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Friction-reducing properties of stearic acid modification of the Cu_2S film on the copper substrate

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ABSTRACT

A simple two-step process was developed to fabricate the dual-layer films on copper substrate for the purpose of lowering friction. The Cu_2S film was fabricated on the surface of the copper substrates by the hydrothermal reaction. A stearic acid overcoat was then prepared on surface of the Cu_2S film. X-ray photoelectron spectroscopy, scanning electron microscopy, Fourier transform infrared microscopy and water contact angle measurements were used to analyze the morphological features, the chemical composition and the hydrophobicity of freshly prepared samples. Moreover, the tribological behavior of the dual-layer films was evaluated by sliding the films against a steel ball under 0.5 N normal load using a reciprocating ball-on-plate tribo-tester. It was found that the stearic acid overcoat on the Cu_2S film led to a significantly decreased friction with greatly extended life.

1. Introduction

Cu_2S (chalcocite), a p-type semiconductor with a bulk band gap of 1.21 eV, has been extensively investigated in solar cells, cold cathodes and nanoscale switches [1–4]. Many different approaches have been developed to synthesize Cu_2S materials with novel and special structures [5–14]. Among them, the hydrothermal reaction presents many advantages for the preparation of high-purity, good-shaped and size-controllable materials [15]. Herein, copper is used both as the reactant of the hydrothermal reaction and the support for Cu_2S films. The self-supported Cu_2S films prepared with current method are much more robust, comparing with other methods in which surface was obtained with initiated growth on different substrates. The Cu_2S film is intrinsically adhered on the copper surface through inter-metal interaction.

We are interested in the potential application of Cu_2S film as the friction-reducing protective coating for copper. This is important because copper and its alloys, as a class of important engineering materials, have poor tribological performance. The application of copper alloys and steel as mating materials for sliding machine elements is very common in many areas of mechanical engineering, such as worm gears, spindle drives and various bushing and guiding devices. The liquid lubricants are normally needed to reduce the friction and wear of copper [16].

It is recognized that long chain fatty acid, dispersed in oil, has been used as a friction modifier for a long time [17]. The first and so far the most authoritative explanation of the phenomenon emerged from the work of Bowden and Tabor [18]. The chemical adsorbed fatty acid molecules on surface of substrate are transformed under tribological condition to a layer of fatty soaps by chemical reaction with the substrates. Low friction was obtained when such a layer was sliding against a solid counterface under certain conditions [19–21].

In this paper, the stearic acid overcoat is deposited on Cu_2S film prepared by hydrothermal reaction on the copper substrate, as a approach to develop a tribological surface-modification route for the lubrication and protection of the copper substrate. The chemical structure and tribological performance of dual-layer films on the copper substrate are characterized.

2. Experimental detail

2.1. Materials

A copper foil (99.9%, 0.25 mm thick) was commercially obtained. Analytical grade reagents stearic acid ($CH_3(CH_2)_{16}COOH$), sulfur, and ethanol were obtained from Aldrich and used without further purification.

2.2. Preparation of Cu_2S film on the copper substrate

Cu_2S film on copper substrate was prepared by the hydrothermal reaction. In a typical procedure, copper foils (99.9%) were firstly treated with 1 M HCl and washed with deionized water before use. A piece of copper foil ($10 \times 10 \times 0.25$ mm) and 1 mmol sulfur powder were placed in a 50 ml autoclave. Then 25 ml distilled water was added. The autoclave was maintained at 180 °C for 12 h and cooled to room temperature naturally. The copper foil was taken out, washed with ethanol and dried in air for the characterization.

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2.3. Preparation of the dual-layer film on the copper substrate

The as-obtained copper substrates were then immersed in an ethanolic solution containing 0.01 M stearic acid at room temperature for 24 h. Upon completion, the copper substrates were lifted from the solution and rinsed with deionized water and ethanol, yielding the dual-layer films on copper substrate after fully drying in air. For a comparison, the same procedure is used to create the stearic acid overcoat on the bare copper substrate.

2.4. Instrumentation

Contact-angle measurements were conducted under static condition with a remote computer-controlled goniometer system (CAM101, KSV Instruments LTD). Deionized water droplets with a volume of about 3.5 μL were prepared at different locations of the to-be-tested surfaces by using a syringe. All contact angle measurements were run under ambient laboratory conditions (temperature about 20 °C, relative humidity about 55%); and five repeat measurements were carried out for each sample. Images of water droplets were analyzed using Imagetool software (University of Texas Health Science Center) to measure the contact angle. The reported sessile drop static water contact angles (WCA) were typically reproducible to ±2° while the tilting angle of the stage was adjusted with a micrometer at a resolution of 0.1°.

The morphology of Cu_2S film on the copper substrate was characterized by means of scanning electron microscopy (SEM, JEOL JSM-5600LV, accelerating voltage 20 kV).

A Fourier transform infrared (FT-IR) microscope (Nicolet iN10) equipped with a diffuse reflectance infrared spectrometric attachment was used to analyze the chemical features of the stearic acid layer atop Cu_2S film of the copper substrate. The IR spectra were acquired over 1024 scans at a resolution of 4 cm^{-1} with a p-polarized beam and calibrated in relation to a bare copper substrate.

The surface chemical states of the films were analyzed on an X-ray photoelectron spectroscopy (Kratos AXIS ULTRA) using with Al Kα radiation.

The friction and wear behavior of the dual films on the copper substrate was tested with a friction and wear tester (UMT-3, CETR Ltd.). Reciprocal sliding tests of a AISI 52100 steel ball (diameter 4 mm) against various to-be-tested films were run at a sliding distance of 5 mm per pass, a room temperature of about 25 °C, a relative humidity of about 40%, an applied load of 0.5 N, and a sliding speed of 10 mm/s. The friction coefficient was recorded automatically by a computer attached to the friction and wear tester. During the whole sliding process, the friction coefficient remained stable for a period of time and then abruptly rose. Three repeat tests were carried out for each specimen. The average friction coefficient, measured at a relative deviation of ±10% is cited in this article.

3. Results and discussion

3.1. Characterization of Cu_2S film on the copper substrate

The surface chemical structure of the Cu_2S film on the copper substrate by the hydrothermal reaction is confirmed by an XPS. High-resolution Cu2p3/2 and S2p peaks for the sample are illustrated in Figs. 1 and 2, respectively. Fig. 1a shows the Cu2p3/2 peak of the clean polished Cu surface. For this surface, the intensity of the satellite peak feature is very low relative to the main photoemission peak with binding energy of 932.7 eV, showing the existence of copper mainly in a metallic (Cu(0)) or cuprous (Cu(I)) because Cu(0) and Cu(I) have, within the resolution of conventional XPS measurements, identical binding energies (±0.1 eV) [22–24]. For the Cu_2S film on the copper substrate as shown in Fig. 1b, almost same spectrum as Fig. 1a is observed. The resulting S2p spectrum (Fig. 2) shows one peak at a binding energy of 161.8 eV, in agreement with the accepted binding energy value for S^{2-} in Cu_2S [25,26]. Therefore, it is reasonable to support the conclusion that the sample is mainly composed of Cu_2S on the copper substrate.

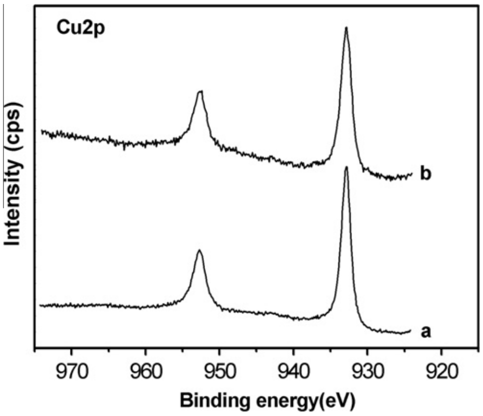

Fig. 1. Cu2p photoelectron spectra for (a) a cleaned copper and (b) the Cu_2S film on the copper substrate.

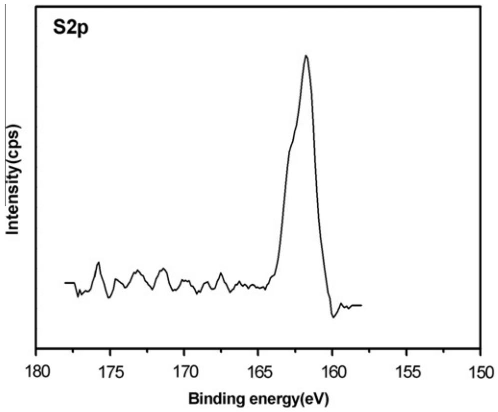

Fig. 2. S2p photoelectron spectra for the Cu_2S film on the copper substrate.

The morphology of the Cu_2S film on the copper substrate is observed by SEM. Fig. 3a is taken from the cleaned copper substrate, showing only polishing scratch surface. The granular-like surface was observed for Cu_2S film on copper substrate (Fig. 3b). It is clearly indicated that the textured surface is formed on the copper substrate after hydrothermal reaction.

3.2. Characterization of the stearic acid overcoat

Contact angle data were collected to determine the relative wettability of the various samples. The bare copper surface possesses hydrophilic properties with a WCA of 65°. The WCA increases to 103° after the bare copper substrate is immersed in a stearic acid solution for 24 h. Such a increase in the WCA of the copper substrate is attributed to the self-assembly of a stearic acid overcoat, leading to significant decrease of the surface free energy, as what have been reported for hydrophobic methyl-terminated thiols on gold [27], silanes on silicon [28], and alkanoic acid on stainless steel substrate [29]. Therefore, it can be inferred that immersion of the copper substrate in the ethanolic solution of stearic acid results in a stearic acid overcoat thereon.

The WCA is 103° for Cu_2S film on the copper substrate after it was hydrothermally treated, showing some hydrophobicity. After the sulfurized copper substrate is immersed in the ethanolic solution of stearic acid for 24 h, the WCA significantly increases to 145°. This demonstrates that the granular-like structure of the Cu_2S film (as shown in Fig. 3b) is critical to bringing about high hydrophobicity. Besides, a water droplet can hardly be attached to the surface, as indicated by a sliding angle of around 5°. The high WCA and the low sliding angle of the as-prepared high hydrophobic organic-inorganic composite film indicate that the water droplets do not penetrate into the grooves but are suspended on the granular-like films.

An FT-IR microscope equipped with a diffuse reflectance infrared spectrometric attachment was used to analyze the chemical feature of the stearic acid overcoats on both bare and sulfurized copper substrates, where solid stearic acid was also analyzed for a comparison. Relevant results are shown in Figs. 4 and 5.