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Optical Surface Plasmon Resonance Monitoring in a High Salinity Environment for Long Duration Sensing Applications

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Abstract

Optical sensing modes such as Surface Plasmon Resonance (SPR) are here applied to the detection surface induced processes and surface corrosion. Our recent studies have investigated the noble metals: silver, copper and gold. We present here results for silver sputter deposited films, with a sputter deposited chromium adhesion layer for exposure to a corrosive environment of standard saline solution over two months. Initial sensor design was achieved using a formalism of Fresnel's optical equations for a uniaxial multi-layered media. Changes in metal film optical properties were measured using the Kretchmann-Raether experimental optical configuration. The study found that after films were exposed to standard saline solution, their reflectivity and relative permittivity changed, detectable as

a shift in the minimum angle and shape of a SPR reflectivity curve whilst the thickness of the silver film was uncorroded.

1. Introduction

Corrosion has always been a major engineering problem and is often described as an oxidisation reaction where pure metal is removed and replaced with a metal oxide. Oxide layers are often weaker and more brittle than pure metals, and as such can lower performance, reduce metal lifespan, and ultimately cause structural failure. In the USA it was estimated corrosion cost the US economy over 276 B$ per annum, 2002 [1]. Whilst in the UK it is believed the direct cost of corrosion may be as high as 4 - 5% of UK GDP (~135 B£), a cost more often than not, passed on to consumers through increased transport, manufacturing and energy production prices. In addition to the vast industry cost caused by corrosion, there have been a number of serious accidents directly related to it. In 1992 a petrochemical pipeline in Guadalajara exploded, creating a 2 km long trench and killing 215 people. The cause of the explosion was traced back to a pipe leak created by corrosion. In the same year a Boeing 747 crashed due to a corroded strut, resulting in further loss of life. Annually thousands of barrels of oil are also spilled into the world's oceans from corroded pipelines. Such accidents can devastate sea life and cost even more to clean up. Corrosion can go undetected for a long time until a key component fails, or has been irreparably damaged, often with catastrophic consequences.

As a result there have been many attempts to create accurate and reliable surface change monitoring devices or corrosion sensors. Despite such efforts, there are still many limitations that such sensors suffer from. One issue all these potential sensors face is that it is hard to detect changes or corrosion at low levels before serious damage has been done. Corrosion often occurs in inaccessible areas such as undersea pipelines or enclosed areas. It is also hard to predict where and when corrosion will occur. Several researchers have tried to examine different optical sensors for corrosion applications [2], including an optical-fibre corrosion sensor based on *Au/Ni-P* layers [3].

This study presents a novel optical method for surface change detection, with corrosion detection in mind, which employs the optical phenomenon of Surface Plasmon Resonance and is currently under patent [4]. The effects of SPR were first documented in 1902 when physicist R.M. Wood observed unusual patterns whilst experimenting with diffraction gratings [5]. He found that when using polarised light, dark bands would appear in the reflected light. These dark bands correspond to light coupling to bound surface plasmon modes. Surface plasmons are due to a collective electron oscillation which is able to interact with incident light. The work of both Otto [6] and Kretschmann [7] in the 1950s and 1960s respectively helped develop a reliable experimental setup where SPR mode-coupling could be achieved consistently. The configuration proposed by Kretschmann is still commonly used today and is the same system that is used in this study, and in our previous work elsewhere [8-9]. In the experimental configuration used here p-polarised, or Transverse Magnetic (TM) polarised light, excites surface plasmon resonance at a well-defined metal-dielectric interface. The definition of corrosion used here includes changes to any of the 3 key parameters: film thickness d, real permittivity ε_r, and imaginary permittivity ε_i, and as such this includes purely surface induced changes of ε_r and ε_i alone, which falls short of complete delamination of the film under study, and can include surface filling factor changes [10].

2. Theoretical Background

It is possible to model SPR mode coupling using computer software written in Fortran 90. Such modelling is important as it allows the user to experiment with thin film parameters such as thickness. Altering thickness, for example, of various sensor layers allows us to find an optimal thickness by design. Another advantage of having the theoretical reflectivity curves as a function of incident angle is they give accurate estimation of the surface plasmon resonance coupling angle. This means the likely scan range can be predicted in advance, saving time. The modelling method can calculate theoretical reflectivities as a function of incident angle for a multi-layered uniaxial media. However, in this paper we consider the layers to be isotropic. The multi-layered system is considered to be a series of uniform isotropic slabs of either dielectric or metal material, with each layer thickness taken to be much less than the wavelength of the incident light. A scattering matrix formalism, first developed by Ko and Sambles [11], overcomes instabilities found in the more conventional transfer matrix method developed by Berreman and Scheffer [12], and by Azzam and Bashara [13]. Both the scattering and transfer matrix methods take account of the various reflection and transmission coefficients occurring at each interface between successive media and uses Fresnel's optical equations. The optical scattering matrix method, developed by Ko and Sambles, couples the incoming optical electromagnetic fields by a matrix which is implicitly stable at all possible incident angles.

An example is shown here for internal reflectivity across a 10 degree angular range, calculated in 2000 steps for a 4 layer system simulated at 652 nm with parameters shown in Table 1 for a high refractive index glass pyramid, chromium adhesion layer, silver layer, and bulk air respectively.

Material	d	ε_r	ε_i
Glass Prism	0.00D00	3.64	0.00
Chromium	2.00D-09	-5.63	31.90
Silver	40.00D-09	-17.50	0.50
Air	0.00D00	1.0006	0.00

Table 1. Typical modelling parameters for optical reflectivity calculations at 652 nm.

Preliminary modelling of the SPR system used optical parameters for both silver and chromium thin films taken from a recognised handbook on optical constants of metals [14].

Fig. 1. SPR theoretical resonance as a function of incident angle at 652 nm at the glass/silver film interface. Series 1 silver with chromium, Series 2 silver only.

3. Methodology

3.1 SPR Experimental Setup

We used the so-called Kretschmann configuration to collect optical experimental reflectivity data (see Fig. 2.). This is the most common SPR experimental arrangement, and has been widely used in bio sensing applications since the first recorded research on this topic [15-17]. In this experimental configuration a thin metal film is usually sputtered or evaporated directly onto the base of a glass prism or pyramid. P-polarised light (or TM radiation) is shone through the pyramid across a range of angles such that the light is totally internally reflected. The laser angle is stepped in increasing internal angle until the light can couple at the glass-metal interface with the surface plasmon resonance and produces an evanescent wave at the underside of the attached metal film [18]. We use silver at the metal/dielectric interface, but gold is often chosen. The optical excitation of a surface plasmon at a gold/air interface has also been used to monitor the thickness of organic fluid layers condensed onto the gold [19].

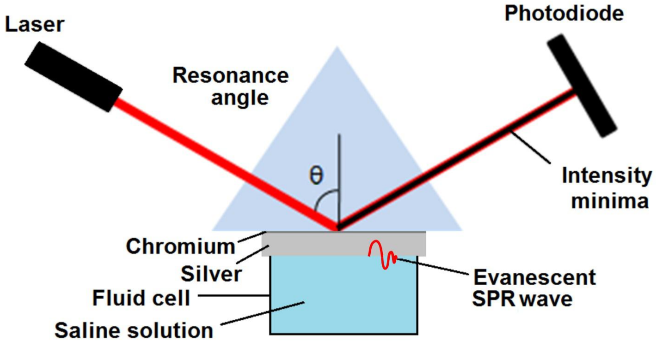

Fig. 2. Schematic diagram of the typical SPR experimental arrangement.

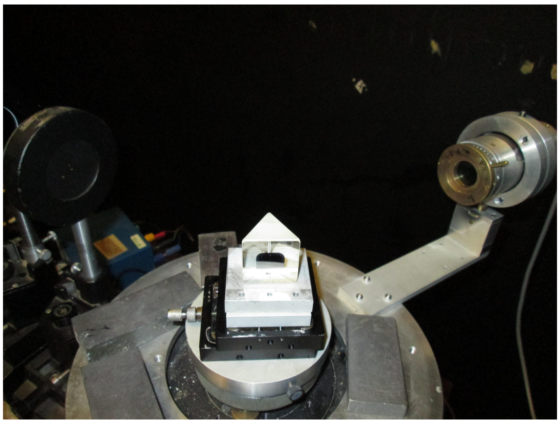

Fig. 3. View of experimental cell mounted on the optical rotation stage.

The experiments were accomplished using an existing SPR experimental arrangement as shown in figure 4. A helium-neon (He-Ne) laser operating at a wavelength of 632.8 nm was used as the light source for all our SPR optical coupling measurements. A customised computer program was created to control the rotary table driver operation and to record detector reflectivity readings from the silicon photodiode detector, written in LabView.

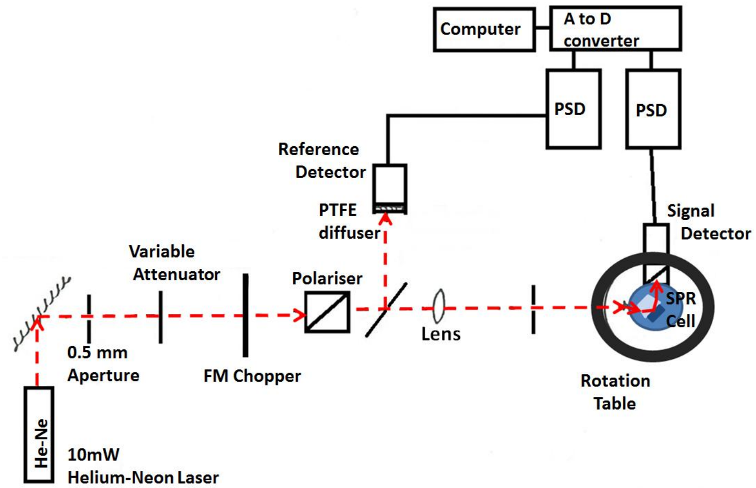

Fig. 4. SPR experimental rotation stage apparatus.

4. Results and Discussion

Before silver deposition a thin chromium adhesion promotion layer was first deposited by sputtering. It is well known that group 1B metals (copper, silver and gold) do not have strong adhesive properties to dielectric materials such as glass. This is because these metals do not have a high affinity for oxygen, and the hydroxyl groups which develop on the glass surface need an oxide bond to form strong adhesion. Thus it is necessary to first deposit a thin adhesion promoting layer such as chromium (a group VIa metal) onto the glass. The chromium forms a covalent oxide bonds at the surface with the hydroxyl groups to promote stronger adhesion. The chromium layer was nominally 2-3 nm thick and deposited by sputtering. An approximately 45 nm silver film was then produced by sputtering on top of the chromium layer. The advantage of using silver was that the deposition rate and optimal thickness were already known from previous studies [20]. In order to sputter both the chromium and silver films directly onto a pyramid shaped prism, a suitable prism holder was designed to support the pyramid substrate in the sputtering chamber (figure 5). The prism holder was water-jet cut out of aluminium in the Plymouth University workshop. The sputtering chamber is part of a Nordiko 6” sputtering machine, achieving pressures of typically 6×10^{-7} mbar after 6 - 7 hours prior to sputtering with a 50 W sputtering power supply maintained to the plasma by careful tuning.

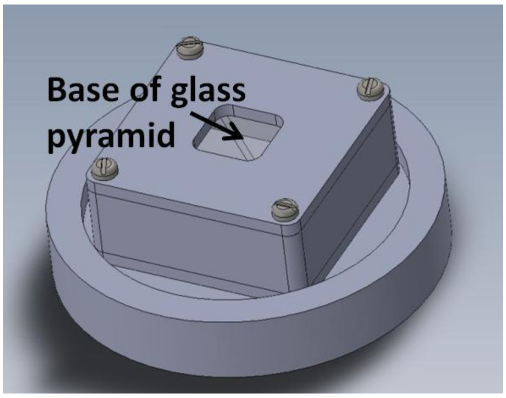

Fig. 5. Prism holder used to support the pyramid shaped substrate for both sputtering depositions in the sputtering chamber.

An initial SPR curve was taken with air as the superstrate media to provide an initial reference measurement and for subsequent theory vs data fitting comparisons. Next, a standard solution of synthetic saline, Vernier Sodium Chloride Standard Solution 35 Parts Per Thousand (PPT), was added to the empty cell through a small aperture in the top of the cell by syringe (approximately 0.8 ml) and then sealed to prevent water evaporation. Optical reflectivity was recorded again for variation of the incident prism coupling angle over as large a region of the SPR curve as was experimentally possible, shown here in Fig. 6., at repeated intervals over the first two months of data acquisition. The SPR reflectivity minimum is shown specifically in Fig. 7.

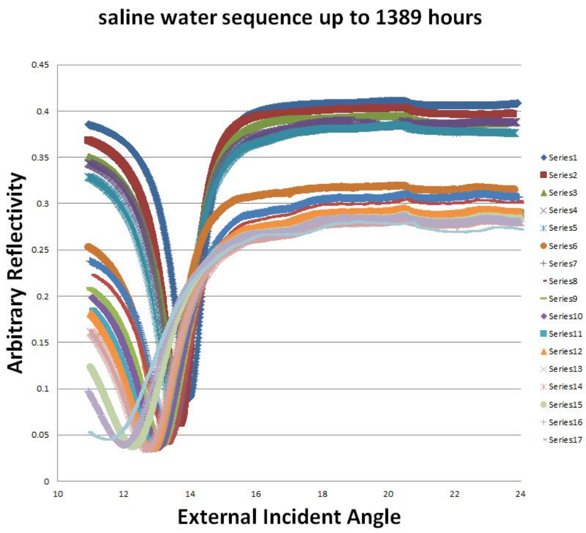

Fig. 6. SPR resonances as a function of incident angle up to 1389 hours of saline solution exposure.

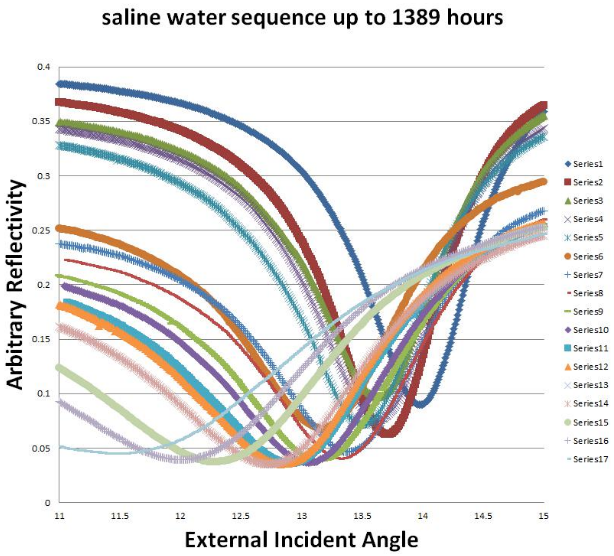

Fig. 7 SPR minimum as a function of external incident angle.

Both Fig. 6. And Fig. 7 show a downward trend in incident angle towards lower incident angle for the SPR minima, both in terms of resonance angle and reflectivity. This effect can be seen more clearly in Fig. 7. which is a plot of the minimum point of each SPR reflectivity curve recorded as a function of external incident angle. The external minimum SPR angle can also be plotted to show its dependence over time from the start of the experimental period, and is shown in Fig. 8.

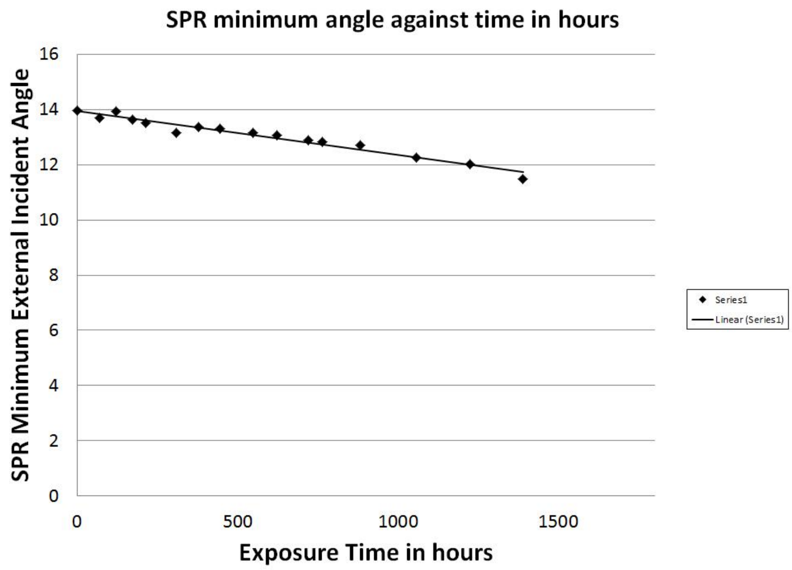

Fig. 8. SPR minimum angle reflectivity angle against time in hours.

The minimum SPR angle plot against time (Fig. 8) shows a very good linear correlation, with a correlation value of $R^2 = 0.9607$, with a linear dependence for the minimum SPR angle, $\theta_{\text{SPR minimum}}$, given by $\theta_{\text{SPR minimum}} = - 0.0016t + 13.953$ where t is the saline exposure time recorded in hours.

Initial $\theta_{\text{SPR minimum}}$ results were observed over the first day or so and are more likely indicative of changes in surface filling rather than silver film permittivity changes or indeed metal layer delamination itself [9]. Further data was acquired from the cell over a surprisingly long 6 months of exposure to salt solution, showing the long term stability of the chromium adhesion layer method. The central sputtered layer of chromium and silver still remained at the end of the full experimental cycle. Delamination of the film did take place from the outside edges moving inwards over time. These results recorded over long monitoring periods were very promising and have shown that it is worth completing further temporal SPR adhesion related experiments.

5. Summary

The measurement of the reflectivity minima of the SPR response has shown that the resonance angle minimum shifts in response over exposure time to lower external angle due to the saline solution. The minimum SPR angle plot against time shows a very good linear correlation, with a correlation value of $R^2 = 0.9607$, with a linear dependence for the minimum SPR angle, $\theta_{\text{SPR minimum}}$, given by:

$\theta_{\text{SPR minimum}} = - 0.0016t + 13.953$ where t is the saline exposure time recorded in hours.

Initial short term time scales results are indicative of salinity related surfacing filling factor changes rather than actual metal film permittivity changes, nor corrosion itself. Sensors can be developed to monitor the resonance angle minimum as the output indicator of surface induced changes, or corrosion. Research has revealed the complex and unstable nature of corroded metal films [13]. It is possible for multiple oxide layers to grow into a film, each with their own distinct properties. In addition to this, it is possible that water penetrated into the thin silver film through voids however well sputtered, further altering its optical properties [21]. Further work will attempt to fit the experimental curves with theoretical models based on Fresnel's reflectivity software. Ultimately the purpose of this sensor is to detect surface induced changes and actual corrosion at low levels – ideally before other sensors can register it. As such any related research should focus more heavily on the short term behaviour of the sensor, days and weeks, rather than over its longer lifetime performance in terms of months or years, which will encompass short term filling factor changes.

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