

**AN AQUEOUS SOLUTION FOR FORMING AN ALKYLTHIOL SELF-
ASSEMBLED MONOLAYER AND A METHOD FOR FORMING THE SAME
USING THE SOLUTION**

5 FIELD OF THE INVENTION

This invention relates to an aqueous solution for forming an alkylthiol self-assembled monolayer and a method for forming the same using the solution. More particularly, this invention relates to an aqueous solution comprising an
10 alkylthiol and a mixture of non-ionic surfactants for forming an alkylthiol self-assembled monolayer on a substrate and a method for forming the same using the solution.

BACKGROUND

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Self-Assembled Monolayers, SAMs are organized monolayer films of organic compounds that are absorbed spontaneously from solution or gas phase onto a solid substrate. Such organic compounds consist of chemical functionalities which possess a special affinity for the targeted substrate. Depending on the choice of
20 organic compounds and the chemical functionalities displayed, the formation of SAMs on the targeted substrate will change the characteristic(s) of the targeted substrate.

Since it is possible to design specific compounds for SAMs formation, this
25 technology provides the possibilities of producing various innovative characteristics to existing surfaces. Indeed, it is known from prior art that SAMs technology have been used to obtain favourable characteristics, such as corrosion prevention and wear protection, on existing materials.

30 Further, it is known from prior art that SAMs formation can occur with metallic substrates. Therefore, the technology involved with SAMs is ubiquitous in the electronic industry. The prior art provides several organic compounds with specific chemical functionality known to bind to specific metals, metal oxides and

semiconductors. In particular, the more common examples are derivations of alkanethiols.

Unfortunately, the bonds formed between the SAMs and the solid substrates are susceptible to oxidation and degradation. This adversely affects the structure, and hence the quality of SAM formation on the substrates. An example of a method used to impede or prevent degradation of the SAM layer is described in US Patent Publication Number 2005/0221081, as published on 6 October 2005 in the names of Liu *et al.* The method described in this publication uses a solvent which may be water, an aqueous solvent, an aqueous buffer, or a mixture thereof. However, as with most methods employed, this method of SAM formation is a slow process, requiring hours and/or days to complete.

Similarly, the formation of alkoxycyanbiphenyl thiols SAMs on gold described in "Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold surface using a lyotropic liquid crystalline medium", as published in 2007 in the name of Ganesh *et al.*, is achieved at room temperature and requires about 15 hours. The slow nature of such SAMs formation is a disadvantage.

In the past, single non-ionic surfactant has been used to solubilise alkylthiol in aqueous solution. The concentration of non-ionic surfactant is at 40% and the process time is similarly slow, requiring at least few minutes to achieve a single molecular layer on, for example, gold surface. The cloudy point of the SAMs working solution is only about 40 to 50°C and the bath life of the SAM solution is only about few days due to oxidation of alkylthiol in the solution.

In general, the methods of forming SAMs on metallic substrates, as described in the prior art, are slow processes and formation generally ranges from several hours to few days. This is attributed to the fact that SAMs have to be absorbed onto the metallic substrate, and spontaneous organization occurs thereafter. Furthermore, the use of alkanethiols and its derivatives, which are the most commonly used compounds for SAMs formation, are usually associated with organic based solvents. Such solvents restrict the use of heat in SAMs formation,

speed processes, such as reel-to-reel process, and adversely affects productivity. In addition, such solvents emit volatile organic chemicals that may be detrimental to health and the environment.

- 5 In light of the above, there is therefore a need to provide a solution and a method for forming SAM on substrate that seek to address at least one of the above problems, or at least to provide an alternative.

SUMMARY OF INVENTION

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The above and other problems are solved and an advance in the art is made by an aqueous solution and a method for forming an alkylthiol self-assembled monolayer in accordance with this invention. The aqueous solution and the method in accordance with this invention have the advantage of forming an alkylthiol self-assembled monolayer in a relatively short period of time. A second advantage of the aqueous solution in accordance with this invention is that the aqueous solution is free of organic solvents and hazardous agents, and this provides an environmentally and user friendly method for forming alkylthiol self-assembled monolayer.

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In accordance with an embodiment of this invention, an aqueous solution for forming an alkylthiol self-assembled monolayer on a substrate is provided. The aqueous solution comprising an alkylthiol and a mixture of non-ionic surfactants for forming micelle networks within the aqueous solution.

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In accordance with some embodiments of this invention, the mixture of non-ionic surfactants comprises two or more non-ionic surfactants selected from a group comprising castor oil polyglycol ether, polyoxypropylene-polyoxyethylene block copolymer, ethoxylated oleyl-cetyl alcohol and polyethylene glycol tert-octylphenyl ether. In certain embodiments of this invention, the mixture of non-ionic surfactants comprises at least three or more of the non-ionic surfactants.

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In accordance with some embodiments of this invention, the mixture of non-ionic

In accordance with some embodiments of this invention, the alkylthiol is in a concentration of 0.01M to 0.05M.

- 5 In accordance with some embodiments of this invention, the aqueous solution further comprises a pH buffer system for controlling pH of the aqueous solution. Preferably, the aqueous solution has a pH of between 3 and 11.

10 In accordance with another embodiment of this invention, a self-assembled monolayer comprising an aqueous solution in accordance with this invention is provided.

15 In accordance with yet another embodiment of this invention, a method for forming an alkylthiol self-assembled monolayer is provided. The method comprises providing a substrate having at least one surface; and applying an aqueous solution comprising an alkylthiol and a mixture of non-ionic surfactants directly or indirectly onto the at least one surface of the substrate.

20 In accordance with some embodiments of this invention, the aqueous solution is applied to the at least one surface of the substrate by immersing the substrate in the aqueous solution for about 5 to 20 seconds.

25 In accordance with a further embodiment of this invention, a further method for forming an alkylthiol self-assembled monolayer is provided. The method comprises mixing an alkylthiol with a mixture of non-ionic surfactants to obtain a solution; diluting the solution with water; heating the solution with agitation to obtain a homogenous aqueous solution; immersing a substrate in the homogenous aqueous solution to coat the substrate; rinsing the coated substrate; and drying the coated substrate.

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In accordance with the further embodiment of this invention, the method further comprises mixing the solution containing the alkylthiol and the mixture of non-ionic surfactants with a pH buffer system. The method also further comprises controlling

In accordance with the further embodiment of this invention, the substrate is immersed in the aqueous solution at a temperature in the range of 20°C to 80°C. The substrate is immersed in the solution for 5 to 20 seconds.

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In accordance with another embodiment of this invention, a self-assembled monolayer obtainable by the method in accordance with this invention is provided.

10 In accordance with yet a further embodiment of this invention, a coated article comprising a substrate and a self-assembled monolayer obtainable by the method in accordance with this invention is provided.

BRIEF DESCRIPTION OF THE DRAWINGS

15 The above and other advantages and features of this invention are described in the following detailed description and are shown in the following drawings:

Figure 1 shows an Electroless Nickel Immersion Gold (ENIG) plated sample after subjecting to sulfur dioxide vapor test. The gold layer has a thickness of 0.028 μm .

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Figure 2 shows an ENIG plated sample which was treated by the aqueous solution of the present invention and after subjecting to sulfur dioxide vapor test. The gold layer has a thickness of 0.028 μm .

25 Figure 3 shows an immersion silver coated copper sample after subjecting to sulfur dioxide vapor test. The silver layer has a thickness of 0.038 μm .

Figure 4 shows an immersion silver coated copper sample which was treated by the aqueous solution of the present invention solution and after subjecting to sulfur dioxide vapor test. The silver layer has a thickness of 0.038 μm .

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Figure 5 shows the polarization curves of different copper samples in 0.5M of sodium chloride solution.

Figure 6 shows the contact angle of a bare copper sample. The contact angle is 85°.

5 Figure 7 shows the contact angle of a copper sample after subjecting to SAM treatment. The contact angle in this case is 136°.

10 Figure 8 shows two copper coupons A and B that have gone through SEM scanning after a 24 hours Neutral Salt Spray test. Copper coupon A is bare copper and copper coupon B is a SAM treated copper.

Figure 9 shows an ENIG plated sample after subjecting to sulfur dioxide vapor test. The gold layer has a thickness of 0.068 µm..

15 Figure 10 shows an immersion silver coated copper sample after subjecting to sulfur dioxide vapor test. The silver layer has a thickness of 0.064 µm.

DESCRIPTION OF THE INVENTION

20 The present invention relates to an aqueous solution for forming an alkylthiol self-assembled monolayer on a substrate. The aqueous solution comprises an alkylthiol and a mixture of non-ionic surfactants.

25 The term "non-ionic surfactants", as used with respect to the present invention, will generally refer to surface active agents which do not dissociate into ions in aqueous solutions, unlike anionic surfactants which have a negative charge and cationic surfactants which have a positive charge in aqueous solution.

30 Suitable non-ionic surfactants include, but are not limited to, castor oil polyglycol ether, polyoxypropylene-polyoxyethylene block copolymer, ethoxylated oleyl-cetyl alcohol and polyethylene glycol tert-octylphenyl ether, etc.

In one embodiment of the invention, the aqueous solution comprises at least two non-ionic surfactants. In a preferred embodiment, the aqueous solution comprises

Preferably, the mixture of non-ionic surfactants is present in a concentration of about 1% to 4% w/v.

5 The term "alkyl" as used herein is as understood by those in the art. Alkyl groups, unless explicitly stated otherwise, refers to straight or branched chain saturated aliphatic groups typically having from 2 to 8 carbon atoms. Alkyl groups can be substituted with by one or more substituent groups, unless explicitly stated otherwise.

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The term "alkylthiol" as used herein has a general formula $R-(CH_2)_n-SH$, where SH is a thiol head group, and n may represent any number from 7 to 17 depending on the desired character of the layer to be formed. R may represent any suitable terminal functional group which will confer a desired character on the SAM, depending on the intended use.

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By using alkylthiols with different terminal functional groups, a wide variety of chemical functionalities can be introduced at the surface of the substrate. Surface properties such as contact angle can be changed over a very wide range of values.

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The term "contact angle" as used herein has its ordinary meaning as known to those skilled in the art. It is the angle at which a liquid interface meets the substrate surface.

25 Suitable alkylthiols that can be used in the present invention include, but are not limited to, those with general formula $R-(CH_2)_n-SH$, where SH is a thiol head group, n represents any number from 7 to 17 and R represents any suitable terminal functional group selected from the group consisting of methyl (CH_3), carbmethoxy (CO_2CH_3), carbethoxy ($CO_2CH_2CH_3$) and carbphenoxy $CO_2CH_2C_5H_6$.

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Preferably, the alkylthiol is present in the aqueous solution in a concentration of about 0.01M to 0.1M, more preferably, about 0.025M.

The aqueous solution of the present invention may further comprise a buffer system for maintaining pH of the aqueous solution within a preferred range. Preferably, the aqueous solution has a pH between 3 and 11, depending on the types of surface that the aqueous solution is applied to. In one embodiment of the invention, the pH of the aqueous solution is maintained within a range of 6.0 to 9.0 when the aqueous solution is applied to a substrate with a gold surface. In another embodiment of the invention, the pH of the aqueous solution is maintained within a range of 8.0 to 11.0 when the aqueous solution is applied to a substrate with a silver surface. In yet another embodiment of the invention, the pH of the aqueous solution is maintained within a range of 3.0 to 6.0 when the aqueous solution is applied to a substrate with a copper surface. In a further embodiment of the invention, the pH of the aqueous solution is maintained within a range of 8.0 to 11.0 when the aqueous solution is applied to a substrate with a nickel or tin surface.

In one embodiment of the invention, the pH buffer system comprises an organic amine and an organic phosphonic acid. The pH range is controlled by varying the ratio of the organic amine and the organic phosphonic acid in the aqueous solution. One skilled in the art will recognize that other suitable buffer system may be used without departing from the present invention.

In one embodiment of the invention, the organic components present in the aqueous solution include alkylthiol, non-ionic surfactants and the components making up the buffer system. In a preferred embodiment, the total organic components concentration in the aqueous solution is from 2 to 20% w/v. More preferably, the concentration of the organic components in the working solution is about 5 to 10% w/v.

Any substrate on which alkylthiol SAM will form using the aqueous solution of the present invention may be used in the invention. The substrate may take any suitable form, for example, a foil, a chip or a wafer of the desired material. Suitable substrate materials include, but are not limited to, pure metals such as gold, silver, copper, bronze, nickel, tin, etc and alloys, as will be appreciated by those of skill in

a layer of substrate material deposited on the substrate by any known deposition process.

As will be appreciated by those of skill in the art, the choice of non-ionic surfactants and the moieties which make up the aqueous solution will be determined in part by the nature of the substrate and/or surface to be coated. In view of the teachings and disclosure contained herein and given the level of skill in the art, it will be within the means of those in the art to select two or more suitable non-ionic surfactants based on the particular substrate and/or surface to be coated for stabilizing the aqueous solution without undue experimentation.

The aqueous solution provided by the present invention is stable as the present invention uses a mixture of non-ionic surfactants instead of a single non-ionic surfactant to solubilize alkylthiol in water, to form micelle networks within the aqueous solution. The alkylthiol in the aqueous solution is stabilized by the micelle networks formed within the solution. The mixture of non-ionic surfactants is homogenously dispersed in the aqueous solution over alkylthiol concentration of about 0.01M to 0.1M. The micelle networks, together with the pH buffer system in the aqueous solution, prevent oxidation of alkylthiol, especially at high temperature (for example, at about 80°C). This makes the aqueous solution of the present invention very stable at high temperature. The high temperature of the aqueous solution helps to accelerate the delivery of the micelle networks to the surface of the substrate to be coated. The micelle networks, together with the pH buffer system in the aqueous solution, allow the aqueous solution to form a single molecular layer effectively at low alkylthiol concentration with short immersion time.

The aqueous solution of the present invention can be used at ambient temperature to about 80°C. The solution is free of organic solvents and hazardous agents. This provides an environmentally and user friendly method for forming alkylthiol self-assembled monolayer on a substrate.

In another aspect of the present invention, a method for forming an alkylthiol self-

with the invention is provided. The method comprises the steps of mixing an alkylthiol with a mixture of non-ionic surfactants to obtain a solution. The solution is then diluted with water to obtain an aqueous solution. The aqueous solution is then heated with vigorous agitation. In a preferred embodiment, the aqueous solution is heated to a temperature of about 40°C to 80°C. The solution can be agitated by stirring or by other means known in the art. The solution is agitated until a homogenous and clear solution is obtained before a substrate is immersed into the aqueous solution to coat the substrate with the aqueous solution. In a preferred embodiment, the solution is agitated for about 30 minutes at a temperature of about 40°C to 60°C.

Preferably, the temperature of the aqueous solution is maintained within a range of 20°C to 80°C, more preferably, the temperature is maintained within 50°C to 65°C.

The immersion time of the substrate in the aqueous solution varies according to the types of substrate and/or surface to be coated. In general, the immersion times varies from about 5 to 20 seconds. For example, in a case where a substrate with gold surface is to be coated, the immersion time can be about 5 to 10 seconds. In a case where a substrate with silver surface is to be coated, the immersion time can be about 5 to 15 seconds. In a case where a substrate with copper surface is to be coated, the immersion time can be about 5 to 20 seconds. In a case where a substrate with nickel and/or tin surface is to be coated, the immersion time can be about 10 to 20 seconds.

After the aqueous solution is coated onto the substrate, the coated substrate is rinsed with water and dried using any suitable methods known in the art. In a preferred embodiment, the coated substrate is dried using hot air. In one embodiment of the invention, the coated substrate is dried at a temperature of about 70°C to 80°C. In another preferred embodiment, the coated substrate is rinsed with warm deionized water at a temperature of about 40°C to 50°C.

In a further aspect of the present invention, a self-assembled monolayer (SAM) formed by using the aqueous solution in accordance with the present invention is

spontaneously upon immersion of a suitable substrate into the aqueous solution of the present invention. The SAM formed using the aqueous solution of the present invention has a more densely defect-free molecular structure as compared to those of the prior art, which are generally formed using organic solvent based solutions.

5 The SAM formed using the aqueous solution of the present invention has a superior hydrophobic property than those of the prior art as the solution of the present invention can significantly increase oxidation resistance and corrosion resistance of any suitable metal surface finishing.

10 For example, the SAM formed on gold or silver surface as a pore blocker can reduce the deposit layer thickness of up to 50% while maintaining the same or even better performance (see Figures 2 and 9 for application on gold surfaces; and Figures 4 and 10 for application on silver surfaces). The SAM can also increase the corrosion resistance and tarnish resistance of the gold and silver surfaces.

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Silver is prone to tarnishing and corrosion, especially when it is exposed to heavily polluted environment. The aqueous solution of the present invention can form SAM on silver surface which can in turn help to increase corrosion resistance and tarnish resistance of the silver surface.

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When the aqueous solution of the present invention is applied to nickel or tin surface, the solution functions as an alternative to chrome passivation solution used in the prior art.

25 Copper is prone to oxidation which will cause failure in conductivity of electrical and electronic devices. The method currently employed in the prior art to prevent copper from oxidizing is to apply silver plating or electroless nickel plating onto the copper surface. The most commonly used silver plating process is the silver cyanide plating process and this process is often very costly, as much time and
30 efforts are required to treat the harmful waste materials produced during the process before the harmful waste materials are disposed into the environment. Electroless nickel plating is not environmentally friendly as it generates bulk waste solutions. The aqueous solution of the present invention can be used to form SAM

cyanide plating process which otherwise will be required if conventional solution is used to form the SAM.

5 The SAM formed on, for example, gold, silver and copper surfaces using the aqueous solution of the present invention exhibits effective protection for the said surfaces as it enhances the corrosion resistance and tarnish resistance of the said surfaces (see Examples below).

10 The aqueous solution of the present invention can be applied to different thickness of substrates or metals, for example, gold or silver deposit layers. Corrosion resistance tests have been carried out. The results show that the aqueous solution of the present invention is excellent pore blocker and it can significantly increase the corrosion resistance of ultra-thin gold or silver deposit layer, for example, of about 10 to 30 nm (see Example 5 below). The results also show that the aqueous
15 solution of the present invention can increase the corrosion resistance of copper surface. In the test, the copper surface coated with the aqueous solution of the present invention is shown not to have been tarnished and/or corroded even after the surface was immersed in tap water or 5% sodium chloride solution for more than one week.

20 The increase of gold and silver prices has forced electronic industry to reduce gold and silver thickness and yet to retain or even improve its performance. The green regulatory also drives industry to look for green process. Currently, lubricant oil or solvent base SAMs are applied for industrial requirements. SAMs aqueous
25 solution, a promising nanotechnology, are attracting much attention due to its environmentally and user-friendly process as well as its cost effectiveness.

30 From the above description of the invention, it can be understood that the aqueous solution and method of the present invention have several advantages. One of which is that the aqueous solution and the method of the present invention can be applied to high speed reel-to-reel application which has a short process time of about 5 to 10 seconds. The SAM in the present invention can be formed in a relatively short period of time as herein described above and it is therefore suitable

Secondly, the aqueous solution of the present invention is more stable than those of the prior art as micelle networks are formed within the aqueous solution to stabilize the solution.

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Thirdly, the aqueous solution can be applied across a very wide temperature range, of about 20°C to 80°C and a wide concentration range, of about 0.01M to 0.1M (alkylthiol) as described hereinabove.

10 Further, the aqueous solution has diversity functions as it can be applied to various metal surfaces. The aqueous solution of the present invention also does not emit volatile organic chemicals as it contains no organic solvents. The solution therefore will not pose any harm to the environment and health. Furthermore, the aqueous solution and the method of the present invention can achieve coating
15 without using any organic stains and with no changes in contact resistance.

The aqueous solution of the present invention incorporates nanotechnologies which provides an environmentally and user friendly method, and cost effective organic finishes as compared to those currently known to be used in the art or
20 under development. The aqueous solution also provides multi-functional coatings for diversified substrates or under-layers. The substrates or surfaces to be coated can simply be immersed in an appropriate manner in the aqueous solution of the present invention, rinsed briefly, if necessary, and dried under suitable condition.

25 The invention will be further described in the following example embodiments of the invention, which do not limit the scope of the invention as set forth in claims.

EXAMPLES

30 EXAMPLE 1

Electroless Nickel and Immersion Gold Plating (ENIG) over a copper substrate

A copper clad laminate test coupon was plated with a layer of electroless nickel using SSC NI-18M chemicals (available from Stella Specialty Chemicals Pte Ltd, Singapore). The copper coupon was properly cleaned and etched before it was immersed in a palladium activator solution. After that, the copper coupon was
5 dipped in a SSC NI-18M electroless nickel bath solution comprising 6 g/L of nickel ions; 210 ml/L of SSC NI-18M additives and balance water at a temperature of about 85°C to 90°C for 20 minutes.

The electroless nickel coated copper coupon was dipped in the immersion gold
10 bath using SSc ImAU-08 chemicals (available from Stella Specialty Chemicals Pte Ltd, Singapore) for 5 and 15 minutes respectively to deposit thin gold layers over the electroless nickel coated copper coupons. The gold layers obtained have a thickness of about 0.028 µm and 0.068 µm respectively.

15 EXAMPLE 2

Immersion Silver Plating (ImAg) over a copper substrate

A copper clad laminate test coupon was plated with a layer of immersion silver
20 using AlphaSTAR chemistry (available from Enthone Inc., West Haven, USA). The copper coupon was properly cleaned and etched before it was immersed in an immersion silver bath comprising 0.5 to 1.0g/L of silver ions; 370 ml/L of AlphaSTAR additives and balance water at a temperature of about 48°C to 55°C for 15 and 30 seconds respectively. The thickness of the immersion silver layers is
25 about 0.038 µm and 0.064 µm respectively.

EXAMPLE 3

Sulfur Dioxide Porosity Testing for ENIG and ImAg Plated Copper Coupons

30 The freshly prepared ENIG and ImAg plated copper coupons in Examples 1 and 2 were placed in a 700 ml glass desiccators containing 20 mL of sulfurous acid (>5%) for 4 hours at ambient temperature. Sulfur dioxide vapor was evolved and

Photographs of the testing coupons were taken after 4 hours of exposure to the sulfur dioxide vapor. The photographs obtained were as shown in Figures 1, 3, 9 and 10. A lot of black spots were formed on the testing coupons surfaces and this indicates the formation of nickel sulfides (NiS_x), silver sulfides (AgS_x), and copper sulfides (CuS_x). This shows that the porosity of thin gold and silver layers is relatively high.

EXAMPLE 4

Applying an Aqueous Self Assembled Monolayers (SAMs) Solution of the present invention to copper coupons

An aqueous SAMs solution containing 5% v/v of concentrated mixture comprising alkylthiol, a mixture of non-ionic surfactants containing castor oil polyglycol ether, polyoxypropylene-polyoxyethylene block copolymer and polyethylene glycol tert-octylphenyl ether, and a buffer system, was diluted with water. The solution was then heated to 60°C to 80°C with stirring to obtain a homogenous solution.

Copper cladded laminate test coupons were properly cleaned and etched before they were immersed in the aqueous solution for 10 to 20 seconds at about 50°C to 60°C. The test coupons were then rinsed with water and dried at a temperature of about 80°C to 90°C.

The contact angle formed between the copper and the water droplet indicates the presence of SAMs (see Figures 6, 7). Figure 6 shows a contact angle of 85° of a bare copper sample. Figure 7 shows a contact angle of 136° of a copper sample after it is subjected to SAM treatment. The contact angle was increased by about 50° and this indicates that the SAMs coated copper surface is hydrophobic.

To determine the protecting ability of SAMs of the present invention, potentiodynamic techniques were applied. Figure 5 shows the polarization curves of the bare copper coupon and the SAMs coated one in 0.5M sodium chloride

anode were significantly decreased. This shows that the SAMs of the present invention are effective corrosion inhibitors.

5 A Neutral Salt Spray (NSS) test, which is an accelerated corrosion test that predicts the corrosion resistance of any coated substrate, was carried out on the coated samples. Figure 8 shows two copper coupons A and B that have gone through SEM scanning after a 24 hours NSS test. Copper coupon A is the bare copper and copper coupon B is the SAMs treated copper. The results show that the surface of coupon A was seriously tarnished and oxidized (color changed and
10 corroded), and the surface of coupon B was tarnish and corrosion free.

EXAMPLE 5

Sulfur Dioxide Porosity Testing for SAMs Treated ENIG and ImAg Plated Copper 15 Coupons

The freshly prepared ENIG and ImAg plated copper coupons in Examples 1 and 2 were dipped in an aqueous SAMs solution of the present invention, which was prepared in accordance with Example 4, for 5 to 15 seconds at 50°C to 60°C. The
20 copper coupons were then rinsed with water and dried at 80°C to 90°C.

The SAMs treated copper coupons were then placed in a 700 ml glass desiccators containing 20mL of sulfurous acid (>5%) for 4 hours at ambient temperature. Sulfur dioxide vapor evolved and formed a sulfidizing atmosphere.

25 Photographs of the testing coupons were taken after 4 hours of exposure to sulfur dioxide vapor. The photographs obtained were as shown in Figures 2 and 4. From the photographs, one can see that there are no black spots formed on the surfaces of the testing coupons and this indicates that the SAMs solution of the present invention is an effective pore blocker and is able to significantly increase
30 corrosion resistance and has anti-tarnish ability. The thin gold layer (0.028 μm , Figure 2) which was treated with SAMs gave a better corrosion resistance than a thicker gold layer (0.068 μm , Figure 9) that is not treated with SAMs of the present

invention. The results were the same for silver layer (see Figure 4 which has a thickness of 0.038 μm and Figure 10 which has a thickness of 0.064 μm).

5 The above is a description of the subject matter the inventor regards as the invention and is believed that others can and will design alternative solutions and methods that include this invention based on the above disclosure.

Claims

1. An aqueous solution for forming an alkylthiol self-assembled monolayer on a substrate, comprising an alkylthiol and a mixture of non-ionic surfactants for forming micelle networks within the aqueous solution.

2. The aqueous solution according to claim 1, wherein the mixture of non-ionic surfactants comprising two or more non-ionic surfactants selected from a group consisting of castor oil polyglycol ether, polyoxypropylene-polyoxyethylene block copolymer, ethoxylated oleyl-cetyl alcohol and polyethylene glycol tert-octylphenyl ether.

3. The aqueous solution according to claim 2, wherein the mixture of non-ionic surfactants comprising at least three or more of the non-ionic surfactants.

4. The aqueous solution according to claim 1, wherein the mixture of non-ionic surfactants is in a concentration of 1% to 4% w/v.

5. The aqueous solution according to claim 1, wherein the alkylthiol is in a concentration of 0.01M to 0.1M.

6. The aqueous solution according to claim 5, wherein the alkylthiol is in a concentration of 0.02M to 0.04M.

7. The aqueous solution according to claim 1, further comprising a pH buffer system for controlling pH of the aqueous solution.

8. The aqueous solution according to claim 7, wherein the aqueous solution has a pH of between 3 and 11.

9. The aqueous solution according to claim 7, wherein the pH buffer system comprising an organic amine and an organic phosphonic acid.

10. A self-assembled monolayer comprising an aqueous solution according to any of claims 1 to 9.

11. Use of the aqueous solution according to any of claims 1 to 9 for preparing a self-assembled monolayer.

12. A method for forming an alkylthiol self-assembled monolayer on a substrate, the method comprising the steps of:

providing a substrate having at least one surface; and

10 applying an aqueous solution comprising an alkylthiol and a mixture of non-ionic surfactants directly or indirectly onto the at least one surface of the substrate.

13. The method according to claim 12, wherein the aqueous solution is applied to the at least one surface of the substrate by immersing the substrate in the aqueous solution for about 5 to 20 seconds.

14. A method for forming an alkylthiol self-assembled monolayer on a substrate, the method comprising the steps of:

20 mixing an alkylthiol with a mixture of non-ionic surfactants to obtain a solution;

diluting the solution with water;

heating the solution with agitation to obtain a homogenous aqueous solution;

immersing a substrate in the aqueous solution to coat the substrate;

25 rinsing the coated substrate; and

drying the coated substrate.

15. The method according to claim 14, wherein the mixture of non-ionic surfactants comprising two or more non-ionic surfactants selected from a group consisting of castor oil polyglycol ether, polyoxypropylene-polyoxyethylene block copolymer, ethoxylated oleyl-cetyl alcohol and polyethylene glycol tert-octylphenyl ether.

16. The method according to claim 15, wherein the mixture of non-ionic surfactants comprising at least three or more of the non-ionic surfactants.

17. The method according to claim 14, further comprising:

5 mixing the solution containing the alkylthiol and the mixture of non-ionic surfactants with a pH buffer system.

18. The method according to claim 17, further comprising:

controlling pH of the solution within a range of 3 to 11.

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19. The method according to claim 14, wherein the substrate is immersed in the aqueous solution at a temperature in the range of 20°C to 80°C.

20. The method according to claim 14, wherein the substrate is immersed in the

15 aqueous solution for 5 to 20 seconds.

21. The method according to claim 12 or 14, wherein the substrate has one or more surfaces provided by a material selected from a group consisting of gold, silver, copper, bronze, nickel and tin.

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22. A self-assembled monolayer obtainable by the method according to any of claims 12 to 21.

23. A coated article comprising a substrate and the self-assembled monolayer

25 according to claim 22.