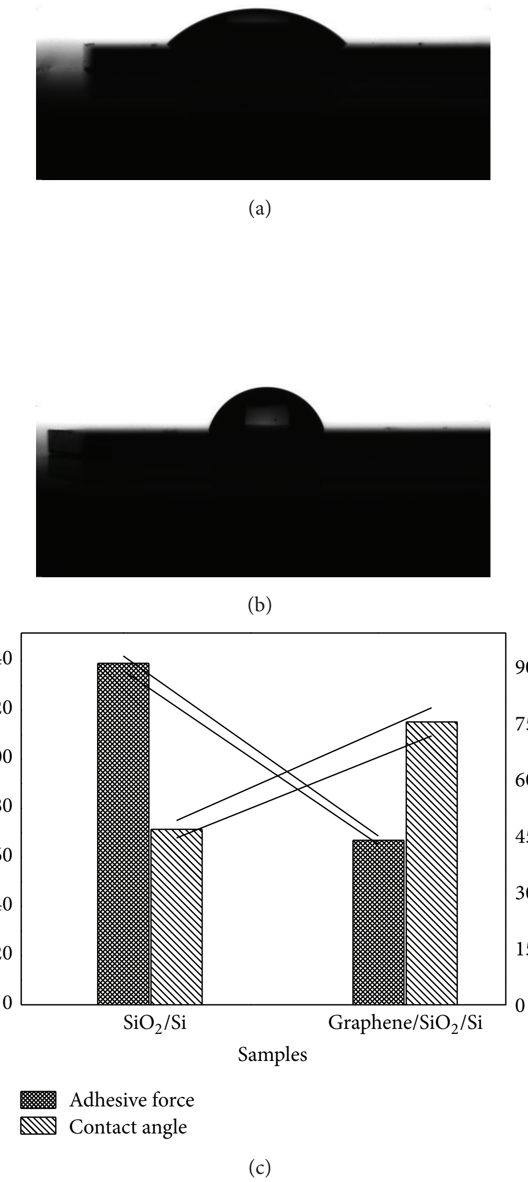


Figure 3: The contact angle of (a) SiO_2/Si substrate and (b) the graphene/SiO_2/Si substrate and (c) the comparative value of the adhesive force and contact angle between them.

3.2. Interaction Effects between Graphene and Pt Cylinder-Array Structure. In order to reveal the effect of graphene on formation mechanisms of Pt cylinders on the SiO_2 film and graphene surfaces, it is necessary to investigate the surface characteristics of two samples. Figures 3(a) and 3(b) show the water contact angle (WCA) of the SiO_2/Si substrate and the graphene/SiO_2/Si. This, respectively, is 47.2° and 76.1° for SiO_2/Si and the graphene, which indicates that the SiO_2/Si substrate is more prone to wetting than graphene/SiO_2/Si. Figure 4 illustrates the schematic diagram of Pt cylinders formation process. From Figures 4(a) and 4(b), we can clearly see that Pt atoms grow as a planar structure and absorb into the surface of SiO_2/Si substrate due to its better wettability, but Pt cylinders keep a weak cohesion with SiO_2/Si substrate due to Van der Waals forces [7]. Relatively, Pt cylinders grow as a shell structure on graphene/SiO_2/Si because of the existence of a wrinkle in graphene, as schematized in Figures 4(c) and 4(d) and reported in theoretical studies [17]. This shrinkage may result from easily noticeable folded regions

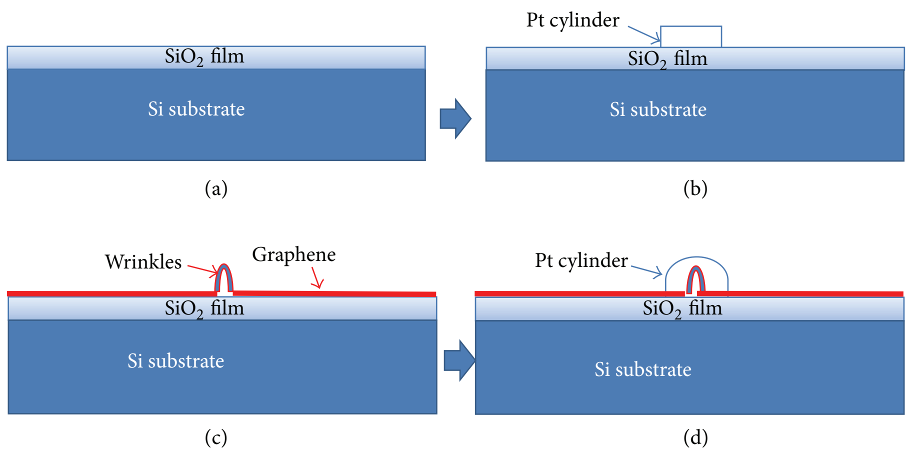


Figure 4: The schematic diagrams of (a) SiO_2/Si substrate, (b) Pt cylinders grown on SiO_2/Si, (c) graphene/SiO_2/Si, and (d) Pt cylinders grown on the graphene/SiO_2/Si, respectively.

as well as from the evolution of dendritic wrinkles, which can affect the growth of Pt cylinders on graphene/SiO_2/Si thus causing reduction in adhesive force: compare 139 nN of SiO_2/Si with 67 nN of graphene/SiO_2/Si. The results reported in Figures 3 and 4 demonstrate that the adhesion forces decrease with increasing contact angles, a finding in good agreement with [7, 18].

3.3. Effect of Graphene as a Middle Layer on Friction and Wear of SiO_2/Si Substrate. In view of the above results, the effect of graphene as a middle layer between Pt and SiO_2 film on the macrotribological properties was investigated. The friction and wear tests were performed on Pt/graphene and Pt/SiO_2 using a ball-on-plate tribometer and under the load of 0.1 N. Figure 5 shows friction behavior of both films. The COF of both Pt/graphene and Pt/SiO_2 is less than 0.2 before 1300 s. Subsequently, the COF of Pt/SiO_2 sharply increases from 0.2 to 1.0. However, that of Pt/graphene remains almost stable to 0.2. Moreover, its wear lifetime is higher than 3500 s which is twice that of Pt/SiO_2. In fact, for Pt/SiO_2, Pt cylinders due to its low hardness can easily be destroyed and extrude outside the wear track. During wear test, only a part of Pt cylinders are transferred to the surface of the steel ball. Simultaneously, the friction occurs between the SiO_2 film and the steel ball partly covered with Pt. The COF of Pt/SiO_2 is affected by Pt due to its low shear strength. As can be seen from Figure 6(a), there is significant wear/scratch damage on the SiO_2/Si substrate. As for Pt/graphene, Pt cylinders act as very strong pinning centers for the sliding of graphene sheets, which had certain pinning effects on graphene sheets and prevented graphene sheets from sliding. Before the Pt cylinder array was rubbed, Pt with the low shear strength can be a lubricating medium and reduces the friction. As indicated in Figure 6(b), after the spoiled Pt extrudes outside the wear track, the friction occurs between graphene and steel counterface covered with Pt transferring films. Although Pt cylinders are easily ploughed or destroyed, the unspoiled Pt cylinders can still remain on the graphene surface. Hence, due to the fact that graphene as a middle layer supports the unspoiled Pt cylinders to prevent

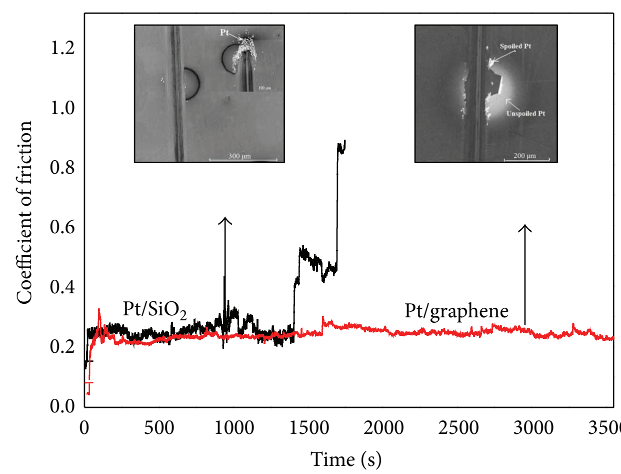
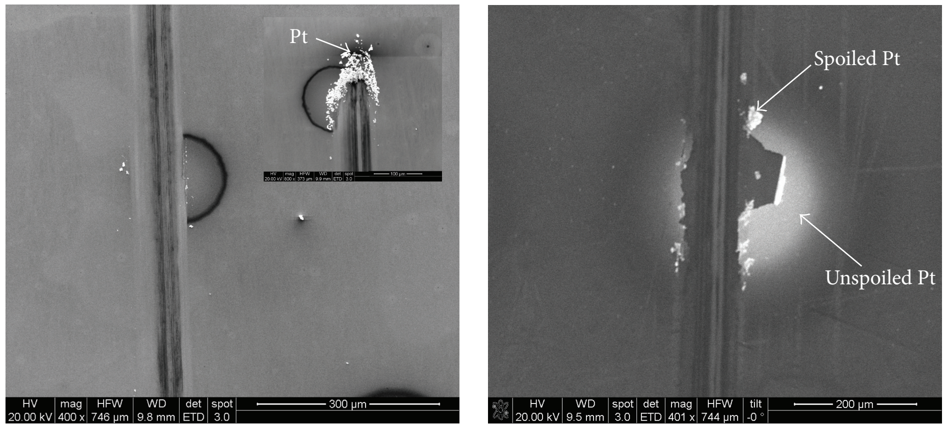


Figure 5: Comparison of friction coefficient of both Pt/SiO_2 and Pt/graphene against steel balls under the load of 0.1 N.

the direct contact between the SiO_2/Si substrate and steel counterface [19], Pt/graphene has a certain role in reducing the friction and improving the wear lifetime.

On the one hand, as for the worn surfaces of Pt/SiO_2 substrate in Figure 6(a), the Raman spectrum presented in Figure 7 indicates that there are no obvious D and G bands on the wear track. Further, the typical Si peaks at 520 cm^{-1} and 964 cm^{-1} can be observed at the center of the wear track which reveals that the spoiled Pt cylinders during wear test extruded outside the wear track thus exposing the SiO_2/Si substrate.

On the other hand, as observable from Figure 6(b), a continuous and compact film forms on the wear track on the Pt/graphene. This is to notice from the Raman spectrum, shown in Figure 7, taken at the center of the wear track, that graphene contrary to SiO_2/Si did not extrude on the two sides of the wear track, and also there are obvious D and G bands at the center of the wear track. The intensity ratio of a D band to that of a G band (I_d/I_g) is around 1.1. I_d/I_g is related to the



(a) (b)

Figure 6: The worn morphologies of (a) Pt/SiO_2 substrate and (b) Pt/graphene.

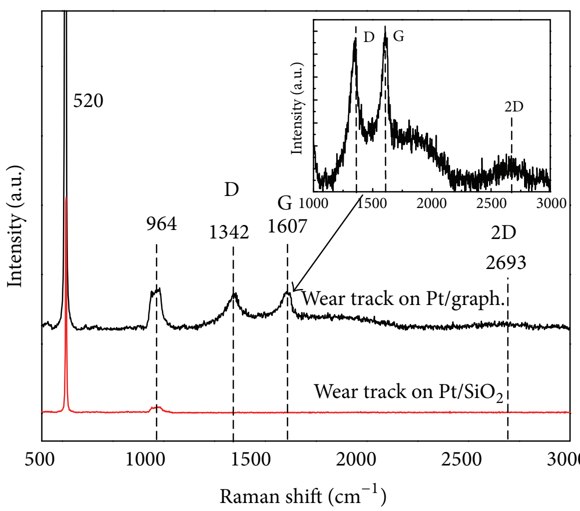


Figure 7: Raman spectra of both Pt/SiO_2 substrate and Pt/graphene/SiO_2 at the center of the wear track after the friction and wear.

changes in the microstructure of graphene surface because it correlates with the sp^3/sp^2 bonding ratio and the size of graphite clusters [20]. Moreover, it can be observed that there is 2D band at ~2700 cm^{-1}, which is regarded as a function of the number of layers. A further increase of the number of layers leads to a significant decrease in the relative intensity of the lower frequency 2D peaks. Therefore, during the friction and wear process, surface states of graphene greatly changed, including defects and composition. Graphene surface oxidation further decreases its surface energy and wear resistance. The interaction between graphene and Pt cylinders prolongs the wear lifetimes.

4. Conclusions

Periodic arrays of Pt cylinders were prepared using magnetron sputtering technology onto SiO_2/Si substrates and also on graphene which was previously deposited onto a SiO_2/Si substrate. The effects of graphene as an adhesive layer on macrotribological properties of Pt/SiO_2 were investigated. The results indicated that the Pt cylinders can play a significant role in decreasing the friction, but graphene as a middle layer enhances the interaction between Pt cylinders and SiO_2 film. Therefore, Pt/graphene does not offer only a low friction coefficient; but it also prolongs the wear lifetime. This study can serve as novel approach to improve the macrotribological behavior of SiO_2/Si substrate.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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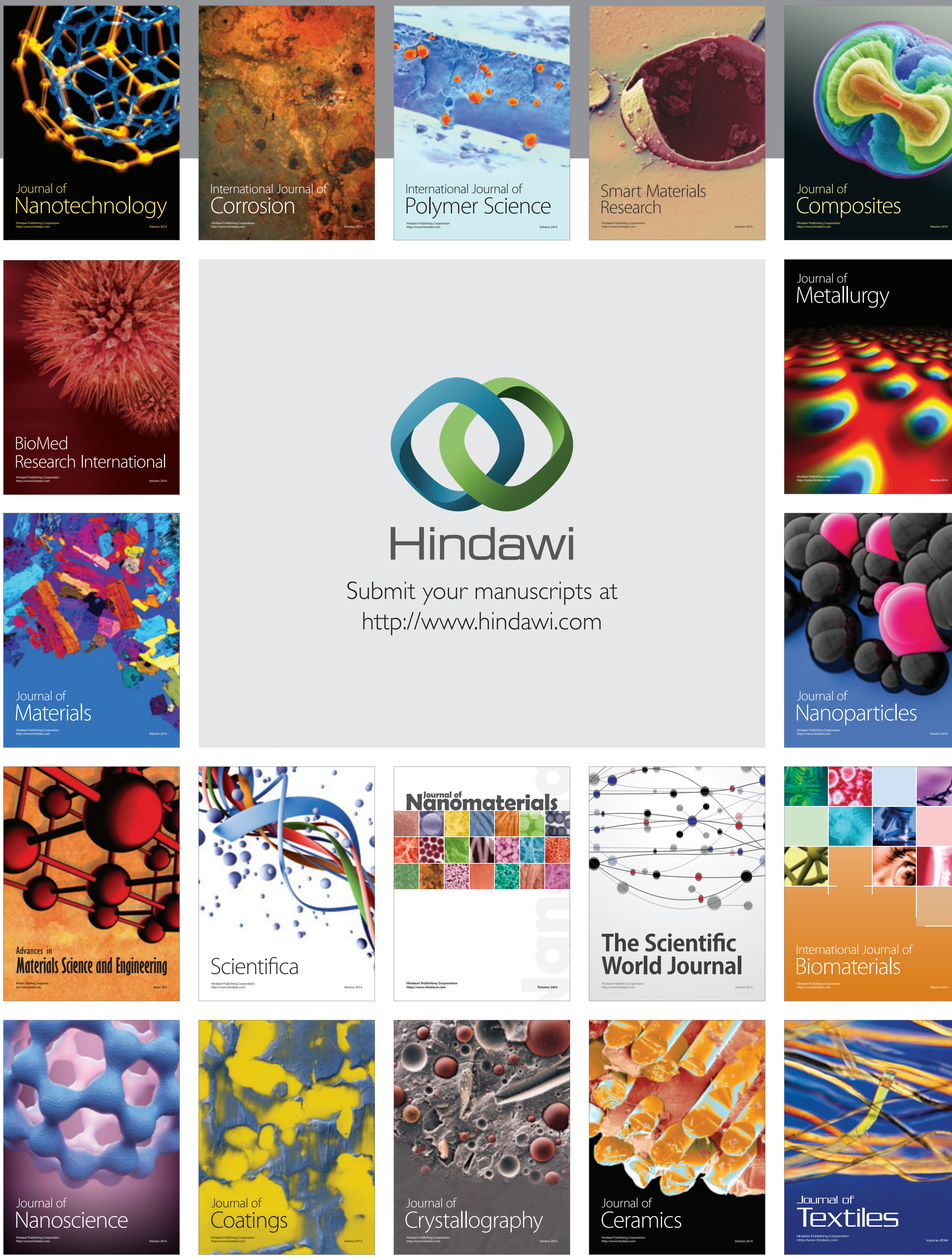
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