STUDY OF OXIDE FILM ON COPPER ELECTRODE BY IN SITU PHOTOTHERMAL SPECTROSCOPY

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Summary

The behavior of an oxide film on a copper electrode in a 0.1 N NaOH solution has been studied by the in-situ photothermal spectroscopy (PTS) method using a polyvinylidene difluoride (PVDF) pyroelectric film as a thermal detector. This study is complemented by photocurrent spectroscopy, XPS, ERD, and cyclic voltammetry methods.

By PTS study, a simple one-dimensional heat transport model is chosen as a theoretical model to analyze the photothermal signal and has been partly proved by some experiments. The photothermal response varies linearly with film thickness and inversely proportional to the chopping frequency f.

From the variations of the **PTS** signal, the redox reaction of copper surface layers between Cu, Cu_2O, and $CuO/Cu(OH)_2$ at different potentials was observed. This proved that the **PTS** method using PVDF film as thermal-detector is a very sensitive and fast response method for measuring surface changes. This **PTS** method has the advantages of simplicity and versatility. It allows a more flexible sample cell arrangement and is free from external acoustic noise, comparing with **PAS** method.

The thermal effect in photocurrent measurement on copper electrode in 0.1M NaOH solution has also been studied by photothermal spectroscopy (**PTS**) method. That part of the photocurrent response due to thermal effect has been separated from the total photocurrent response, and the real part of photocurrent response due to photo effect has been obtained by deducting I_{th} from I_{total}.

By photocurrent study, the Cu_2O layer is p-type and band gap energy is about 2.43 eV by the experiment of photocurrent dependence on photon energy of incident light. The flat band potential is about 0.3 mv by photocurrent spectrum and −341mv. The difference may be due to the deviation between theoretical equation and practical situation.

XPS and **ERD** study were performed on the surface oxide layer which formed at different potential corresponding to the anodic voltammetric peak. **XPS** result shows that CuO layer was formed round the anodic peak II, and a duplex layer of CuO and $Cu(OH)_2$ was formed round the anodic peak III. The element H in surface layer formed at potential round the anodic peak III could be detected by **ERD**.

The cyclic voltammetry at different potential window was carried out on Cu electrode in 0.1 N NaOH solution. The results that peak I corresponds to the simple oxidation of Cu_2O from Cu, peak II corresponds to the formation of CuO from Cu_2O and direct from Cu, and peak III corresponds to the formation of duplex layer of Cu(II). Another experiment where the oxide layer formed at constant potential of peak II and III was cathodic scanned back to −1150 mv was performed. The result shows, combined with **SEM** on the surface layer formed in different potential for different time, that the major formation at peak I and III is completed within 15 min, while in peak II, the surface coverage increase with the time increasing and the major phase is CuO which was formed direct from Cu.

Chapter 1

General Introduction

1.1 In Situ Characterization of Electrochemical Process

1.1.1 Overview

The infusion of multidisciplinary interest in electrochemical research in the recent past has given rise to new opportunities for innovation and research in application areas such as electrocatalysis, electrodeposition, corrosion, batteries, fuel cells, and rapidly developing semiconductor industrial. Alongside this, need for molecular level information on the structure of the electrode-electrolyte interface, mechanism and kinetics of electrochemical process on electrodes and electrolytes during the conduct of electrochemical reactions also has clearly been identified.

The electrode-electrolyte interface, often called the interphase, is the heart of electrochemistry. It is the site of enormous electric fields and chemical forces that determine electrochemical reactions. It is also the site of electron transfer, from a region in which only electrons move freely to a region where ions move freely and where electrons must travel "piggyback" on some molecule. The electrode-electrolyte interphase is the region where the properties of both phases differ from their bulk value. An essential element in understanding this interphase is the use of in situ spectroscopic methods to directly obtain molecular information about the interfacial region. Such techniques have not been as well developed

for the solid – liquid interface as they have been for the solid – gas (vacuum) interface, which, in comparison, has been extensively studied. This is partly because there are many sensitive surface techniques for the solid – vacuum interface, such as Auger electron spectroscopy (**AES**), ultraviolet and x-ray photoelectron spectroscopy (**UPS** and **XPS**), secondary ion mass spectrometry (**SIMS**), low-energy electron diffraction (**LEED**), and high-resolution electron energy loss spectroscopy (**HREELS**). However, such techniques require ultrahigh – vacuum environments.

Although electrochemists can use electrochemical methods to study solid—liquid interfacial processes, the electrochemically measurable parameters, such as current and potential, yield information regarding only the rate of reaction, the influence of diffusion, concentration, temperature, and so on. They cannot give information about the chemical identity, structure, configuration, and orientation of surface species. Therefore, there is a great need for techniques that can probe both kinetic and structural characteristics of a surface reaction. Ideally, such a technique would be combination of an electrochemical system with a spectroscopic method capable of being used in situ, that is, while electrochemical process are taking place.

Following is the brief introduction to some of in situ spectroscopic techniques and their applications.

1.1.2 Ellipsometry

Ellipsometry is an optical technique for characterizing surfaces and thin films. The technique involves the reflection of polarized (generally monochromatic) light from the surface under study and the measurement of the change in the state of polarization caused by the reflection. The measurements usually involve elliptically polarized light, a fact that is recognized in the present name of the technique, and yield two parameters that characterize the change in the state of polarization.

Ellipsometer measurements are often extremely sensitive to the presence of very thin surface layers (including fractional monolayers), to changes in their thickness (or coverage), and to changes in surface topography at an atomic scale. The range of film thicknesses that can be observed is very large (reaching to several wavelengths optical thickness), and the surfaces being studied may be immersed in any optically transparent medium, including liquids. These characteristics make the use of ellipsometry for electrochemical studies particularly attractive.

Although the reflection of polarized light has been studied for more than a century, as pointed out in the historical review by Hall [1], the term ellipsometry was not introduced until 1945, by Rothen [2], who described in his recollections [3] that he thought the otherwise appropriate term, Polarimetry, had been given a restricted meaning by chemists for the measurement of optical rotation. Significant early work by Vasicek employed the terms polarimetry or polarization spectroscopy [4,5].

The applications of ellipsometry cover a wide range of studies of electrochemistry, such as anodic oxidation [6], gas-phase oxidation [7], corrosion [8,9], cathodic metal deposition [10], reduction of oxides [11], adsorption process [12], electronic materials [13], and other studies.

Ellipsometry will continue to be used for measurements on surfaces, particularly solid—liquid and solid—gas interfaces, for which its capabilities are unique. It will provide real time, in situ information on the formation, breakdown, and removal of surface layers or on the cleaning, etching, and annealing of solids. The spectroscopic properties of bulk solids and surfaces will be determined more readily to derive chemical composition, ordering, electronic structure, and the distribution of materials in composite and inhomogeneous systems.

The combination of ellipsometer measurements with other techniques will be of continued interest for the detailed study of surfaces and thin films.

1.1.3 Surface-Enhanced Raman Spectroscopy

The Raman effect is due to the interaction of photons with the vibrations of chemical bonds. These wavelengths are in the IR region but the excitation source for observation of the Raman effect is often in the visible region. The major part of incident light passes through the system without change of photon energy (Rayleigh effect); if there is energy exchange with the system the Raman effect is observed.

In 1974, Fleischmann et al. [14] first reported the surface Raman spectra of pyridine adsorbed on a silver electrode that had been electrochemically roughened. Fleischmann et al. also gave a possible model for the structure of the double layer between the silver electrode and its electrolyte solution contained pyridine and potassium chloride. These results were of great interest since they showed that Raman spectroscopy could be used in situ to obtain molecular information at an electrode surface. However, the fact that a giant surface enhancement was occurring was not realized until 1977, as noted in the work of Jeanmaire and Van Duyne [15] and Albrecht and Creighton [16]. They independently found that with only a single pretreatment voltage pulse or triangular sweep, the Raman signal per adsorbed pyridine molecule was roughly six orders of magnitude larger than that of an isolated molecule in solution. Thus, the signal from pyridine that Fleischmann et al. [14] had observed could not be attributed to only an increase in surface area of their roughened electrode. This surprising discovery touched off a flurry of experimental and theoretical activity. Since then **SER** scattering and other interactions of EM radiation with surfaces have been intensely studied.

The **SERS** effect has been observed for many different interfaces and environments. **SER** scattering in an electrochemical system, that is, electrode-electrolyte interface, has been most widely investigated. Most **SER** scattering studies have been obtained on silver because silver shows the largest enhancement. Copper [17] and gold [18] have also shown **SERS** enhancements. In addition, some form of enhanced surface scattering has been claimed for platinum [19], nickel [20], aluminum [21], lithium and sodium [22-24], and semiconductors [25]. However, the giant Raman enhancement effect that is commonly

referred to as **SERS** is mainly limited to the coinage metals. With all the various possibilities for development in sensitivity, time resolution, the new **SERS** active substrates, it would appear that **SERS** will continue to be a field of spectroscopy with a great amount of activity.

1.1.4 Ultraviolet – Visible Reflectance Spectroscopy

Specular reflectance spectroscopy has much in common with ellipsometry and while in theory it is a less informative technique, in practice it is certainly more versatile and has proved more useful to electrochemists. Its major advantages are its much faster response, and therefore greater suitability in kinetic studies, its optical simplicity, and the ease with which the wavelength may he varied. Like ellipsometry it has, until very recently, been restricted to the **UV** – visible spectral range and it is such studies that are discussed here. Recent developments in the extension of this technique to the study of vibrational spectroscopy will be considered later.

The essence of the reflectance spectroscopy experiment is to shine a monochromatic light beam, that is also usually plane polarized, at a defined angle of incidence at an electrode surface, and to measure the intensity of the reflected beam as a function of an experimental variable such as wavelength, potential, or time. The same model as is used in ellipsometry, i.e. substrate/interphase/ambient phase, is usually used to describe the reflecting interface and if the optical constants of these regions are known it is then a fairly simple matter, using the Fresnel equations, to calculate the reflectivity. For systems of electrochemical interest, e.g. specific ion adsorption, the reflectance changes will be small and virtually impossible to

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detect and quantify by direct measurement. A number of approaches have therefore been followed to enhance the sensitivity.

Perhaps the simplest way of doing this is to use a cell configuration that permits multiple reflections between parallel working electrodes. This was first done by Takamura and co-workers [26, 27] in the early 1970s, to investigate a number of processes on gold electrodes, including oxide formation, anion adsorption, and underpotential deposition. Relatively large reflectivity changes were observed but no quantitative data treatment was attempted. The reflectance spectroscopy also can be applied in the study of solution free species [28,29], adsorption studies [30], and underpotential deposition [31], etc.

1.1.5 Infrared Reflectance Spectroscopy

The techniques discussed so far have been applied largely in the **UV** – visible region of the spectrum, and whilst these have revealed much interesting information they lack molecular specificity. A need therefore exists, particularly in the study of adsorbates, for a technique that can supply such molecular structural information; i.e. an in-situ vibrational spectroscopy. The extension of several **UV** – visible techniques into the infrared spectral region has been attempted but these attempts have been largely unsuccessful. Recently modulated reflectance spectroscopy has been successfully used in the infrared region.

The apparatus required is very similar to that for **UV** – visible studies except, of course, that glass optics cannot be used and therefore, for example, silica or silicon cell windows are required. The **IR** source is a Nernst filament and an **IR** detector replaces the photomultiplier

or photodiode. The first successful demonstration of this technique was by Bewick and co-workers in 1980, [32] and since then several further reports have appeared from this group. The first studies were of the thionene radical cation, indole adsorption on Pt, and hydrogen adsorption on Pt. This last example is of particular interest and several further reports have appeared covering also adsorption on Rh [33-36].

That any results can be obtained at all for this system is remarkable in view of the presence of the aqueous solution. However, by pushing the electrode hard against the window of the cell, trapping a thin electrolyte layer, there is an adequate spectral window. The changes in reflectivity caused by changes in an absorbate are very small and therefore, in order to obtain an adequate sensitivity, the lock-in amplifier output is not recorded directly but is signal averaged for many sweeps over a period of up to several hours. In the strongly hound hydrogen region, only an increase in reflectivity is detected, as is also seen in the **UV** – visible, but for the weakly bound hydrogen a band at 1.95 μm is observed. This is clearly at too high an energy for a Pt – H stretch and therefore, from isotopic substitution studies, it has been suggested that it arises from a $v_2 + v_3$ combination band, for an hydrated adsorbed proton. The predominant water species is identified as a dimer.

The other major area of study in Bewick's group has been the electrocatalytic oxidation of small organic fuels, e.g. methanol in aqueous solution [37]. In particular they have identified the poisoning species as bridge-bonded CO whilst no COH was detected. In conjunction with this interest, they have studied CO adsorption on Pt, Rh, and Au electrodes [38] and have detected both linearly and bridge-bonded CO on these metals.

The potential-modulated reflectance technique necessarily produces as its output the difference in the spectra at two potentials. An alternative approach, polarization modulation, permits the recording of a surface spectrum at a single potential. This technique relies on the surface selection rule that s-polarized radiation is insensitive to an adsorbed layer. The difference in spectra recorded with s- and p-polarized light may therefore be attributed to surface effects. Russell and co-workers [39] have used this approach to study CO adsorption on Pt and their results confirm those obtained by potential modulation.

A further recent development in this area is the use of FTIR to study adsorbed acetonitrile on Pt. Davidson and co-worker [40] have studied this system and have reported how the spectrum for the CN bond varies with potential. It is certain that IR-reflectance spectroscopy will receive much attention in the future and it will probably become a very widely applied technique.

1.1.6 Surface X-Ray Absorption Spectroscopy, EXAFS and NEXAFS

Various structural probes of electrode surfaces and interfaces have been used in the past. Among these, x-ray absorption spectroscopy is a particularly suitable technique in that it is sensitive to short-range order about specific elemental species in disordered as well as crystalline materials. Since some of the thin films that form on electrodes are understood to be noncrystalline [41], this is a significant capability. Using this technique, radial distribution functions can be derived about one or more important atomic centers without solving the entire structure. It can be applied to the in situ examination of the electrode – electrolyte interface; it allows a determination of the changes that occur in the structure of

the films on electrodes ex situ when they are removed from the electrolyte; and it serves for the characterization of species in the electrolyte.

An x-ray absorption edge spectrum is usually divided into several regions. The first is the pre-edge region and includes the actual absorption edge. This region is where the near-edge absorption fine structure, or **NEXAFS**, is seen. It consists of spectral features within a few tens of electronvolts of the edge. These features are due to core electron transitions to unoccupied bound orbital and to effects such as excisions. The **NEXAFS** can be directly related to the absorbing atom's density of final states multiplied by the transition probability to such states. In the second region, which extends to several tens of eV above the absorption edge, multiple scattering takes place. In the third region, which extends from approximately 50 to 1000 eV above the edge, the plane wave approximation, the restriction to single scattering paths, and the approximate treatment of inelastic scattering losses generally apply, and the extended x-ray absorption fine structure is seen. This fine structure is the **EXAFS**. It is due to the interference of the outgoing electron waves with the waves backscattered by the neighboring atoms in the photoionization process. This fine structure can be simply related to the atomic arrangement around the absorbing atom.

Because **EXAFS** and **NEXAFS** offer the possibility of examining electrode surface while electrochemical processes are taking place, the recent development of these techniques has resulted in their application to a number of important electrochemical problems, such as the passive films on Fe [42-46] and Mg [47-49], corrosion inhibitors [50-52] and batteries [53, 54].

1.1.7 Photothermal Deflection Spectroscopy

Photothermal deflection spectroscopy (**PDS**) is a versatile in situ surface-sensitive technique applicable to the study of electrochemical interfaces. This technique was original developed by Boccara, Fournier, and Badoz [55, 56]. **PDS** is also called photothermal beam deflection spectroscopy (**PBDS**) or mirage effect spectroscopy. **PDS** can measure the absorption spectrum of electrode surface species with submonolayer sensitivity, the absorption spectrum of electrolyte species, and the concentration gradients near the electrode surface.

Photothermal techniques are quite versatile. Besides the most common use, measuring either homogeneous-phase or interfacial absorption spectra, photothermal techniques have been applied to chromatography, fluid dynamics, and material characterization [57-61]. The principles of all the photothermal techniques are similar. Fig.1.1 shows a basic **PDS** system. The basis of **PDS** is the detection of refractive-index gradients in the electrolyte adjacent to the electrode. These gradients are measured by the deflections of a probe beam passing through the gradients. This section will discuss the aspects of **PDS** applicable to electrode surfaces.

PDS has several advantages compared to existing spectroelectrochemical techniques. First, **PDS** used a relatively low-intensity excitation light of approximately 10^{-2} W cm^{-2} to probe the interface. The risk of inducing changes in the surface chemistry is much smaller than with the high-intensity laser techniques using up to 10^{5} W cm^{-2}, e.g., Raman and Secondharmonic Generation (SHG). Second, **PDS** is applicable to any electrochemical

interface. The electrode surface is required to be only approximately planar; polished, smooth, porous, and rough surfaces can be studied. Last, the advantages of in situ techniques cannot be understated [62]. Only the in situ techniques can monitor transient processes. The in situ techniques do not require the removal of the electrode from the electrochemical environment, which can alter the identity or structure of the surface species. Armstrong and Muller [63] have studied copper electrodeposits with in situ scanning tunneling microscopy (**STM**) and have shown that the microtopography changes after I mm at open circuit. This demonstrates the problem of removal of electrodes from the electrochemical environment, a problem not encountered by in situ techniques.

PDS can be widely used in electrochemical systems, such as electrochemical oxidation and reduction of platinum in 0.1 M perchloric acid [64], copper in 0.1 M KOH [65,66], photocorrosion of CdTe single crystals in acidified $SnCl_2$ electrolyte at open circuit [67], etc.

The results discussed above demonstrate the versatility of the **PDS** technique for in situ and nonintrusive spectroelectrochemical measurements. The technique uses low-intensity illumination, which is safe for use with any photoinactive electrode, to measure the surface absorption spectrum. Changes in the interfacial absorption coefficient and concentration gradients attributable to the reaction of submonolayer quantities have been measured.

PDS excels where reflection spectroscopies fail*:* As the reflectivity of the electrode decreases, as with dispersed platinum or carbon, the reflection signal decreases whereas the **PDS** signal increases. The ability to separate the electrolyte absorption from the surface

absorption based on the phase difference is a major advantage compared to reflection-based spectroscopies.

PDS is a promising technique for obtaining in situ vibrational spectra of electrode surfaces. Raman spectrospcopy is an alternative method of obtaining vibrational spectra, but, because the Raman scattering selection rules are different than the absorption selection rules, an absorption technique is needed. Also, the surface enhancement required for monolayer studies by Raman methods is applicable only to certain metals.

PDS is a relatively new spectroscopy and its application to electrochemical systems is even more recent. This chapter illustrates the wealth of information about electrochemical systems the technique provides. A goal for the future is increased sensitivity. This would allow faster electrochemical processes to be studied.

1.1.8 Scanning Tunneling Microscopy

Several recent investigations have demonstrated scanning tunneling microscopy/micro-scope (**STM**) to be a powerful new technique for electrode surface characterization with atomic resolution in situ at surfaces under potentiostatic control [68,69]. It is already well established in surface physics that the technique is unique in its ability to determine both the structural and the local electronic properties of surfaces of metals and semiconductors in ultra-high vacuum (UHV) [70,71].

Understanding the electrochemical reactivity of noble metals such as platinum (Pt) and gold (Au) is very important in modern electrochemistry [72-76]. Although many structure sensitive methods on an atomic scale such as low-energy-electron diffraction (**LEED**) have been used to characterize electrochemically treated electrodes under UHV conditions [72-76], it is always necessary to transfer the electrode from the electrolyte solution to the UHV environment. This ex-situ experiment may involve structural surface changes during the transfer of the electrode.

Semiconductor/liquid interfaces are also interesting and important systems for characterization in the field of photoelectrochemistry [77,78]. Although tremendous efforts have been made during the last twenty years to obtain a better understanding of photoelectrochemical reactions, there is not much information available about structures and electric properties of semiconductor electrodes with atomic resolution in electrochemical environments.

Since Hansma and co-workers first demonstrated that **STM** can operate in electrolyte solutions [79], much progress has been made in exploring the possibilities of **STM** for characterizing the solid/liquid interface with atomic resolution. The objective of this chapter is to briefly highlight some of the recent progress from this laboratory and others on in-situ **STM** with atomic resolution. It is not possible to review all of the published accounts of in-situ **STM** results in this format. The reader is referred to more comprehensive reviews published elsewhere [68, 69].

In the present work, we use the following in situ techniques, such as Photothermal Spectroscopy (**PTS**), Photocurrent Spectroscopy, and accompanied by some ex-situ surface analysis method, such as **XPS**, **ERD**, and **SEM** to study the oxide film of copper.

1.2 Photothermal Spectroscopy

1.2.1 Introduction

The search for spectroscopic methods whose can be used for opaque sample has led to investigations of techniques such as Photoacoustic Spectroscopy (**PAS**) and Photothermal Spectroscopy (**PTS**). We first discuss **PAS** here and later the **PTS** in chapter 2.

In 1880, Alexander Graham Bell studied the "optoacoustic" effect [80]. He discovered that when a periodically interrupted beam of sunlight shines on a solid in an enclosed cell, an audible sound could be heard by means of a hearing tube attached to the cell. Motivated by Bell's discovery, Tyndall [81] and Rontgen [82] found that an acoustic signal could also be produced when a gas in an enclosed cell was illuminated with chopped light. Bell [83] subsequently experimented with a variety of solids, liquids, and gases and his work generated a brief flurry of interest. Later he renamed this effect the "photoacoustic effect" to distinguish it from "acousto-optic effect". Unfortunately, the photoacoustic effect was evidently regarded as a curiosity of no practical value as was soon forgotten.

Fifth yeas later, PAS since became a well-established technique for gas sample [84]. The use of this method on monophase samples is reviewed in the cited literature [85, 86]. From 1975, PAS method has been used to study the electrochemical reaction at the interface between electrode and electrolyte.

1.2.2 Principles

In **PAS**, the sample is illuminated by a modulated light source. The incident light is absorbed and through nonradiative processes heats the sample. Because the light is chopped, the temperature rise is periodic at the chopping frequency. It is this periodic temperature rise ($<10^{-3}$ K) at the surface of the sample causes the generation of elastic waves in the sample. This elastic wave can be detected by a microphone [87-90] or piezoelectric transducer [91] attached to the back of the sample. However, this signal is rather small and thus the background noise hides this "photoacoustic" signal. To overcome this problem, the signal can more easily be detected through a "lock in" technique.

1.2.3 Experimental Setup

The experimental arrangement for PAS using different cell is similar, including light source, chopper, **PAS** cell with different detector, potentiostat, lock-in amplifier, and X-Y record. Fig. 1.2 shows the photoacoustic cell and the experimental setup for **PAS** [92] with piezoelectric transducer as a detector and Fig. 1.3 shows the PAS cell with microphone as detector [93]. Another PAS setup and cell are shown in Fig. 1.4 described by J. K. Dohrmann [94] using double-beam.

The light source in Fig.1.2 is an Ar ion laser. This type of laser has the advantage of emitting a coherent source of high intensity monochromatic light. However if we are performing spectrometric investigation, we need another optical source such as a dye laser. The most common light source for this spectrometric measurement is a Xe lamp, as shown in Fig.1.4, because of its high intensity of light as a wide variety of wavelengths. With the aid of a monochromater or interference filter, we can obtain monochromatic light.

The incident light is chopped by a mechanical chopper for low frequency use (<1 kHz) or an acousto-optic modulator for high frequency use (>10 kHz). This chopped light illuminates the electrode surface through an electrolyte. Generated elastic wave can be detected by a piezoelectric transducer attached to the back of the sample that converts the elastic wave to a voltage signal. This voltage signal at the chopping frequency is attenuated by a "lock-in" amplifier. So through this process the signal-to-noise ratio can be enlarged.

1.2.4 Applications

PAS can be applied to the solid/liquid interface. A. Fujishima and his co-workers [95] used **PAS** to investigate the oxidation and reduction of gold electrode in $HClO_4$ solution. Under anodic polarization, an oxide film was formed on the Au electrode and the corresponding PAS signal shows an increase. While continuous cathodic polarization reduces the oxide film so the corresponding photoacoustic signal returns to the initial level. Other applications were done to electroplating, especially copper deposition on gold [96], nickel plating with scanning laser beam [97]. In situ PAS can also be used to investigate the

semiconductor electrode surface [98]. The working electrode was a CdS single crystal. Under cathodic polarization (-2.0 Vvs. SCE) in 1 M KCl, CdS decomposes as follows

$$CdS + 2e^- \rightarrow Cd + S^{2-}$$

Eventually Cd metal is deposited on the surface of the electrode. After cathodic polarization, **PAS** signal amplitude increases in the region of longer wavelengths. This is due to the absorption of deposited Cd. Thus through this technique, electrochemical decomposition of semiconductor electrode in dark can be estimated in situ. Similarly photoelectrochemical reactions can be estimated using **PAS** [99, 100].

1.3 Photocurrent Spectroscopy

1.3.1 Introduction

Photoeffects in electrochemical systems have been recognized for a long time, and the phenomenon that an additional current can be stimulated by irradiation with light, the Bequerel effect, is named after its discoverer [101]. The electrodes with Bequerel effect were, in fact, metal electrodes that were covered with an oxide film. Since then, there have been continuous efforts to utilize this photoeffect in order to study properties of passive metal electrodes. Because of a limited understanding of the involved processes and also limited experimental means, results and interpretations were only qualitative and remained controversial. During the last 10-15 years, however, photo-electrochemistry with semiconductor electrodes has undergone an enormous advancement that has been largely due to the search for materials for liquid junction solar cells [102 – 105]. Besides affording a

much better understanding of a large number of systems and the processes involved in photoelectrochemical reactions, photoelectrochemistry emphasizes that solid-state properties are of great importance to electrochemical behavior. The application of photoelectrochemistry to the study of passive films is based on the recognition that even very thin films constitute their own phase with their specific properties. Consequently, photoelectrochemistry can be used as an in situ technique to characterize passive films with respect to their optical and electronic properties.

In this section an attempt will be made to give an overview of the possibilities photoelectrochemistry offers for the investigation of passive films. Relevant theoretical background will be described, including aspects of photoelectrochemistry of amorphous materials since passive films are often highly disordered. The literature will be reviewed with the object being to distinguish noble metals, on which usually very thin films are formed (which may not be categorized as passive films in a stricter sense), transition metals on which passive films of intermediate thickness are formed and which are of importance for corrosion studies, and valve metals, on which very thick films can be formed due to the possibility of high film formation potentials because of high breakdown potentials.

1.3.2 Theory

A photoelectrochemical reaction on a passive metal electrode can be described in the following simplified way. If light with a suitable energy hv is absorbed by the passive film, electrons can be excited from occupied electronic states into unoccupied ones,

$$hv \rightarrow e^- + h^+ \tag{1}$$

As a consequence, the charge distribution in the film is changed, which can result in a current at constant potential or a potential change at constant current which includes the open circuit condition where $i = 0$. The current results from an electrochemical reaction at the electrode/electrolyte interface. The changed charge distribution can also be measured as a change of the electrode capacity.

Depending on the properties of the passive film with respect to its conduction type, different energetic conditions can be distinguished for an n-type or p-type semiconducting or an insulating film. Fig.1.5 gives a schematic representation for crystalline films without, as yet considering any effects caused by an absorption that involves localized states. Under the conditions of a depletion layer built up at the film/electrolyte interface in a semiconducting film, the electron hole pair is separated in the electric field of the space charge layer. The condition of a depletion layer is the one where a photoeffect would be observed. In the case of a p-type semiconducting film (Fig. 1.5a), the electron migrates to the surface from where it can react with an unoccupied (acceptor) state in the electrolyte that is represented by an oxidized chemical species. The hole flows to the backside contact; the resulting current is cathodic. For an n-type film (Fig. 1.5b) the situation is reversed. The hole migrates to the surface, reacting with an occupied (donor) state while the electron moves to the backside contact: the photocurrent is anodic. In an insulating film (Fig 1.5c) the potential gradient is constant within the film and depending on the sign of the field the photocurrent is anodic or cathodic. In general, a change in the sign of the field changes the sign of the photocurrent. The potential at which this sign change occurs is called the flatband potential, U_{fb}. It is consequently accessible by photoelectrochemical techniques and can be compared with

values obtained from capacity measurements. In addition to an excitation in the passive film, an excitation can happen in the underlying metal as well. For thin passive films and insulating films this has been observed and will be described later. Excitation occurs most probably from or to the Fermi level in the metal with a consecutive emission of a hot electron or hole. Internal photoemission into the passive film might also occur; it is illustrated in Fig. 1.5c for the emission of a hot electron. It should be emphasized that photoemission is not limited to insulating films but can also happen with n-type and p-type passive films.

The following description of the photoresponse will be restricted to the photocurrent, although the measurement of photopotentials is equivalent. Since, however, most measurements nowadays are performed under potentiostatic control it has become more common to measure photocurrents. Disregarding any recombination, the photocurrent of a crystalline semiconductor can be expressed by [106,107]

$$I_{ph} = eqI_0\{1 - \exp[-\alpha d_{sc}(e/kT)^{1/2}(U - U_{fb})^{1/2}]/(1+aL)\} \tag{2}$$

E denotes the electronic charge, q the quantum efficiency, I_0, the incident photon flux disregarding any reflections at the electrode/electrolyte interface, a the absorption coefficient, *U* the electrode potential and U_{fb} the flatband potential. The Debye length, d_{sc} is determined by important semiconductor quantities such as the dielectric constant, ε and the doping concentration, *N,* which is the donor concentration, *Nd,* for an n-type semiconductor and the acceptor concentration, N_a, for a p-type material. It is given by

$$d_{sc} = (e\varepsilon_0 kT/e^2 N)^{1/2} \tag{3}$$

The diffusion length of the minority carriers, *L,* is expressed by

$$L = (D\tau)^{1/2} \qquad\qquad (4)$$

Where, D is the diffusion coefficient of the minority carriers and t is their lifetime. Equation (2) is derived under the assumption that the charge transfer at the electrode/electrolyte interface is not rate determining. Simplifications in Equation (2) are possible under certain conditions whose will be discussed later.

The photoelectrochemical behavior of passive films is largely influenced by their electronic properties. These properties as obtained from other techniques, such as capacity measurements and electron transfer reactions, will be reviewed briefly. Then, characteristics of the absorption behavior of thin films will be discussed, followed by a more detailed description of the wavelength and potential dependence of the photocurrent for crystalline and amorphous films.

Wavelength dependence of the photocurrent

The absorption coefficient, a, of a crystalline material depends on the photon energy in the following manner

$$\alpha = A\ (hv - Eg)^n/hV \qquad\qquad (5)$$

For allowed transitions which are the most likely to be observed in our case, $n = 1/2$ describes direct transitions, and $n = 2$ is characteristic of indirect transitions, which require a phonon participation [108, 109]. The type of transition can also be determined from photocurrent spectra as long as $i_{ph} \propto \alpha$ holds. The minimum energy required for indirect transitions, E^i_g, can be evaluated from $(iPhhv)^{1/2}$ vs hv plots, and that for direct transitions, E^d_g, from $(iph\ hv)^2$ vs hv plots. This information allows us to identify the material forming

the passive film. It also might be used to estimate to what extent the band structure in the passive film is developed with respect to bulk properties of the same material. (An example for the latter case will be given later for passive titanium.)

Potential dependence of the photocurrent

At constant wavelength, where a is constant, Equation (2) describes the potential dependence of the photocurrent for a crystalline semiconductor. Under certain conditions simplifications of Equation (2) are possible. For a diffusion length much larger than the width of the space charge layer, $L >> d_{sc}(e/kT)^{1/2} (U - U_{fb})^{1/2}$, the photocurrent becomes potential independent as can be seen from Equation (2). Such a behavior is commonly found with bulk semiconductor electrodes whose are either single crystals or well crystallized materials. For the reverse case, where $\alpha\ d_{sc}(e/kT)^{1/2} (U - U_{fb})^{1/2} << 1$, the exponential function can be expanded, and Equation (2) changes to [107]

$$iph = const.\ \alpha d_{sc}(e/kT)^{1/2} (U - U_{fb})^{1/2} \qquad (6)$$

Behavior in accordance Equation (6) can be identified from $i^2_{ph}\ vs\ U$ plots. The slope depends on the photon energy since a is a function of hv and the extrapolation to $iph = 0$ should yield the flatband potential U_{fb}. In several cases U_{fb} values obtained from such extrapolations were higher by several hundred millivolts than U_{fb} values obtained from capacity measurements. In the presence of surface states or when recombination is included in the derivation, different relations between photocurrent and electrode potential have been discussed [110-113]. Even for high recombination rates, the $i_{Ph}(U)$ relation is at most linear for crystalline semiconductors[112].

1.3.3 Experimental

The experimental techniques used in photoelectrochemical studies of passive films commonly use a combination of equipment used for passivation studies and that used for photoelectrochemical research with semiconductors. In Fig. 1.6 a block diagram of a typical experimental set-up is outlined. It is shown for a potentiostatic measurement with a monochromatic light source in the form of a polychromatic lamp and monochromator. In order to measure photopotentials, a galvanostat can be used or open circuit conditions can be applied. The light source can also be polychromatic (usually xenon or tungsten lamps) for preliminary measurements, *ie* in order to test under what conditions photoeffects can be expected. The advantage of the polychromatic source is its usual high intensity and its spectrum covering a wide range of wavelengths. Disadvantages are that possible heat effects may exist, especially with high power lamps, which have to be distinguished from photoeffects. A high power monochromatic light source is the laser that has clear advantages. It can be applied to studies of the potential dependence of the photocurrent, especially where absorption coefficients are small, and to studies of sub-band gap or close-to-band gap responses. Measurements of spectra with a laser (dye laser) are usually tedious even if the equipment is available. Polychromatic sources, *eg* xenon lamps with quartz bulbs, which have a considerable output even below 250 nm, together with a modern monochromator with digitally addressable scan rate, 2. range *etc.* are more convenient. If the photoresponse is large enough it can be measured directly. A convenient way is to use slowly chopped light, e.g. 0.1 Hz. Currents under dark and illuminated conditions are both recorded and, in addition, any transient behavior pertinent for the given frequency will be shown as well. In most cases, however, photocurrents are fairly small requiring methods with a better signal-

to-noise ratio, for instance the lock-in technique. In this case the frequency control of the chopper sends a reference signal, ji, to the lock-in amplifier and the current equivalent signal, *I,* feeds the input of the lock-in amplifier. Since lock-in amplifiers tend to pick up noise, usually measurements with and without light are necessary in order to make a base line correction. The output of the lock-in amplifier can be used for the measurement of photocurrent spectra and photocurrent potential curves. In order to obtain intensity-corrected spectra, the intensity *vs* wavelength of the light source has to be determined. This can be done by using a detector with known spectral response or a flat response in the desired wavelength range, e.g. a thermopile or a pyroelectric detector. Then the photocurrent can be transformed into quantum efficiencies with respect to incident radiation or, if the absorption is known, internal quantum efficiencies can be calculated. Because of various calibration curves and base line corrections, it is of advantage to use a microcomputer for data aquisition that also allows for an easier handling of the data

1.3.4 Examples

More recent work of photoelectrochemistry with passivated electrodes will now be reviewed (For older work the review of Kuwana [114] with its comprehensive bibliography should be consulted). Emphasis will be put on illustrative examples in order to demonstrate the various types of behavior of passive films. Some of the recent work that tries to point out the impact of an amorphous character of the passive film on photoelectrochemical behavior will be discussed. In the examples noble metals (including lb group metals), transition metals and valve metals will be distinguished. In the section on valve metals, passive films

modified by ion implantation will be included since they exhibit interesting structural properties those are reflected in their photoelectrochemical behavior.

Copper. The first detailed results for passivated copper electrodes were obtained by Paatsch [115]. He studied the influence of inhibitors on the corrosion behavior of copper using photopotential and photocurrent measurements in 0.1 M NaOH. While it was not clear that anodic photocurrents occured, cathodic photocurrents, associated with the oxide reduction, were observed. Such photocurrents are observed in neutral and basic solutions after the Cu(II)-oxide [$CuO/Cu(OH)_2$] reduction. The reduction of the Cu_2O film in a cyclic voltammogram is enhanced under illumination [116]. This indicates, in accordance with bulk properties of Cu_2O, that this film is p-type conducting. The absorption spectrum of Cu_2O [117,118] shows an extensive peak structure which derives from a number of different bands contributing to the absorption spectrum. This is still reflected in a photocurrent spectrum which was obtained in I M NaOH after reduction of the $CuO/Cu(OH)_2$ layer (Fig. 1.7) [119]. The various peaks obtained in the photocurrent spectrum can be related to the peaks in the absorption spectrum of Cu_2O [117]. Using the absorption data of Brahms and Nikitine [117] and combining it with the data in Fig. 1.6 (*d* = 2 nm), a quantum efficiency with respect to the absorbed number of photons can be estimated, which is approx. 2000. A similarly high value for oxide-covered gold electrode was estimated by Watanabe and Gerischer [120]. A recent study of copper in phosphoric acid by Pointu *eL al.* [121], which was mainly performed in the potential regime where polishing occurs, showed anodic photocurrents. The spectra, however, do not allow for an identification of the film because of a wavelength spacing of only about 50 nm which does not give a good enough resolution.

In a later interpretation, a band structure model was discussed with conductivity types changing within the film [122].

1.3.5 Conclusions

In the given description of the background of the photoelectrochemical behavior of passive films, it was shown that the stoichiometry and structural properties of the film are well reflected in photoelectrochemical data. Amorphous and crystalline films are different in their spectral behavior as well as in the potential dependence of the photocurrent due to the participation of localized states in amorphous films. The question, therefore, as to whether the passive film is amorphous or crystalline should be answerable by means of photoelectrochemistry, the specific advantages being that the radiation used in the experiment is not damaging to the film and that it is an *in situ* technique. Some of the more recent examples reviewed from the literature demonstrate this. To further exploit this potential, more elaborate techniques such as time resolved laser pulse analysis, as was done very recently by Plieth and coworkers [123,124] for oxide-covered platinum and passive iron, respectively, the analysis of photocapacities or the development of surfaceimaging should be applied to passive films.

1.4 References

[1] A. C. Hall, *Surf. Sci.*, 16 (1969) 1

[2] A. Rothen, *Rev. Sci. Instrum.*, 16 (1945) 26

[3] A. Rothen, *NBS Misc. Pub.*, 256 (1964) 7

[4] A. Vasicek, *Phys.Rev.*, 57 (1940) 925

[5] A. Vasicek, *J. Opt. Soc. Am.,* 37 (1947) 145

[6] W. Paik and Z. Szklarska-Smialowska, *Surf. Sci.,* 96 (1980) 401

[7] L. J. Hanekamp, W. Lisowski, and G. A. Bootsma, *Surf. Sci.,* 118 (1982) 1

[8] J. Kruger, *J. Electrochem. Soc.,* 110 (1963) 654

[9] Z. Szklarska-Smialowska and R. W. Staehle, *J. Electrochem. Soc.,*121 (1974) 1146

[10] J. Horkans, B. D. Cahan, and E. Yeager, *J. Electrochem. Soc.,* 122 (1975) 1585

[11] J. L. Ord, Z. Q. Huang, and D. J. De Smet, *J. Electrochem. Soc.,* 2076 (1985) 2076

[12] B. E. Conway, H. Angerstein-Kozlowsks, and L. Laliberte, *J. Electrochem. Soc.,*121 (1974) 1596

[13] D. E. Aspnes, *Surf. Sci.*, 101 (1980) 84

[14] M. Fleischmann, P. J. Hendra, and A. McQuillan, *J. Chem. Phys. Lett.,* 26 (1974) 163

[15] D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.,* 84 (1977) 1

[16] M. G. Albrecht and J. A. Creighton, *J. Am. Chem. Soc.,* 99 (1980) 351

[17] R. L. Panl, A. J. McQuillan, P. J. Hendra, and M. Fleischmann, *J. Electroanal.Chem.,* 66 (1975) 248

[18] B. H. Loo and T. E. Furtak, *Chem. Phys. Lett.,* 71 (1980) 68

[19] H. Yamada and Y. Yamamoto, *Chem. Phys. Lett.,* 77 (1981) 520

[20] A. V. Bobrov, Ya. M. Kimel'fel'd, and L. M. Mostovaya, *J. Mol. Struct.,*60 (1980) 431

[21] P. F. Liao and M. B. Stern, *Opt. Lett.,* 7 (1982) 483

[22] P. A. Lund, R. R. Smardzewski, and D. E. Tevault, *Chem. Phys. Lett.*, 89 (1982) 508

[23] P. A. Lund, D. E. Tevault, and R. R. Smardzewski, *J. Phys. Chem.*, 88 (1984) 1731

[24] W. Schulze, B. Breithaupt, F. Frank, and F. W. Froben, *Surf. Sci.*, 156 (1985) 963

[25] J. F. Brazdil and E. B. Yeager, J. Phys. Chem., 85 (1981) 2194

[26] T. Takamura, K. Takamura, W. Nippe, and E. Yeager, *J. Electrochem. Soc.*, 117 (1970) 626

[27] T. Takamura, K. Takamura, and E. Yeager, *J. Electroanal. Chem. Interfacial Electrochem.,* 29 (1971) 279

[28] A. Bewick, G. J. Edwards, J. M. Mellor, and B. S. Pons, *J. Chem. Soc., Perkin Trans. 2,* (1977) 1952

[29] A. Bewick, J. M. Mellor, and B. S. Pons, *Electrochim. Acta,* 25 (1980) 931

[30] B. E. Conway and S. Gottesfeld, *J. Chem. Soc. Faraday Trans. 1,* 70 (1974) 1793

[31] J. D. E. McIntyre and W. F. Peck, *Faraday Discuss. Chem. Soc.,* 56 (1973) 122

[32] A. Bewick, K. Kunimatsu, and B. S. Pons, *Electrochim. Acta,* 25 (1980) 465

[33] A. Bewick, and K. Kunimatsu, *Surf. Sci.,* 101 (1980) 131

[34] A. Bewick, K. Kunimatsu, J. Robinson, and J. W. Russell, *J. Electroanal. Chem. Interfacial Electrochem.,* 119 (1981) 175

[35] A. Bewick and J. W. Russell, *J. Electroanal. Chem. Interfacial Electrochem.,*132 (1982) 329

[36] A. Bewick and J. W. Russell, *J. Electroanal. Chem. Interfacial Electrochem.,* 142 (1982) 337

[37] B. Beden, A. Bewick, K. Kunimatsu, and C. Lamy, *J. Electroanal. Chem. Interfacial Electrochem.,* 121 (1981) 343

[38] B. Beden, A. Bewick, K. Kunimatsu, and C. Lamy, *J. Electroanal. Chem. Interfacial*

Electrochem., 142 (1982) 345

[39] J. W. Russell, J. Overend, K. Scanlon, M. W. Severson, and A. Bewick*, J. Phys. Chem.,* 86 (1982) 3066

[40] T. Davidson, B. S. Pons, A. Bewick, and P. P. Schmidt, *J. Electroanal. Chem. Interfacial Electrochem.,* 125 (1981) 237

[41] C. L. McBee and J. Kruger, *Electrochim. Acta,* 17 (1972) 1337

[42] J. Kruger, G. G. Long, M. Kuriyama, and A. I. Goldman, *passivity of Metals and Semiconductors,* p. 163. Elsevier, Amsterdam, 1983

[43] G. G. Long, J. Krufer, D. R. Black, and M. Kruiyama, *J. Electroanal. Chem.,* 150 (1983) 603

[44] G. G. Long, J. Kruger, D. R. Black, and M. Kuriyama, *J. Electrochem. Soc.* 130 (1983) 240

[45] G. G. Long, J. Kruger, M. Kuriyama, D. R. Black, E. N. Farabaugh, D. M. Sanders, and A. I. Goldman, *Proceedings of the International Conference on Metallic Corrosion,* Vol. 3, p. 419. National Research Council of Canada, Ottawa, 1984.

[46] G. G. Long, J. Kruger, and M. Kuriyama, *Passivity of Metals and Semiconductors* (M. Froment, ed), p. 139. Elsevier, Amsterdam, 1983.

[47] B. X. Yang, J. Kirz, and I. McNulty, *Proc. SPIE—Int. Soc. Opt. Eng.,* 689, (1986) 34

 48] R. W. Wood, *Philos. Mag.* 4 (1902) 396

[49] B. X. Yang, J. Kirz, and S. Xu, *Nucl. Inst. and Meth.* A258 (1987) 141

[50] J. K. Hawkins, H. S. Isaacs, S. M. Heald, J. Tranquada, G. F. Thomson, and G. F. Wood, *Corros. Sci.* 27 (1987) 391

[51] M. Koudelkova, J. Augustinski, and H. Berthou, *J. Electrochem. Soc.* 124 (1977) 1165

[52] M. F. Abd Rabbo, J. A. Richardson, G. C. Wood, and C. K. Jackson, *Corros. Sci.,* 16 (1976) 677

[53] J. McBreen, W. E. O'Grady, K. I. Pandya, R. W. Hoffman, and D. E. Sayers, *Langmuir*, 3 (1987) 428

[54] J. McBreen and W. E. O'Grady, *Natl. Synchrotron Light Source Annu. Rep.,* P. 289 (1986)

[55] A. C. Boccara, D. Fournier, and J. Badoz, *Top. Meet. Photoacoustic Spectrosc.,* Ames, Iowa (1979).

[56] A. C. Boccara, D. Fournier, and J. Badoz, *Appl. Phys. Lett.* 36 (1980) 130

[57] N. M. Amer**,** *J. Phys. (Orsay, Fr.)* 44 (1983) C6-185

[58] D. Fournier, A. C. Boccara, N. M. Amer, and R. Gerlach, *Appl. Phys. Lett.* 37, (1980) 591

[59] J. A. Sell, *Photothermal Investigations of Solids and Fluids.* Academic Press, Berkeley, California, 1989.

[60] A. C. Boccara, D. Fournier, W. Jackson, and N. M. Amer, *Opt. Lett.* 5 (1980) 377

[61] H. L. Fang and R. L. Swofford, "The Thermal Lens in Absorption Spectroscopy." *Ultrasensisitve Laser Spectroscopy* (D. S. Kliger, ed.). Academic Press, San Francisco, California, 1983.

[62] *"In Situ Characterization of Electrochemical Processes,"* Publ. NMAB 438-3. National Materials Advisory Board, Commission on Engineering and Technical

[63] M. J. Armstrong and R. H. Muller, *J. Electrochem. Soc.*, 136 (1989) 584

[64] D. Fournier, A. C. Boccara, N. M. Amer, and R. Gerlach, *Appl. Phys. Lett.* 37, (1980) 591

[65] A. C. Boccara, D. Fournier, W. Jackson, and N. M. Amer, *Opt. Lett.* 5 (1980) 377

[66] R. E. Russo, F. R. McLarnon, J. D. Spear, and E. J. Cairns, *J. Electrochem. S*oc., 134 (1987) 2783

[67] B. S. H. Royce, D. Voss, and A. Bocarsley, *J. Phys. (Orsay, Fr.)* 44 (1983) C6-325

[68] R. Sonnenfeld, J. Schneir and P. K. Hansma, *Modern Aspects of Electrochemistry*, Vol 21, Plenum Press, New York, 1990, pp. 1-28

[69] T. R. I. Cataldi, I. G. Blackham, and G. Andrew, D. Briggs, *J. Electroanal. Chem.*, 290 (1990) 1

[70] Proceedings of the 5th International Conference on STM, *J. Vac. Sci. Technol.*, B9 (1991) 401

[71] Proceedings of the 6th International Conference on STM, *Ultroamicroscopy,* Vol. 42-44 (1992)

[72] D. M. Kolb, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 11, John Wiley and Sons, New York, 1978, pp. 125-271

[73] D. M. Kolb, *Ber Bunsengesn. Phys. Chem.*, 92 (1988) 1175

[74] A. Mamelin, Modern Aspects of Electrochemistry, Vol. 16, Plenum Press, New York, 1985, pp. 1-101

[75] P. N. Ross and F. T. Wagner, *Advances in Electrochemistry and Electrochemical Engineering,* Vol. 13, John Wiley and Sons, New York, 1984, pp. 69-112

[76] A. T. Hubbard, *Langmuir*, 6 (1990) 97

[77] H. Gerischer, *Electrochim. Acta*, 35 (1990) 1677

[78] R. Memming, *Electroanalytical Chemistry*, Vol. 11, Marcel Dekker, New York, 1979, pp. 1-84

[79] R. Sonnenfeld and P. K. Hansma, *Science*, 232 (1986) 211

[80] A. G. Bell, *Am. J. Sci.*, 20 (1880) 305

[81] J. Tyndall, *Proc. R. Soc. London*, 31 (1881) 307

[82] W. C. Rontgen, *Philos. Mag.*, 11 (1881) 308

[83] A. G. Bell, *Philos. Mag.*, 11 (1881) 510

[84] M. L. Viengerov, *Dokl. Akad. Nauk. SSSR*, 19 (1938) 687

[85] Y.-H. Pao, Ed: *Optoacoustic Spectroscopy and Detection*, Academic Press, Inc., New York, 1977

[86] A. Rosencwaig, *Analytic Chemi*stry, 47 (1975) 592A

[87] L.-G. Rosengren, *Appl. Opt.*, 14 (1975) 1960

[88] R. Gerlach and N. M.. Amer, *Appl. Phys.*, 23 (1980) 319

[89] M. S. Shumate, R. T. Menzies, J. S. Margolis, L.-G. Rosengren, *Appl. Opt.*, 15 (1980) 2480

[90] A. Rosengwaig, *Photoacoustics and Photoacoustic Spectroscopy*, P. 137, John Wiley & Sons, New York, 1980

[91] S.Yoshihara, A.Aruchamy and A. Fujishima, *Bull. Chem. Soc. Jpn.*, 61 (1988) 1017

[92] S. Yoshihara, R. Takahashi, M. Okamoto, E. Sato and A. Fujishima, *Electrochim. Acta,* 36 (1991) 1959

[93] M. J. Adams and G. F. Kirkbrignt, *Analyst*, 102 (1977) 281

[94] U. Sander, H.-H. Strehblow and J. K. Dohrmann, *J. Phys. Chem*, 85 (1981) 447

[95] A. Fujishima, H. Masuda and K. Honda, *Bull. Chem. Soc. J*pn, 53 (1980) 1542

[96] A. Fujishima, H. Masuda and K. Honda, *Chem. Lett.*, 1979, 1963

[97] S. Yoshinara, E. Sato and A. Fujishima, *Ber. Bunsenges. Phys. Che*m., 94 (1990) 603

[98] H. Masuda, A. Fujishima, and K. Honda, *Chem. Lett*., 1980, 1153

[99] H. Masuda, S. Morishita, A. Fujishima, and K. Honda, *J. Electroanal. Chem*., 121 (1981) 363

[100] S. Yoshihara, A. Aruchamy, and A. Fujishima, *Bull. Chem. Soc. J*pn., 61 (1988) 1017

[101] E. Becquerel, *Cr. hebd. Séanc. Acad. Sci.,* Paris 9 (1839) 561

[102] Yu. Ya. Gurevich, Yu. V. Pleskov and Z. A. Rotenberg. *Photoelectrochemistry.* Consultants Bureau, New York (1980).

[103] S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes.* Plenum Press, New York (1981).

[104] A. Heller (Ed.), *Semiconductor Liquid-Junction Solar Cells.* The Electrochemical Society. Princeton, New Jersey (1977).

[105] W. L. Wallace, A. J. Nozik, S. K. Deb and R. H. Wilson (Eds), *Photoelectrochemistry: Fundamental Processes and Measurement Techniques.* The Electrochemical Society Princeton, New Jersey (1982)

[106] W. W. Gaertner, *Phys. Rev*. 116 (1959) 84

[107] M. A. Butler, *J. appl. Phys.* 48 (1977) 1914

[108] R. H. Bube, *Photoconductivity of Solids.* Wiley, New York (1967)

[109] J. I. Pankove, *Optical Processes in Semiconductors.* Dover, New York (1975)

[110] R. H. Wilson, *J. appl. Phys.* 48 (1977) 4292

[111] J. Reichman, *Appl. Phys. Lett.* 36 (1980) 574

[112] W. J. Albery, P. N. Bartlett, A. Hamnett and M. P. Dare-Edwards, *J. elect rochem. Soc.* 128 (1981) 1492

[113] D. Haneman and J. F. McCann, *Phys. Rev. B* 25 (1982) 124

[114] T. Kuwana, in *Elect roanalytical Chemistry* (Edited by A. J. Bard), Vol. 1. Marcel

Dekker, New York (1966)

[115] W. Paatsch, *Ber. Bunsenges Phys. Chem.*, 81 (1977) 645

[116] U. Sander, H-H. Strehblow and J. K. Dohrmann, *J. phys. Chem.* 85 (1981) 447

[117] S. Brahms and S. Nikitine, *Solid State Comm.* 3 (1965) 209

[118] S. P. Tandon and J. P. Gupta, *Phys. stat. Sol.* 37 (1970) 43

[119] U. Stimming, in *Passivity of Metals and Semiconductors* (Edited by M. Froment),

p. 509. Elsevier, Amsterdam (1983).

[120] T. Watanabe and H. Gerischer, *J. electroanal. Chem.* 117 (1981) 185

[121] B. Pointu, M. Braizaz, **P.** Poucet, J. Rousseau and N. Muhlstein, *J. electroanal.*

Chem. 122 (1981) 111

[122] B. Pointu, M. Braizaz, P. Poucet and J. Rousseau, *J. electroanal. Chem.* 15 (1983)

65,79

[123] W. J. Plieth and K. J. Foerster, in *Surface Studies with Lasers, Chemical Physics*,

Vol. 33 (Edited by F. R. Aussenegg et al.), Springer, New York

[124] A. Felske and W. J. Plieth, *Ext. Abstracts*, 36 th I.S.E. Meeting, Salamanca, Spain

(1985)

Fig. 1.1 A basic **PDS** system. The source provides broadband light that is dispersed by the monochromator. The narrowband excitation light leaving the monochromator is modulated by a mechanical chopper and focused onto the electrode. The probe beam passes parallel to the electrode surface. Deflections of the probe beam are detected with the position detector (PD).

Fig. 1.2 Schematic diagram of (a) the photoacoustic cell and (b) the experimental arrangement.

Fig. 1.3 PAS cell with microphone as detector

Fig. 1.4a Diagram of the double-beam PAS setup

Fig. 1.4b PAS cell with microphone: (M) microphone, (WE) working electrode, (QW) quartz window. The counter and reference electrodes are not shown.

Fig. 1.5 Schematic representation of an illuminated p-type (a) and n-type (b) passive film under depletion conditions and of an insulating film under flat band conditions with a simultaneous excitation in the film (hv$_1$) and in the underlying metal (hv$_2$) (c).

Fig. 1.6 Schematic representation of an experimental set-up for photoelectrochemical studies of passive films

Fig. 1.7 Photocurrent spectrum of the passive film on copper electrode after reduction of the CuO/Cu(OH)$_2$ film

Chapter 2

In-situ Photothermal Spectroscopy of Oxide Film on Copper Electrode in NaOH Solution

2.1 Introduction

Photothermal Spectroscopy (**PTS**) is a spectroscopic technique particularly useful for obtaining spectra of highly absorbent sample, e.g., metal or semiconductor electrode, by measuring directly the temperature change which occur upon absorption of radiation.

Photothermal Spectroscopy (**PTS**) and Photoacustic Spectroscopy (**PAS**) have the similar principles. When the light is absorbed by the surface of electrode, there is temperature change at the electrode/electrolyte interface and this temperature change will raise the elastic waves and then the pressure change. Measuring directly the temperature change is **PTS**, and measuring the pressure change is **PAS**. So **PTS** is more directly than **PAS** in terms of theory.

In 1977, Bard et al first introduced the technique of **PTS** where a thermistor in contact with a sample was employed to detect temperature changes caused by radiationless transitions resulting from the absorption of light by the sample [1]. Bard et al also reported

in 1977 their application on the characterization of various semiconductor materials (single crystal and polycrystalline) and the study of photoelectrochemical reactions at semiconductor electrodes [2]. Bard et al also successfully reported in 1980 the application of **PTS** to in-situ study on metals and electrodes [3,4]. Except the above study reports, there had been seldom other practical applications of **PTS** in electrochemical research in the following 10 years due to the limitation of sensitivity of this method, the lower limit for detection was of the order of 75-100 monolayers in some case [3] while the sensitivity for **PAS** was only several monolayers [5]. As Bard et al pointed out, the sensitivity of **PTS** could be improved by instrumental changes such as more intense light sources, e.g. laser, more sensitive thermal detectors, and light modulation or signal-averaging techniques [3].

In 1984, Mandelis developed a new **PTS** method using pyroelectric polyvinylidene difluoride (PVDF) film detector to investigate the properties of Ho_2O_3 powder and to monitor the kinetics of the chemical reaction of CuO with HCl [6]. Till 1989, Jiang et al began to report the new **PTS** experimental set up with PVDF as thermal detector to study in-situ the surface properties of an electrode [7-10]. The method was similar to that used for the investigation of photo-oxidation of ions on semiconductor electrode introduced in 1990 by Dohrmann et al [11].

The objective of this chapter is to present the **PTS** experimental set up with PVDF film as a thermal detector, the theoretical treatment of photothermal signal, and the application of investigation on the copper electrode.

2.2 Experimental

2.2.1 Experimental Setup

The experimental set up for **PTS** using different cell is similar [3,9], including light source, chopper, **PTS** cell with different detector, potentiostat, lock-in amplifier, and X-Y record. Fig. 2.1 shows the experimental set up for **PTS** with PVDF film as a thermal-detector. The light source was an Ar^+ laser and the exciting rediation was 488.0 nm with 200 mw power. The electrochemical, in-situ **PTS** measurement was carried out with an EG&G M273A Potentiostat/Galvanostat, an EG&G M5210 lock-in amplifier, and an EG&G M651 light chopper

2.2.2 PTS Cell

The PTS cell is shown in Fig. 2.2 [8]. The electrochemical cell was manufactured from a piece of Teflon bar. A copper foil (purity 99.95%) of thickness 0.025mm, a platinum wire and an Hg/HgO/0.1M NaOH were sued as working electrode, counter electrode and reference electrode, respectively. The reference electrode was located near the copper foil. The potentials reported in this paper are referred to this electrode. When the detector tube was assembled into the back hole of the cell, the upper face of the PVDF pyroelectric film was contact very close with the back side of the working electrode foil (Fig. 2.2b). Therefore, the heat produced at the front side of the electrode foil by absorption of incident light could be transported to PVDF film and then transformed into an electric signal, which was finally measured by a lock-in amplifier.

2.2.3 Chemicals

Copper foil used as substrate and electrode material (Goodfellow) was polished with #1200 of emery paper, alumina (0.3 μm), ultrasonic clean for 5 min, rinsed with D.I water, and then treated in 50 v/v% HNO_3 for few second and thoroughly rinsed with 99.5% ethanol and D.I water before use. All reagents were A.R grade and the solutions were made up with deionized water.

2.3 Results and Discussion

2.3.1 Theoretical Model

Even though there are already a lot of reports of theoretical analyses on **PAS** [11-13], such analyses on **PTS** are comparatively lesser. R. Tom et al discussed the thermal diffusion in **PTS** in 1979 [14]. In some theoretical analyses of **PAS**, modeling of thermal diffusion can also be found [12,13]. In this experiment, metallic materials were used as electrode, thus light can only effect on its surface layer but not penetrate into its inner part, and hence a simple model can be proposed.

Suppose that the electrode surface is at position of x = 0, and its thickness is d. Light is directed perpendicularly to the electrode surface and the intensity at the electrode surface is I_λ. Because of chopping by a mechanical chopper, I_λ varies cosinoidally.

$$I_\lambda = I_0 \cos\omega t \qquad (1)$$

Where I_0 is amplitude of the intensity of light, ω is angular velocity, and take the absolute value of the cosine part in the formula. Since the thermal conductivity of metals is much higher than that of liquids (Cu: $\lambda = 380$ w.m^{-1}.K^{-1}, H$_2$O: $\lambda = 0.6$ w.m^{-1}.K^{-1}), thus it can be presumed that the heat generated on the surface travels into the metal part at a larger ratio. Apart from this, the electrode thickness is much smaller than its surface dimension, thus it can be regarded as a one-dimensional process of thermal diffusion. Under low frequency, thermal conduction of PVDF film is relatively better than that of under high frequency, hence the whole system could be approximated as a semi-infinite thermal diffusion process.

If the initial temperature of the specimen is assumed to be at standard zero level, and if the increasing temperature on the surface of the specimen at the initial stages is neglected, and only the stage at which equilibrium temperature is established on the specimen surface is considered, the surface temperature at this time is

$$T_{x=0} = T_0 \cos(\omega t - \theta) \qquad (2)$$

Where T_0 is the amplitude value, θ is the phase difference. Under such condition, the temperature distribution of the inner part of the electrode can be obtained [15].

$$T = T_o e^{-bx} \cos(\omega t - bx - \theta) \qquad (3)$$

Where
$$b = \left(\frac{\omega}{2\alpha} \right)^{1/2} \qquad (4)$$

And
$$\alpha = \frac{k}{\rho c} \qquad (5)$$

α is the thermal diffusion constant of the solid specimen, k is the thermal conductivity, ρ is density and c is the specific heat capacity.

Under stable conditions, the heat energy generated by light absorption from the surface is equal to the heat energy conducted out. As mentioned previously, under our experiment, light is absorbed by either the surface of the metallic electrode or the oxide film on the surface. If it is assumed that the chopping speed of light is not fast enough, this will not affect the light-thermal conversion efficiency of the surface, then the heat generated H_0 on the surface is directly proportional to I_λ,

$$H_o = \varepsilon I_\lambda = \varepsilon I_o \cos \omega t \tag{6}$$

ε is the light-thermal absorption coefficient of the specimen for incident light. It is related to light absorption coefficient and surface reflectance.

If the portion of heat conducted into the liquid is neglected, the heat energy conducted from the surface to the inner part of the electrode can be obtained from heat conduction Fourier's law

$$H' = -k(\frac{\partial T}{\partial x})_{x=0} \tag{7}$$

Substituting (3) into the above formula

$$H' = -kT_0 b e^{-bx} \left[\sin(\omega t - bx - \theta) - \cos(\omega t - bx - \theta) \right] \tag{8}$$

Since,
$$\sin \alpha - \cos \alpha = -\sqrt{2} \cos(\alpha + \frac{\pi}{4}) \tag{9}$$

Thus,
$$H' = \sqrt{2} kT_0 b e^{-bx} \cos(\omega t - bx - \theta + \frac{\pi}{4}) \tag{10}$$

When x = 0, we get,
$$H' = \sqrt{2} kT_o b \cos(\omega t - \theta + \frac{\pi}{4}) \tag{11}$$

Although there is phase difference between heat generated and heat diffused, their absolute values are the same, so the module of H_0 and H' are equal.

That is
$$\varepsilon I_0 = \sqrt{2}kT_0 b . \tag{12}$$

Substituting into (3), and the temperature distribution of the inner part of the electrode is

$$T = \frac{\varepsilon I_o}{\sqrt{2}kb} e^{-bx} \cos(\omega t - bx - \theta) \tag{13}$$

For the case where heat energy is conducted into the liquid, the above formula should be multiplied with the distribution ratio coefficient of heat energy conducting into the electrode's inner part. The temperature that the PVDF film detected is the temperature at the back surface (i.e. $x = d$).

Here
$$T_{x=d} = \frac{\varepsilon I_o}{\sqrt{2}kb} e^{-bd} \cos(\omega t - bd - \theta) \tag{14}$$

the voltage output of the PVDF film is related to the temperature distribution inside the film. It is not only decided by the temperature to be detected, but also directly proportional to $\omega^{-1/2}$ when the thickness of the film is larger than its thermal diffusion wavelength. If the thermal-electricity conversion coefficient of thermal sensor is ξ, the voltage V of the thermal probe is

$$V = \frac{\varepsilon \xi I_o}{\sqrt{2}kb\omega^{1/2}} e^{-bd} \cos(\omega t - bd - \theta) \tag{15}$$

if the electronic materials is fixed, the voltage is the function of the optical property ε of the electrode's surface substance. The property of the surface substance can thus be determined. In order to prove the above relationship, the following experiments are performed.

The Relationship of ∇ and ω

The module of V, ∇ can be obtained from lock-in amplifier. Substitute (4) into (15) and take the module of it

$$\nabla = \frac{\varepsilon \xi I_o \alpha^{\frac{1}{2}}}{k\omega} \exp-(\frac{\omega}{2\alpha})^{\frac{1}{2}}d \qquad (16)$$

Where $\dfrac{\varepsilon \xi I_0 \alpha^{1/2}}{k}$ is constant for the fixed system. Thus ∇ is proportional to

$\omega^{-1}\exp-(\dfrac{\omega}{2a})^{\frac{1}{2}}d$. The different ∇ can be obtained by changing the chopping frequency f

($\omega = 2\pi f$). Table 2.1 shows the experiment result.

f/Hz	5	10	15	20	30	40	50
$10^2 \times f^{-1}$	20	10	6.67	5.0	3.33	2.5	2.0
$\omega = 2\pi f$	31.4	62.8	94.2	125.7	188.5	251.3	314.2
$\nabla/\mu v$	1840	780	570	360	130	75	62
$10^3 \times \omega^{-1}\exp-(\frac{\omega}{2a})^{\frac{1}{2}}d$	31.3	15.5	10.3	7.69	5.09	3.79	3.02

Tab.2.1 Value of ∇ at different ω, $\lambda = 488.0$ nm, d = 0.0025 cm.

The α of Cu is 0.34 cm^2.s^{-1} [9]. The thickness of Cu used is 0.0025 cm. The relationship of

∇ and $\omega^{-1}\exp-(\dfrac{\omega}{2a})^{\frac{1}{2}}d$ is shown in Fig.2.3. In this experiment, $\exp-(\dfrac{\omega}{2a})^{\frac{1}{2}}d \approx 1$ (Tab.

2.2), therefore, ∇ is direct proportional to ω^{-1} or f^{-1} ($\omega = 2\pi f$), which is shown in Fig.2.4.

Both Fig.2.3 and Fig.2.4 show that the relationship is linear when ω is lower and the

extended line passes through the origin. When ω is higher, the thermal conductivity of

PVDF film is reduced, and hence affects the existence of its semi-infinite thermal diffusion, the experimental values are deviated [9].

f/Hz	5	10	15	20	30	40	50
$\exp-(\frac{\omega}{2a})^{1/2}d$	0.983	0.976	0.971	0.967	0.959	0.953	0.948

Tab.2.2 Value of $\exp-(\frac{\omega}{2a})^{1/2}d$ at different f, λ = 488.0 nm, d = 0.0025 cm.

The Relationship of Photothermal Signal and Specimen Thickness d

From (16), $\qquad \lg \nabla = -0.434bd + \lg \dfrac{\varepsilon \xi I_o}{\sqrt{2}kb\omega^{1/2}}$ $\qquad\qquad$ (17)

lg∇ and specimen thickness d is linearly related. By changing the number of pieces, *N*, used for the Cu electrode, the thickness (d = N x 0.0025) of the electrode can be changed. The result is shown in Table 2.3 and Figure 2.5, and good linear relationship is observed. Of course, this includes the influence of the air gap between two Cu pieces.

N	1	2	3	4	5
∇/μv	780	650	250	150	62
lg∇	2.89	2.81	2.40	2.18	1.79

Tab.2.3 Value of lg∇ at different N. N is the number is copper foil, λ = 488.0 nm, f = 10 Hz

2.3.2 PTS Spectrum

Under the illumination of a laser, the in-situ photothermal spectrum, simultaneously with the cyclic voltammatry (CV) on copper electrode in 0.1 M NaOH solution were carried out, shown in Fig. 2.6.

The CV curve is similar to the reported behaviour of copper [17-21]. Three anodic peaks (I, II and III) and two cathodic peaks (IV and V) were observed, as shown in Fig.2.6 (a). Anodic peak I corresponds to the formation of a layer of Cu_2O, peak II corresponds to the formation of CuO on the Cu_2O underlayer and peak III corresponds to the formation of a duplex layer of Cu (II) (CuO and/or $Cu(OH)_2$). On the reverse scan, the cathodic peak IV and V corresponds to the reduction of Cu (II) to Cu_2O and Cu_2O to Cu, respectively.

The in-situ PTS spectrum is shown in Fig.2.6 (b). It is very similar to the PAS spectra reported by J. K. Dohrmann and his co-workers [21]. The PTS signal is zero when the surface of copper is under dark and is about 17.0 (relative value) when it is under the illumination of a laser. This reflects the high temperature of the surface when the light is absorbed by the surface of copper. As the positive potential sweep, the PTS signal is kept the same value till anodic peak I where PTS signal starts to rise with the formation of Cu_2O. This rising corresponds to the formation and growth of the Cu_2O layer, because the light absorption of Cu_2O is larger than that of Cu [21,22]. The initial decrease around anodic peak II can be attributed either to an initial oxidation of Cu_2O to give less absoptive CuO or to an initial oxidative dissolution of the layer in the strongly alkaline electrolyte [21,22]. With the formation and growth of the duplex layer of Cu(II) (CuO and/or $Cu(OH)_2$) at around

anodic peak III, PTS signal gradually increased. During the reverse scan, the PTS signal remains constant and then rises at cathodic peak IV with the reduction of Cu(II) to Cu_2O because of the larger absorption of Cu_2O than that of Cu(II) [21,22]. At cathodic peak V, PTS signal goes down to the original value with the reduction of Cu_2O to Cu.

2.4 Conclusions

A photothermal spectroscopy (PTS) method using a polyvinylidene difluoride (PVDF) pyroelectric film as thermal-detector has been studied on theoretical model analysis and in-situ application of oxide layer on a metal electrode.

The theoretical model, simple one-dimensional heat transport model, was used to analyze the photothermal signal and has been party proved by some experiments. The photothermal response is linear with film thickness and inverse proportional to the chopping frequency f when the frequency is lower.

From the variations of the **PTS** signal, the redox reaction of copper surface layers between Cu, Cu_2O, and $CuO/Cu(OH)_2$ at different potentials was observed. This proved that the PTS method using PVDF film as thermal-detector is very sensitive and fast response for measuring surface changes. This PTS method has the advantages of simplicity and versatility. It allows a more flexible sample cell arrangement and is free from external acoustic noise, compare with **PAS** method.

2.5 Reference

[1] G. H. Brilmyer, A. Fulishima, K. S. V. Southanam and A. J. Bard, *Anal. Chem.*
49 (1977) 2057

[2] A. Fulishima, G. H. Brilmyer, and A. J. Bard, in "Semiconductor Liquid-Junction
Solar Cells", A. Heller, Ed., Electrochemical Society, Inc., Princeton, N. J.
(Proceedings Vol. 77-3), 1977, pp 172

[3] G. H. Brilmyer and A. J. Bard, *Anal. Chem.*, 52 (1980) 685

[4] A. Fulishima, H. Masuda, K. Honda, and A. J. Bard, *Anal. Chem.*, 52 (1980) 682

[5] H. Masuda, A. Fulishima, and K. Honda, *Bull. Chem. Soc, Jpn*, 53 (1980) 1542

[6] A. Mandelis, *Chem. Phys. Lett.*, 108 (1984) 388

[7] Z. Jiang, Y. Xiang and J. Wang, *Extended Abstracts of the Fifth Chinese
Electrochemistry Conference*, 1989, Chinese Electrochemistry Society, Ji Nan, No.
1A12

[8] Z. Jiang, Y. Xiang, J. Wang, *J. Electroanal. Chem.*, 316 (1991) 199

[9] Z. Jiang, Y. Xiang, J. Wang, and J. Wu, *Acta Chimica Sinica*, 50 (1992) 372

[10] Z. Jiang, X. Zhang, and Y. Xiang, *J. Electroanal. Chem.*, 351 (1993) 321

[11] J. Rappich, N.-S. Schaaf, and J. K. Dohrmann, *J. Electroanal. Chem.*, 279 (1990)
123

[12] A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, 47 (1976) 64

[13] M. J. Adams and G. F. Kirkbright, *Analyst*, 102 (1977) 281

[14] A. C. Tam, *Rev. Modern Phys.*, 58 (1986) 381

[15] R. Tom, T. A. Moore, and S. H. Lin, *Chem. Phys. Lett.*, 66 (1979) 390

[16] H. S. Carslaw, J. C. Jaeger, "*Conduction of Heat in Solids*", 2nd Edn., Clarendon Press, Oxford, 1986

[17] U. Collish and H.-H. Strehblow, *J. Electroanal. Chem.*, 210 (1986) 213

[18] L. M.Abrantes, L. M.Castillo, C. Norman and L. M.Peter, *J. Electroanal. Chem.*, 163 (1984) 209

[19] A. Aruchamy, G.-D. Zhou and A. Fulishima, *J. Electroanal. Chem.*, 244 (1988) 333

[20] U. Collisi and H.-H. Strehblow, *J. Electroanal. Chem.*, 284 (1990) 385

[21] U. Sander, H.-H. Strehblow and J.K. Dohrmann, *J. Phys. Chem.*, 85 (1981) 447

[22] R. E. Russo, F.R. Mclarnon, J.D. Spear and E.J. Cairns, *J. Electrochem. Soc.*, 134 (1987) 2783

light source   chopper   cell   potentiostat

lock-in amplifier   X-Y-Y record

Fig. 2.1 Block diagram of the photothermal spectroscopy system

Fig. 2.2 Electrochemical cell. (a) Pyroelectric transducer: (1) PVDF film; (2,5) stainless steel; (3) lead; (4) Teflon; (6) BNC cable. (b) Photothermal spectroscopy electrochemical cell: (1) PVDF film; (2) working electrode; (3) counter electrode; (4) reference electrode; (5) quartz window; (6) silicon rubber ring; (7) Teflon; (8) pyroelectric transducer.

$$10^{-3} x \omega^{-1} \exp - \left(\frac{\omega}{2\alpha} \right)^{1/2} d$$

Fig.2.3 Relationship between ∇ and $\omega^{-1} \exp - (\frac{\omega}{2a})^{\frac{1}{2}} d$. $\lambda = 488.0$ nm, d = 0.0025cm.

Fig.2.4 Relationship between ∇ and f. λ = 488.0 nm, d = 0.0025cm.

Fig.2.5 Relationship between lg ∇ and specimen thickness d (d = N x 0.0025cm). N is the number of copper foils, λ = 488.0 nm, and f = 10 Hz.

Fig. 2.6 Cyclic voltammogram (a) and PTS spectrum (b), on copper electrode in 0.1M NaOH. Potential scan rate = 5mv/s, f = 10 Hz, λ = 488.0 nm.

Chapter 3

A Study of Thermal Effect in Photocurrent Measurement on Copper Electrode in NaOH Solution by In-situ Photothermal Spectroscopy Method

3.1 Introduction

Copper has been extensively studied because of its relation to the field of corrosion and the electric industry. Although it has been studied for over half a century, the electrochemical behaviour of copper in alkaline solution continues to excite interest and controversy. During the past decades, in-situ spectrum techniques have been wildly used in this project. Photoelectrochemical method based on measurement of photopotential or photocurrent, mostly the photocurrent, due to illumination is one of them [1-9]. Photocurrent measurements have a distinct advantage in the determination of thin film electronic properties, such as type of conductivity, band gaps and nature of optical transitions. But the thermal effect which may confuse with electronic properties in photocurrent measurement has not been reported yet.

Photothermal Spectroscopy (**PTS**) and Photoacoustic Spectroscopy (**PAS**) are two useful in-situ techniques for surface analysis. **PTS** and **PAS** are under the same fundamentals. When light is absorbed by the surface of the electrode, the photo energy will be transferred

to thermal energy and there will be temperature change at the surface of the electrode. Making use of the measurement of the temperature change to study the surface of the electrode is the application of Photothermal Spectroscopy. If the thermal energy is further transferred to acoustic energy, that is the Photoacoustic Spectroscopy. So **PTS** is more directly than **PAS** in viewpoint of method of measurement. **PAS** was used to investigate in-situ properties of surface layers formed on metal electrodes, such as those on copper [10]. **PTS** using a thermistor as thermometer was also used to study in-situ the properties of the electrode surface [11,12]. The thermistor was located near the working electrode and measured the temperature change of the electrode. However, the method was not completely successful because the sensitivity of the thermistor was not very high.

In 1984, Mandelis first reported his work on increasing PTS sensitivity by using PVDF film [13, 14] as a thermal detector [15]. From 1989, other experimental set up on PTS application by using PVDF film to study in-situ the surface properties of an electrode by Zhiyu Jiang [16-20] and Dohrmann [21].

In this chapter, we reported the study of thermal effect in photocurrent measurement on copper electrode in 0.1M NaOH with a laser as a light source by the in-situ thermal technique.

3.2 Experimental

3.2.1 PTS Spectrum

The electrochemical cell and the test procedure for the in-situ **PTS** study have been described chapter 2. A copper foil (purity 99.95%) of thickness 0.0025cm, a platinum wire and an Hg/HgO/0.1M NaOH were sued as working electrode, counter electrode and reference electrode, respectively. The reference electrode was located near the copper foil. The potentials reported in this paper are referred to this electrode.

In order to get thermal signal, a pyroelectric PVDF film thermodetector was placed behind the working electrode. When light irradiated on the surface of the working electrode was absorbed with non-radiative relaxation, heat was produced. This heat was transported to the pyroelectric thermodetector and transformed to an electric signal that was finally measured by a lock-in amplifier. For **PTS** spectra, light was irradiated on interface of Cu/NaOH, as shown in Fig. 3.1(a).

3.2.2 Photocurrent Measurement and Thermal Effect Study

Fig. 3.2 shows the photocurrent measurement set up. For the **PTS** and photocurrent measurement, the light was irradiated on the interface of Cu/NaOH, while for the experiment of determination of thermal effect, the light was irradiated on the interface of Cu/air, the opposite side of Cu/NaOH, as shown in Fig. 3.1(a) and (b).

The electrochemical, in-situ **PTS** and photocurrent measurement was carried out with an EG&G M273A Potentiostat/Galvanostat, an EG&G M5210 lock-in amplifier and an EG&G

M651 light chopper. A chopping frequency of 10 Hz was used in all experiments. The light source was an Ar^+ laser and the exciting rediation was 488.0 nm with 200 mw.

3.2.3 Chemicals

Copper foil used as substrate and electrode material (Goodfellow) was polished with #1200 of emery paper, alumina (0.3 μm), ultrasonic clean for 5 min, rinsed with D.I water, and then treated in 50 v/v% HNO_3 for few second and thoroughly rinsed with 99.5 % ethanol and D.I water before use. All reagents were A.R grade and the solutions were made up with deionized water.

3.3 Results and Discussion

3.3.1 PTS Spectrum

Under the illumination of a laser, the in-situ photothermal spectrum, simultaneously with the cyclic voltammatry (**CV**) on copper electrode in 0.1 M NaOH, was carried out, shown in Fig. 3.3 (a) and (b). The CV curve is the same as that described in chapter 2 (p. 51) [1, 2, 4, 22, 23].

The in-situ PTS spectrum is shown in Fig. 3.3 (a). The detailed discussion in this spectrum is described in chapter 2 (p.51). The PTS signal is zero without light and is about 17.0 (relative value) when it is under the illumination of a laser. The different value of PTS

signal at different peak reflects the different composition or structure of the surface and hence the different temperature [23, 24].

During the whole cyclic scan, the high **PTS** signal, 17.0 or over than 17.0, reflects the high temperature of the surface of electrode when the light is absorbed by the surface of copper. As pointed by Arrhenius, $k = A \cdot \exp(-Ea/RT)$, rising in temperature will make an exponential rising in the rate of reaction and so in the current response. The thermal effect in photocurrent measurement is due to this reason.

3.3.2 Thermal Effect in Photocurrent Measurement

Fig. 3.3 (c) shows the photocurrent response on copper electrode in 0.1 M NaOH solution under the illumination of a laser. There are three peaks on positive scan and two peaks on the negative scan. It is believed, compared with cyclic voltammogram, that some of peaks correspond to the presence of p-Cu_2O, while others reflect the reactions related to the cyclic voltammatry. This implies that there might be two kinds of effect in photocurrment measurement: photo effect and thermal effect. The former is due to the presence of p-Cu_2O, and the latter is come from the high temperature at the surface when the light is absorbed by the surface of electrode. We refer to this photocurrent response including photo effect and thermal effect as total current and label it as I $_{total}$.

In order to identify the photo effect and thermal effect in the photocurrent measurement, an experiment, shown in Fig. 3.1 (b), was carried out in which the current response only due to thermal effect was measured when the Cu/air interface (the opposite side of Cu/NaOH

interface) was under the illumination of a laser. Fig. 3.3 (d) and (a) shows this part of current response and simultaneous cyclic voltammogram. A comparison of these two curves shows that the current response obtained from such experiment should be due to the thermal effect, because every peak in curve (d) reflects the reaction related to curve (a). We refer to this part of current response as thermal current and label it as I_{th}. When photocurrent was measured where the Cu/NaOH interface is under the illumination of a laser, there should be the same thermal effect. In these two experiments, the thermal current response is some different due to the different surface. The surface in the determination of thermal effect is always Cu, while it varies from Cu to Cu_2O and $CuO/Cu(OH)_2$ with the potential sweep in photocurrent measurement. Comparing with PTS signal from zero (dark) to 17.0 (illumination), 17.0 (Cu) to 18.5 (Cu_2O) are not much different. So it is believed that the current response (I_{th}) in these two experiments is almost the same.

The real component of the photocurrent, labelled as I_{ph}, due to photo effect is obtained by deducting the I_{th} from I_{total} as shown in Fig. 3.3 (e). A comparison of curve (e) and curve (a) shows that, on the positive scan, the onset of the anodic photocurrent at -0.30v reflects the formation of Cu_2O. The disappearance of photocurrent response was observed at $+0.3$ v in Fig. 3.3 due to either the formation of Cu(II) from Cu_2O or the flat-bank potential of p-Cu_2O at $+0.3$ v [1, 4, 25], since a thin layer of Cu_2O exists between the Cu(II) layer and the Cu electrode [5,22]. On the reverse scan, cathodic photocurrent begins at 0.30v which corresponds to the flat-band potential of p-Cu_2O [1, 4, 25], and increases with the reduction of Cu(II) to Cu_2O. Cathodic photocurrent is observed even at potential more negative than the reduction peak IV where Cu_2O is reduced to Cu metal, because some unreduced Cu_2O

layer still exists on the electrode between Cu metal and the surface copper formed in the process of Cu_2O reduction [4, 26].

3.4 Conclusions

The thermal effect in photocurrent measurement on copper electrode in 0.1M NaOH solution has been studied by a photothermal spectroscopy (**PTS**) mehtod using a polycinylidene difluoride (PVDF) pyroelectric film detector. That part of the photocurrent response due to thermal effect has been separated from the total photocurrent response, and the real part of photocurrent response due to photo effect has been obtained by deducting I_{th} from I_{total}. From our results, we suggest that the thermal effect be considered firstly when you want to use photocurrent spectra to study electronic properties of some semiconductor specimens.

3.5 References

[1] U. Collish and H.-H. Strehblow, *J. Electroanal. Chem.*, 210 (1986) 213

[2] L. M.Abrantes, L. M.Castillo, C. Norman and L. M.Peter, *J. Electroanal. Chem.*, 163 (1984) 209

[3] G.-D. Zhou, H. Shao and B.H. Loo, *J. Electroanal. Chem.*, 421 (1997) 129

[4] A. Aruchamy, G.-D. Zhou and A. Fujishima, *J. Electroanal. Chem.*, 244 (1988) 333

[5] A.D. Modestov, G.-D. Zhou and H.-H. Ge, *J. Electroanal. Chem*., 375 (1994) 293

[6] A. Aruchamy and A. Fulishima, *J. Electroanal. Chem*., 272 (1989) 125

[7] A.D. Modestov, G.-D. Zhou and H.-H. Ge and B.H. Loo, *J. Electroanal. Chem*., 380 (1995) 63

[8] A.D. Modestov, G.-D. Zhou, Y.-P. Wu, T. Notoya and D.P. Schweinsberg, *Corrosion Science*, 36 (1994) 1931

[9] H. Shao and G.-D. Zhou, *Acta Chimica Sinica*, 54 (1996) 325

[10] U. Sander, H.-H. Strehblow and J. K. Dohrmann, *J. Phys. Chem*., 85 (1981) 447

[11] G.H. Brilmyer, A. Fujishima, K.A.V. Santhanam and A.J. Bard, *Anal. Chem*., 49 (1977) 2057

[12] A. Fujishima, H. Masuda, K. Honda and A. J. Bard, *Anal. Chem*., 52 (1980) 682

[13] H, Yamazaki, J. Ohwaki, T. Yamada and T. Kitayama, *Appl. Phys. Lett*., 39 (1981) 772

[14] Y. Dupin, Z. Augru, Y.-W. Zhao, *J. Phys. D. Appl. Phys*., 21 (1988) 641

[15] A. Mandelis, *Chem. Phys. Lett*., 108 (1984) 388

[16] Z.-Y. Jiang, Y. Xiang and J.-T. Wang, *Extended Abstracts for the Fifth Chinese Electrochemistry Conference*, 1989, *Chinese Electrochemistry Society*, Ji Nan, No. 1A12

[17] Z.-Y. Jiang, Y. Xiang and J.-T. Wang, *J. Electroanal. Chem*., 316 (1991) 199

[18] Z.-Y. Jiang, Y. Xiang, J.-T. Wang, J.-G. Wu, B.-W. Shi and S.-P. Shen, *Acta Chimica Sinica*, 50 (1992) 372

[19] Z.-Y. Jiang, Y. Xiang, B. Qian and C.-H. Jin, *J. Electroanal. Chem*., 361 (1993) 257

[20] Z.-Y. Jiang, X.-Q. Zhang and Yang Xiang, *J. Electroanal. Chem*., 351 (1993) 321

[21] J. Rappich, N.S. Schaaf and J.K. Dohrmann, *J. Electroanal. Chem.*, 279 (1990) 123

[22] U. Collisi and H.-H. Strehblow, *J. Electroanal. Chem.*, 284 (1990) 385

[23] U. Sander, H.-H. Strehblow and J.K. Dohrmann, *J. Phys. Chem.*, 85 (1981) 447

[24] R.E. Russo, F.R. Mclarnon, J.D. Spear and E.J. Cairns, *J. Electrochem. Soc.,*134 (1987) 2783

[25] G. Nagasubramanian, A.S.Gioda and A.J. Bard, *J. Electrochem. Soc.*, 128 (1981) 2158

[26] S.M. Wilhelm, Y.Tanizawa, C.-Y. Liu and N. Hackerman, *Corrosion Scien*ce, 22 (1982) 791

Fig. 3.1 Diagram of measurement of (a) PTS and photocurrent response, (b) thermal effect in photocurrent measurement

light source   chopper   cell   potentiostat

resistance

lock-in amplifier   X-Y-Y record

Fig. 3.2 Block diagram of photocurrent measurement set up

Fig. 3.3 PTS spectrum (a), Cyclic voltammogram (b), Total photocurrent (c), Thermal current (d), and Real component of photocurrent (e) on copper electrode in 0.1M NaOH. Potential scan rate = 5mv/s, f = 10 Hz, λ = 488.0 nm, p = 200 mw.

Chapter 4

The Oxide Film on Copper Electrode in NaOH Solution: Photoelectrochemical Study

4.1 Introduction

Semiconducting oxide layers formed on many metals by thermal oxidation, anodization and corrosion reactions have been investigated extensively in various photoelectrochemical (**PEC**) studies [1-3]. **PEC** measurements have often been used to characterize the electronic nature of the films with respect to their conductivity, optical transitions and interface energetics from the photocurrent and photopotential behavior of the semiconductor oxide/electrolyte interface, by anology with the Schottky barrier [4-6]. PEC studies provide reliable results if the photoeffects do not alter the composition and properties of the films drastically.

The oxide layer formed on copper electrode appears to consist of a simple Cu_2O or a duplex layer Cu_2O/CuO, $Cu(OH)_2$ [7-9]. The p- or n-type semiconducting characters of bulk oxides or anodic films change appreciably with the conditions of their preparation [10]. Usually, the oxide layers display **PEC** behavior consistent with the p-type conductivity of the oxides known from their bulk solids. However, in some cases where Cu_2O is the corrosion product layer, **PEC** studies have revealed anodic photocurrents, indicating n-type

conductivity [10,11]. Also, in some cases, a change from cathodic to anodic photocurrents was found with increasing electrode potential [10, 12, 13].

In this chapter, a **PEC** study was performed on oxide layer formed in 0.1 N NaOH solution. From the potential and wavelength dependence of the photocurrent, the flat band potential and band gap are deduced.

4.2 Experimental

4.2.1 PEC Measurement

The photoelectrochemical cell, voltammetry, and photocurrent measurement have been described in chapter 2 and chapter 3, respectively. A copper foil (purity 99.95%) of thickness 0.0025cm, a platinum wire and an Hg/HgO/0.1M NaOH were sued as working electrode, counter electrode and reference electrode, respectively. The reference electrode was located near the copper foil. The potentials reported in this paper are referred to this electrode. The **PEC** measurement was carried out with an EG&G M273A Potentiostat/Galvanostat, an EG&G M5210 lock-in amplifier and an EG&G M651 light chopper. A chopping frequency of 10 Hz was used in all experiments. The light source was an Ar^+ laser.

4.2.2 Photoelectrochemical Properties Measurement

Photocurrent dependence on the photon energy of the incident light (E_g) and dependence on the potential (φ_{ft}) were carried out on Cu_2O oxide film formed on copper electrode in 0.1 N NaOH solution. The oxide film was grown potentiostated for 120 min at -320 mv, which corresponding to the formation of Cu_2O film on copper electrode.

4.2.3 Chemicals

Copper foil used as substrate and electrode material (Goodfellow) was polished with #1200 of emery paper, alumina (0.3 μm), ultrasonic clean for 5 min, rinsed with D.I water, and then treated in 50 v/v% HNO_3 for few second and thoroughly rinsed with 99.5 % ethanol and D.I water before use. All reagents were A.R grade and the solutions were made up with deionized water.

4.3 Results and Discussion

4.3.1 Photocurrent spectrum

Under the illumination of a laser, the photocurrent spectrum, simultaneously with the cyclic voltammatry (**CV**) on copper electrode in 0.1 M NaOH, was carried out, shown in Fig. 4.1.

The **CV** curve is similar to the reported behavior of copper (described in chapter 3 and the reference therein). Three anodic peaks (I, II and III) and two cathodic peaks (IV and V) were observed, as shown in Fig. 4.1(a). Anodic peak I corresponds to the formation of a

layer of Cu_2O, peak II corresponds to the formation of CuO on the Cu_2O underlayer and peak III corresponds to the formation of a duplex layer of Cu (II) (CuO and/or $Cu(OH)_2$). On the reverse scan, the cathodic peak IV and V corresponds to the reduction of Cu (II) to Cu_2O and Cu_2O to Cu, respectively.

Photocurrent spectrum was shown in Fig. 4.1 (b). This spectrum, as described in chapter 3 at p.67 [9, 13-17] is the total photocurrent response. The real component of the photocurrent is shown in Fig. 4.1 (c).

The polarity of the photocurrent was also tested by use of light interrupt method as shown in Fig. 4.2. The light was interrupted every 20 second when measuring I_{ph} with anodic scan at potential of -0.2 v to 0.0 v. When the light was on, the oxide current decreased. It means that photocurrent is cathodic photocurrent, which reflects the p-type semiconductor properties of Cu_2O layer.

4.3.2 Photocurrent Dependence on the Photon Energy of Incident Light ((E_g)

Pure Cu_2O oxide film was formed at potential of –320 mv. The photoelectrochemical properties at this potential are only result from Cu_2O. Tab. 4.1 shows the experiment data of photocurrent dependence on photon energy of incident light.

Where, λ is the wavelength of incident light, p is the power of incident light, V_{ph} is reading in lock-in amplifier, and I_{ph} is the photocurrent.

λ/nm	p/mw	V_{ph}/mv	$I/A \times 10^3$	$I_{ph}/A \times 10^7$	$\eta \times 10^5$	$h\upsilon$/eV	$(\eta h\upsilon)^2 \times 10^9$
457.9	20	0.63	7.38	6.3	8.54	2.71	53.6
476.5	100	2.7	38.4	27	7.03	2.60	33.5
488.0	380	8.4	149	84	5.63	2.54	20.5
496.5	70	1.1	28.0	11	3.93	2.50	7.17
501.7	15	0.2	6.07	2.0	3.30	2.47	6.66
514.5	280	1.8	116	18	1.55	2.41	1.40

Tab. 4.1 Photocurrent dependence on photon energy of incident light, R = 1kΩ

Calculation:

photon energy (u) = h υ = h c/λ (1)

incident light density (I_0) = p/(u)   (2)

incident light current (I) = e I_0 = ep/u   (3)

photocurrent (I_{ph}) = V_{ph}/R   (4)

photocurrent quantum efficiency (η) = I_{ph}/I   (5)

The plot of (h υ) vs (η h υ)^2 is shown in Fig. 4.3. The band gap energy E_g of the surface layer of Cu_2O was determined from the intercept on the curve. It is about 2.43 ev, which agrees with the E_g value reported for p-type thin film of Cu_2O [9, 13,15].

4.3.3 Photocurrent Dependence on the Potential (φ_{fb})

In order to get flat band potential of Cu_2O film, a measurement of photocurrent dependence on potential was carried out on oxide firm also formed at potential of –320 mv, which corresponding formation of Cu_2O. Tab. 4.2 shows experiment data.

The plot of I_{ph}^2 vs φ is shown Fig. 4.4 and φ_{fb} was determined as potential when $I_{ph} = 0$. It is about –341mv, which is not agree with the value of $\varphi_{fb} = 0.3$ mv in Fig. 4.2. This may be due to the deviation between theoretical equation and practical situation. Many researchers have reported their study on the modification of the equation [18-23].

φ/mv	V_{ph}/mv	I_{ph}x10^6	I_{ph}^2x10^{12}
-350	2.4	2.4	5.76
-375	3.1	3.1	9.61
-400	3.9	3.9	15.21
-425	4.9	4.9	24.01
-450	5.8	5.8	33.64
-475	6.2	6.2	38.44
-500	7.1	7.1	50.41
-525	7.4	7.4	54.76
-550	7.9	7.9	62.41
-575	8.4	8.4	70.56
-600	8.8	8.8	77.44

Tab.4.2 Photocurrent dependence on potential, $\lambda = 488.0$ nm, p = 380 mw, R = 1 kΩ

4.4 Conclusions

The photoelectrochemical study was carried out on Cu_2O oxide surface layer formed on copper electrode in 0.1 N NaOH solution. The Cu_2O layer is p-type and band gap energy is about 2.43 eV by the experiment of photocurrent dependence on photon energy of incident light. The flat band potential is about 0.3 mv by photocurrent spectrum and −341mv. The difference may be due to the deviation between theoretical equation and practical situation.

4.5 Reference

[1] K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.*, 124 (1977) 215

[2] U. Stimming*, Electrochim. Acta*, 31 (1986) 415

[3] S. R. Morrison, *Electrochemistry at Semiconductors and Oxideized Metal Electrodes*, Prenum Press, New York, 1980

[4] W. W. Gaertner, *Phys. Rev*., 116 (1959) 84

[5] H. Gerischer*, in H. Eyring (Ed.), Physical Chemistry: An Advanced Treatise*, Vol. IXA, Academic Press, New York, 1970, p. 463

[6] J. Reichman, *Appl. Phys. Lett*., 36 (1980) 574

[7] H.-H. Strehblow and B. Titze, *Electrochim. Acta*, 25 (1980) 839

[8] H.-D. Speckmann and H.-H. Strehblow, *Werkst. Korros*., 35 (1984) 512

[9] U. Collisi and H.-H. Strehblow*, J. Electroanal. Chem*., 210 (1986) 213

[10] U. Bertocci, *J. Electrochem. Soc*., 125 (1978) 1598

[11] F. Di Quarto, S. Piazza and C. Sunseri, *Electrochim. Acta*, 30 (1986) 315

[12] E. K. Oshe and I. L. Rozenfeld, *Sov. Electrochem*., 4 (1968) 1080

[13] S. M. Wilhelm, Y. Tanizawa, Chang-Yi Lin and N. Hackerman, *Corros. Sci.*, 22 (1982) 791

[14] A. Aruchamy, G.-D. Zhou and A. Fujishima, *J. Electroanal. Chem.*, 244 (1988) 333

[15] G. Nagasubramanian, A.S.Gioda and A.J. Bard, *J. Electrochem. Soc.*, 128 (1981) 2158

[16] A.D. Modestov, G.-D. Zhou and H.-H. Ge, *J. Electroanal. Chem.*, 375 (1994) 293

[17] U. Collisi and H.-H. Strehblow, *J. Electroanal. Chem.*, 284 (1990) 385

[18] R. H. Wilson and A. Heller, *Electrochemical Society*, 77 (1979) 63

[19] D. Laser and A. J. Bard, *J. Electrochem. Soc.*, 123 (1976) 1833

[20] S. Fonash, M. Rose, K. Corby, J. Jordan, W. L. Wallace, A. J. Nozik, S. K. Deb, and R. H. Wilson, (ed.), *The Electrochemical Society*, 82-3 (1982) 24

[21] J. F. Mcann, D. Haneman, W. L. Wallace, A. J. Nozik, S. K. Deb, and R. H. Wilson, (ed.), *The Electrochemical Society*, 82-3 (1982) 80

[22] E. Buhks, F. Willianms, W. L. Wallace, A. J. Nozik, S. K. Deb, and R. H. Wilson, (ed.), *The Electrochemical Society*, 82-3 (1982) 1

[23] H. Tributsch, *The Fifth International Conference on Photochemical Conversion and Storage of Solar Energy*, Osaka, August 26-31, (1984) 10

Fig. 4.1 Cyclic voltammogram (a), Total photocurrent (b), and Real component of photocurrent (c) on copper electrode in 0.1M NaOH. Potential scan rate = 5mv/s, f = 10 Hz, λ = 488.0 nm, p = 200 mw.

Fig. 4.2 On and Off current

Fig. 4.3 Photocurrent dependence on photon energy of incident light, R = 1kΩ

Fig. 4.4 Photocurrent dependence on potential, $\lambda = 488.0$ nm, p = 380 mw, R = 1 kΩ

Chapter 5

The Oxide Film on Copper Electrode in NaOH Solution:

XPS and ERD Studies

5.1 Introduction

Anodic oxidation of copper in alkaline solutions has attracted a great deal of attention due to its relevance to the understanding of corrosion mechanisms of copper. The characterization of oxidation and reduction of copper using in-situ techniques and the composition of oxide films on copper are two of the most interesting topics in the study of corrosion of copper.

Photothermal Spectroscopy (**PTS**) is one of the useful in-situ techniques for surface analysis. When light is absorbed by the surface of the electrode, the photo energy is transferred to thermal energy and there is temperature change at the surface of the electrode. Making use of the measurement of the temperature change to study the surface of the electrode is the application of Photothermal Spectroscopy. Chapter 2 described the details of **PTS** and its in-situ application on characterization of oxidation and reduction of copper electrode by using PVDF film as a thermometer.

Although a lot of work has been done in the composition of oxide films, it continues to excite interest and controversy. There are three copper oxide and hydroxide compounds whose are known to be stable as bulk solids at ambient temperatures. They are Cu_2O (cuprous oxide), CuO (cupric oxide), and $Cu(OH)_2$ (cupric hydroxide). All three of these materials have been suggested as being present in various forms on copper electrode surfaces in alkaline solutions indicate that at least one monovalent and two divalent soluble copper species are expected to be formed in alkaline electrolytes. S. T. Mayer et al reported their studies using Raman spectroscopy that the formation of Cu_2O occurs at potentials corresponding to the first anodic voltammetric peak, and a porous layer of $Cu(OH)_2$ composed of fine needle-like crystals is formed at the second voltammetric peak [1]. H.-H. Strehblow et al reported their **XPS** and **ISS** studies that a duplex structure of the oxide is found with copper (I) oxide at the metal surface covered by copper (II) hydroxide for sufficiently positive potentials [2]. D. T. Schwartz and co-workers pointed out by use of Raman spectroscopy that a thin Cu_2O film formed as oxidation of the copper surface was initiated, increasing the potential produced a $Cu(OH)_2$ layer on top of the Cu_2O film, and further oxidation at higher potentials converted the Cu_2O film to a CuO underlayer that coexisted with the $Cu(OH)_2$ overlayer [3].

X-ray photoelectron spectroscopy (**XPS**) is one of the most commonly used surface analysis technique used to study the oxide film. Beside **XPS**, ion-beam analysis has been demonstrated to be a powerful technique for sensitive measurements of the atomic composition and impurity concentrations in the near-surface regions of solids. The most commonly used techniques are ion-backscattering and nuclear reaction analysis.

Rutherford Backscattering Spectrometry (**RBS**) is the most famous in ion-backscattering techniques. In ion-backscattering analysis, light ions such as H or He with energies of ~ 1-3 MeV are incident on the sample under investigation and ions backscattered at some well-defined angle are detected. Analysis of the energy distribution of these backscattered ions yields the near-surface depth distribution of atomic species with masses greater than that if the projectile beam. Hydrogen (^{1}H) is the most difficult atomic species to profile. Because of its light mass, ion-backscattering can not be used. While forward-scattering elastic recoil detection (**ERD**) analysis can provides accurate measurements of ^{1}H concentration in the near-surface region of solid using 3 MeV tandem accelerator. The experimental arrangement we used for ERD is illustrated schematically in Fig. 5.1 [4].

The purpose of this study was to determine the composition of oxide films at different potentials. Besides the **XPS** study, Elastic Recoil Detection (**ERD**) were performed in this study. **ERD** is the unique surface analysis method that can detect the hydrogen element in thin films. We hope the results of **XPS** and **ERD** are consistent.

5.2 Experimental

5.2.1 Electrochemical Cell and Cyclic Voltammetry

The electrochemical cell and the test procedure for cyclic voltammetry study in this experiment have been described in chapter 2. A copper foil (purity 99.95%) of thickness 0.025mm, a platinum wire and an Hg/HgO/0.1M NaOH were used as working electrode,

counter electrode and reference electrode, respectively. The reference electrode was located near the copper foil. The potentials reported in this paper refer to this electrode. Cyclic voltammetry were carried out with EG & G M273A Potentiostat/Galvanostat.

5.2.2 XPS and ERD

The three oxide film samples were grown potentiostated on copper foils for 120 min at –320mv, -120mv and 200mv, respectively. Then the foils were kept in 99.5% ethanol before **XPS** and **ERD** study.

The surface electronic states of oxide film on copper were detected by **XPS** performed by the Perkin Elmer PHI 5000C ESCA system with the Al Kα radiation (1486.6ev) at a base pressure of 1.0$\times$ 10-9 Torr. The dimension of the samples was approximately 10 mm diameter. They were degassed in the pretreatment chamber for 2.0 h and then they were transferred to the test chamber for XPS study. The charging effect of the samples was corrected by using the contaminant carbon (C1s=284.6ev).

The element H in oxide films on copper was detected by **ERD** performed on a 3 MV tandem accelerator at Fudan University. Fig. 5.2 shows the schematically experimental apparatus. Details of the system for this **ERD** study were reported by Zhao et.al. [5].

5.2.3 Chemicals

Copper foil used as substrate and electrode material (Goodfellow) was polished with #1200 of emery paper, alumina (0.3 μm), ultrasonic clean for 5 min, rinsed with D.I water,

and then treated in 50 v/v% HNO_3 for few second and thoroughly rinsed with 99.5 % ethanol and D.I water before use. All reagents were A.R grade and the solutions were made up with deionized water.

5.3 Results and Discussion

5.3.1 PTS Spectrum and Cyclic Voltammogram

The cyclic voltammogram (CV) on copper electrode in 0.1 M NaOH is shown in Fig.5.3. The CV curve is similar to the reported behaviour of copper [6-10]. Three anodic peaks (I, II and III) and two cathodic peaks (IV and V) are observed, as shown in Fig. 5.3. (a). It is generally accepted that the anodic peak I corresponds to the formation of a layer of Cu_2O, peak II and peak III corresponds to the formation of a douplex layer of Cu (II) (CuO and/or $Cu(OH)_2$) on the Cu_2O underlayer. On the reverse scan, the cathodic peak IV and V corresponds to the reduction of Cu (II) to Cu_2O and Cu_2O to Cu, respectively.

5.3.2 XPS

Fig.5.4 (a), (b) and (c) show the Cu2p and O1s XPS spectra of oxide films formed at potential of anodic voltammetric peak I, II and III, respectively. The $Cu2p_{3/2}$ peak at 932.0 ev and O1s peak at 530.5 ev in Fig.5.4 (a) correspond to the copper in Cu_2O and oxygen in Cu_2O [11], while the O1s peak at 532.6 ev may to due to the oxygen in adsorbed water [12-14]. So the oxide film formed at potential of anodic peak I is mainly composed of Cu_2O. The

binding energy values of separate peaks and the corresponded compounds are showed in the following Table.

For the XPS spectra of film formed at potential of anodic peak II in Fig.5.4 (b), the binding energy values at 932.0 ev ($Cu2p_{3/2}$) and 530.7 ev (O1s) represent Cu_2O [11], 933.4 ev ($Cu2p_{3/2}$) and 529.5 ev (O1s) represent CuO [11], while 532.6 ev (O1s) represent O_{ad} [12-14]. So the composition of the surface layer of oxide film formed at potential of anodic peak II is Cu_2O and CuO, which is summarized in Tab.5.1.

Fig.5.4 (c) is the Cu2p and O1s spectra of oxide film formed at potential of anodic peak III. The two peaks at binding energy of 933.4 ev ($Cu2p_{3/2}$) and 935.2 ev represent CuO and $Cu(OH)_2$ [11], while 529.7 ev (O1s), 531.1 ev and 532.7 ev (O1s) represent CuO, $Cu(OH)_2$ and O_{ad} [12-14]. Hence the surface layer of oxide film formed at potential of anodic peak III is the duplex layer of CuO and $Cu(OH)_2$.

Sample	I	II	III
$Cu2p_{3/2}$	932.0 — Cu_2O	932.0 — Cu_2O 933.4 — CuO	933.4 — CuO 935.2 — $Cu(OH)_2$
O1s	530.5 — Cu_2O 532.6 — O_{ad}	529.5 — CuO 530.7 — Cu_2O 532.6 — O_{ad}	529.7 — CuO 531.1 — $Cu(OH)_2$ 532.7 — O_{ad}

Table 5.1 $Cu2p_{3/2}$ and O1s binging energies of separate peak and related compounds

5.3.3 ERD

Fig. 5.5 shows the **ERD** spectrum of oxide film formed at potential of anodic peak III. Element H was detected only in the film formed at potential of anodic peak III. This result was in good consistent with **XPS** which told that $Cu(OH)_2$ was formed only at potential of anodic peak III.

5.4 Conclusions

XPS and **ERD** study were performed on the surface oxide layer which formed at different potential corresponding to the anodic voltammetric peak. **XPS** result shows that CuO layer was formed round the second peak, and a duplex layer of CuO and $Cu(OH)_2$ was formed round the third peak. The element H in surface layer formed at potential round the peak III could be detected by **ERD**.

5.5 References

[1] S.T. Mayer and R.H. Muller, *J. Electrochem. Soc.,* 139 (1992) 426

[2] H.-H. Strehblow and B. Titze, *Electrochimica Acta,* 25 (1980) 839

[3] D.T. Schwartz and R.H. Muller, *Surface Science,* 248 (1991) 349

[4] G.-Q Zhao, Y.-H. Ren Z.-Y. Zhou G.-H. Tang and J.-Y. Tang, *Nuclear Instruments and Methods in Physics Research,* B48 (1990) 513

[5] B.L. Doyle and P.S. Peercy, *Appl. Phys. Lett.,* 34 (1979) 812

[6] U. Collish and H.-H. Strehblow, *J. Electroanal. Chem.*, 210 (1986) 213

[7] L. M.Abrantes, L. M.Castillo, C. Norman and L. M.Peter, *J. Electroanal. Chem.*, 163 (1984) 209

[8] A. Aruchamy, G.-D. Zhou and A. Fulishima, *J. Electroanal. Chem.*, 244 (1988) 333

[9] U. Collisi and H.-H. Strehblow, *J. Electroanal. Chem.*, 284 (1990) 385

[10] U. Sander, H.-H. Strehblow and J.K. Dohrmann, *J. Phys. Chem.*, 85 (1981) 447

[11] R.E. Russo, F.R. Mclarnon, J.D. Spear and E.J. Cairns, *J. Electrochem. Soc.,* 134 (1987) 2783

[12] C.D.Wagner, W.M.Riggs, L.E.Davis, J.F.Moudler and G.E.Muilergery, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN (1979) 82

[13] W.Kantek and J.G.Gordon, *J.Electrochem. Soc*., 137 (1990) 2672

[14] D.W.Shoesmith, S.Sunder, M.G.Bailey, G.J.Wallace, and F.W.Stanchell, *J. Electranal. Chem*., 143 (1983) 153

[15] Y.-Q. Feng, W.-K. Teo, K.-S. Siow, Z.-Q. Gao, K.-L. Tan, and A.-K. Hsieh, *J. Electrochem. Soc*., 144 (1997) 55

Fig. 5.1 Schematic illustration of the ERD experimental arrangement

Fig. 5.2 Schematic diagram of the experimental apparatus of ERD analysis

E/V vs Hg/HgO/0.1 M NaOH

Fig.5.3 Cyclic voltammogram on copper electrode in 0.1M NaOH.
Potential scan rate = 5mv/s

Fig.5.4 XPS spectra of oxide film formed at potential of (a) anodic peak I, (b) anodic peak II, and (c) anodic peak III.

Fig. 5.5 ERD spectrum of film formed at potential of anodic peak III

Chapter 6

The Oxide Film on Copper Electrode in NaOH Solution:

Voltammetry and SEM Studies

6.1 Introduction

The electrochemical behavior of copper in alkaline has been investigated on many occasions since the first work of Muller [1]. Form detailed examination by electrochemical and surface analytical methods, this oxide layer appears to consist of a simple Cu (I) or a duplex layer of Cu (I)/Cu (II) film [2, and references therein]. Most detailed electrochemical studies have been concentrated on the first stage of copper oxidation [3-6] when surface products are formed containing Cu (I) only. The second stage of oxidation is more complex, involving the formation of a mixture of oxides and hydroxide in Cu (I) and Cu (II) stages. Although this topic has been extensively studied [7-12], no general agreement has been reached pertaining to the phases formed during anodic polarization in the Cu (II) region.

In this chapter, the identity of the formation of the oxide film has been investigated by voltammmtry method and scanning electron microscope (SEM) method.

6.2 Experimental

6.2.1 Voltammetry

The photoelectrochemical cell and voltammetry measurement have been described in chapter 2 and chapter 3, respectively. A copper foil (purity 99.95%) of thickness 0.0025cm, a platinum wire and an Hg/HgO/0.1M NaOH were sued as working electrode, counter electrode and reference electrode, respectively. The reference electrode was located near the copper foil. The potentials reported in this paper are referred to this electrode. The voltammetry measurement was carried out with an EG&G M273A Potentiostat/Galvanostat.

6.2.2 SEM

The oxide film samples were grown potentiostated on copper foils for 5, 15, 30, 60, 90, and 120 min at –320mv, -120mv and 200mv, respectively. Then the foils were kept in 99.5% ethanol before **SEM** study.

6.2.3 Chemicals

Copper foil used as substrate and electrode material (Goodfellow) was polished with #1200 of emery paper, alumina (0.3 μm), ultrasonic clean for 5 min, rinsed with D.I water, and then treated in 50 v/v% HNO_3 for few second and thoroughly rinsed with 99.5 % ethanol and D.I water before use. All reagents were A.R grade and the solutions were made up with deionized water.

6.3 Results and Discussion

6.3.1 Voltammetry

In order to understand the behaviors of the copper electrode, it is necessary to explore the correspondence between the anodic and cathodic peaks. Cyclic voltammograms at different potential window were obtained on copper electrode in 0.1 N NaOH solution and shown in Fig. 6.1. Curve (a) shows the CV of potential window at -1150 to -400 mv. It indicates a simple oxidation − reduction system, oxidation peak I at -470 mv corresponds to the formation of Cu_2O [13-17],

$$2\ Cu + 2\ OH^- - 2e \rightarrow Cu_2O + H_2O \qquad \text{(peak I)}$$

Reduction peak V at -700 mv corresponds to the reduction of Cu_2O to Cu [13-17],

$$Cu_2O + H_2O + 2e \rightarrow 2\ Cu + 2\ OH^- \qquad \text{(peak V)}$$

Fig. 6.1 (b) shows the CV of potential at -1150 to -200 mv. Oxidation peak II corresponds to the formation of CuO (chapter 5), combined with formation of Cu_2O,

$$2\ Cu + 2\ OH^- - 2e \rightarrow Cu_2O + H_2O \qquad \text{(peak II)}$$

$$Cu + 2\ OH^- - 2e \rightarrow CuO + H_2O \qquad \text{(peak II)}$$

Reduction peak IV corresponds to the reaction of CuO to Cu_2O as follows,

$$2\ CuO + H_2O + 2e \rightarrow Cu_2O + 2\ OH^- \qquad \text{(peak IV)}$$

Reduction peak V corresponds to the reactions

$$CuO + H_2O + 2e \rightarrow Cu + 2\ OH^- \qquad \text{(peak V)}$$

$$Cu_2O + H_2O + 2e \rightarrow 2\ Cu + 2\ OH^- \qquad \text{(peak V)}$$

Fig. 6.1 (c) and (d) show the CV curves of potential window at -1150 to -100 mv, and -1150 to $+450$ mv, respectively. Oxidation peak III corresponds the formation of complex Cu(II) oxidation layer.

$$Cu_2O + 2\ OH^- - 2e \rightarrow 2\ CuO + H_2O \qquad \text{(peak III)}$$

$$Cu_2O + 2\ OH^- + H_2O - 2e \rightarrow 2\ Cu(OH)_2 \qquad \text{(peak III)}$$

The reduction reactions in peak IV and V could be the followings, respectively.

$$2\ CuO + H_2O + 2e \rightarrow Cu_2O + 2\ OH^- \qquad \text{(peak IV)}$$

$$2\ Cu(OH)_2 + 2e \rightarrow Cu_2O + H_2O + 2\ OH^- \qquad \text{(peak IV)}$$

and that in peak V:

$$Cu_2O + H_2O + 2e \rightarrow 2\ Cu + 2\ OH^- \qquad \text{(peak V)}$$

In order to study the behavior of oxidation layer in potential at peak II and III, an experiment that formed a oxide layer at potential of peak II and III for different time of 5, 15, 30, and 60 min and then linear sweep reduction back to -1150 mv was carried out in 0.1 N NaOH solution. Fig. 6.2 shows the reduction curves that the oxide layer was formed at -240 mv which corresponding to the formation of Cu_2O/CuO and then linear sweep back to -1150 mv. The reactions corresponding to peak IV and V are mentioned above. The potential difference between Fig. 6.1 and Fig. 6.2 may be due to the different composition and structure of oxide layer in those two oxide situations. Fig. 6.2 shows that peak IV is almost the same in (a) to (d), while the potential in peak V shifted from -1000 mv in (a) to -1100 mv in (d) and also the quantity increased from (a) to (d). This means that major oxidation in peak II is the formation of CuO directly from Cu, not from Cu_2O as the time increased.

Otherwise the quantity of peak IV should increase with the time from 5 min to 60 min. SEM (next section) also shows such result.

Fig. 6.3 shows the reduction curves that oxide layer was formed at 100 mv which corresponding to the formation of duplex layer of $CuO/Cu(OH)_2$ for 5, 15, 30, and 60 min and then linear sweep reduction back to -1150 mv. It shows that there is no significant difference with time increasing. That means the major oxidation is completed within 5 mins. SEM also shows the same result.

6.3.2 SEM

SEM was carried out for oxide layer potentiostated formed at different potential corresponding to peak I, II, and III for different forming time of 5, 15, 30, 60, and 120 min. Fig. 6.4 compares the morphology of oxide layer formed at different potential but for the same time of 5 min (a, b, and c), and 120 min (d, e, and f), respectively. SEM results show that the size and morphology of the surface crystals are dependent of potential no matter the minimum coverage at 5 min or the maximum coverage at 120 min. This means that the oxide layer formed at different potential has different composition.

The changes surface coverage for various time at constant potential are shown in Fig. 6.5 for peak I, Fig. 6.6 for peak II, and Fig. 6.7 for peak III, respectively. The **SEM** result in Fig. 6.5 shows that there is no significant change in surface coverage for oxide layer formed in peak I from range of 15 to 120 min, though there is some changes from the range of 5 to 15 min. It means that the major formation of Cu_2O from Cu is completed within 15 min. The

similar situation occurred in Fig. 6.7. It means that the major formation of duplex layer of Cu(II) is completed within 15 min, which is inconstant with the result shown in Fig. 6.3. Fig. 6.6 shows the different situation. The crystal phase which represents Cu2O increases with the time and because the major phase after 30 min. It is inconstant with the result shown in Fig. 6.2.

6.4 Conclusions

The cyclic voltammetry at different potential window was carried out on Cu electrode in 0.1 N NaOH solution. The results that peak I corresponds to the simple oxidation of Cu_2O from Cu, peak II corresponds to the formation of CuO from Cu_2O and direct from Cu, and peak III corresponds to the formation of duplex layer of Cu(II). Another experiment where the oxide layer formed at constant potential of peak II and III was cathodic scanned back to -1150 mv was performed. The result shows, combined with **SEM** on the surface layer formed in different potential for different time, that the major formation at peak I and III is completed within 15 min, while in peak II, the surface coverage increase with the time increasing and the major phase is CuO which was formed direct from Cu.

6.5 Reference

[1] E. Muller, *Z. Electrochem.*, 13 (1907) 133

[2] H.-H. Strehblow and B. Titze, *Electrochim Acta*, 25 (1980) 839

[3] M. J. Dignam and D. B. Gibbs, *Can. J. Chem.*, 48 (1970) 1242

[4] V. Ashworth and D. Fairhurst, *J. Electrochem. Soc.*, 124 (1977) 506

[5] S. Fletcher, R. G. Barradas, and J. D. Porter, *J. Electrochem. Soc.*, 125 (1978) 1960

[6] J. M. M. Droog, C. A. Anderliesten, P. T. Anderliesten, and G. A. Bootsma,
    J. Electroanal. Chem., 111 (1980) 61

[7] A. Hickling and D. Taylor, *Trans. Faraday Soc.*, 44 (1948) 262

[8] J. S. Halliday, *Trans. Faraday Soc.*, 50 (1954) 171

[9] A. M. Shams EI Din and F. M. Abd EI Wahab, *Electrochim Acta*, 9 (1964) 113

[10] N. A. Hampson, J. B. Lee, and K. I. Macdonald, *J. Electroanal. Chem.*, 32 (1971)
    165

[11] B. Miller, *J. Electrochem. Soc.*, 116 (1969) 1675

[12] D. D. Macdonald, *J. Electrochem. Soc.*, 121 (1974) 651

[13] J. Ambrose, R. G. Barradas, and D. W. Shoesmith, *Electroanalytical Chemistry and
    Interfacial Electrochemistry*, 47 (1973) 47

[14] A. M. Castro Luna De Medina, S. L. Marchiano, and A. J. Arvia, *Journal of Applied
    Electrochemistry*, 8 (1978) 121

[15] Y. A. El-Tantawy, F. M. Al-Kharafi, and A. Katrib, *J. Electroanal. Chem.*, 125
    (1981) 321

[16] S. M. Abd El Haleem, and Badr G. Ateya, *J . Electroanal. Chem.*, 117 (1981) 309

[17] M. Perez Sanchez, M. Barrera, S. Gonzalez, R. M. Soutot, R. C. Salvarezza, and A.
    J. Arvia, *Electrochimica Acta*, 35 (1990) 1337

Fig. 6.1 Cyclic voltammetry in different potential window on copper electrode in 0.1 N NaOH solution, (a) –1150 to –400 mv, (b) –1150 to –200 mv, (c) –1150 to 100 mv, and (d) –1150 to 450 mv, potential scan rate = 5 mv/s,

Fig. 6.2 Linear potential sweep reduction for oxide layer formed in –240 mv for (a) 5 min, (b) 15 min, (c) 30 min, and (d) 60 min on copper electrode in 0.1 N NaOH solution, potential scan rate = 5 mv/s.

Fig. 6.3 Linear potential sweep reduction for oxide layer formed in +100 mv for (a) 5 min, (b) 15 min, (c) 30 min, and (d) 60 min on copper electrode in 0.1 N NaOH solution, potential scan rate = 20 mv/s from 100 to –350 mv and 5 mv/s from –350 to –1150 mv.

(a)-peak I	(d)-peak I
(b)-peak II	(e)-peak II
(c)-peak III	(f)-peak III

Fig. 6.4 SEM x5000 of oxide layer formed on copper electrode in 0.1 N NaOH solution for same time of 5 min at different potential of (a)-peak I, (b)-peak II, (c)-peak III; and 120 min of (d)-peak I, (e)-peak II, (f)-peak III

(a)

(b)

(c)

(d)

(e)

Fig. 6.5 SEM x5000 of oxide layer formed at potential of peak I on copper electrode in 0.1 N NaOH solution for different time, (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, and (e) 120 min

(a)   (b)

(c)   (d)

(e)

Fig. 6.6 SEMx5000 of oxide layer formed at potential of peak II on copper electrode in 0.1 N NaOH solution for different time, (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, and (e) 120 min

Fig. 6.7 SEM x5000 of oxide layer formed at potential of peak III on copper electrode in 0.1 N NaOH solution for different time, (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, and (e) 120 min

List of **Publications**

1. <u>Hongmin Li</u>, Koksiong Siow and Zhiyu Jiang, "Oxide Film of Copper in NaOH — PTS, XPS and ERD Study", *The 7th Ibero-American Congress of Corrosion and Protection, 4th Nace Latin-American Region Corrosion Congress* (Cartagena de Indias, Colombian, September 2000)

2. <u>Hongmin Li</u>, Koksiong Siow and Zhiyu Jiang, "Study of Thermal Effect in Photocurrent Measurement of Copper by In-situ Photothermal Technique", *The 14th International Corrosion Conference* (Cape Town, South Africa, October 1999)

3. <u>Hongmin Li</u> and Koksiong Siow, "Emphasis of Application of Mathematics in Teaching of Physical Chemistry", *2000 International Chemical Congress of Pacific Basin Societies* (Honolulu, Hawaii, USA, December 2000)

4. <u>Hongmin Li</u> and Koksiong Siow, "Determination of Two-component Liquid-solid Phase Diagram: An Introduction to a New Simple Method", *2000 International Chemical Congress of Pacific Basin Societies* (Honolulu, Hawaii, USA, December 2000)