A REVIEW ON EFFECT OF ELCTROETCHING ON COPPER SUBSTRATE TO ACHIEVE SUPERHYDROPHOBICITY

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ABSTRACT

The interest in highly water-repellent surfaces has grown in recent years due to the desire for self-cleaning surfaces. A super-hydrophobic surface is one that achieves a water contact angle of 150 ^{o} or greater. This article explores the different approaches used to construct super-hydrophobic surfaces and identifies the key propertiesof each surface that contribute to its hydrophobicity.The models used to describe surface interaction with water are considered, with attention directed to the methods of contact angle analysis. A copper substrate was etched in the mixed solution by different methods to generate a desired roughened structure and surface contact angle. The morphology and microstructure of as-prepared etched Cu surface were observed with a field-emission scanning electron microscope, and its friction-reducing and anticorrosion abilities were evaluated in relation to water contact angle measurements, X-ray diffrac-tion (XRD), X-ray photoelectron spectroscopy (XPS), potentiodynamic polarizationand electrochemical impedance spectroscopy techniques. Wettability of solid surfaces is an important property and depends both on surface roughness and on surface chemistry.

Keyword: *hydrophobic effect, lotus effect, self-cleaning, super-hydrophobicity, surface chemistry, water-repellent materials*

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1. INTRODUCTION

Wetting is one of the most important properties of liquid/fluids to spread over a solid substrate. Wetting a solid by liquid is of great technological importance. Some applications require a good wetting between liquid and substrate surface such as soldering, printing, whereas some others demand poor wetting (or repellence) such as painting and solar panels. Contact angle is a measure of the degree of wetting or wettability of a surface by a liquid [**1**].

A surface is classified as either hydrophilic (loving water) or hydrophobic (scared of water) by how it interacts, or sticks to water drops. Usually, if the contact angle of water is smaller than 90° (or significantly low), the surface is regarded as hydrophilic. A surface which exhibits liquid drop with a contact angle over 90° is considered as hydrophobic. However, few surfaces are repellent to water droplet i.e., extremely difficult to wet. A super-hydrophobic surface is one that repels water to such an extent that the contact angles obtained are extremely high; they are generally defined as surfaces with water contact angles above 150°, but it has also been less commonly adopted as 150° [**2**]. This is also referred to as the lotus effect.

Figure 1 : Lotus leaf showing superhydrophobic property

Superhydrophobic surfaces were first observed on plants and animals [**3**]. Such surfaces have received interest in many fields such as water-repellent, self-cleaning, contamination-inhibiting and anti-icing. Superhydrophobic surfaces are generally produced by roughening or by fabrication of a micro or nano rough surface **[4]**.

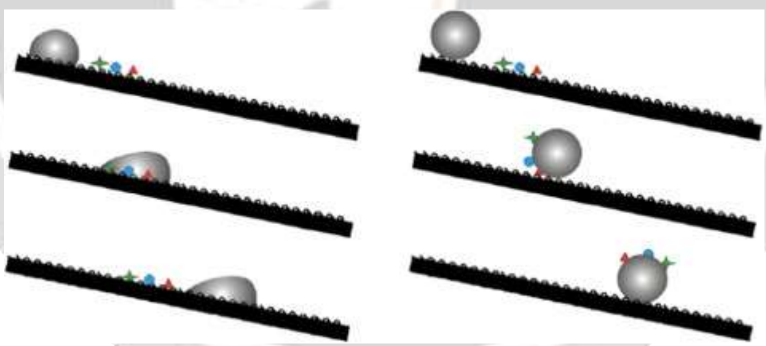

Figure 2: Self Cleaning ability of superhydrophobic surface.

Copper [Cu] has excellent property such as good ductility, electrical and thermal conductivity. Due to these properties Cu is often used in production of electrical conductors, heat exchangers, plumbing applications etc. In spite of these advantages copper is highly susceptible to corrosion i.e. oxidation [**5, 6**]. Copper (Cu) is the preferred metal for creating multilevel interconnects structures in ultra-large scale integrated circuits due to its high electrical conductivity and resistance to electromigration. One of the major challenges in Cu applications is the prevention of Cu corrosion and the resulting increase in resistivity, which leads to inferior device performance and failure [**7**]. These artificial super-hydrophobic surfaces have been fabricated mostly by tailoring surface topography and using techniques such as electrochemical deposition, chemical etching, phase separation, chemical vapor deposition, sol–gel processing, and so on [**8].** Most of those methods are subject to certain limitations, such as severe conditions, tedious fabrication, expensive materials, and poor durability, which block superhydrophobic surfaces to be applied into industries smoothly. The major concerns of electrodeposited conducting polymer coatings are water permeability and weak adhesion **[9,10].**

2.ElectroEtching

Electroetching process is the process of removing a layer on a metal surface through a chemical reaction and is an effective method for obtaining rough surfaces. Chemical etching is one of the oldest nontraditional machining processes. It uses strong chemical solution, which is called etchant, to remove unwanted workpiece material by controlled dissolution. The process is widely used in electronics, precision engineering and medical industries to produce micro-components. It is also a useful process in removing material from sheet components to reduce weight. The process is sometimes called chemical machining, chemical milling, wet etching, etching. Copper, as one of the major commercial engineering materials, is extensively used in various industries such as electronics, automotive and chemical industries because of its excellent electrical and thermal conductivities, good strength and fatigue resistance, high corrosion resistance and ease of fabrication.

2.1 Etching on copper by oxidation assisted surface acid process:

A copper substrate was etched in the mixed solution of (NH4_2S2O8 and HCl by oxidation-assisted surface acid etching process to generate a desired roughened structure (coded as etched Cu). Resultant etched Cu surface was then immersed in silver nitrate solution to allow incorporation of silver sub micro-particles through replacement reaction to afford a lotus-leaf-like structure (denoted as etched Cu–Ag). Etched Cu–Ag surface was finally modified with stearic acid (abridged as STA) to provide etched Cu–Ag composite coating with superhydrophobicity (coded as etched Cu–Ag/STA). The morphology and microstructure of as-prepared etched Cu–Ag surface were observed with a field-emission scanning electron microscope, and its friction-reducing and anticorrosion abilities were evaluated in relation to water contact angle measurements. It was found that the as-prepared etched Cu–Ag surface is composed of micro-protrusions and sub micro-mastoids with dual-scale structure similar to that of the lotus leaf. Besides, etched Cu–Ag/STA composite coating has a static water contact angle of 160.5_ and shows very low adhesion for water droplet, and it possesses good friction-reducing ability. The evaluation of its anticorrosion ability indicates that the superhydrophobic surface has a certain anticorrosion ability against the solution whose pH values are within 5~9. Moreover, the water contact angles(WCAs) of the superhydrophobic surface almost remain the same after immersion in the solution with different pH values, but its contact angle hysteresis values (CAHs) increase slightly thereafter.

2.2 Etching of copper by polymer plating:

The 6-(*N*-allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium) (ATP)was used to fabricate polymeric thin film on pure copper plate to achieve super-hydrophobic surface.The copper plates were pretreated to gain rough surfaces by chemical etching before polymer plating.The polymer plating process of ATP on copper in Na2CO3 aqueous solution and the growth mechanism ofpoly(6-(*N*-allyl-1,1,2,2-tetrahydro-perfluorodecyl) amino-1,3,5-triazine-2,4-dithiol) (PAT) thin film was studied by means of cyclic voltammetry. The polymeric film was investigated by using X-ray photoelectronspectroscopy (XPS), and the etched surfaces were observed by atomic force microscopy (AFM). A contact angle meter was applied to measure the contact angles with distilled water drops at ambient temperature. The experimental results indicated that the polymeric film formed on rough copper surface exhibits super-hydrophobic property with a distilled water contact angle of 155◦. The wettability ofcopper surfaces was discussed on the basis of both Wenzel and Cassie theories. The etching and polymerplating processes are time-saving, inexpensive, environmental and fairly convenient to carry out. Itis expected that this technique will advance the production of super-hydrophobic materials with new applications in large scale. Moreover, this kind of thin film can be used as a dielectric material due to its insulated feature.

2.3 Etching on copper by pretreating it with *n*-tetradecanoicacid:

Pretreated by a *n*-tetradecanoic acid (CH3(CH2)12COOH) etch, the super-hydrophobic film was formed on the fresh copper surface. The filmstructure was probed with contact angle measurement and scanning electron microscopy(SEM). The results suggest that the structure of the film is similar to haulm or flower and the seawater contact angle is larger than 150°. Moreover, the corrosion resistance of bare and modified samples in seawater were investigated by cyclic voltammograms(CV) and electrochemical impedance spectroscopy(EIS). Experimental results show that the corrosion rate of Cu with super-hydrophobic surface decreases dramatically because of its special microstructure. The concentration of around 0.06M and the immersion time of 10days are ideal for the formation of stable flowerlike structure. Therefore, our study is of great importance for constructing microscale structures endowed with resistance to corrosion. And experimental results prove that the super-hydrophobic surface can improve the corrosion resistance of copper significantly. It is believed that this method should be easily applied to large scale production of super-hydrophobic engineering materials with ocean industrial applications.

2.4 Etching on copper with calcination process:

Superhydrophobic surfaces on copper substrates are prepared by combining the etchingand calcination treatment processes. The surface morphologies, wettability, chemical composition andcorrosion resistance are characterized by means of scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), water contact angle, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The micro-nano catkin-like structure formed on the copper substrate showed a contact angle of 157.6◦after etching in an ammonia solution for 20 h, calcinations in air at 340◦C for 10 min and immersion in an ethanol solution containing stearic acid for 3 h. The superhydrophobic film on the copper substrate exhibited a good corrosion resistance a in 3.5 wt.%NaCl aqueous solution with potentiodynamic polarization and EIS measurements. This method could provide an effective route to fabricate superhydrophobic surface with inhibitive andself-cleaning properties for various applications.

2.5 Etching on copper by HNO3 technique:

Superhydrophobic rough structure was prepared on copper wafer via HNO3 etching technique with the assistance of Cetyltrimethyl Ammonium Bromide (CTAB) and ultrasonication. After modification of1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDTES), the copper wafer showed stable superhydrophobicity. The morphologies, chemical compositions and hydrophobicity of the substrates were analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and water contact angle measurement, A facile CTAB and ultrasonication assisted HNO3 etching technique was established to fabricate rough structure on the copper wafer. The investigation showed that it was the joint action of CTAB surfactant and ultrasonication that caused the formation of dense and spherical micropits. After being modified with FDTES, the surface displayed stable superhydrophobicity both in a wide temperature range and in the corrosive liquids with a wide pH range. Compared with the traditional methods, the method we used here is simple and inexpensive. Moreover, the addition of surfactant into etching reagent greatly expands the applications of chemical etching in constructing appropriate roughness on solid material surfaces.

2.6 Etching of copper surface graft polymerisation:

With the objective of developing materials with repellent surfaces by combining both low surface energy and rough structure, superhydrophobic fluoropolymer films were prepared via surface graft polymerisation from copper substrates. A vinyl-terminated trimethoxysilane was firstly immobilised on the etched copper surface to introduce active carbon–carbon double bonds. Subsequent graft polymerisation of 2,2,3,4,4,4-hexafluorobutyl acrylate (HFBA), in the presence of a polymerisation initiator 4,40-azobis-(4-cyanpentanoic acid), yielded the fluoropolymer films on the copper substrates. The resultant P(HFBA)-grafted surfaces not only exhibited desired superhydrophobic property with water contact angle above 150°, but substantially improved the corrosion resistance of copper substrates.

3. CONCLUSIONS

In summary, stable and robust superhydrophobic copper materials is obtained by electroetching process. The superhydrophobic materials show excellent superhydrophobicity, mechanical durability and chemical stabilities. Meanwhile, the superhydrophobic surfaces exhibit excellent oil/water selectivity in the oil spill clean and ice-overresistance. The superhydrophobic film on the copper substrate exhibited a good corrosion resistance a in 3.5 wt.%NaCl aqueous solution with potentiodynamic polarization and EISmeasurements. After performing the above technique the copper surfaces shows the property superhydrophobic surfaces which are applicable for different purposes.

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