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Structure and nanotribology of thermally deposited gold nanoparticles on graphite

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ABSTRACT

We present experiments involving the structural and frictional characterization of gold nanoparticles (AuNP) thermally deposited on highly oriented pyrolytic graphite (HOPG). The effect of thermal deposition amount, as well as post-deposition annealing on the morphology and distribution of gold on HOPG is studied via scanning electron microscopy (SEM) measurements, while transmission electron microscopy (TEM) is utilized to confirm the crystalline character of the nanoparticles. Lateral force measurements conducted via atomic force microscopy (AFM) under ambient conditions are employed to investigate the nanotribological properties of the gold nanoparticles as a function of normal load. Finally, the increase in lateral force experienced at the edges of the nanoparticles is studied as a function of normal load, as well as nanoparticle height. As a whole, our results constitute a comprehensive structural and frictional characterization of the AuNP/HOPG material system, forming the basis for nanotribology experiments involving the lateral manipulation of thermally deposited AuNPs on HOPG via AFM under ambient conditions.

1. Introduction

Despite the fact that friction is ubiquitous in nature, the fundamental physical principles that govern this interesting phenomenon are still not well understood. While the macroscopic laws of friction involving a linearly proportional relationship between the normal load (F_n) and the friction force (F_f) arising between two objects in contact have been well established since hundreds of years thanks to pioneering experiments by Amontons, Coulomb and others, the macroscopically observed proportionality constant μ (the so-called *friction coefficient*) cannot be derived from first principles as it constitutes a complex function of interface structure, chemistry and environmental factors including temperature and humidity [1]. Moreover, the unavoidable multi-asperity nature of interfaces formed by two macroscopic objects in contact [2] complicates the physical interpretation of macroscopic friction experiments, leading to substantial difficulties in the determination of the actual contact area (A) between the two objects, among others.

To overcome the above-mentioned difficulties associated with macroscopic tribology (the science of friction, wear and lubrication) experiments, the research field of nanotribology has been introduced relatively soon after the invention of the atomic force microscope (AFM) [3,4]. The AFM, which can be thought of as a very high-resolution *mechanical* microscope, allows the recording of (sub-)nanometer-scale topography as well as normal and lateral forces experienced by a very sharp single asperity (radii of curvature usually on the order of <10 nm) in the form of a tip at the end of a micro-machined $Si/SiO_2/Si_3N_4$ cantilever during the raster-scanning of a given sample surface under slight contact (normal forces on the order of a few to tens of nN) [5]. Thanks to the single-asperity nature of the contact formed between the AFM tip and the sample surface, various nanotribology experiments conducted on a large number of sample surfaces over the last couple of decades have resulted in the precise determination of the effect of normal load, sliding velocity and temperature on frictional behavior at the nanoscale [6–8]. Moreover, phenomena such as stick-slip [9] and superlubricity [10] have been observed and largely explained, in many cases with substantial support from theory and computational work [11].

Among the material systems investigated nanotribologically using an AFM-based approach, nanoparticles on layered substrates such as highly oriented pyrolytic graphite (HOPG) [12,13] are of particular interest, primarily due to the fact that they readily present a heterogeneous sample surface where the effect of changing experimental parameters such as normal load on frictional

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behavior can be compared and contrasted on the nanoparticles themselves and the substrates. Moreover, there has been a recent increase in nanotribology experiments involving the deliberate lateral manipulation of nanoparticles on structurally well-defined substrates such as HOPG and the measurement of the associated frictional forces, as a model approach to study frictional effects in devices featuring sliding components on nano- and micrometer scales [14–19]. Consequently, the need for a comprehensive nanometer-scale characterization of the structural and frictional properties of such sample systems arises as a prerequisite for the correct interpretation of the above-mentioned nano-manipulation experiments, among others.

Motivated by the discussion above, we present in this contribution a comprehensive characterization of the structural and nanotribological properties of thermally deposited gold nanoparticles (AuNP) on HOPG substrates. The particular choice of this sample system is motivated by recently reported nano-manipulation experiments involving AuNPs under ultrahigh vacuum (UHV) conditions [18], as well as the fact that the growth mechanisms of AuNPs on HOPG have been studied via various approaches in the past [20–24]. In the following sections of this work, the effects of thermal deposition amount, as well as post-deposition annealing on nanoparticle morphology and distribution are discussed via scanning electron microscopy (SEM) measurements. Results reveal that a transformation in morphology from small, non-uniformly dispersed gold islands that are coalesced to form channeled thin films on HOPG to much larger, well-faceted, mostly hexagonal AuNPs with much lower substrate coverage takes place upon post-deposition annealing. Furthermore, high-resolution transmission electron microscopy (TEM) images are utilized to confirm the crystalline character of the hexagon-shaped AuNPs. An extensive nanotribological analysis involving a number of AuNPs via AFM performed in ambient conditions allows the characterization of the friction force measured on the nanoparticles and the HOPG substrate as a function of normal load. Finally, an analysis of the increase in lateral force experienced at AuNP edges is presented as a function of normal load and nanoparticle height, revealing a linearly increasing trend for both parameters.

It is important to emphasize at this point that the results reported in this paper form a much-needed basis in terms of a comprehensive structural and tribological characterization for future nano-manipulation experiments to be conducted using the AuNP/HOPG material system under ambient conditions. In fact, it is observed that many AuNPs are frequently manipulated on the HOPG substrate during AFM measurements, opening the route towards the quantitative characterization of interfacial friction between crystalline surfaces. On the other hand, the present focus has been placed on immobile AuNPs stuck between HOPG steps and other structural features, suitable for a comprehensive structural and frictional characterization via AFM and other techniques.

2. Experimental

2.1. Sample preparation

HOPG substrates have been prepared by mechanical cleaving in air via adhesive tape and immediately transferred into the vacuum chamber of a thermal evaporation system (Vaksis PVD Vapor–3S). Thermal evaporation of 999.9 purity gold on HOPG substrates took place at a base pressure on the order of 5×10^{-6} Torr and at a deposition rate of 0.1 Å/s for total deposited amounts between 1 Å and 40 Å. During deposition, the HOPG substrate was held at room temperature. After deposition, the gold-coated HOPG substrates were removed from the evaporation system for optional post-deposition annealing and further analysis via SEM, TEM and AFM. Post-deposition annealing at temperatures ranging from 400 °C to 650 °C and for annealing times on the order of 30 min to 4 h took place in a quartz tube furnace (Alser Teknik/ProTherm).

2.2. Sample characterization via SEM and TEM

Prior to structural and nanotribological characterization by AFM, samples prepared as detailed in the previous section have been analyzed via SEM (FEI Quanta 200 FEG, typically operated at 10 kV) to study the morphology and the distribution of AuNPs on HOPG. Additionally, high-resolution TEM (FEI Tecnai G2 F30, typically operated at 300 kV) has been utilized to confirm the crystalline structure of AuNPs via direct imaging as well as electron diffraction. The TEM samples have been prepared by mechanical cleavage of a thin layer of the gold-covered HOPG sample and subsequent sonication in ethanol, followed by drop-casting on a Cu grid (300 mesh).

2.3. Nanotribological measurements performed via AFM

Complementary to SEM and TEM measurements, AFM experiments have been utilized to characterize the structure as well as the nanotribological properties of the AuNP/HOPG sample system. A commercial AFM instrument (PSIA XE-100) has been operated under ambient conditions and in the contact mode to simultaneously measure the topography of the sample surface and the lateral forces arising between the tip and the sample during scanning. A single silicon cantilever (Nanosensors PPP-CONTR series, radius of curvature ≈ 10 nm) has been used for all AFM measurements. To reliably determine the normal as well as the lateral forces detected during AFM measurements, the cantilever has been calibrated according to the methods reported by Sader et al. [25] and Varenberg et al. [26], respectively, resulting in a normal spring constant k of 0.23 N/m and a calibration constant α of 15.0 nN/V for the lateral force signal. While the details of both calibration techniques are described in the respective references, let us indicate here that the Sader et al. method allows the practical calculation of normal spring constants of AFM cantilevers based on a measurement of resonance frequency, quality factor and plan-view dimensions, taking into account the effect of the surrounding fluid medium (air) on cantilever oscillation via a hydrodynamic function [25]. On the other hand, the Varenberg et al. method, sometimes referred to as the improved wedge method, involves the measurement of the forward and backward lateral force signals on the sloped and flat faces of a commercial calibration grating with known feature sizes and dimensions, effectively allowing the calculation of lateral force calibration constants using force equilibrium arguments in conjunction with the determination of friction loop width and offset values at fixed normal loads [26]. In accordance with literature, the reported friction forces in our experiments have been calculated by considering the half-width of the friction loops formed by the recording of lateral forces during forward and backward scans [27].

3. Results and discussion

3.1. Effect of deposition amount and post-deposition annealing on morphology

In order to obtain a heterogeneous sample system suitable for nanotribological investigation via AFM consisting of individual AuNPs of defined shape and reasonable lateral separation on HOPG, the first preparation step involved the thermal evaporation of gold onto freshly cleaved HOPG substrates. The growth kinetics and morphological characteristics of thin films of gold on HOPG have received particular attention in the past, where typically non-uniform surface coverages have been observed due to the relatively low surface energy exhibited by the HOPG substrate [20–24]. While

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