Tribology International 44 (2011) 906–915

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

# Adhesion and friction of nanoparticles/polyelectrolyte multilayer films by AFM and micro-tribometer

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ARTICLE INFO

*Article history:*
Received 28 September 2010
Received in revised form
6 March 2011
Accepted 9 March 2011
Available online 17 March 2011

*Keywords:*
Polyelectrolyte multilayer film
Nanoparticles
Adhesion
Friction

ABSTRACT

The in situ CuS nanoparticle/polyelectrolyte multilayer (NPs/PEM) films have been prepared using the layer-by-layer method and the in situ synthesize method. The NPs/PEM films were characterized by atomic force microscope (AFM), ultraviolet–visible (UV–vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM). It was found that the adhesive forces between probe and sample are decreased by compositing in situ CuS nanoparticles. From the investigation of the nano- and micro-tribological behaviors, the NPs/PEM film has a lower friction force and a better anti-wear property than the pure polyelectrolyte multilayer film.


## 1. Introduction

Over the previous decades, there are some methods for deposition of ultrathin films on a substrate such as layer-by-layer (LBL), Langmuir–Blodgett (LB), spin coating, sputtering, and so on [1–3]. Layer-by-layer (LBL) method developed by Decher et al. [4–6] consists of alternate dipping of the substrate in oppositely charged polycation and polyanion electrolyte solutions. The LBL method is simple and cheaper, easy to automate, and friendly to the environment. Especially, the film can be deposited on a wide variety of substrates, and devices with complex architectures can be coated uniformly over large areas. The LBL film is a novel material studied extensively in recent years due to their numerous potential applications, versatility, and simplicity [1].

The LBL technique is ideally suited to combat the tribological challenges in microelectromechanical systems (MEMS). Up to now, the tribological properties of polyelectrolyte multilayer (PEM) film were studied popularly. Pavoor et al. [7,8] has reported that the deposition of a poly(acrylic acid) and poly(allylamine hydrochloride) polyelectrolyte multilayer film using the LBL technique, and the capacity for polyelectrolyte multilayer film induced wear reduction at large scales under the dry state. The PEM film is able to decrease the adhesive force on a surface, and to modify the friction surface and reduce the friction force [9–11]. And, nanoparticles were applied in tribology of ultrathin film. Graphite oxide, $TiO_2$, $SiO_2$, Ag nanoparticles, and so on composite polyelectrolyte multilayer films have been investigated to enhance the wear life of PEM film [12–15]. It was found that these films can improve the tribological performance greatly.

It has been reported that CuS were used as oil additive and filling material to improve the tribological property [16–18]. In this paper, the adhesion and friction of the in situ CuS nanoparticles/polyelectrolyte multilayer (NPs/PEM) film have been investigated by AFM and micro-tribometer.

## 2. Experiment

### 2.1. Materials

All materials were used without further purification. The polyelectrolytes used in this studies were poly(diallyl dimethylammonium chloride) and poly(acrylic acid), hereafter referred to as PDDA and PAA, supplied by Aldrich Chemical Co., American. The averaged molecular weight (*Mw*) of the PDDA and PAA used in the experiments were 100,000–200,000 and 30,000, respectively.

Mili-Q ultrapure water was used for preparation of all aqueous solutions, and during rinsing procedures ( > 18 MΩ cm, Milipore Mili-Q). Copper chloride ($CuCl_2$) and Sodium sulfide ($Na_2S$) were supplied by Sinopharm Chemical Reagent Co., Ltd. All the other reagents are analytical reagents. Prior of deposition, the glass and quartz substrates were cleaned according to the following procedures:

(1) The substrates were ultrasonic treated in acetone, chloroform, and anhydrous ethanol (volume ratio = 3:3:1) bath for 30 min

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doi:10.1016/j.triboint.2011.03.007

first and rinsed to eliminate the residues on substrates using de-ionized water flushing.

(2) The substrates were treated in an 80 °C piranha solution (98%$H_2SO_4$/30%$H_2O_2$, volume ratio=7:3) bath for 1 h (*caution: piranha solution reacts violently with organic solvents and is a skin irritant. Extreme caution should be exercised when handling piranha solution*). The piranha treatment allows removal of residues of organic and inorganic impurities from the substrates and makes the slides completely hydrophilic at the same time, through making the substrates to be hydroxylated. In the end, the substrates were rinsed with plenty of de-ionized water and dried with nitrogen to prepare for the deposition of polyelectrolytes.

### 2.2. Instruments

Ultraviolet–visible (UV–vis) absorption spectrums of films were recorded on a Unico 2102 UV–vis spectrophotometer, which was used to monitor the influence of absorbance on the in situ nanoparticle/polyelectrolyte multilayer film.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with the PHI-5300 spectroscope using Al Kα ($h\nu$=1486.6 eV) X-ray radiation. The vacuum inside the analysis chamber was $1.333 \times 10^{-8}$ Pa during the analysis. The binding energy (*BE*) of C1s (284.8 eV) was used as the reference.

Contact angle measurements were conducted using the sessile drop technique performed on a contact angle goniometer (JC2000A, China) at 25 °C.

A NanoMan VS (VEECO) atomic force microscopy was used to evaluate the morphology of the MD films by tapping mode, and it was operated under air-ambient temperatures (25 ± 1 °C) and a relative humidity of 20% using commercial silicon nitride probes (spring constant 0.2022 N/m, which was checked by the AFM instrument). AFM has been used extensively to measure adhesive force between surfaces at nano-scale [19–21]. The adhesive force between the AFM tip and the film surface by force-curves mode under ambient condition is shown in Fig. 1. $a \rightarrow b$ is the probe approaching the sample surface gradually, and the micro-cantilever of the probe does not bend with the force between the sample surface and probe zero. $b \rightarrow c$ is probe contacting with the sample surface suddenly due to the surface tension when both close infinitely, and then the micro-cantilever is curved downward slightly. $c \rightarrow d$ is loading process where the downward micro-cantilever transforms into without any bending, then curved upward, and the degree of bending gradually increases.

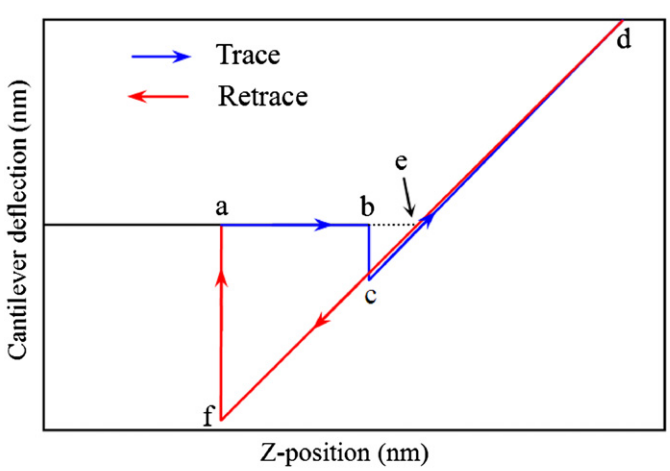


**Fig. 1.** A typical force–distance plot and schematic illustration for adhesion force calculation.

The probe retraces to unload when achieving the Point '*d*', $d \rightarrow f$ is the unloading process, where the bending degree of micro-cantilever upward decreases to zero (Point '*e*'), then the micro-cantilever bends downward gradually due to the adhesive force between the probe and the sample surface. The probe will pull-off the sample surface suddenly when the adhesive force equals to the bending force of the micro-cantilever (Point '*f*'). The Point '*a*' indicates no bending occurs after the probe pulling off the sample surface. The adhesive force (pull-off force) was calculated by multiplying the cantilever spring constant by the horizontal distance between Points '*e*' and '*a*' [19]

$$F_a = K \times l_{ae} \tag{1}$$

The friction forces of PEM and NPs/PEM films were measured using the friction force mode of AFM (FFM) [22]. Fig. 2 shows the working principles of FFM, and the main components are a thin cantilever with a probing tip ($L$ is the lever length of cantilever; $w$ is the lever width of cantilever, $h$ is the lever thickness, $\iota$ is the height of the tip mounted at the end of the cantilever). The size of the AFM probe is listed in Table 1. The laser beam deflection caused by the cantilever is determined by a quadrant photodiode of the optical system. The normal load and the frictional force are proportional to the normal and torsional deflections of the cantilever, which are recorded simultaneously via the output of the photodiode detector. The signal $V_{A+B}-V_{C+D}$ is the measurement for normal bending and $V_{A+C}-V_{B+D}$ for the torsional deflection of the cantilever. When the lateral force $F_y$ is applied at the tip, as in the case of the AFM cantilever, lateral deflection is accompanied by twisting or torsion along the cantilever axis [23].

$$F_y = k_{yT}\Delta y \tag{2}$$

$k_{yT}$ is the bending stiffness. $\Delta y$ is the deflection in the $y$ direction.

For a wide, thin cantilever ($b \gg h$) experiencing a rotation $\phi$. The torsional stiffness of the beam $k_\phi$, is given as

$$M = k_\phi \phi \tag{3}$$

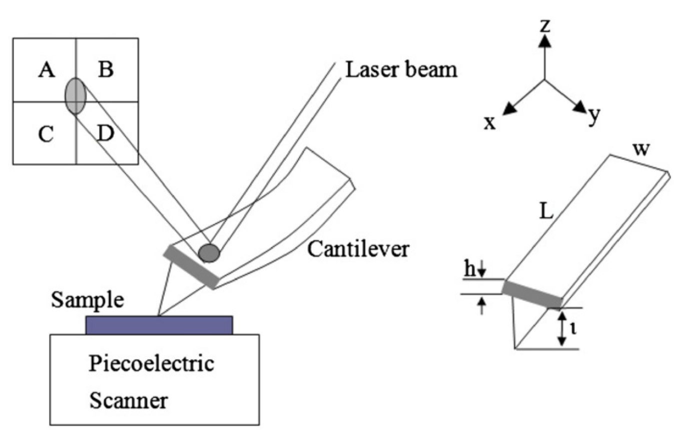


**Fig. 2.** The working principles of FFM, and the main components a thin cantilever with a probing tip.

**Table 1**
The size of the AFM probe.

| $L$ (μm) | $w$ (μm) | $h$ (μm) | $\iota$ (μm) |
|---|---|---|---|
| 130 | 25 | 1 | 8 |