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**ANALYTICAL APPLICATIONS
OF
PHOTOTHERMAL SPECTROSCOPIES**

by
Runde Guo, M.Sc.

**A dissertation submitted to the Faculty of Graduate Studies
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy**

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ISBN 0-315-54410-4

The undersigned recommend to the Faculty of Graduate Studies acceptance of the dissertation "Analytical applications of photothermal spectroscopies" submitted by Runde Guo, M.Sc., in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Chairman, Department of Chemistry

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Abstract

Photothermal spectroscopy (PTS) can be applied to several unique chemical analyses. A solid film sampling technique has been developed for the determination of trace elements in dilute solutions with gas-microphone photoacoustic spectroscopy (PAS). First, an analyte was extracted from its aqueous solution into an organic solvent. Then, the organic extract was evaporated in a sample cup under flowing air, forming a thermally-thin solid film sample on the cup bottom. When determined with gas-microphone PAS, a 2–3 orders of magnitude increase in analytical sensitivity was achieved as a result of the concentration of the analyte from a thermally thick sample (dilute solution) to a thermally thin sample (solid film). The enhanced sensitivity was demonstrated with trace amounts of Cd(II), Co(III), Ni(II), Pd(II), Sb(V) and Tl(III). Even though the power of the He–Ne laser employed was only 17 mW and the complexing agents might not be the optimum selection for the elements studied, the experimental detection limits were all below 1 ng except for Ni(II) as Ni(PAN)₂.

The solid film sampling technique has been applied for the determination of Pd(II) in water. After extracting Pd(II) as palladium dithizonate into CCl₄, 500 µL of the extract was converted into a solid film sample by an automated film sample preparation device. The resulting detection limit was 0.04 ppb of Pd(II) in water, with a precision of 3.2% relative standard deviation.

A transverse photothermal deflection spectroscopy (PDS) technique was used for the nondestructive determination of implant doses in B⁺– and BF₂⁺–implanted silicon wafer samples. Nonlinear PDS signals were observed and proven to arise from

two— or possibly three—photon absorptions under intense laser illumination. A new theoretical model has been derived for the nonlinear PDS analysis of ion—implanted silicon wafers, wherein the nonlinear PDS signal amplitude is related to the implant dose in a silicon wafer through the defects created by ion implantation. When this model was used to the experimental data, a linear relationship was obtained for the log—log plot between the increase in PDS signal amplitude (ΔV) and the implant dose, and a detection limit of 1×10^{12} ions cm^{-2} was found for both B^+ and BF_2^+ implants.

Acknowledgements

First of all, I would like to express my most sincere thanks to my supervisor, Dr. Edward P.C. Lai, for his financial support, academic advice and consultation during the course of my thesis work over the past years. I appreciate very much for his determination to accept me as his graduate student in a situation which called for trust and tactfulness, without which I could not have started the work for this dissertation in Carleton University.

I wish to thank Dr. C.L. Chakrabarti for offering me an opportunity to work for him in the first two years of my graduate studies, and for the partial financial support during that period as well as for his kind assistance on a number of occasions afterwards.

I wish also to extend my gratitude to Dr. B.R. Hollebhone and Dr. D.R. Wiles for their kind suggestions and encouragements which were invaluable for a foreign student trying to adapt to a completely new and different environment.

I would like to express my appreciation to Dr. Chandrasekhar and Dr. Ravi Gandhi for their kindness in reading the manuscript of my thesis and making suggestions for improvement; and to Miss Tory Vandermoot who rendered me some much needed help.

My thanks are also owing to Mr. P.C. Pertels, who generously allowed me to use his equipments for my research project.

I am very grateful to my wife and my daughter for their understanding and

patience. They had done everything they could to make the home atmosphere cheerful after my long hours of work.

I am deeply indebted to my parents, especially my mother who died of cancer after suffering quietly for a year in order to spare me agony and distraction. She had given me all that a mother could give and had little return from me. Therefore, I wish to dedicate this thesis to my mother.

I would like to extend my thanks to Northern Telecom Electronics Ltd. for providing the ion-implanted silicon wafers for my experiments.

Finally, I have to thank the Chinese Academy of Sciences for the partial financial support during my first two years of graduate studies in the department. Without that financial support, I could not have come to Carleton University to achieve my goal. Thanks must be given to my friends and some of my former colleagues in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, who had given generous support to my family after my arrival in Canada.

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Glossary

A – absorbance;

B – bulk modulus (dynes cm^{-2});

h – light path length in a sample (cm);

C – specific heat ($\text{cal g}^{-1} \text{K}^{-1}$);

c – concentration (mol L^{-1});

c_0 – velocity of sound in a gas;

ϵ – strain;

E_g^d – direct gap energy of a semiconductor (eV);

E_g^i – indirect gap energy of a semiconductor (eV);

E_p – phonon energy (eV);

$i = \sqrt{-1}$;

I_0 – the intensity of an incident monochromatic light (W cm^{-2});

I_r – the intensity of reflected light beam (W cm^{-2})

$J = 4.184 \text{ joules cal}^{-1}$;

k – Boltzmann constant;

k' – wave vector for the acoustic wave in a gas ($= \frac{\omega}{c_0}$);

l – sample length/thickness (cm);

l_c – length of PAS cel channel (cm);

l_β – optical length of a sample (cm);

l_0 – length/thickness of a fluid (usually gas) (cm);

l_2 – length/thickness of backing material (cm);

M – mass (g) or thermal mass (cal K^{-1});

N_i – dosage of an implant (ions cm^{-2})

or concentration of a dopant (atoms cm^{-3});

n_0 – refractive index without thermal disturbance;

P_a – ambient pressure (atm);

p – stress (dynes cm^{-2});

ℓ – the path length of deflected probe beam (cm);

$Q(r,t)$ or $Q(x,t)$ – heating function due to laser illumination;

r – distance from the center of a laser beam;

$\vec{r}$ – position vector;

r_0 – laser beam diameter (cm);

S – sample surface area or sample cup bottom area (cm^2)

S_c – cross-sectional area of PAS cell channel (cm^2);

T – temperature (K);

T_a – ambient temperature (K);

t – time (s);

$u(x,t)$ – the x component of particle displacement;

u – experimental constant for ion-implanted wafers;

V – PAS or PDS signal amplitude (V);

v_1 – volume of PAS cel chamber (cm^3);

v_2 – volume of microphone chamber (cm^3);

α – thermal diffusivity ($\text{cm}^2 \text{s}^{-1}$);

α – optical absorption coefficient for indirect one-photon absorption;

β – optical absorption coefficient (cm^{-1});

β -- absorption coefficient for direct two photon absorption (cm W^{-1})

ϵ -- molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$);

η -- efficiency of heat conversion from absorbed optical energy;

κ -- thermal conductivity ($\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$);

μ -- thermal diffusion length (cm);

ρ -- density (g cm^{-3});

τ_0 -- laser pulse duration (s);

ϕ -- angular deflection of probe beam (rad);

ϕ_n -- normal beam deflection (rad);

ϕ_t -- transverse beam deflection (rad);

ω -- chopping frequency (rad s^{-1}); and

ω_{H} -- Helmholtz resonance frequency (Hz).

CHAPTER 1

Introduction

Photothermal spectroscopies (PTS) are based on various photothermal effects that may be generated in the interactions of electromagnetic radiation and matter. The most popular photothermal effects after optical irradiation are temperature rise, photoacoustic wave generation, refractive index change and infrared radiation variation. Investigations of the photothermal effects of electromagnetic radiation have played an important role in the discovery and understanding of many natural phenomena, such as mirages. Even though the first scientific reports on photothermal effects appeared by the end of the 19th century [1], the applications of these effects became significant only in the 1970's when the innovation of powerful lasers furnished scientists with new tools to tackle many difficult projects that could not have been done before. In these past two decades photothermal spectroscopies have developed rapidly, and many books and review articles have been published on various topics of photothermal spectroscopies [2–13]. Photoacoustic spectroscopy (PAS) [2, 7, 10], photothermal deflection spectroscopy (PDS) [3, 14, 15], thermal lensing spectroscopy [5, 6, 16], laser calorimetry [17, 18], photothermal radiometry [19, 20], and various other photothermal spectroscopic techniques [21–24] have become very important areas in analytical chemistry.

Compared with conventional absorption measurements, PTS methods offer several significant features: (1) high sensitivity which can be achieved by increasing

the power of the incident light below the saturation regime or damage threshold because the absorbed power or energy is measured in PTS studies instead of the relative change of light intensity in conventional absorption spectrometry. By using PTS methods, absorption of $10^{-7} - 10^{-8} \text{ (cm}^{-1}\text{)}$ can be detected; (2) versatility to various kinds of samples that cannot be determined with conventional absorption spectrometry, such as solid, powder, suspension, and smear. (3) capability of surface imaging and depth profiling of a sample; (4) local probing of samples as a laser beam can be focused into a very small region (a few micrometers in diameter); (5) remote sensing, noncontact monitoring or nondestructive analysis in a hostile environment.

The above features have made PTS techniques very attractive to scientists for a wide range of applications. Some unique characteristics of photothermal spectroscopies for analytical chemistry will be demonstrated later in this thesis.

Chapter 2

Theory of Photoacoustic Spectroscopy

(1) Photoacoustic Effects

The photoacoustic effects were first observed by Alexander Graham Bell in 1880 when he tested his photophone device [1]. After almost one century the photoacoustic effects were "refound" in the 1970s. Since then they have been applied widely and become a unique tool for chemists and physicists alike.

The basic processes underlying these effects are quite simple. When a sample is irradiated by a modulated optical beam, some optical energy will be absorbed by the sample if the sample has a finite absorptivity at the wavelength of the incident light. In subsequent thermal deexcitation processes, the sample converts the absorbed optical energy into heat. The heat deposited in the sample is transmitted to the surroundings by two mechanisms. The first mechanism involves heat diffusion from the heated region of the sample to the surroundings. For instance, the heat deposited in the first thermal diffusion length below the sample surface can be transferred to the adjacent layer of gas. As the light beam is modulated, the sample surface will undergo heating and cooling periodically. The adjacent layer of gas will therefore undergo expansion and contraction periodically, too. In this way, the indirect photoacoustic waves are produced in the gas and can be determined by the gas-microphone PAS method.

In the second mechanism, the local heat energy deposited in the sample may be coupled to the vibrational modes of the sample material itself (i.e., the sample's

phonon spectrum) in a thermoelastic process, which is generally nondissipative. The stresses generated in this process due to the periodical heating of the sample will vary periodically and can be measured by using a piezoelectric transducer attached to the sample. These are direct photoacoustic waves. The speed of the energy transfer in this process is governed by the speed of sound in the sample material.

Both direct and indirect PAS methods have been widely applied for spectroscopic studies, trace analysis, thermal property studies, surface imaging, depth profiling and other works [25–37]. Theories have been developed well for both direct and indirect PAS measurements. Here we mainly follow Rosencwaig's work [36] to present the PAS theory in this chapter.

(2) Temperature variations in a gas–microphone PAS system

A typical system in gas–microphone photoacoustic spectroscopy can be represented by Fig. 1. A sample is supported by a backing material that is non absorbing to the incident light. The sample is adjacent to a gas which is also non absorbing to the incident light. When the light beam passes through the non absorbing gas phase to irradiate the sample surface, the sample absorbs a certain amount of optical energy and is excited. Subsequently, the sample will release a major portion or all of the absorbed optical energy as thermal energy in nonradiative relaxation processes. The heat generated within the sample will be conducted to the gas and to the backing material due to the existence of a temperature gradient. The appropriate description of the energy transfer processes in the studied system is essential for understanding the PAS effects and for developing its further applications

Fig. 1: Schematic representation of a typical gas-microphone PAS system.

in analytical chemistry. Thermal conduction equations have been used to describe the heat transfer processes in the system. By solving thermal conduction equations under given experimental conditions the temperature distribution (i.e., energy distribution) in the system can be obtained. Then, the PAS signal can be related to the properties of the system studied.

Generally speaking, there are two kinds of systems in heat conduction: one with an internal heat source and the other without. Heat conduction processes in both systems can be described by the following thermal conduction equations [38]:

$$\nabla^2 T + \frac{Q(r,t)}{\kappa} = \frac{1}{\alpha} \frac{\delta T}{\delta t} \quad \text{with heat source} \quad (2-1)$$

and

$$\nabla^2 T = \frac{1}{\alpha} \frac{\delta T}{\delta t} \quad \text{without heat source} \quad (2-2)$$

where T = temperature (K);

κ = thermal conductivity ($\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$);

α = thermal diffusivity ($\text{cm}^2 \text{s}^{-1}$);

t = time (s);

and $Q(r,t)$ = thermal generation rate of the heat source (J s^{-1} or cal s^{-1}).

In the PAS system shown in Fig. 1, region 1 is active in which optical energy is converted to thermal energy. Therefore, region 1 can be considered as having an internal heat source and be described by Eq. (2-1). The other two regions have no internal heat sources and their heat conduction processes must be described by Eq.(2-2). Under the conditions that convection and radiation processes are negligible in the system during heat transfer and that the sample itself is homogeneous, the

thermal diffusion equations for the system in Fig. 1 are as follows [36]:

$$\nabla^2 T_0 - \frac{1}{\alpha_0} \frac{\delta T_0}{\delta t} = 0 \quad 0 \leq x \leq l_0 \quad \text{Region 0} \quad (2-3a)$$

$$\nabla^2 T_1 - \frac{1}{\alpha_1} \frac{\delta T_1}{\delta t} = - \frac{Q(r,t)}{\kappa} \quad -l \leq x \leq 0 \quad \text{Region 1} \quad (2-3b)$$

$$\nabla^2 T_2 - \frac{1}{\alpha_2} \frac{\delta T_2}{\delta t} = 0 \quad -(l+l_2) \leq x \leq -l \quad \text{Region 2} \quad (2-3c)$$

with the boundary conditions:

$$T_0|_{x=0} = T_1|_{x=0} ; \quad T_2|_{x=-l} = T_1|_{x=-l} ;$$

$$\kappa_0 \frac{\delta T_0}{\delta x} \Big|_{x=0} = \kappa_1 \frac{\delta T_1}{\delta x} \Big|_{x=0} ; \quad \text{and} \quad \kappa_2 \frac{\delta T_2}{\delta x} \Big|_{x=-l} = \kappa_1 \frac{\delta T_1}{\delta x} \Big|_{x=-l} \quad (2-4)$$

where the subscript i indicates the parameters in region i ($i = 0, 1$, and 2),

x is a position along the light beam pathway (cm);

l is the sample length or thickness (cm);

l_0 is the thickness of the gas column (cm);

and l_2 is the thickness of the backing material (cm).

In order to solve these equations a heating function must be specified in the system to replace $Q(r,t)$ in Eq. (2–3b), the thermal generation rate of the internal heat source in region 1 (i.e., the rate of optical energy deposited as thermal energy in the region). The heating function $Q(r,t)$ is related to the light source which is used to stimulate the system from its ground state to an excited state

Various lasers and incoherent light sources have been used to provide optical energy to the PAS system. When a continuous wave laser (cw laser) or an incoherent light source is used to provide the excitation beam, the incident light beam is modulated using a mechanical chopper. The generation of PAS signals is an average effect of temperature rise in the sample. The intensity of a modulated light beam varies with time periodically. Therefore, the absorbed optical energy varies with time periodically as well, and the heat generation rate can be represented by a sinusoidal function of time as follows [36]:

$$Q(x,t) = \frac{1}{2} \eta \beta I_0 e^{-\beta x} \operatorname{Re}(1 + e^{-i\omega t}) \quad (2-5)$$

where η - efficiency of heat conversion from the absorbed optical energy;

β - optical absorption coefficient (cm^{-1});

I_0 - intensity of the monochromatic incident light (W cm^{-2});

ω - chopping frequency (rad s^{-1});

$i = \sqrt{-1}$;

and Re stands for the real part of an imaginary number.

With this heating function specified above, the temperature variations in the PAS system and hence the PAS signal can be found. Solving the partial differential equations in heat transfer processes is one of the most important aspects in PTS theories. Various approaches to solving these equations have been reported in the literature [3, 18, 22, 36, 39]. When a cw laser or an incoherent light source is used in PAS studies, the heat generation rate within the sample (i.e., region 1) can be represented by Eq.(2-5). By substituting Eq.(2-5) into Eq.(2-3b), Eqs.(2-3) can be solved to find the temperature variation in each region of the PAS system shown in Fig.

1. As the 3-dimensional thermal diffusion equations are tedious to solve and have similar solutions to those of 1-dimensional equations [40], solving the thermal diffusion equations under 1-dimensional conditions would be suitable for most PAS studies.

Assuming the heat conversion efficiency (η_1) to be 1, which is true for many non-fluorescent samples of interest in PAS, Eq.(2-3) becomes

$$\frac{\delta^2 T_0}{\delta x^2} = \frac{1}{\alpha_0} \frac{\delta T_0}{\delta t} \quad (2-6a)$$

$$\frac{\delta^2 T_1}{\delta x^2} = \frac{1}{\alpha_1} \frac{\delta T_1}{\delta t} - \frac{1}{2\kappa} \beta I_0 e^{-\beta x} (1 + \cos \omega t) \quad (2-6b)$$

$$\frac{\delta^2 T_2}{\delta x^2} = \frac{1}{\alpha_2} \frac{\delta T_2}{\delta t} \quad (2-6c)$$

Under the above mentioned conditions the general solutions for the temperature rise in each region is obtained from R-G theory [36]:

$$T_0(x,t) = \left(1 - \frac{x}{l_0}\right) F + \mathcal{J}_0 e^{-\sigma_0 x} e^{i\omega t} \quad 0 \leq x \leq l_0 \quad (2-7a)$$

$$T_1(x,t) = b_1 + b_2 x + b_3 e^{\beta x} + (\Xi e^{\sigma_1 x} + \Lambda e^{-\sigma_1 x} - \Gamma e^{\beta x}) e^{i\omega t} \quad -l \leq x \leq 0 \quad (2-7b)$$

$$T_2(x,t) = -(x + l + l_2) W_0 + W_1 e^{\sigma_2(x + l_2)} e^{\epsilon \omega t} \quad -(\ell + l_2) \leq x \leq -\ell \quad (2-7c)$$

where $\mathcal{J}_0$, Ξ , Λ , Γ , and W_1 are complex valued constants, b_1 , b_2 , b_3 , W_0 , and F are real valued constants. $\sigma = (1 + \epsilon) a$ with $a = \left(\frac{2\alpha}{\omega}\right)^{-1/2}$, $b_3 = \frac{I_0 \eta}{2\beta \kappa_1}$, and $\Gamma = \frac{\beta I_0}{2\kappa_1(\beta^2 - \sigma_1^2)}$.

By using the boundary conditions given in Eq.(2-4), all the coefficients in the Eq.(2-7) can be found. The explicit solution of $\mathcal{J}_0$, the complex amplitude of the periodic temperature rise in the solid-gas boundary ($x = 0$) is given by

$$\mathcal{J}_0 = \frac{\beta I_0}{2\kappa_1(\beta^2 - \sigma_1^2)} \left[\frac{(\gamma-1)(b+1)e^{\sigma_1 \ell} - (\gamma+1)(b-1)e^{-\sigma_1 \ell} + 2(b-\gamma)e^{-\beta \ell}}{(g+1)(b+1)e^{\sigma_1 \ell} - (g-1)(b-1)e^{-\sigma_1 \ell}} \right] \quad (2-8)$$

where $b = \frac{\kappa_2 a_2}{\kappa_1 a_1}$, $g = \frac{\kappa_0 a_0}{\kappa_1 a_1}$, and $\gamma = (1-\epsilon) \frac{\alpha_1}{2a_1}$.

Thus, Eq.(2-8) can be evaluated for specific parameter values, yielding a complex number whose real and imaginary parts, $\mathcal{J}'_0$ and $\mathcal{J}''_0$, respectively determine the in-phase and quadrature components of the periodic temperature variation at the sample surface ($x = 0$). Specifically the actual temperature at $x = 0$ is given by

$$\mathcal{T}(0,t) = \varphi_0 + F_0 + (\mathcal{J}'_0 \cos \omega t - \mathcal{J}''_0 \sin \omega t) \quad (2-9)$$

where φ_0 is the ambient temperature at the PAS cell walls, and F_0 is the increase in temperature due to the steady-state component of the absorbed heat.

(3) PAS signal generation

Once the temperature variation caused by an electromagnetic radiation is known, the photoacoustic signal can be derived from thermoelastic theory [36]. In a gas-microphone PAS system, the air absorbs heat uniformly over the sample surface at the plane $x = 0$. As a result, there is a temperature rise at and near the surface in the air and the subsequent strain (ϵ) due to temperature rise may be written as

$$\epsilon = \frac{\delta \mathcal{U}(x,t)}{\delta x} = \zeta T(x,t) \quad (2-10)$$

where $\mathcal{U}(x,t)$ is the x component of particle displacement at time t ;

ζ is the coefficient of linear thermal expansion;

and $T(x,t)$ is the temperature rise above the initial temperature;

In the presence of both heating and stress (p), the usual stress-strain relation $p = B \epsilon$ becomes

$$p = B \epsilon - B \zeta T(x,t) \quad (2-11)$$

where B is the bulk modulus (dynes cm^{-2}).

The equation of motion for an elastic wave travelling in the gas is

$$\begin{aligned} \rho \frac{\delta^2 \mathcal{U}(x,t)}{\delta t^2} &= \frac{\delta p}{\delta x} \\ &= B \frac{\delta^2 \mathcal{U}}{\delta x^2} - B \zeta \frac{\delta T}{\delta x} \end{aligned} \quad (2-12)$$

where ρ is the density of the gas (g cm^{-3}).

The velocity of sound in the gas is given by $c_0 = \sqrt{B/\rho}$, and the above equation becomes

$$\frac{\delta^2 \mathcal{U}}{\delta x^2} - \frac{1}{c_0^2} \frac{\delta^2 \mathcal{U}}{\delta t^2} = \zeta \frac{\delta T}{\delta x} \quad (2-13)$$

If the gas does not absorb the incident light, and is in contact with the light-absorbing sample at the boundary $x = 0$, then the temperature variation (a.c. component) in the gas is given by Eq.(2-7a)

$$T_{\text{a.c.}}(0,t) = \mathcal{T}_0 e^{-\sigma_0 x} e^{i\omega t} \quad (2-14)$$

where $\mathcal{T}_0$ is the temperature at the sample-gas interface ($x = 0$) and x is positive $0 \leq x \leq l_0$. The general solution for $\mathcal{U}(x,t)$ is then

$$\mathcal{U}(x,t) = \mathcal{U}_0(x) e^{i\omega t} \quad (2-15)$$

Equation (2-13) can be written as

$$\frac{\delta^2 \mathcal{U}_0(x)}{\delta x^2} + k'^2 \mathcal{U}_0(x) = \zeta \frac{\delta T}{\delta x} \quad (2-16)$$

where $k' = \frac{\omega}{c_0}$ is the wave vector for the acoustic wave in the gas.

The general solution for $\mathcal{U}_0(x)$ is as follows:

$$\mathcal{U}_0(x) = A_c e^{-\epsilon k' x} + D_c e^{\epsilon k' x} - \zeta_0 \mathcal{J}_0 \left(\frac{\sigma_0}{(k'^2 + \sigma_0^2)} \right) e^{-\sigma_0 x} \quad (2-17)$$

where A_c and D_c are constants to be determined from the following boundary conditions:

$$\mathcal{U}(0) = 0, \text{ and } \mathcal{U}(\ell_0) = 0 \quad (2-18)$$

which means that the sample and the cell window have impedances high enough to damp the acoustic wave in the gas phase to zero at the gas-solid boundaries immediately. Thus, the constants A_c and D_c are found to be

$$A_c = \zeta_0 \mathcal{J}_0 \left(\frac{\sigma_0}{k'^2 + \sigma_0^2} \right) \left(\frac{e^{\epsilon k' \ell_0} - e^{-\sigma_0 \ell_0}}{e^{\epsilon k' \ell_0} - e^{-\epsilon k' \ell_0}} \right) \quad (2-19)$$

$$D_c = \zeta_0 \mathcal{J}_0 \left(\frac{\sigma_0}{k'^2 + \sigma_0^2} \right) \left(\frac{e^{-\epsilon k' \ell_0} - e^{-\sigma_0 \ell_0}}{e^{\epsilon k' \ell_0} - e^{-\epsilon k' \ell_0}} \right) \quad (2-20)$$

Then, substituting Eq. (2-19) and (2-20) into Eq. (2-17) and solving for $\mathcal{Z}_0(x)$ and $p_0(x)$ according to Eq. (2-10) and (2-12), it is obtained:

$$\begin{aligned} \mathcal{Z}_0(x) = \frac{\delta \mathcal{U}_0}{\delta x} = & \epsilon \zeta_0 \mathcal{J}_0 \left(\frac{k' \sigma_0}{k'^2 + \sigma_0^2} \right) \\ & \left[\frac{(e^{-\sigma_0 \ell_0} - e^{\epsilon k' \ell_0}) e^{-\epsilon k' x} + (e^{-\sigma_0 \ell_0} - e^{-\epsilon k' \ell_0}) e^{\epsilon k' x}}{e^{\epsilon k' \ell_0} - e^{-\epsilon k' \ell_0}} \right] \end{aligned} \quad (2-21)$$

$$\begin{aligned}
 p_0(x) = & \epsilon B \zeta'_0 \mathcal{J}_0 \left(\frac{k' \sigma_0}{k'^2 + \sigma_0^2} \right) \\
 & \left[\frac{(e^{-\sigma_0 l_0} - e^{\epsilon k' l_0}) e^{-\epsilon k' x} + (e^{-\sigma_0 l_0} - e^{-\epsilon k' l_0}) e^{\epsilon k' x}}{e^{\epsilon k' l_0} - e^{-\epsilon k' l_0}} \right] \\
 & - B \zeta'_0 \mathcal{J}_0 \left(\frac{k'^2}{k'^2 + \sigma_0^2} \right) e^{-\sigma_0 x}
 \end{aligned} \quad (2-22)$$

In a practical PAS cell, the gas column length l_0 is much smaller than the acoustic wavelength, $l_0 \ll k'^{-1}$, and from the above equations we have

$$g(x) \approx \zeta'_0 \mathcal{J}_0 \left[e^{-\sigma_0 x} - \frac{(1 - e^{-\sigma_0 l_0})}{\sigma_0 l_0} \right] \quad (2-23)$$

$$p(x) \approx -B \zeta'_0 \mathcal{J}_0 \left(\frac{1 - e^{-\sigma_0 l_0}}{\sigma_0 l_0} \right) \quad (2-24)$$

The stress or pressure in the gas, $p(x)$, is thus compressive and independent of the position x . Furthermore, when the gas column over the sample surface is long enough to be thermally thick ($l_0 \gg \sigma_0^{-1}$), which is the normal case in PAS studies, we obtain

$$p(x) \approx - \frac{B \zeta'_0}{\sigma_0 l_0} \quad (2-25)$$

The pressure experienced by the microphone is equal and opposite to the pressure on the gas which has the properties that $B = \gamma_h P_a$ and $\zeta' = \frac{1}{T_a}$, where P_a is the ambient pressure (atm.), T_a is the ambient temperature (K); γ_h is the ratio of specific heats; and

$\mathcal{T}_0$ is the temperature rise on the sample surface, given in Eq. (2-8). The pressure measured by the microphone, i.e., the PAS signal, is also a function of time. Therefore, the PAS signal can be exclusively given by

$$\begin{aligned} q = -p(x,t) &= \frac{\gamma_h P_a}{T_a \sigma_0 l_0} \mathcal{T}_0 e^{i\omega t} \\ &= \frac{\gamma_h P_a}{\sqrt{2} T_a l_0 a_0} \mathcal{T}_0 e^{i(\omega t - \pi/4)} \end{aligned} \quad (2-26)$$

By substituting Eq. (2-8) into Eq. (2-26) a full expression of PAS signal is obtained as follows:

$$\begin{aligned} q &= \frac{\gamma_h P_0}{\sqrt{2} T_0 l_0 a_0} \frac{\beta l_0}{2\kappa_1(\beta^2 - \sigma_1^2)} \\ &\quad \left[\frac{(\gamma-1)(b+1)e^{\sigma_1 l} - (\gamma+1)(b-1)e^{-\sigma_1 l} + 2(b-\gamma)e^{-\beta l}}{(g+1)(b+1)e^{\sigma_1 l} - (g-1)(b-1)e^{-\sigma_1 l}} \right] e^{i(\omega t - \pi/4)} \end{aligned} \quad (2-27)$$

Similarly the PAS signals determined by using a piezoelectric transducer can also be derived from the thermoelastic theory (see Chapter 10 in ref. 2).

In Eq. (2-27) the amplitude of the PAS signal generated in the system is related to the optical and thermal properties of the PAS system. By using specific parameters of a system, the PAS signal amplitude can be mathematically simulated

Therefore, the effect of a parameter of the system on the PAS signal can be evaluated using this equation.

(4) Special Cases in PAS

In practice Eq. (2-27) is inconvenient to use in describing the physical meaning of PAS signals. In the real world of PAS studies, six special cases have been considered to be the most significant [2, 4]. As shown in Fig. 2, these cases may be divided into two groups according to the optical opaqueness of the sample as determined by the relation of the optical absorption length (l_β) to the length (i.e., thickness) of the sample (l). In each group of optical opaqueness, three cases are considered according to the relative magnitude of the thermal diffusion length (μ) of the sample to the physical length (l) and the optical absorption length (l_β), where

$$\mu = \sqrt{\frac{2\alpha}{\omega}} \quad (2-28)$$

$$l_\beta = \frac{1}{\beta} \quad (2-29)$$

(a) Optically transparent samples ($l_\beta > l$):

As a sample is optically transparent, the incident light will be partly absorbed throughout the whole length of the sample while the rest is transmitted through the sample.

If a sample is thermally thin (cases 1-a and 1-b), all the optical energy absorbed by the sample can be transferred from the sample to the adjacent gas for the generation of the PAS signal. In the two cases the PAS signal amplitude is

1. Optically Transparent

2. Optically Opaque

Fig. 2: Special cases in gas-microphone PAS.

proportional to the sample absorption (βl) and has an ω^{-1} dependence.

In a thermally thick sample (case 1-c), even though the sample absorbs optical energy along the whole sample length, only the optical energy absorbed within the first thermal diffusion length can contribute to the PAS signal. The PAS signal amplitude is not proportional to the total absorption by the sample, instead, it is proportional to the absorption in the first thermal diffusion layer of the sample and has a frequency dependence of $\omega^{-3/2}$.

(b) Optically opaque samples ($l_{\beta} < l$):

When a sample is optically opaque, most of the incident light is absorbed within a distance that is smaller than the sample length, and essentially no light is transmitted.

If the sample is also thermally thin (case 2-a), the sample will seem to be optically saturated and the PAS signal amplitude will be independent of the optical absorption coefficient of the sample and will be only related to the thermal properties of the backing material.

If the sample is thermally thick (case 2-b), with the thermal diffusion length being larger than the optical absorption length of the sample ($\mu > l_{\beta}$), the PAS signal amplitude will be independent of the optical absorption of the sample and will be related to the thermal properties of the sample itself.

In both the above cases (2-a and 2-b), the PAS signal amplitude varies as ω^{-1} .

In the last special case (2-c), the sample is optically opaque and thermally thick, with its thermal diffusion length being less than its optical absorption length

The PAS signal expression in this case is similar to that for case (1-c). Only the optical energy absorbed within the first thermal diffusion length contributes to the PAS signal. This is a very interesting and important case. The sample is optically opaque but not photoacoustically opaque. The PAS signal amplitude is still proportional to β , is dependent on the thermal properties of the sample, and varies as $\omega^{-3/2}$.

Chapter 3

Photoacoustic Determination of Trace Elements with Solid Film Sampling

(1) Introduction

In the past two decades, the PAS has become an important tool of analytical chemistry. PAS techniques have been used in spectroscopic studies, in monitoring the deexcitation processes, and in probing thermoelastic and other physical properties of samples in the solid state [41–43]. Specifically, Goede et al. investigated isovalent impurities in II – IV semiconductors [44]; Varlashkin et al. studied spectra of powder materials by using the FTIR/PAS technique [45]; Hursh and Kuwana detected monolayer coverage of copper phthalocyanine sublimates on glass [46]; Holter and Perkampus conducted a PAS investigation on thin copper phthalocyanine films [47].

Leyden and co-workers determined Cu(II) and Fe(III) as then N-2-aminoethyl-3-aminopropyl trimethoxysilane complexes in two-component samples immobilized on silica gel using their photoacoustic response functions [48, 49], however, the precision of their results are not good.

Although PAS is very sensitive in solid-state analysis, its application to the liquid state is limited by the requirement of a powerful laser source. Recently, using a 1.6 W argon ion laser, Kitamori et al. were able to determine cobalt below 1 ng L^{-1} after extracting cobalt from its aqueous solution into an organic solvent to increase the cobalt concentration for piezoelectric PAS detection [50]. It is clear that the ultimate degree of analyte preconcentration would be achieved by reducing the solvent volume

to zero, resulting in a solid sample. It will be shown from PAS theory later that such a conversion of a sample, from being thermally thick to being thermally thin, can enhance the analytical sensitivity of gas–microphone PAS detection by 2–3 orders of magnitude [51].

In this chapter, a technique is demonstrated for preparing solid film samples from sample solutions in order to achieve high sensitivity in gas–microphone PAS determinations.

(2) Converting thermally thick samples into thermally thin ones

In analytical chemistry one deals with dilute solutions of analytes on most occasions. The analyte species in such solutions may absorb optical energy all along the incident light path. However, only the optical energy absorbed within the first-thermal-diffusion layer below the sample surface can be transferred as heat to the adjacent gas in a gas–microphone PAS cell and generate a PAS signal.

The thermal diffusion length of a sample solution is dependent on the thermal properties of the solvent. From Eq.(2–28), at the chopping frequency of 100 Hz, the thermal diffusion lengths calculated for water, ethanol and chloroform are 2.1×10^{-2} , 1.7×10^{-2} and 1.6×10^{-2} mm, respectively. If the solution has a thickness of 10 mm, it is thermally thick ($\mu < l$). The ratio of the optical energy used to generate the PAS signal to the total optical energy absorbed by the solution will be approximately 10^{-3} , while the remaining absorbed energy is wasted with respect to PAS signal generation. Consequently the gas–microphone PAS technique is not sensitive for liquid samples.

If one can gather all the analyte species from the bulk of the solution into the first—thermal—diffusion—length layer, the entire optical energy absorbed by the analyte species will contribute to the production of PAS signal. By converting a thermally thick sample into a thermally thin one, the detection sensitivity of gas—microphone PAS can be increased by as much as 2–3 orders of magnitude.

In gas—microphone PAS the signal amplitude (V) for a thermally thin and optically transparent sample ($\mu > l$ and $l_\beta > l$) can be derived from Eq. (2-27) in Chapter 2, to be [36, 47]

$$V = K q = K' I_0 (1 - e^{-\beta l}) \quad (3-1)$$

where K and K' are constants under given experimental conditions. If $\beta l < 0.1$, then by expanding $e^{-\beta l}$ into the power series of βl and truncating the high—order terms of βl , the above equation can be approximated to

$$V \approx K' I_0 \beta l \quad (3-2)$$

Up to this step it has been shown that the PAS signal amplitude is proportional to the absorption of monochromatic light at a specific wavelength by the sample. As absorbance is the conventional parameter used in analytical spectrometry we would like to express the sample absorption in absorbance units as follows. When a monochromatic beam of light passes through an isotropic medium, the beam intensity will be attenuated by the medium if the medium absorbs the light. Then, the intensity (I) of the beam after passing through the medium is related to the original intensity of

the incident beam (I_0) by the following equation:

$$I = I_0 e^{-\beta l} \quad (3-3)$$

The absorbance (A) of the medium is given by

$$A = -\log \frac{I}{I_0} = \log (e^{\beta l}) \approx 0.4342 (\beta l) \quad (3-4)$$

or

$$\beta l = 2.303 A \quad (3-5)$$

Substituting Eq.(3-5) into Eq.(3-2) obtains

$$V \approx 2.303 K' I_0 A = K'' I_0 A \quad (3-6)$$

Eq. (3-6) shows that the PAS signal amplitude is proportional to the intensity of the incident light beam and to the sample absorbance.

According to Beer–Lambert law, the absorbance of a solution is related to the molar absorptivity (ϵ) of the light-absorbing analyte species, the concentration of the species in the solution (c) and the light pathlength in the solution (b):

$$\begin{aligned} A &= \epsilon b c \\ &= \epsilon \frac{n}{S} \end{aligned} \quad (3-7)$$

In the above equation, the product of b and c has the units of moles cm^{-2} since $b c = \frac{n}{S}$, where n is the mole number of the species and S is the cross-sectional

area (cm^{-2}) of the solution. For a solid film sample prepared in a sample cup, the area of the film sample (S) is constant, being confined by the size of the cup bottom, (5-mm diameter, see Fig. 3). By using these relations, Eq.(3-6) can be rewritten as

$$V = K'' I_0 \epsilon \frac{n}{S} = K''' I_0 \epsilon n \quad (3-8)$$

where K''' is a combined proportionality constant. Obviously, for a given species and a given light source (i.e., constant ϵ and I_0), V is directly proportional to n (in moles) in a solid film sample that is optically transparent ($\beta l < 0.1$) and thermally thin. Equation (3-8) thus serves as the basic equation for quantitative PAS measurements of solid film samples.

(3) Experimental

Equipment:

The experimental set-up for PAS measurement is shown in Fig. 4. A He-Ne laser (Melles Griot 05-LHR-981, San Marcos, CA) with an output power of 17 mW at 632.8 nm was used as the excitation light source. The laser beam was modulated by a mechanical chopper (PTI OC4000, Princeton, NJ). A mirror and a convex lens were used to adjust the position and size of the laser spot which covers the whole bottom area of the sample cup. The PAS cell was based on the Helmholtz resonator design, as shown in Fig. 5, with a cell volume of 2.6 cm^3 . The PAS cell body was made of aluminium which has little optical absorption at the laser wavelength of 632.8 nm. The cell window material was a circular fused-quartz plate that was fixed to the cell top by

Fig. 3: Sample cup.
All dimensions are in mm.

Fig. 4: Experimental set-up of photoacoustic spectrometer.

Fig. 5: PAS cell.

a = retainer ring; b = fused-quartz window; c = rubber O-ring;
 d = aluminum cell body; e = bolt and nut; f = brass bottom plates;
 g = mirror; h = solid film sample on the cup bottom; and
 i = microphone and preamplifier.

a retainer ring. An O-ring was used between the window and the cell body to provide air-tightness. A brass plate was attached to the perimeter of the cell bottom with epoxy resin. Another brass plate as the base board supporting the sample, was mounted to the first brass plate with bolts and nuts. Two O-rings were inserted between these two brass plates to provide air-tightness, preventing any environmental noise from transferring through air into the cell. On the base plate was a mirror which was used to reduce the background noise level (due to laser light absorption by the brass material), typically from 50 mV to 3 mV. In addition, the mirror reflected the transmitted light backwards to make a second pass through the thin film sample. As the film is thermally thin, this back illumination approximately doubled the PAS signal amplitude, hence increasing the analytical sensitivity.

A condenser microphone (Bruel & Kjaer 4132, Naerum, Denmark) and an impulse precision sound level meter (Bruel & Kjaer 2209) with an octave filter set (Bruel & Kjaer 1613) constituted the detector system. The acoustic wave generated from the periodic optical heating of the sample exerts a pressure on the microphone. This pressure causes the displacement of the microphone diaphragm, producing a proportional voltage signal in the preamplifier circuit. In order to reduce noise in the voltage signal, the microphone and sound level meter system was supported by a 14-cm styrofoam-sponge pad to isolate the system from bench vibrations which generate noise. The PAS cell was directly mounted to the microphone through its microphone chamber, with no extra support as to avoid undesirable transmission of vibrations.

A function generator (Wavetek 164, San Diego, CA) and an oscilloscope (B+K Precision, Chicago, IL) were used to control and monitor the scanning of chopping frequency in a study of the frequency characteristics of the gas-microphone PAS cell.

The PAS cell had a resonant frequency of 490 Hz (shown in Fig. 6) which is very close to the value calculated using the following equation [52]

$$\omega_H = c_0 \left[\frac{S_c (v_1 + v_2)}{l_c v_1 v_2} \right]^{1/2} \quad (3-9)$$

where ω_H is the Helmholtz resonance frequency;

S_c is the cross-sectional area of the PAS cell channel;

l_c is the length of the channel;

and v_1 and v_2 are the volumes of the PAS cell and microphone chambers.

However, the resonant frequency was not really utilized in this PAS work for it did not result in the best signal-to-noise ratio. As shown in Table I, when three chopping frequencies were compared 200 Hz gave the lowest noise level and hence the largest signal-to-noise ratio. Consequently, 200 Hz was selected as the working chopping frequency in all subsequent PAS measurements.

A lock-in amplifier (Stanford Research System 510, Palo Alto, CA) processed the modulated PAS signal and discriminated against noise. A computer software (Stanford Research System 510) was used to collect experimental data and to perform autophase calculations. The lock-in amplifier consists of two parts: a filter part and a phase-correlation part. In the first part, noise components which are due to the electrical line frequency, its harmonics and due to ambient acoustic wave are eliminated by the line filters and band filters. Only the signal components in a narrow frequency range around the chopping frequency are allowed to pass to the second part of the lock-in amplifier for further processing. In the second part, the signal component will be compared with the reference signal. Only those components with

Fig. 6: Frequency characteristics of the PAS cell tested with BGSbCl_6 , ---
a = 0 ng; b = 68 ng; c = 136 ng; d = 272 ng; e = 465 ng.

Table I: Comparison of noise levels at three chopping frequencies

Noise Level (peak-to-peak), mV					
Frequency (Hz)	Time Constant				
	1 s	3 s	10 s	30 s	100 s
100	87.0	56.9	37.9	15.8	9.5
200	10.5	6.5	2.6	1.5	1.0
490	75.9	55.3	18.7	18.7	9.2

the same phase as the reference signal can be amplified and detected. Other out-of-phase components cancel each other because they have no phase correlation with the reference signal. The autophase calculation performed with the lock in amplifier allows one to measure the maximum amplitude of a signal at the correct phase angle.

Reagents:

All chemicals used were of analytical-reagent or ACS spectral pure grade. The water used was deionised to a resistivity of 18 M Ω cm with a Miller-02 water purification system (Millipore Corporation, Mississauga, Ontario, Canada). The complexing agents used were brilliant green (BG), dithizone (H₂Dz), and 1-(2-pyridylazo)-2-naphthol (PAN), which were obtained from Fisher Scientific Company (Fair Lawn, NJ). The selection of these complexing agents and the corresponding metal ions was governed mainly by their availability and no attempt was made to optimize the complexation systems studied. The only consideration was that the metal complexes must have a high absorption at the the He-Ne laser wavelength (632.8 nm), so that PAS signals could be generated from the complex samples with the moderate power of the He-Ne laser.

Procedure:

(i) Extraction – As the complexing agents were commonly used ones, all the extraction procedures were adopted from various literature sources [53–56] with minor modifications for operational simplicity. Only standard solutions were used in this work.

Extraction of BGSbCl₆ (or BGTlCl₄) – An aliquot of standard Sb(III)/ Tl(I)

solution was pipetted into a 100 mL–separatory funnel containing 10 mL of 1:1 HCl [or 1:2 HCl for Tl(I)]. 1 mL of cerium(IV) sulfate solution (0.1 M in 1 M H₂SO₄) was transferred into the funnel and the contents were mixed for 1 minute. The excess of cerium(IV) was reduced by dropwise addition of 1% hydroxyl–ammonium chloride solution until the yellow color disappeared. Without delay, the mixture was diluted with 25 mL of water (no dilution was needed for thallium), and 10 mL of benzene plus 0.5 mL of 0.5% BG solution were added into the solution. The funnel was shaken for 2 minutes and the organic phase was filtered through a filter paper into a flask. Another 10 mL of benzene plus 0.5 mL of BG solution were added into the funnel to extract any residual Sb(V)/Tl(III), and the organic phase was filtered into the flask. The organic extract in the flask was used to prepare solid film samples for PAS determination of antimony or thallium.

Extraction of Cd(HDz)₂ – An aliquot of standard Cd(II) solution was pipetted into a 100 mL–separatory funnel containing 45 mL of water and 5 mL of 1 M NH₃ – 1M NH₄Cl buffer solution. 5 mL of 0.01% dithizone solution in chloroform was added into the funnel and the funnel was shaken for 2 min. Then the organic phase was drained through a filter paper into a flask for later use.

Extraction of Ni(HDz)₂ – An aliquot of standard Ni(II) solution was pipetted into a 100 mL–separatory funnel containing 50 mL of water and 2 mL of 1:1 ammonia. 5 mL of 0.01% dithizone solution in chloroform was added into the funnel for extraction. The funnel was shaken for 2 minutes and the organic phase was filtered through a filter paper into a flask for later use.

Extraction of Pd(HDz)₂ – An aliquot of standard palladium(II) solution was pipetted into a 100 mL – separatory funnel containing 50 mL of water and 2 mL of 1:1 HCl. The aqueous solution was extracted with 5 mL of 0.01% dithizone solution

chloroform for 10 minutes. Then, the organic phase was washed with two 4-mL portions of 1:50 ammonia and the organic phase was filtered through a filter paper into a flask for later use.

Extraction of $\text{Co(PAN)}_2\text{Cl}$ – An aliquot of standard cobalt(III) solution was pipetted into a 100 mL – separatory funnel containing 50 mL of water and 4 drops of 6N HCl. 0.5 mL of 0.005 M PAN solution and 5 mL of chloroform were added into the solution and the funnel was shaken for 3 minutes. 15 minutes were allowed for the phases to separate. The organic phase was then filtered into a flask for later use.

Extraction of Ni(PAN)_2 – An aliquot of standard nickel(II) solution was pipetted into a beaker containing 40 mL water and 3 mL of 1M NH_3 – 1M NH_4Cl buffer solution . 0.5 mL of 0.005 M PAN solution was added into the solution and the solution was heated up to approximately 60 °C. After cooling to room temperature, the solution was quantitatively transferred into a 100–mL separatory funnel and the solution was extracted with two 5–mL portions of chloroform. The organic phase was filtered into a flask for later use.

Extraction of Pd(PAN)Cl – An aliquot of standard palladium(II) solution was pipetted into a 100–mL separatory funnel containing 40 mL of water. Then 2N HCl was added, by drops, into the solution until the pH range of the solution reach between 2–5. 5 mL of CHCl_3 was added into the funnel and the funnel was shaken for 5 minutes. The organic phase was filtered into a flask for later use.

(ii) **Evaporation of the Organic Solvents** – After each extraction, the concentration of a metal in the organic extract was determined by using both spectrophotometry and atomic absorption spectrometry, which was used as the standard value to calculate the amount of the metal ion in its solid film samples.

To prepare a solid film sample, 10 – 50 μL of an organic extract containing a certain amount of a metal ion was transferred with an Eppendorff microliter pipet into a sample cup of the dimensions shown in Fig. 3. The sample cup was made from glass and its bottom was a thin circular glass plate (about 0.5mm in thickness) which was normally used as a microscopic cover glass (Corning Glass Works, New York). This thin glass plate was attached to the cup body by using cyanoacrylate glue. The organic solvent in the organic extract was evaporated by blowing air over the cup for 3 minutes. After that the solid film on the cup bottom was ready for PAS measurements. A relatively thick solid film sample could be obtained either by using an organic extract with a high concentration of the metal complex ion, or by transferring a large amount of organic extract, in several portions, to the same sample cup with intermediate solvent evaporation.

The thickness of solid film samples was measured with a digital micrometer (Mitutoyo ID-110 ME digimatic indicator, Japan) which has a lowest count of 1 μm . The absorbance value of the solid film samples was measured according to the equation $A = \log\left(\frac{I_0}{I}\right)$. A He-Ne laser was used as the light source to provide I_0 at the wavelength of 632.8 nm; a photodiode was used as the detector to measure I_0 and I , and a set of neutral density filters was used as standard to calibrate the experimental set-up.

(iii) PAS measurement of solid film samples – The solid film sample on the bottom of the cup was placed in the gas-microphone cell, as shown in Fig. 5. The sample cup sat on a mirror that was used to reduce background absorption and noise. The chopping frequency was set at 200 Hz. The time constant of the lock-in amplifier was chosen between 1 and 30 s. Autophase calculation was done for each

sample to read the maximum signal amplitude and to monitor the phase angle shift. All the data was collected using a computer (IBM PC XT).

(4) Result. and Discussion

(a) Extraction

In this study liquid-liquid extraction was used as the method to pre-concentrate an analyte from its aqueous solution into an organic solvent, and the organic extract was the starting material for the preparation of solid film samples since the organic solvents used are more volatile than water. No attempts were made to separate the analyte of interest from potential interfering species because only pure standard solutions of each metal were used in this study.

Brilliant green (BG) was used as the complexing agent in the extractions of Sb(V) and Tl(III). The solid dye is usually in the form of chloride, (BG)Cl. As shown below, in acid solution (BG)H²⁺ predominates; in neutral solution, (BG)⁺; and in alkaline solution, the colorless carbinol form (BG)OH:

The optimal range of HCl concentration for the extraction of chloro anions, depends upon the metal. In 1:1 HCl medium, Sb(V) and Tl(III) exist as $SbCl_6^-$ and $TlCl_4^-$. The dye cation, $(BG)^+$, green in colour, forms slightly soluble ion-association complexes with $SbCl_6^-$ and $TlCl_4^-$. Although the ion pairs are extractable into various organic solvents, benzene was used in this study because it produces extraction blanks with the lowest absorbance [55]. Note that brilliant green is not very selective for Sb(V) and Tl(III) but also combines with $GaCl_4^-$, $AlCl_4^-$, $CuCl_2^-$, AgI_2^- , TaF_6^- , ReO_4^- and other singularly charged complex anions. Thus, additional separations are necessary if these anions coexist with $SbCl_6^-$ and $TlCl_4^-$ in complicated samples.

Dithizone (H_2Dz), or Diphenylthiocarbazone is one of the most important complexing agents used by analytical chemists for heavy metals. In its solution dithiozone has two forms in tautomeric equilibrium as shown below:

Therefore, the absorption spectrum of dithizone in an organic solution shows two peaks and the absorption peak at the longer wavelengths corresponds to the thione form [53].

Dithizone was used for the extractions of Cd(II), Ni(II) and Pd(II) from their aqueous solutions. Dithizone contains two active hydrogen atoms, each of which can be replaced by an equivalent of metal. When one hydrogen of each dithizone molecule is replaced, a primary dithizonate complex is formed. When both are replaced, a secondary dithizonate is formed. The structure of a primary dithizonate of the metal M(II) is depicted as follows:

where M represents one of Cd(II), Ni(II) or Pd(II) ions. The chelate complex can be extracted into an organic solvent such as CCl_4 or CHCl_3 . Chloroform was used in this study.

1-(2-pyridylazo)-2-naphthol (PAN) is the most widely used pyridylazo reagent for spectrophotometric determination of Co(III) and other metal ions. The structure of PAN molecule is shown below:

In acidic solutions the pyridine nitrogen is protonated and in basic solutions the H of the OH group is ionized.

PAN was used in this work for the extractions of Co(III), Ni(II) and Pd(II). The chelates of PAN have the metal atom (or oxo- or hydroxo-metal cation) bonded to O of the OH group (H replaced), to pyridine N and to azo N as illustrated by the following structures:

or

where M represents Pd(II) ion in the upper case and M represents Ni(II) or Co(III) ion in the lower case .

The characteristics of the extracts results are shown in Table II. The

Table II:

Characteristics of the Organic Extracts

Element	Complex	Organic Solvent	Molar Absorptivity at a Peak Wavelength [*] (L mol ⁻¹ cm ⁻¹)	Molar Absorptivity at 632.8 nm ^{**} (L mol ⁻¹ cm ⁻¹)
Tl	BGTlCl ₄	C ₆ H ₆	$\epsilon_{640} = 1.06 \times 10^5$ ^{***}	1.01×10^5
Sb	BGSbCl ₆	C ₆ H ₆	$\epsilon_{640} = 7.0 \times 10^4$ ^{***}	6.5×10^4
Cd	Cd(HDz) ₂	CHCl ₃	$\epsilon_{520} = 8.7 \times 10^4$	5.8×10^3
Co	Co(PAN) ₂ Cl	CHCl ₃	$\epsilon_{630} = 1.96 \times 10^4$	1.93×10^4
Ni	Ni(HDz) ₂	CHCl ₃	$\epsilon_{670} = 2.0 \times 10^4$	1.9×10^4
	Ni(PAN) ₂	CHCl ₃	$\epsilon_{575} = 5.1 \times 10^4$	1.5×10^3
Pd	Pd(HDz) ₂	CHCl ₃	$\epsilon_{620} = 4.25 \times 10^4$	3.3×10^4
	Pd(PAN)Cl	CHCl ₃	$\epsilon_{678} = 1.41 \times 10^4$	1.0×10^4

Reference 53 : ** Calculated from the peak molar absorptivity and the measured absorbances at the peak wavelength and at 632.8 nm; and *** Reference 54 .

absorption spectra for these complexes in organic solutions are shown in Fig. 7 – Fig. 13. The molar absorptivities ($\epsilon_{632.8}$) of these organic solutions at the wavelength of He Ne laser (632.8 nm) were calculated from the following equations:

$$A = \epsilon l C$$

$$\text{and} \quad \frac{A_{632.8}}{A_{\max}} = \frac{\epsilon_{632.8}}{\epsilon_{\max}} \quad (3-10)$$

where $A_{\max}$ and $A_{632.8}$ are spectrophotometrically measured absorbance values at the maximum absorption wavelength and at 632.8 nm respectively, and $\epsilon_{\max}$ is the molar absorptivity of the complex studied at a peak absorption wavelength, as given in Table II. The $\epsilon_{632.8}$ value of each complex will be used later in the discussion on the analytical sensitivity of PAS measurements on solid film samples.

(b) Solid film samples

After evaporating the organic solvent off the sample cup, a solid film sample was obtained on the bottom of the sample cup. The film samples formed from different organic complex solutions showed certain surface patterns. These patterns were probably determined by the crystallization properties of the complexes since crystallization might take place accompanying the solvent evaporation. The thickness of each solid film sample did not look uniform visually; however, the differences in thicknesses were so small that the PAS signals for solid films made from the same amount of analyte were almost identical to each other.

Fig. 7: Absorption spectrum of BGShCl₆/BGTlCl₄ in C₆H₆.

Fig. 8: Absorption spectrum of $\text{Cd}(\text{HDz})_2$ in CHCl_3 .

Fig. 9: Absorption spectrum of $\text{Ni}(\text{HDz})_2$ in CHCl_3 .

Fig. 10: Absorption spectrum of $\text{Pd}(\text{NDz})_2$ in CHCl_3 .

Fig. 11: Absorption spectrum of $\text{Co(PAN)}_2\text{Cl}$ in CHCl_3 .

Fig. 12: Absorption spectrum of Ni(PAN)_2 in CHCl_3 .

Fig. 13: Absorption spectrum of Pd(PAV)Cl in CHCl_3 .

The film samples formed in the sample cups were thermally thin as was evident from the following estimation. The thermal diffusivities (α) for most solid organic compounds are of the order of $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ [47]. Therefore, at a chopping frequency of 200 Hz, the thermal diffusivities for most solid organic compounds would be

$$\mu = \sqrt{2\alpha/\omega} = 13 \text{ } \mu\text{m}$$

The complexing agents used in this study are organic compounds and would have thermal diffusivities close to $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ in the solid state. When they combine with metal ions, the thermal diffusivities of the resulting complexes should not decrease significantly for the complexing agents have larger molecular weights and sizes than the metal ions. Therefore, the value of 13 μm can be safely used as the criterion to estimate whether or not a solid film sample is thermally thin at the chopping frequency of 200 Hz.

It is shown in Fig. 14, for instance, that the PAS linear dynamic range for cobalt as $\text{Co(PAN)}_2\text{Cl}$ extends up to 500 ng of Co(III) which is contained in 4.7 μg of the complex. Ideally, the mass of the complex in a film sample is related to the thickness, area (i.e., the bottom area of the sample cup) and density of the film sample. Unfortunately, the density of the complex was not known accurately, so an approximate value, the density of water ($\rho = 1.0 \text{ g cm}^{-3}$) had to be used for comparison purposes:

Mass of complex containing 500 ng of Co(III), $M = 4.7 \text{ } \mu\text{g}$;

Film sample area = bottom area of sample cup, $S = 0.196 \text{ cm}^2$;

$\therefore$ film sample thickness, $l = \frac{M}{\rho S} = 0.24 \text{ } \mu\text{m}$, which is almost two orders of magnitude smaller than the thermal diffusion length estimated above. Similar

Fig. 14: Standard calibration graphs for (a) Tl as HgTlCl_4 , (b) Sb as HgSbCl_5 , (c) Co as $\text{Co(PAN)}_2\text{Cl}$, (d) Pd as Pd(PAN)Cl .

Horizontal scale represents the amount of metal in a complex.

calculations can be made for the other complexes studied. In the linear dynamic ranges, all the film samples were thermally thin, having thicknesses of at least one order of magnitude smaller than 13 μm .

Another piece of evidence for thermally thin film samples came from the fact that the PAS signal amplitudes for the films made from 4.7 μg of $\text{Co}(\text{PAN})_2\text{Cl}$ and 3.9 μg of $\text{Pd}(\text{PAN})\text{Cl}$ had a chopping frequency dependence of ω^{-1} (Fig. 15 and 16), whereas a thermally thick, optically transparent sample has a theoretical frequency dependence of $\omega^{-3/2}$ [36]. Thus, it was confirmed that all the film samples falling in the linear dynamic ranges were thermally thin.

The absorption spectra of the complex film samples were observed to be very similar in profile to those of the complexes in the corresponding organic solvents. The absorption peak positions were slightly shifted as shown in Table III. Such small shifts in absorption peak positions are a common phenomenon, mainly due to the solvent effect [57]. As the absorption peak shifts are generally less than 10 nm, the peak absorption wavelength measured from the organic solution of a complex, which are often known in the literature, can generally be used as a convenient guide to select the laser excitation wavelength for a given complex analyte in a solid film sample.

The stability of four metal complexes $\text{Cd}(\text{HDz})_2$, $\text{Co}(\text{PAN})_2\text{Cl}$, BGSbCl_6 and BGTlCl_4 were tested. The results, as shown in Fig. 17, indicated that the film samples were very stable under normal laboratory conditions of temperature, pressure and light. Therefore, the PAS measurement on a solid film sample can be made as many times as required without any fear of sample decomposition or changes in analyte concentration.

(c) Noise in gas-microphone PAS system

There are mainly three kinds of noise in the gas-microphone PAS system,

Fig. 15: Frequency dependence of PAS signal amplitude for 500 ng of $\text{Co(III)} \text{ in a } \text{Co(PAN)}_2\text{Cl}$ solid film sample.

Fig. 16: Frequency dependence of PAS signal amplitude for 1,060 ng of Pd(II) in a Pd(PAN)Cl solid film sample.

Table III:

Shift of Absorption Peaks in Solid Films

Element	Complex	Absorption Peak Wavelength (nm) in Organic Solution	Absorption Peak Wavelength (nm) in Solid Film	Absorption Peak Shift (nm)
Tl	BGTlCl ₄	638.5	633.8	-5
Sb	BGSbCl ₆	638.9	634.0	-5
Cd	Cd(HDz) ₂	517.1	529.0	+12
Co	Co(PAN) ₂ Cl	627.4	627.0	0
Ni	Ni(PAN) ₂	569.0	582.2	+13
Pd	Pd(HDz) ₂	635.0	640.0	+5
	Pd(PAN)Cl	620.5	620.0	-1

Fig. 17: The stability of solid film samples.

a = 41 ng Sb as BGSbCl_6 ; b = 23 ng Tl as BGTlCl_4 ;

c = 20 ng Co as $\text{Co(PAN)}_2\text{Cl}$; d = 50 ng Cd as Cd(HDz)_2 .

which may limit the detection sensitivity of the PAS method: environmental noise, photoacoustic noise and electronic noise.

The environmental noise can arise from ambient acoustics or vibrations from the building and the mechanical chopper. There was no specific acoustic isolation in our PAS system as long as there were no loud noise source in the neighbourhood to overload the microphone. In order to reduce vibrational noise, the PAS detector was supported by a sponge–styrofoam pad to isolate the system from bench vibrations. The mechanical chopper was also supported with a styrofoam pad and was placed as far away as possible from the detector.

The photoacoustic noise may be generated from the absorption of the He–Ne laser radiation by the PAS cell window and the cell walls. In our PAS system a fused–quartz plate was used as the cell window, which has negligible absorption at the wavelength of the He–Ne laser. A mirror was put on the bottom of the PAS cell chamber (Fig. 5) to effectively reduce the light absorption by the brass bottom plate.

There are three types of electronic noise: Johnson noise, shot noise and flicker noise. Johnson noise (or thermal noise) originates from a resistor (or conductor), in which a basic fluctuation of electrons always exists because of thermal agitation. Johnson noise has a white power spectrum; that is, its power density (W Hz^{-1}) is independent of frequency. The noise associated with such fluctuations can be expressed by a root–mean–square voltage (V_{rms}) as follows [57]:

$$V_{\text{rms}} = \sqrt{4kTR \Delta f} \quad (3.11)$$

where R is the resistance (Ω) and Δf is the frequency bandwidth (Hz) over which a measurement is made.

Shot noise is associated with random variations in the number of charged

particles crossing a junction or arriving at a electrode. Shot noise originated in transistors, vacuum tubes and photomultiplier tubes can be described by [57]

$$i_{\text{rms}} = \sqrt{2Ie \Delta f} \quad (3-12)$$

where I is the current due to some "single-event" type process and e is the charge on an electron. Shot noise also has a white power density spectrum. Ordinarily, shot noise is small in magnitude and may be neglected in comparison with Johnson noise.

The third type of noise is flicker noise (also called $\frac{1}{f}$ noise), the power density of which decreases with the reciprocal of the increasing frequency. Such noise is typical of the low frequency (i.e., long-term) drifts common in transducers, amplifiers, and analog components.

In a real electronic instrumentation system, all three types of noise are likely to be encountered. Flicker noise can usually be greatly reduced by choosing a relatively high reference frequency. As for white noise which is band-limited by the frequency response of the measurement system. Noise reduction may be effected by the time constant selected. The data shown in Table I (on p.32) indicate that in our PAS system there is a quadratic decrease in noise level with increasing time constant at each chopping frequency. Recall that the time constant (τ_c) of the low-pass filter in the lock-in amplifier is related to its resistance (R) and capacitance (C) by

$$\tau_c = R C \quad (3-13)$$

By changing R and/or C the lock-in amplifier can be set at various τ_c values. Since the effective instrument bandwidth (Δf) is related to the time constant by the expression [57]

$$\Delta f = \frac{1}{4\tau_c} \quad (3-14)$$

it is clear that increasing the time constant (τ_c) can reduce the frequency bandwidth (Δf). As the noise voltage (V_{rms}) has a dependence upon $\sqrt{\Delta f}$, it can be related to τ_c :

$$V_{rms} \propto \sqrt{\Delta f} \propto \sqrt{\frac{1}{4\tau_c}} \quad (3-15)$$

Therefore, by using a 100 times longer time constant, the white noise can be reduced by a factor of 10, which provides a good opportunity to achieve a better detection sensitivity for the PAS measurement. The data in Table I clearly verify that electronic white noise is the most significant type of noise under the experimental conditions. In practice, there is a trade-off between noise reduction and system response speed, because the measurement time is given by (or equal to) five time constants.

(d) Analytical figures of merits

Standard calibration curves were obtained for the complexes studied, as shown

Table IV:

**Analytical Figures of Merit for PAS Determination of
Trace Metals with Solid Film Sampling**

Element	Complex	Sensitivity (mV ng ⁻¹)	Detection Limit (ng) *	Upper Limit of Linear Dynamic Range (ng)
Tl	BGTlCl ₄	3.4 ± 0.2	0.20 ± 0.02	~ 300
Sb	BGSbCl ₆	2.8 ± 0.1	0.20 ± 0.01	~ 300
Cd	Cd(HDz) ₂	0.8 ± 0.1	0.80 ± 0.05	> 180
Co	Co(PAN) ₂ Cl	1.5 ± 0.1	0.40 ± 0.01	~ 500
Ni	Ni(HDz) ₂	1.9 ± 0.1	0.30 ± 0.02	> 400
	Ni(PAN) ₂	0.3 ± 0.1	2.3 ± 0.3	> 1000
Pd	Pd(HDz) ₂	1.5 ± 0.1	0.40 ± 0.01	> 340
	Pd(PAN)Cl	0.8 ± 0.1	0.80 ± 0.05	~ 800

* Calculated by dividing three times the standard deviation of the background signal by the sensitivity.

thermally thick. For example, 2200 ng of Sb(V), as BGSbCl_6 , corresponded to a solid film with a measured thickness of 20 μm which was larger than the estimated thermal diffusion length of 13 μm . In this particular case, both optical and thermal properties of the sample were responsible for the complete saturation of the PAS signal. Although the contribution of thermal diffusion length to PAS signal saturation could be reduced by using a lower modulation frequency of the incident light, a wider linear dynamic range would probably not be accommodated because the onset of negative deviation from linearity was governed solely by the high optical absorption of the solid film sample.

The PAS sensitivity for each metal, which can be determined from the slope of its standard calibration graph in the linear dynamic range, is related to the absorption coefficient (β) or the molar absorptivity (ϵ) of its complex at 632.8 nm, according to Eq. (3-2) and (3-8). A graph of PAS sensitivity versus ϵ at 632.8 nm is shown in Fig. 18. There is general increase in sensitivity with an increasing ϵ value. Ignoring experimental errors, the scattering of data points about a hypothetical straight line relationship may be explained by the possibility that the heat conversion efficiency is not always equal to 1, as assumed in the PAS theory (Chapter 2). Hence, Eq. (3-1) should include a heat conversion factor ($0 \leq \eta \leq 1$) which represents the percentage of optical absorption that is converted to a PAS signal:

$$S = K I_0 \eta (1 - e^{-\beta l}) \quad (3-16)$$

Fig. 18: Relationship between PAS sensitivity and molar absorptivity at 632.8 nm.

a = Ni(PAN)_2 , b = Cd(HDz)_2 , c = Pd(PAN)Cl , d = Ni(HDz)_2 , e = $\text{Co(PAN)}_2\text{Cl}$,

f = Pd(HDz)_2 , g = AgSCl_5 , and h = AgCl_4 .

Therefore, the deviations of data points from the dotted line suggests differences in η values for the complexes studied, which are an intrinsic property of molecular structures beyond the scope of this work.

(5) Conclusion

This chapter by no means attempts to show the highest possible sensitivity of the PAS method for the metal ions studied, as the He–Ne laser used in the experiments represents only a very moderate power among commercially available lasers and as the complexing agents may not yet have been optimised. The primary purpose here is to demonstrate the advantage of performing PAS on solid film samples. By converting the sample from a solution to a solid film, the PAS signal amplitude can be increased by 2–3 orders of magnitude and the resulting detection limits for the metal ions studied have been lowered to less than 1 ng. Further increase in PAS sensitivity can be expected from using either a laser of higher power or a complexing agent that forms with an analyte a chelate of higher molar absorptivity.

Chapter 4

PAS Determination of Palladium (II) in Water by Dithizone Extraction and Solid Film Sampling

(1) Introduction

Palladium exists in various natural minerals, soils and rocks and its abundance in the earth's crust has been calculated to be 0.01 – 0.02 p.p.m [58]. The losses of palladium to the environment occur mainly through human activities in the smelting and refining of copper and precious metals, the manufacturing of chemicals and the use of palladium catalysts in automobile mufflers. Palladium and its compounds do not cause any recognised acute or chronic toxic effects in humans. However, the carcinogenicity of Pd(II) compounds in rats and mice and their toxicity to mammals, microflora, fish and higher plants are causes for environmental concern [59]. As such, Pd(II) is considered to be an environmental pollutant [60].

Various methods have been reported for the determination of palladium in geological materials, metals, alloys, catalysts and biological samples [61- 63]. In order to determine trace amounts of Pd(II) in environmental sample, a method of high sensitivity with a low detection limit is required. Towards this end, Ci and Wan suggested a high-sensitivity color reaction for the determination of Pd(II) [62]. The resulting ion association complex of Pd(II) with potassium iodide and butylrhodamine B had a high molar absorptivity of $1.4 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 610 nm. Beer's law was obeyed in the concentration range 4 – 56 ng mL⁻¹. Unfortunately, this reaction suffers

interferences from Ag(I), Au(III), Cu(II) and Hg(II) ions, and the instability of the complex leads to large deviations between the results.

A sensitive PAS method was detailed in Chapter 3 for the determination of heavy metal ions at the nanogram level [51]. It was derived from the Rosencwaig-Gersho theory that the PAS signal is directly proportional to the absorbance in a thermally thin sample [36], which in turn is related to the amount of light absorbing species in the sample. The great advantage of performing PAS measurements on solid samples rather than on sample solutions is that the former provides a sensitivity that is 2–3 orders of magnitude higher than that obtained for the latter. In addition, solid film sampling technique is significant to the performance of photochromism-induced PAS in the determination of trace mercury(II) as its dithizonate in solid film samples [64] since in the solid state only mercury (II) dithizonate shows photochromism and the potential interferences due to photochromism from other metal dithizonate species are negligible in the solid state, which normally occur in the liquid state [53].

The above PAS method has been adapted for the determination of trace palladium(II) in tap water [65]. A device was designed for the automated preparation of solid film samples and several operating parameters were optimised so that the preparation procedure was time-saving and produced more precise PAS results than manual preparations.

(2) Experimental

Reagents:

The reagents and solvents used were all of analytical reagent grade or better. Dithizone solution in carbon tetrachloride (0.005% m/m) was prepared by dissolving 15 mg of purified dithizone in 200 mL of CCl_4 . The Pd(II) stock solution (1.000 mg mL^{-1}) was prepared from palladium chloride and a working solution (2.00 $\mu\text{g mL}^{-1}$) was freshly prepared daily by appropriate dilution of the stock solution. Deionised water (resistivity = 18 $\text{M}\Omega\text{ cm}$) was used throughout.

Extraction:

A water sample of 100 mL containing less than 2.5 μg of Pd(II) ions was placed in a 250-mL separatory funnel and 4 mL of 1:1 HNO_3 were added, followed by 100 mL of 0.005% dithizone solution in CCl_4 . The funnel was shaken for 10 min, and then 5 minutes were allowed for phase separation. The organic extract was subsequently washed (by shaking for 20 s) with 2.5 mL of 4 M HCl plus 0.2 mL of 0.1 M tin(II) chloride solution, two 2.5 mL-portions of deionised water and finally two 2.0 mL-portions of 1:50 ammonia solution.

In order to prepare an extraction blank, 100 mL of deionised water were treated with the same extraction procedure as above.

Solid film preparation:

The device, shown in Fig. 19, was used to prepare solid film samples for PAS measurement. To prepare a solid film sample, an aliquot of the organic extract (> 500 μL) was loaded into the 1 mL-syringe. The syringe was connected through plastic

Fig. 19: Automated device for preparation of solid film samples.

a = computer; b = syringe pumped with stepping motor; c = syringe;
 d = micrometer translation stage; e = stainless-steel syringe needle;
 f = sampling mirror; g = aluminium platform; h = hot plate;
 i = thermocouple; j = preamplifier and voltmeter.

tubing to a 22-gauge stainless steel syringe needle with a flat tip that was hung vertically above a sampling mirror. A micrometer translation stage was used to adjust the height of the needle tip from the mirror surface. The mirror was sitting on an aluminium platform that was heated by a hot-plate. A thermocouple was used as a probe to measure the temperature of the mirror surface. By choosing the dial setting on the hot-plate, a constant temperature of the mirror surface within the range 90-100 °C could eventually be obtained, as shown in Fig. 20. The computer controlled stepping motor was then used to drive the syringe, which delivered the organic extract onto the mirror surface. As each drop of the organic extract touched the hot mirror surface, the organic solvent was rapidly evaporated, leaving behind a solid palladium dithizonate as a residue. At the end of extract delivery, a circular solid film sample approximately 3.5 mm in diameter was formed on the mirror surface. Then the solid film sample with the mirror substrate was transferred into a PAS cell for the PAS measurement.

Photoacoustic spectrometry

The instrumental setup for PAS measurement has been described in detail in Chapter 3, as shown in Fig. 4. A He-Ne laser of 17-mW output power (at 632.8 nm) was used as the light source to generate a PAS signal from the solid film sample. The PAS cell used here had a reduced volume of 0.20 cm³ (see Fig. 21), so that its resonant frequency changed to 660 Hz, at which the noise level is equal to that at the chopping frequency of 200 Hz. However, the signal amplitude of the same solid film sample at the resonance frequency is slightly higher than that at 200 Hz. This resonance frequency was therefore used to give the optimum signal-to-noise ratio.

Fig. 20: Heating curve of a sampling mirror on the hot-plate.

Fig. 21: The modified PAS cell of reduced volume.

a = retainer ring; b = window; c = O-ring; d = cell body; e = bolt and nut;
 f = brass bottom plates; g = solid film; h = aluminium cylinder; i = sampling mirror;
 j = microphone and preamplifier.

(3) Results and Discussion

(a) Extraction blank

A blank can only cause an additive error. Therefore, the blank signal only affects the intercept of a calibration curve, not the slope of the calibration curve. In a real sample analysis, the blank problem has to be solved to correct for any matrix interferences.

The extraction of $\text{Pd}(\text{HDz})_2$ is a slow process and a large excess of dithizone is usually required for a fast and quantitative extraction of palladium dithizonate. Then a large amount of free dithizone will coexist in the organic phase with the complex $\text{Pd}(\text{HDz})_2$ after the extraction. As the absorption spectrum of dithizone is very similar to that of $\text{Pd}(\text{HDz})_2$ (see Fig. 22), the presence of dithizone in the organic extract of $\text{Pd}(\text{HDz})_2$ will significantly affect the PAS measurement of $\text{Pd}(\text{HDz})_2$. Hence it is necessary to remove free dithizone from the organic extract before preparing solid film samples for the determination of Pd(II) as its dithizonate.

Conventionally, dilute aqueous ammonia had been used to wash free dithizone from the organic extract [54]. However, it was observed that after washing with 1:50 ammonia solution, the extraction blank still showed significant absorption in the wavelength range 350–570 nm and definite absorption at the laser wavelength, 632.8 nm, as shown in Fig. 23a. The resulting solid film blank from this solution produced a background PAS signal as high as 100 mV and associated proportional noise.

It has been reported [53] that dithizone is subject to oxidation by air, by products formed in the photodecomposition of organic solvents, and by oxidants in the sample solution. Several dithizone oxidation products can be formed, most of which are yellow in dilute solution. Bis-1,5-diphenylformazan-3-yl disulphide is an

Fig. 22: Absorption spectra of (a) dithizone in CCl_4 and (b) palladium dithizonate in CCl_4 .

Fig. 23: Absorption spectra of extraction blanks.
 (a) after washing with 1:50 NH_3 solution; and (b) after washing first with 4 M HCl containing 0.01 M SnCl_2 and then with 1:50 NH_3 solution.

analytically important oxidation product and this disulphide has strong absorption at 450 nm ($\epsilon = 4.8 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$) which may be responsible for the absorption spectrum of the blank (see Fig. 23a). This disulfide can be readily reduced back to dithizone by certain reducing reagents. For example, by washing with SnCl_2 , any disulphide present in the organic extract will be reduced to dithizone. Then, the free dithizone can be removed by washing the organic extract again with 1:50 ammonia solution. For this reason, 4 M HCl solution containing about 0.01 M SnCl_2 was used to wash the organic extract. Consequently, an almost clear extraction blank could be obtained (see Fig. 23b).

In addition, it was observed that the PAS signal amplitude of a solid film blank was determined by the concentration of dithizone in the CCl_4 solution used for extraction. It could be decreased by several tens of millivolts to 6 mV after changing the dithizone concentration from 0.005 to 0.0001% and using the above reduction treatment. As 1 mL of 0.0001% dithizone solution contains enough dithizone to extract 20 ng of Pd(II) from 100 mL of water, it was used to prepare the ten solid film blanks for the determination of the PAS detection limit.

(b) Automatic preparation of solid film samples

The mirror surface temperature is the most important parameter in the preparation of solid film samples, as it determines how fast the organic solvent is evaporated from the mirror surface and hence the rate at which the organic extractant can be delivered onto the mirror without spreading too far. A low temperature would require a long time to prepare a single solid film sample, whereas too high a temperature could cause "bump" evaporation on the mirror surface, in which some organic extract was lost, and could decompose the $\text{Pd}(\text{HDz})_2$ complex in the solid film.

sample, as dithizone has a decomposition temperature of 169 °C [66]. In this work the mirror surface temperature was controlled within the range 90–100 °C, so that a maximum extract delivery rate of 0.71 $\mu\text{L s}^{-1}$ could still be used to produce solid film samples within a finite small size. As a result, it took only 12 minutes to prepare a solid film sample from 500 μL of organic extract. Moreover, the solid films prepared by this technique were found to be stable for more than 2 days under normal laboratory conditions.

The height of the needle tip from the mirror surface is another important parameter in the preparation of solid film samples. It was set at 0.45 mm in these experiments with the aid of a micrometer translation stage. It was observed that the organic extract could not be delivered directly onto the mirror if the height was greater than 0.50 mm. In such an instance, the liquid drop would grow at the needle tip until it became large enough to fall by gravity. The subsequent splash on the mirror surface would result in a disperse solid film sample. On the other hand, if the needle tip was too close to the mirror surface, some of the organic extract would climb up the outside of the needle and be evaporated to dryness there, thus losing the analyte for the final PAS measurement.

By using the parameters specified above, the resulting solid film sample was a circular spot of 3.5 mm in diameter, which could be fully covered by the He–Ne laser beam in the PAS cell. It was observed that the distribution of analyte inside the circle did not significantly affect the amplitude of PAS signal as long as the solid film sample is thermally thin in every region. This technique of solid film sample preparation is crucial to the successful determination of trace amounts of Pd(II), as the PAS signal amplitude generated from a solid film sample is 2–3 orders of magnitude higher than that produced by the liquid organic extract used to make the solid film sample. In

addition, compared with the previous method of solid film formation in a glass cup [51], the present technique is automated, is more efficient and does not require specially-made glass cups.

(c) Standard calibration graph

By following the experimental procedure described above, a series of solid film standards were prepared. They were used to obtain a calibration graph for the PAS measurement of Pd(II), which is shown in Fig. 24. The lower horizontal scale represents the amount of Pd(II) in a solid film sample. The corresponding concentration of Pd(II) in the original water sample could be calculated from the volume ratio of organic phase to water sample (1:100) used in the extraction step and from the volume of the organic extract (500 μ L) used to prepare a solid film sample. This concentration in water is represented by the upper horizontal scale in Fig. 24. Several analytical figures of merit can be obtained from this graph. First, the sensitivity of the PAS technique can be determined from the slope of the linear calibration curve to be 1.4 mV ng⁻¹. Second, the detection limit can be calculated (by dividing three times the standard deviation of the signals obtained from ten solid film blanks by the sensitivity) to be 2 ng of Pd(II), which corresponds to 0.04 ppb of Pd(II) in the water sample. Third, the linear dynamic range can be seen to extend beyond 200 ng. Fourth, the relative standard deviation of six replicate analyses for 100 ng of Pd(II) in water was 3.2%.

In comparison with the method of Ci and Wan [62], the present PAS method has a lower detection limit, a larger linear dynamic range and better precision. It also offers a detection limit approximately 1000-times lower than that of flame atomic absorption spectrometry, which normally has a sensitivity of approximately 0.1 ppm of

Fig. 24: Standard calibration graph for PAS determination of Pd(II).

Pd(II) [62]. Note that the upper limit of the linear dynamic range for this PAS method is governed by the condition that the sample be thermally thin [51]. This means that the thickness of the solid film sample can be at most 6.9 μm for a chopping frequency of 660 Hz in order to produce a PAS signal that is within the linear dynamic range. However, this limit can be easily increased, if necessary, by using a chopping frequency lower than 660 Hz. On the other hand, the upper limit in terms of Pd(II) concentration in a water sample can be increased simply by using either a larger volume ratio than 1:100 between the organic phase and the water sample in the extraction step, or a smaller volume of organic extract than 500 μL for the preparation of the solid film.

(d) Interfering species and analysis of palladium(II) in water

When dithizone was used as the complexing reagent, only Ag(I), Au(III), Cu(II), Hg(II) and Pt(II) ions could be co-extracted with Pd(II) ion from an acidic aqueous solution into the organic phase (CCl_4) [67]. In the determination of Pd(II) in tap water, Cu(II) was considered to be the major potential interfering ion. Even though copper(II) dithizonate is formed faster than palladium(II) dithizonate, it is relatively unstable. If the extraction of palladium and copper dithizonates is carried out for 10 minutes, the Pd(II) ions will either combine with free dithizone or displace an equivalent amount of Cu(II) ions from copper dithizonate. Finally, any residual copper(II) dithizonate can be decomposed and washed away with 4 M HCl solution containing 0.01 M SnCl_2 while palladium(II) dithizonate remains intact in the organic extract [67]. In one experiment, up to 20 mg of Cu(II) ions were observed to have no interference effect on the extraction (and subsequent PAS determination) of 100 ng Pd(II) ions in 100 mL of tap water. This corresponds to a Cu(II) concentration of 200

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ppm, which is much higher than the range of Cu(II) concentration usually found in aqueous environmental samples.

When water samples contain significant amounts of Ag(I), Au(III), Hg(II) or Pt(II) ions, these ions can be separated from Pd(II) by adopting the methods described by Marczenko et al [67].

Tap water was used as the sample for the determination of its Pd(II) content by the present PAS method. The concentration of Pd(II) in tap water, however, was found to be below the detection limit of the method, i.e., less than 0.04 ppb. In a separate experiment, the recovery of 200 ng of Pd(II) added to 100 mL of tap water (which corresponded to 100 ng of Pd(II) in the solid film sample) averaged 96% in three replicate determinations.

(4) Conclusion

A technique has been developed to automatically prepare solid film samples for the PAS determination of trace amounts of Pd(II) in water samples after extraction with 0.005% dithizone solution in CCl₄. The PAS method can be used to determine Pd(II) at a concentration of 0.04 ppb in an aqueous solution. Apparently there are still two approaches for improving the detection limit: (a) using a more powerful laser than the present 17-mW instrument as the excitation source and (b) employing a complexing agent that either forms a Pd(II) complex of higher molar absorptivity or permits a higher preconcentration factor than 100 in the extraction process.

Chapter 5

Theory of Pulsed Laser Transverse Photothermal Deflection Spectroscopy (PDS)

(1) Introduction

Since the first report on PDS technique by Boccara et al. in 1980 [68], the technique has seen rapid development and applications in many fields.

As one member of the PTS family, PDS shares most of the common features but it also has its own characteristics. Comparisons have been made elsewhere between PDS and the other PTS techniques [3]. In essence, the collinear PDS technique has a higher sensitivity than PAS methods, but its application is limited to transparent samples only. On the contrary, the transverse PDS technique can be used for opaque sample and has a sensitivity 100 times higher than that of PAS [69].

As PDS signal is dependent on both optical and thermal properties of a sample, this technique has naturally been used in the measurements of optical absorption coefficients [70, 71] and thermal diffusivities [72, 73]. In particular, nonlinear thermal diffusivities were observed in solid samples [74, 75]. PDS is also a suitable technique for nondestructive evaluation of industrial materials. Welded seams [76], vertical interfaces such as cracks and other thermal barriers [77], and corrosion in metals by hot lubricant [78] could be detected by PDS.

The detector of a PDS instrument requires no physical contact with samples, so the technique can be used to monitor flow streams, vapours and aerosols, determining the flow velocity or the concentration of absorbing species in them [79].

PDS can also be used as a remote diagnostic tool for hostile environment and combustion process [80].

PDS measurements are based on the change of refractive index with temperature in a medium. As a liquid state usually has a higher temperature coefficient of refractive index than the gaseous state, the PDS technique becomes more sensitive when the probe beam is propagated through a liquid medium rather than a gas. Pamler et al. developed a rapid scanning FTIR-PDS technique for solid-liquid interface detection, and they measured the absorption spectra of prepared electrodes in CCl_4 to take advantage of its high temperature coefficient of refractive index [81]. Similarly, Varlashkin et al. reported on a special arrangement wherein solid sample were submerged in a liquid to enhance the PDS detection sensitivity [82], and Wagner et al. could investigate a photoelectrochemical process at an electrode-electrolyte interface [83].

Numerous advances in the PDS science have appeared in the recent literature. The technique was employed for microbore liquid chromatographic detection [84] and for the densitometric determination [85]. Hadamard transformation was combined with PDS technique for sample surface imaging [86] and the resultant linear dynamic range and resolution capability were discussed [87]. Furthermore, Mandelis et al. reported their mirage-effect spectrometer design and its performance [88]. Bialkowski et al. proposed new methods for data processing and for error reduction in pulsed laser PDS [89,90]. Lepoutre et al. calculated PDS signals under three dimension heat conduction conditions [91].

The theories of PDS have been developed by Jackson et al. [3] and Murphy et al. [14, 15]. Collinear and transverse PDS models were based on different spatial arrangements between the pump beam and the probe laser beams. Usually CW lasers

were used as excitation sources, which provide very stable output powers. Nonetheless, the theory for pulsed-laser transverse PDS is derived here for the first time to serve as a basis for the development of a nonlinear PDS technique with a pulsed-laser excitation. A pulsed laser source can provide a high density in very short time to generate two- or multi-photon absorption [92].

(2) Temperature variations in a typical transverse PDS system due to pulsed heating

A typical transverse PDS system is shown schematically in Fig. 25. A sample is supported by a non-absorbing backing material and the sample surface is covered by a gas (usually air) which is non-absorbing at the wavelength of the pump laser. The PDS system is divided into three regions analogous to the PAS system in Fig. 1. Then, the temperature distribution in each region must satisfy Eq. (2-3) and the boundary conditions in Eq. (2-4). The pump laser beam illuminates the sample surface perpendicularly while the probe laser beam (usually from a He – Ne laser) is parallel to the sample surface without thermal disturbance from the pump laser and travels along the direction of x axis. The vertical offset of the probe beam from the sample surface is z_0 and y_0 is the transverse offset of the probe beam from the center of the pump laser.

The temperature solutions have been derived by Jackson et al. [3] and Murphy et al. [14, 15] from their different approaches where cw lasers were used as the pump lasers. When a pulsed laser of Gaussian intensity profile is used in the above described PDS system, the heating function, $Q(r,t)$, should have the following form

Fig. 25: Schematic representation of a typical transverse PDS system.

(a) side view, and (b) top view.

$$Q(r,z,t) = \begin{cases} \frac{2\beta \eta P_0 t}{\pi r_0^2 \tau_0} e^{-2r^2/r_0^2} e^{\beta z} & (0 < t < \tau_0, 0 > z > -\ell) \\ 0 & (t > \tau_0) \end{cases} \quad (5-1)$$

where P_0 is the laser power at each pulse (W cm^{-2});

τ_0 is the laser pulse duration (s);

r_0 is the radius of the laser spot on the sample surface;

and r is the radius from the center of the pump laser beam to the point concerned on x - y plane and $r = (x^2 + y^2)^{0.5}$.

This heating function should be substituted into Eq. (2-3) to solve the thermal conduction equations.

The time domain equations from Eq. (2-3) can be solved in Laplace space 's' by taking their Laplace transforms. This reduces the partial differential equations in (x,y,z,t) to a set of ordinary differential equations in (x,y,z) . The Laplace transforms of Eq.(2-3) with the heating function in Eq.(5-1) can be expressed as follows

$$\begin{aligned} \frac{d^2 \hat{T}^i(x,y,z,s)}{d(x,y,z)^2} - \frac{s}{\alpha_i} \hat{T}^i(x,y,z,s) \\ = - \frac{2\beta \eta P_0}{\kappa_i \pi r_0^2 \tau_0} \left[\frac{1 - \exp(-s\tau_0)}{s} \right] \exp\left(\frac{-2r^2}{r_0^2}\right) e^{\beta z} \end{aligned}$$

$$i = 1 \quad 0 < z < -\ell \quad (\text{sample}) \quad (5-2a)$$

$$\frac{d\hat{T}^2(x,y,z,s)}{d(x,y,z)^2} - \frac{s}{\alpha_i} \hat{T}(x,y,z,s) = 0 \quad i = \begin{cases} 0 & \infty > z > 0 & (\text{air}) \\ 2 & -\infty < z < -l & (\text{backing material}) \end{cases} \quad (5-2b)$$

where a caret is used to indicate the Laplace transforms of a function.

Since the laser pulse duration is very short ($< 10^{-9}$ s) each pulse heat can be considered as an instantaneous heating source. Therefore, Green's function was used to solve the temperature gradient on the sample surface [3]. The heat loss from any point above the illuminated sample spot to the surrounding gas is proportional to the temperature at that point [14]. As a result, the temperature gradient on every x - y plane(parallel to the sample surface and at various z positions) in the air would then keep a Gaussian profile, but the Gaussian profile becomes flatter with increasing in z value. Therefore, it is only necessary and convenient to solve Eq. (5-2) in one-dimensional to determine the temperature gradient in the air along the z axis by using the following boundary conditions

$$\text{at } z = 0, \quad \hat{T}_1 = \hat{T}_0 \text{ and } \kappa_1 \frac{\delta \hat{T}_1}{\delta z} = \kappa_0 \frac{\delta \hat{T}_0}{\delta z}$$

$$\text{at } z = -l, \quad \hat{T}_1 = \hat{T}_2 \text{ and } \kappa_1 \frac{\delta \hat{T}_1}{\delta z} = \kappa_2 \frac{\delta \hat{T}_2}{\delta z}$$

$$\begin{aligned}
 & \text{at } z = \infty, & \frac{\delta \hat{T}_0}{\delta z} &= 0 \\
 & \text{and at } z = -\infty, & \frac{\delta \hat{T}_2}{\delta z} &= 0
 \end{aligned}$$

The temperature expressions should have the following forms

$$\hat{T}_0 = c_0 \exp(-a_0 z) \quad (5-3a)$$

$$\hat{T}_1 = c_1 \exp(a_1 z) + c_2 \exp(-a_1 z) + Y \exp(\beta z) \quad (5-3b)$$

$$\hat{T}_2 = c_3 \exp(a_2 z) \quad (5-3c)$$

$$\text{where } Y = \frac{2\beta \eta P_0 \alpha_1}{\kappa_1 \pi r_0^2 \tau_0} \left[\frac{1 - \exp(-s\tau_0)}{s(s - \alpha_1 - \beta^2)} \right] \exp\left(\frac{-2r^2}{r_0^2}\right); \quad a_i = \left(\frac{s}{\alpha_i}\right)^{0.5} \text{ with } i = 0, 1, 2;$$

and all the c_i are functions of s . Note that the term $\left(\frac{\alpha_i}{s}\right)^{0.5}$ is the equivalent of thermal diffusion length (μ) in the cases where a cw laser serves as the pump laser.

By using the boundary conditions the coefficients c_i can be found for the individual expressions of $\hat{T}_i$.

$$c_1 = Y \left[\frac{(a_0 \kappa_0 + \beta \kappa_1)(a_1 \kappa_1 - a_2 \kappa_2) e^{-a_1 \ell} - (a_0 \kappa_0 + a_1 \kappa_1)(\beta \kappa_1 - a_2 \kappa_2) e^{-\beta \ell}}{(a_1 \kappa_1 - a_0 \kappa_0)(a_1 \kappa_1 - a_2 \kappa_2) e^{-a_1 \ell} - (a_0 \kappa_0 + a_1 \kappa_1)(a_1 \kappa_1 + a_2 \kappa_2) e^{a_1 \ell}} \right] \quad (5-4)$$

$$c_2 = \Upsilon \left[\frac{(a_0\kappa_0 + \beta\kappa_1)(a_1\kappa_1 + a_2\kappa_2) e^{a_1\ell} - (a_1\kappa_1 - a_0\kappa_0)(\beta\kappa_1 - a_2\kappa_2) e^{-\beta\ell}}{(a_1\kappa_1 - a_0\kappa_0)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} - (a_0\kappa_0 + a_1\kappa_1)(a_1\kappa_1 + a_2\kappa_2) e^{a_1\ell}} \right] \quad (5-5)$$

then

$$c_0 = c_1 + c_2 + \Upsilon = \Upsilon \left\{ \frac{(a_0\kappa_0 + \beta\kappa_1)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} + (a_1\kappa_1 + a_2\kappa_2)(\beta\kappa_1 - a_1\kappa_1) e^{a_1\ell}}{(a_1\kappa_1 - a_0\kappa_0)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} - (a_0\kappa_0 + a_1\kappa_1)(a_1\kappa_1 + a_2\kappa_2) e^{a_1\ell}} + \frac{2a_1\kappa_1(\beta\kappa_1 - a_2\kappa_2) e^{-\beta\ell}}{(a_1\kappa_1 - a_0\kappa_0)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} - (a_0\kappa_0 + a_1\kappa_1)(a_1\kappa_1 + a_2\kappa_2) e^{a_1\ell}} \right\} \quad (5-6)$$

The temperature $\hat{T}_0$ in the air layer can be expressed by using Eq. (5-3a) and Eq. (5-6) exclusively. However, we only consider opaque samples on which the transverse PDS technique is usually applied. With samples being opaque, i.e., $e^{-\beta\ell} \approx 0$, the temperature in the air layer can be written as:

$$\hat{T}_0 = \Upsilon \left[\frac{(a_0\kappa_0 + \beta\kappa_1)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} + (a_1\kappa_1 + a_2\kappa_2)(\beta\kappa_1 - a_1\kappa_1) e^{a_1\ell}}{(a_1\kappa_1 - a_0\kappa_0)(a_1\kappa_1 - a_2\kappa_2) e^{-a_1\ell} - (a_0\kappa_0 + a_1\kappa_1)(a_1\kappa_1 + a_2\kappa_2) e^{a_1\ell}} \right] e^{-a_0z} \quad (5-7)$$

For PDS studies on opaque samples, two cases are considered, in which a sample may be either thermally thin or thermally thick

In the case of thermally thin samples, $e^{\pm a_1\ell} \approx 1$ as $a_1\ell \ll 1$. Then,

$$c_0 = \gamma \frac{(\beta \kappa_1 - a_2 \kappa_2)}{(a_0 \kappa_0 - a_2 \kappa_2)} \quad (5-8)$$

and

$$\hat{T}_0 = \gamma \frac{(\beta \kappa_1 - a_2 \kappa_2)}{(a_0 \kappa_0 - a_2 \kappa_2)} e^{-a_0 z} \quad (5-9)$$

By substituting A and a_i values (as functions of s) into Eq. (5-9) and carrying out the inverse Laplace transform, the time-dependent temperatures in the air layer are obtained as follows:

$$T_0 = \left(\frac{2 \beta \eta P_0}{\pi r_0^2 \tau_0} \right) e^{-\frac{2r^2}{r_0^2}} e^{-a_0 z} \frac{\sqrt{\alpha_0} \kappa_2 \alpha_1}{\kappa_0 \sqrt{\alpha_2} - \kappa_2 \sqrt{\alpha_0}} \left[\frac{1}{\alpha_1 \beta^2} (e^{\alpha_1 \beta^2 t} - 1) + \right.$$

$$\left. \left(\frac{\beta \kappa_1 \sqrt{\alpha_0 \alpha_2}}{\kappa_0 \sqrt{\alpha_2} - \kappa_2 \sqrt{\alpha_0}} \right) \int_0^t \sqrt{\alpha_1 \beta^2} e^{\alpha_1 \beta^2 \tau} \operatorname{erf}(\sqrt{\alpha_1 \beta^2} \tau) d\tau \right]$$

$$0 < t < \tau_0 \quad \text{and} \quad 0 < z < \infty \quad (5-10)$$

and

$$T_0 = \left(\frac{2 \beta \eta P_0}{\pi r_0^2 \tau_0} \right) e^{-\frac{2r^2}{r_0^2}} e^{-a_0 z} \left\{ \frac{\kappa_2 \sqrt{\alpha_0}}{(\kappa_0 \sqrt{\alpha_2} - \kappa_2 \sqrt{\alpha_0}) \beta^2} [(e^{\alpha_1 \beta^2 t} - 1) - \int_0^t (e^{\alpha_1 \beta^2 (\tau - \tau_0)} d\tau)] + \right.$$

$$\left. \left(\frac{\kappa_1 \alpha_2 \sqrt{\alpha_0 \alpha_1}}{\kappa_0 \sqrt{\alpha_2} - \kappa_2 \sqrt{\alpha_0}} \right) \left[\int_0^t e^{\alpha_1 \beta^2 \tau} \operatorname{erf}(\sqrt{\alpha_1 \beta^2} \tau) d\tau - \int_0^t e^{\alpha_1 \beta^2 (\tau - \tau_0)} \operatorname{erf}(\sqrt{\alpha_1 \beta^2} (\tau - \tau_0)) d\tau \right] \right\}$$

$$t > \tau_0 \quad \text{and} \quad 0 < z < \infty \quad (5-11)$$

where $\text{erf } x$ stands for the ordinary error function, i.e.,

$$\text{erf } x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\sigma^2} d\sigma$$

In the case of thermally thick samples $e^{\pm a_1 l} \approx 0$, then, $\hat{T}$ becomes

$$\hat{T}_0 = \Upsilon \left(\frac{a_1 \kappa_1 - \beta \kappa_1}{a_0 \kappa_0 + a_1 \kappa_1} \right) e^{-a_0 l} \quad (5-12)$$

Then by substituting Υ and a_i values into Eq. (5-12) and carrying out the inverse Laplace transform, the time-dependent temperatures are obtained:

$$T_0 = \left(\frac{2 \beta \eta P_0}{\pi r_0^2 \tau_0} \right) e^{-\frac{2r^2}{r_0^2}} e^{-a_0 z} \left[\frac{\kappa_1 \alpha_1 \sqrt{\alpha_0}}{(\kappa_0 \sqrt{\alpha_1} + \kappa_1 \sqrt{\alpha_0})} \right] \\ \left\{ \left[\frac{1}{\alpha_1 \beta^2} (e^{\alpha_1 \beta^2 t} - 1) \right] - \left[\frac{2\beta \sqrt{\alpha_1}}{\sqrt{\pi}} \int_0^t \sqrt{\tau} e^{\alpha_1 \beta^2 (t-\tau)} d\tau \right] \right\} \\ 0 < t < \tau_0 \quad \text{and } 0 < z < \infty \quad (5-13)$$

and

$$T_0 = \left(\frac{2 \beta \eta P_0}{\pi r_0^2 \tau_0} \right) e^{-\frac{2r^2}{r_0^2}} e^{-a_0 z} \left[\frac{\kappa_1 \alpha_1 \sqrt{\alpha_0}}{(\kappa_0 \sqrt{\alpha_1} + \kappa_1 \sqrt{\alpha_0})} \right] \\ \left\{ \frac{1}{\alpha_1 \beta^2} \left[e^{\alpha_1 \beta^2 t} - e^{\alpha_1 \beta^2 (t-\tau_0)} \right] - \frac{2\beta \sqrt{\alpha_1}}{\sqrt{\pi}} \left[\int_0^t \sqrt{\tau} e^{\alpha_1 \beta^2 (t-\tau)} d\tau \right] \right. \\ \left. + \int_0^t \sqrt{(\tau-\tau_0)} e^{\alpha_1 \beta^2 (t-\tau+\tau_0)} d\tau \right\} \quad t > \tau_0 \quad \text{and } 0 < z < \infty \quad (5-14)$$

In general, the above temperature solutions may be divided into three parts. The first part is the coupling between the laser beam and the sample (a function of laser power and sample properties), the second part is a function of positions and the third part is basically a function of time (which involves the complicated thermal coupling in the system studied). Therefore, one can use the general expression as follows

$$T_0 = F_{l-s}(P_0, r_0, \tau_0, \beta, \eta) F_p(r, z) F(t, \alpha_i, \kappa_i, \dots) \quad (5-15)$$

For simplification and convenience one can deal with these functions separately under different experimental conditions. In the next chapter the above inference will be used to develop the nonlinear PDS signal.

(3) Photothermal deflection of the probe beam

The refractive index of a medium is, in general, a function of temperature and pressure. As the pressure effect is about 10^{-10} orders of magnitude smaller than the temperature effect [3, 14], one can neglect the pressure effect and write

$$n(r, t) = n_0 + \Delta n(r, t) = n_0 + \left. \frac{\delta n}{\delta T} \right|_{T_a} (T - T_a) \quad (5-16)$$

where n_0 is the refractive index of the medium without thermal disturbance from the laser illumination;

and $\frac{\delta n}{\delta T}$ is the temperature coefficient of the refractive index of the medium.

The light rays can be defined as the orthogonal trajectories to the geometrical wave-fronts: $\psi(x,y,z) = \text{constant}$. Then the properties of light rays can be related to the refractive index of a medium by the following differential equation [93]

$$\begin{aligned} \frac{d}{d\ell} \left(n_0 \frac{d\vec{r}}{d\ell} \right) &= \text{grad. } n \\ &= \frac{\delta}{\delta \vec{r}} [n(\vec{r}, t)] \end{aligned} \quad (5-17)$$

where $\vec{r}$ is the position vector of a point (say, q) on a ray; and

ℓ is the length of the ray measured from a fixed point (p in Fig. 25) to another point (q in Fig. 25);

and $d\vec{r}$ and $d\ell$ are the elementary increments of $\vec{r}$ and ℓ .

Since the photothermal deflection generated by laser illumination is usually small, the angular deviation (ϕ) from the original light propagation direction is small too and can be approximated to

$$\phi \approx \frac{d\vec{r}}{d\ell} \quad (5-18)$$

Integrating Eq.(5-17) over the path-length of the ray, ℓ , gives

$$\frac{d\vec{r}}{d\ell} = \frac{1}{n_0} \int_{\ell} \frac{\delta}{\delta \vec{r}} [n(\vec{r}, t)] d\ell \quad (5-19)$$

From Eq. (5-18) and (5-19), one obtains

$$\phi \approx \frac{d\vec{r}}{d\ell} = \frac{1}{n_0} \int \frac{\delta n}{\delta T}|_{T_a} \frac{\delta T}{\delta \vec{r}} d\ell \quad (5-20)$$

The temperature coefficient of the refractive index varies little along the light path and the term, $\frac{\delta n}{\delta T}|_{T_a}$ can be taken as a constant to move out of the integral. For simplicity, $\frac{\delta n}{\delta T}$ is used instead of $\frac{\delta n}{\delta T}|_{T_a}$. Therefore,

$$\phi = \frac{1}{n_0} \frac{\delta n}{\delta T} \int \frac{\delta T}{\delta \vec{r}} d\ell \quad (5-21)$$

This equation shows that the photothermal deflection signal is generated by the temperature gradient vertical to the light pathway. In the transverse PDS experiments, the probe beam propagates only in the gas medium (usually air). By substituting the temperature distribution in the air into Eq. (5-21), the relationship between the PDS signal and the optical and thermal properties in a system can be easily established.

There are two kinds of photothermal deflections in transverse PDS experiments, normal and transverse relative to the sample surface. The normal photothermal deflection signal takes place in a plane vertical to the sample surface (i.e., x-z plane) and the PDS signal can be expressed as follows:

$$\phi_n = -\frac{\ell}{n_0} \frac{\delta n}{\delta T} \int_{x_0}^{\infty} \frac{\delta T}{\delta z} dx$$

or

$$\phi_n = -\frac{\ell}{n_0} \frac{\delta n}{\delta T} \int_{x_0}^{\infty} \frac{\delta T_0}{\delta z} \frac{dr}{\sqrt{1-(y_0/r)^2}} \quad (5-22)$$

The transverse photothermal deflection occurs in a plane parallel to the sample surface (i.e., x-y plane) and the PDS signal can be expressed as:

$$\phi_t = \frac{\ell}{n_0} \frac{\delta n}{\delta T} \int_{x_0}^{\infty} \frac{\delta T_0}{\delta y} dx$$

or

$$\phi_t = \frac{\ell}{n_0} \frac{\delta n}{\delta T} \int_{x_0}^{\infty} \frac{\delta T_0}{\delta y} \frac{dr}{\sqrt{1-(y_0/r)^2}} \quad (5-23)$$

By substituting the suitable temperature solutions from Eq. (5-10), (5-11), (5-13) or (5-14) into Eq. (5-22) or (5-23), mathematical evaluations can be made to find the dependence of the PDS signal amplitude upon the optical and thermal properties as well as upon experimental parameters. Such evaluations have been done by several authors for cw laser source [3, 14, 15]. Similarly the pulsed laser transverse PDS signal can also be analysed numerically by substituting values for all the variables in the appropriate equations.

In summary, the equations in this chapter have been developed in order to help express the pulsed PDS signal behavior in nonlinear optical absorption discussed in the next chapter.

Chapter 6

Nonlinear PDS Analysis of Ion-Implanted Silicon Wafers

(1) Introduction

Silicon is a very important semiconductor material, owing to its excellent electronic properties, high abundance in our planet (second to oxygen) and low cost of manufacturing silicon crystals of high purity. More significantly, the electronic properties of crystalline silicon can be modified by introducing a certain amounts of other elements into silicon crystal lattice. Ion implantation is a major and modern technique useful for this purpose. Implant dose is an important parameter in ion implantation processes as it affects the properties of the final products of ion-implanted silicon wafers. However, the control of ion implantation processes has always been a complex and difficult task [94]. Relative and absolute dose accuracy is not easy to obtain. The relative dose accuracy is no better than 10% and the absolute dose accuracy performance can be expected to be somewhat worse than this level [95].

As process requirements for advanced integrated circuit (IC) manufacture become more demanding, the need for monitoring and controlling the implantation process as a defence against operational, equipment, and process error becomes increasingly important [95]. The conventional methods used for the characterization of ion-implanted silicon wafers (such as transmission electron microscopy, Rutherford backscattering and X-ray topography) are destructive, and the tests can only be performed on specially prepared test specimen. Therefore, the results do not directly represent the true characteristics of the real ion-implanted products of silicon wafers.

Obviously, nondestructive analysis methods are absolutely necessary for the close control of ion implantation process and for the enhancement of the quality and yield of ion-implanted wafers.

Several methods have been used for the nondestructive analysis of ion-implanted silicon wafers. Narayan et al. [96] compared spectroscopic ellipsometry (SE) with cross-section transmission electron microscopy for the characterization of oxygen-ion-implanted silicon. They concluded that SE was a very important nondestructive technique for assessing the quality of ion-implanted wafers. Witowski et al. performed optical reflectance measurements for the examination of semiconductors [97]. The dopant profile parameters in arsenic-implanted and annealed silicon were measured by Wagner and Schaefer using infrared spectroscopy [98]. By measuring the infrared reflectance and transmittance of boron-implanted and laser-annealed silicon, Engstrom found that the optical properties varied essentially linearly with the implant dose [99]. The activated carrier density profiles and elastic scattering rates in B^- and BF_2^+ -implanted silicon wafers were measured by Young et al. using an infrared attenuated total reflection technique [100].

In the visible range, silicon wafers are opaque and the measurements of transmittance is impossible. Several PAS techniques have been applied successfully to the characterization of silicon wafers. Papa et al. determined the thermal conductivity in an ion-implanted silicon layer by PAS technique [101]. Zammit et al. used the gas-microphone PAS technique to measure the optical and thermal properties in ion-implanted silicon and gallium arsenide as a function of implanted Si^+ dose [102]. The PAS technique was also used by Macfarlane et al for 2-dimensional mapping on silicon material surface [103]. In our laboratory, a piezoelectric transducer have been used as the detector for the PAS examination of BF_2^+ -implanted silicon wafers [104].

On the other hand, PDS is another photothermal spectroscopic technique which can be applied for nondestructive analysis of silicon wafers. The advantages of PDS over PAS have been discussed by Jackson et al. [3] and Amer et al.[69]. In general, PDS is about 100 times more sensitive than PAS technique, is less sensitive to scattered light and has smaller background signal than PAS. In addition, the complicated gas coupling or transducer attachment physics in PAS is eliminated in PDS instrumentation. A PDS system was designed and used by Frosio et al. for the study of a-Si [105]. PDS techniques were also used by several laboratories in the studies of optical properties of defect states and transportation in hydrogenated amorphous silicon [106–110]. Recently, Zenkevich et al. determined the implant dose in silicon wafers implanted with Bi^+ , Fe^+ , or Ti^+ by using Ar^+ -ion-laser PDS method, and they achieved a detection limit of 1×10^{12} ions cm^{-2} in implant dose [111].

In this chapter, the PDS technique was used as a nondistructive method to investigate B^+ – and BF_2^+ –implanted silicon wafers. Laser induced nonlinear absorption was observed and a model is proposed to interpret the experimental results.

(2) The Model

Many optical absorption processes may take place in semiconductor materials under optical irradiation [112, 113]. The optical properties of a semiconductor are determined to a great extent by its crystalline structure, or energy band configuration. The absorption coefficients of a semiconductor at a given photon energy (wavelength) is generally proportional to the probability of the transition from the initial state to the final state, to the density of electrons in the initial state and to the density of available (empty) final state [112]. Crystalline silicon is a semiconductor material with an indirect gap energy of 1.1 eV and a direct gap energy of 3.4 eV. When crystalline silicon is illuminated by visible light rays (with photon energy of 1.8–3.1 eV), the phonon-assisted indirect one-photon absorption normally occurs. At the same time, the direct two-photon absorption may also take place, predominating over the phonon-assisted indirect two-photon absorption since the later is a third-order process.

Ion implantation may change the optical properties of crystalline silicon substrate in all three aspects. In ion implantation processes an accelerated ion enters the lattice of a substrate and in slowing down and coming to rest in the substrate loses its energy by electronic repulsion and nuclear collisions. In collisions having energy transfers above a threshold of 15 eV, the implanted ions displace Si atoms from their lattice sites, otherwise implanted ions will take interstitial positions in the substrate [114]. A dose of boron ions below $4 \times 10^{16} \text{ cm}^{-2}$ does not generate continuous amorphization of crystalline silicon [115], but their implantation in silicon does increase the disorder in the substrate. The implantation of BF_2^+ will result in the ion-implanted products being similar to B^+ -implanted silicon wafers as BF_2^+ decomposes immediately at the surface of the substrate. Technically, BF_2^+ is more

convenient to use for implantation in a shallow layer below the substrate surface [116]. In both cases the generated defects or disorders in the substrate can enhance the optical absorption processes by creating new states within the band gap, allowing more transitions to take place, or by disturbing the phonon population and therefore changing the phonon-assisted indirect one-photon absorption probability [117].

If we consider ion implantation processes as a perturbation to the silicon crystalline lattice, then the optical and electronic properties of ion-implanted silicon wafers can be obtained by modifying those of crystalline silicon. In this way, the optical absorption coefficients of an ion-implanted silicon wafer may be expressed as the sum of the absorption coefficients of crystalline silicon and a perturbation term which is related to the ion implantation process. Therefore, we can write

$$\alpha_i = \alpha_c + \Delta\alpha \quad (6-1)$$

$$\beta_i = \beta_c + \Delta\beta \quad (6-2)$$

where α and β are the absorption coefficients for the indirect one-photon absorption (cm^{-1}) and direct two-photon absorption (cm W^{-1}) respectively. The subscripts i and c indicate an ion-implanted silicon wafer and crystalline silicon, and $\Delta\alpha$ and $\Delta\beta$ are the perturbations to the corresponding absorption processes due to ion implantation. The higher order absorption processes can be treated in the same way, if they exist.

As the next step we want to find how the perturbation terms ($\Delta\alpha$ and $\Delta\beta$, etc.) are related to the implant dosage since our purpose is to eventually measure the implant dose by using PDS technique. Actually this is a very difficult task because the relationship between the perturbation terms ($\Delta\alpha$ and $\Delta\beta$) and the ion dose may be

highly dependent on various implantation conditions. Three clues were obtained from the literature. First, Mahan reported that the energy gap of doped silicon, which determines the probability of optical transition processes, is dependent on some power of the impurity concentration [118]. Secondly, Street [119] proposed a model in which the defect density (which increases the electron density in the initial state) varied as the square root of the dopant concentration in ion-implanted amorphous silicon. Furthermore, it is found that the concentration of free electrons from thermal ionization, (N) is related to the dopant concentration by the following equation [120]

$$N = (a N_i)^{0.5} \text{EXP} (-E_i/2kT) \quad (6-3)$$

where a is a constant for a given crystal at a given temperature T ;

N_i is the dopant concentration (atoms cm^{-3});

E_i is the ionization energy of the implanted species (eV);

and k is the Boltzmann constant.

Therefore, the density of final states which is available (empty) for optically-induced transition is reduced proportionally to $N_i^{0.5}$ due to the existence of electrons from thermal ionization.

Considering all the above cases, we propose that the perturbation to optical absorption coefficients due to ion implantation is related to a certain power of the implant dose for the indirect one-photon and direct two-photon absorption processes, which can be expressed as follows:

$$\Delta\alpha = \mathcal{A} N_i^u \quad (6-4)$$

$$\Delta\beta = \mathcal{B} N_i^u \quad (6-5)$$

where $\mathcal{A}$ and $\mathcal{B}$ are constants related to the properties of crystalline silicon;

N_i is the implant dose (or concentration); and

u is an experimental parameter which may be dependent upon the implant species, the crystalline substrate and implantation conditions, such as temperature, energy and orientation.

When the above absorption processes are considered in silicon wafer samples, the maximum optical energy absorbed by a wafer sample from a pulsed laser illumination is obtained at the end of each laser pulse, which is related to the maximum PDS signal of interest. Assuming a square pulse form, as the pulse duration is shorter than 10^{-9} s, the absorbed optical energy from each laser pulse can be written as follows [121]

$$E(r, \tau_0) = [\alpha I(r) + \beta I^2(r)] \mu \tau_0 S \quad (6-6)$$

where $I(r)$ is the laser beam intensity (W cm^{-2}) as a function of r ;

and S is the area illuminated by the pump laser beam (cm^2).

Then, assuming that all absorbed optical energy is converted to heat and that no high energy emission occurs from the excited levels of the semiconductor, the maximum temperature rise on the sample surface due to the optical absorptions from each laser pulse can be given by [122]

$$T(r, \tau_0) = \frac{E(r, \tau_0)}{M J} = \frac{\tau_0}{\rho C J} [\alpha I(r) + \beta I^2(r)] \quad (6-7)$$

where $J = 4.184 \text{ joules cal}^{-1}$; and M is the thermal mass of the illuminated area (M

$\rho C \mu S$) [36].

Therefore, the temperature gradient produced on the sample surface at time τ_0 can be expressed as follows

$$\frac{\delta T(r, \tau_0)}{\delta \vec{r}} = \frac{\tau_0}{\rho C J} \left[\alpha \frac{\delta I(r)}{\delta \vec{r}} + 2 \beta I(r) \frac{\delta I(r)}{\delta \vec{r}} \right] \quad (6-8)$$

The temperature gradient generated in the gas phase can be found by a procedure similar to that used in chapter 5. For simplicity, the temperature gradient generated due to heat transfer in the thin layer of gas close to the sample surface can be treated by the following equation [85]

$$\frac{\delta T_0(r, \tau_0)}{\delta y} = \frac{\kappa_1}{\kappa_0} \frac{\delta T_1(r, \tau_0)}{\delta y}$$

$$\text{and} \quad \frac{\delta T_0(r, \tau_0)}{\delta y} = \frac{\kappa_1}{\kappa_0} \frac{\tau_0}{\rho C J} \left[\alpha \frac{\delta I(r)}{\delta y} + 2 \beta I(r, z) \frac{\delta I(r)}{\delta y} \right] \quad (6-9)$$

The temperature gradient in the y direction is responsible for the transverse deflection PDS signal. However, we cannot find the temperature gradient in the z direction directly from the above equations, as r is not related to z . This problem can be solved if we refer to the temperature solutions [Eqs. (5-10), (5-11), (5-13), and (5-14) in chapter 5], in which the temperature in the gas phase is related to a position in the z direction through the term $e^{-a_0 z}$. Then we may relate $\frac{\delta T_0(r, z)}{\delta z}$ to $\frac{\delta T_1(r)}{\delta r}$ through the following equation

$$\frac{\delta T_0}{\delta z} = e^{-\alpha_0 z} F(\alpha_i, \kappa_i) \frac{\delta T_1}{\delta r} \quad i = 0 \text{ or } 1 \quad (6-10)$$

In the experimental configuration shown in Fig. 25 we have

$$\frac{\delta T_0}{\delta z} = \frac{\kappa_1 \tau_0 e^{-\alpha_0 z}}{\kappa_0 \rho C J} F(\alpha_i, \kappa_i) \left[\alpha \frac{\delta I(r)}{\delta y} + 2\beta I(r, z) \frac{\delta I(r)}{\delta y} \right] \quad (6-11)$$

where $F(\alpha_i, \kappa_i)$ is the thermal coupling function between the sample and the air, and it only depends upon thermal properties of the sample and air. The function can be found from the temperature solutions in chapter 5 and is constant under given experimental conditions.

The photothermal deflection signal, ϕ , can be expressed from Eq. (5-21)

$$\phi = \frac{1}{n_0} \frac{\delta n}{\delta T} \int \frac{\delta T(\vec{r}, t)}{\delta \vec{r}} d\vec{r}$$

Usually the interaction length between the probe beam and the pump laser beam is very short so that the temperature gradient along the interaction length (l) can be assumed as a constant [85, 121], hence

$$\phi = -\frac{l}{n_0} \frac{\delta n}{\delta T} \frac{\delta T}{\delta \vec{r}} \quad (6-12)$$

By using a similar simplification, Eq. (5-22) and (5-23) can be modified into the following forms:

$$\phi_n = -\frac{l}{n_0} \frac{\delta n}{\delta T} \frac{\delta T_0(r, z, \tau_0)}{\delta z} \quad (6-13)$$

and

$$\phi_t = -\frac{l}{n_0} \frac{\delta n}{\delta T} \frac{\delta T_0(r, z, \tau_0)}{\delta y} \quad (6-14)$$

where $l = \int_{x_0}^{x'} \frac{dr}{\sqrt{1-(y_0/r)^2}}$

The voltage signal from the photodiode detector generated by the photothermal deflection of the probe beam can be written as:

$$V = R \phi \quad (6-15)$$

where R is a proportionality constant which is dependent on the pathlength (ℓ) and on the sensitivity of the detector used (photodiode or position sensor).

From the above equations one can obtain the difference in PDS signal amplitude, ΔV , between the crystalline silicon substrate and an ion implanted silicon wafer sample for the transverse-deflection PDS mode:

$$\Delta V = V_i - V_c = -\frac{l}{n_0} \frac{\kappa_1 \tau_0 R}{\kappa_0 \rho C J} \frac{\delta n}{\delta T} \frac{\delta I(r)}{\delta y} [\Delta \alpha + 2 \Delta \beta I(r, z)] \quad (6-16)$$

or for normal-deflection PDS mode:

$$\Delta V = -\frac{l}{n_0} \frac{R \kappa_1 \tau_0 e^{-a_0 z}}{\kappa_0 \rho C J} F(\alpha_i, \kappa_i) \frac{\delta n}{\delta T} \frac{\delta I(r)}{\delta y} [\Delta \alpha + 2 \Delta \beta I(r, z)] \quad (6-17)$$

By substituting Eq.(6-4) and (6-5) into Eq. (6-16) and (6-17), and we get

$$\Delta V = \mathcal{K} N_i^u \quad (6-18)$$

where $\mathcal{K}$ is a constant under a given experimental condition, i.e., for transverse deflection PDS

$$\mathcal{K} = \frac{l}{n_0} \frac{R}{\kappa_0} \frac{\kappa_1}{\rho} \frac{\tau_0}{C} \frac{1}{J} \frac{\delta n}{\delta T} \frac{\delta I(r)}{\delta y} [\mathcal{K} + 2 \mathcal{K} I(r)] \quad (6-19)$$

or for normal deflection PDS

$$\mathcal{K} = \frac{l}{n_0} \frac{R}{\kappa_0} \frac{\kappa_1}{\rho} \frac{\tau_0}{C} \frac{e^{-a_0 z}}{J} F(\alpha_i, \kappa_i) \frac{\delta n}{\delta T} \frac{\delta I(r)}{\delta y} [\mathcal{K} + 2 \mathcal{K} I(r)] \quad (6-20)$$

Therefore, in general, we have the following formula

$$\log (\Delta V) = \log \mathcal{K} + u \log (N_i) \quad (6-21)$$

which means that a linear relationship should exist between the logarithm of PDS signal difference and the logarithm of implant dose, and that the value, u , can be found from the slope of the expected straight line experimentally.

(3) Experimental

The experimental set-up used in the photothermal deflection spectroscopic work is shown in Fig. 26. A pulsed nitrogen laser-pumped dye laser (Photon Technology International, PL2300/PL202, London, Ontario, Canada) was used as the pump light source. The laser generates pulses of 500-ps duration at a repetition rate of up to 20 pulses per second. The pump light beam was directed by a front surface mirror to a plano-convex lens (L_1) which focused the beam onto the surface of a silicon wafer sample. The degree of the focusing was adjustable by moving the lens L_1 , which was attached to a translation stage driven by a computer-controlled stepping motor. The wafer sample was placed on a platform whose height with respect to the probe beam was adjusted with a micrometer translation stage so as to maximize the photothermal deflection signal generated from the wafer sample. The probe beam was obtained from a He-Ne laser (Spectra-Physics model 157, Mountain View, California, U.S.A.) and passed parallel to the wafer sample surface. A lens of 20 cm focal length was placed between the probe laser and the sample-supporting stage. This lens (L_2) was used to focus the probe beam above the sample spot irradiated by the pump laser beam, and the lens L_2 was also adjustable by using a micrometer translation stage to change the probe beam direction horizontally, i.e., transversely across the pump laser beam. Two mirrors were used to increase the path length of the deflected probe beam from the sample to the photodiode detector (EG & G, UV100BQ, Waltham, Massachusetts, U.S.A.). A 1-mm slit was used in front of the detector to allow only a small portion of the probe beam cross-section to fall on the photodiode surface. The voltage output signal from the photodiode was amplified by a preamplifier before being sent to a boxcar averager (Stanford Research System SR250, Palo Alto, California,

U.S.A.). An oscilloscope was also used to visually monitor the transient PDS signal output from the photodiode detector. Data acquired using boxcar averager was finally stored in an IBM PC–XT computer.

The silicon wafer samples were obtained from Northern Telecom Electronics (Ottawa, Ontario, Canada). The substrate was n–type, <100> Czochralski–grown silicon with a resistivity of 3–7 Ω cm. The first group of wafer samples was implanted with various doses of boron ion (B^+) at 20 keV by using a Nova high current implanter at room temperature. The second group of the wafer samples was implanted with various doses of boron difluoride ions (BF_2^+) at 90 keV. Some furnace–annealed ion–implanted wafers were also used for comparison purposes. The specific values of implant doses for the wafers were provided by the manufacturer.

(4) Results and Discussion:

(a) Optimization of PDS detection system

The detector was a photodiode which did not respond directly to the deflection of the probe beam (angular deflection). Instead, it monitored the intensity variation due to the deflection of a probe beam portion that fell on the photodiode surface (absolute deflection). Therefore, the relative position of the horizontal slit to the center of the deflected beam has certain effects on the PDS signal, as shown in Fig. 27. The PDS signal amplitudes look like almost inversely symmetric about the center of the probe beam. When the slit is higher than the beam center, the signal amplitude is positive, i.e., an increasing light intensity was detected by the photodiode, and

Fig. 27: Effect of slit position on PDS signal amplitude.

vice versa. The PDS signal amplitude became zero as the slit was close to the center of the deflected probe beam since there is no change in the light intensity which fell onto the surface of the detector. As well, the delay time of the PDS signals also changed with changing the relative positions. This is due to the fact that the deflected probe beam became quite wide, as pointed by Aarnodt et al. [15], the larger probe beam can be decomposed into a bundle of infinitesimal light filaments. The output signal depends on the particular mode of detection used and shows its maximum amplitude value at a given delay time that is related to the heat transfer in the air layer. Experimentally the horizontal slit was always set at the position where the maximum positive PDS signal can be measured.

The relative position (height) of the photodiode with respect to the slit is also adjustable so that after passing through the slit the probe beam may fall on the most sensitive area of the photodiode surface, thereby generating a maximum PDS signal. The result, as shown in Fig. 28, indicates that the increase in the light intensity is larger when the deflected probe beam was fallen onto the edge of the photodiode, that is, the probe beam was partially onto and partially off the photodiode surface.

The height of the probe beam above the silicon wafer sample surface, i.e., the vertical offset z_0 , has a significant effect on the PDS signal amplitude. The distance between the probe beam and the wafer surface must be less than the thermal diffusion length of the air in order to probe the change of refractive index in the air. When the probe beam is propagating closer to the wafer surface, the PDS signal will become larger [3, 14]. Under our experimental conditions an optimum distance was found to be 0.13–0.15 mm, which gives a maximum PDS signal, as shown in Fig. 29.

A 20-cm focal length lens was used between the probe laser and the sample, which serves two purposes, (1) to focus the probe beam over the sample spot irradiated

Fig. 28: Optimization of the photodiode position.

Fig. 29: Optimization of the height of the probe beam above the sample surface.

by the pump light beam, preventing the probe beam from grazing the sample surface [14], and (2) to finely adjust the horizontal position of the probe beam relative to the center of the pump laser beam. As the focused probe beam was scanned across the diameter of the pump beam in one direction, with simultaneous readjustment of the photodiode for signal optimization, the PDS signal amplitude showed a maximum value at the middle of the scan (Fig. 30a). This result is consistent with the theory that the normal PDS signal amplitude is maximum when the centers of the probe beam and pump beam coincide. In Fig. 30, curve b was obtained when lens L_1 was at a loosely-focusing position. The two peaks on curve b were probably caused by different modes of the pump laser. Comparing the two curves in Fig. 30, one finds that the intensity profile of the pump beam will change to a certain extent with the focusing lens L_1 . By scanning the probe beam across the pump beam one can obtain the intensity profile of the pump beam in the scanning direction [121].

(b) Calibration of linear response of the PDS instrument

A set of neutral density filters (NDF) were used as standards to calibrate the response of the PDS instrumentation. These filters were made from quartz plates with one side coated with inconel alloy material to various extents. The absorbance value of each filter produced by the coated inconel layer was checked by using the following equation:

$$T = \frac{I_t}{(I_0 - I_r)} \quad (6-22)$$

Therefore the absorbance value of each filter can be found from:

Fig. 30: Optimization of the horizontal position of the probe beam relative to the pump laser beam center.

The focal point of the pump beam was (a) on the sample surface and (b) 70 mm away from the surface.

$$A = -\log T = \log \left(\frac{I_0 - I_r}{I_t} \right) \quad (6-23)$$

where T is the transmittance of a filter.

I_r is the intensity of the light beam reflected by a filter;

and I_t is the intensity of the light beam transmitted through a filter.

The experimentally measured absorbance values have shown a linear correspondance to the nominal value of optical density (nearly 1:1). Therefore, it is reasonable to use these neutral density filters as standard absorbers for calibrating the linear response of the PDS instrumentation. The results, as shown in Fig. 31, have verified that the PDS system does have a linear response to the increasing optical density values of the neutral density filters from 0 to 0.40. However, the calibration curve begins to deviate from the linearity as the optical density value becomes larger than 0.40. This is a normal phenomenon in photothermal spectroscopies [22, 36], as the linear relationship is based on the assumption that a sample is weakly absorbed at the wavelength of the pump laser.

(c) Nonlinear PDS signals from silicon wafers

Theoretically, the absorption coefficients, α and β , of crystalline silicon are dependent to some extent on the wavelength of the pump laser (i.e., photon energy $h\nu$) according to the following equations [112, 123]:

$$\alpha = A' (h\nu - E_g^i \pm E_p)^2 \quad (5-24)$$

$$\beta = B' (2h\nu - E_g^d)^{1/2} \quad (6-25)$$

Fig. 31: PDS system response calibration curve.

where A' and B' are constant related to the properties of crystal silicon;
 E_g^i and E_g^d are the indirect and direct gap energy of a semiconductor;
 and E_p is phonon energy involved.

Experimentally, Jellison et al. [117] have proven that the differences in absorption coefficients between crystalline silicon and boron–implanted silicon have a wavelength dependence, as shown in Fig. 32, and that the changes in absorption coefficients due to the same implant dosage are wavelength dependent. These are larger (on the order of 10^5 cm^{-1}) in the wavelength region of 400–500 nm than in any other region. On the other hand, the PDS signal amplitude depends not only on the absorption coefficient but also on the intensity of the pump laser beam (W cm^{-2}). Particularly two– or multi–photon absorption PDS signals are strongly dependent on the second or higher power of the intensity of the pump laser beam. Our dye laser has the highest output power at the wavelength of 500 nm. Furthermore, to avoid laser–induced damage to the silicon wafer samples, it is desirable to choose the pump laser wavelength as far as possible from the electronic band edge i.e., short wavelength transmission cutoff (3.4 eV for silicon) [124]. When these three factors were compromised, 500 nm was chosen as the working wavelength for the determination of implant dosages in ion–implanted wafers.

The optical absorption properties of silicon have been well studied. Theoretical calculations of two–photon and three–photon absorption coefficients were done for semiconductor material of indirect band gap like silicon [123, 125]. Experimentally, two–photon absorption was observed at the wavelength of 1.06 μm by Reintje and McGroddy [126]. In a laser calorimetric study on semiconductors, Stewart and Bass found the saturation of one–photon absorption in silicon and the increase of its total absorption due to two– and multi–photon absorption processes [127]. In

Fig. 32: Wavelength dependence of absorption coefficients of (a) c-Si and (b) B^+ -implanted Si.

addition, Aydinli et al. [128] found that under intense pulsed laser excitation the absorption coefficient of silicon in the range of 1.3 – 3.3 eV increased dramatically, and they attributed this to the presence of self-confined plasma in silicon.

Therefore, in order to study the importance of the effects of the pump laser intensity on the PDS signal amplitude, an experiment was carried out, in which the focusing lens, L_1 , for the pump laser was moved by the computer-controlled stepping motor translation stage to change the focusing degree. In this way, the sample area irradiated by the pump laser was varied, thereby changing the photon density of the laser radiation on the sample surface. The variation of the PDS signal amplitude is shown in Fig. 33. When the sample surface was far away from the focal point of the pump laser, the PDS signal increased very slowly with the increasing focusing. When the sample surface was close to the focal point of the dye laser, i.e., the pump laser was sharply focused on the sample surface, the PDS signal amplitude increased abruptly. Further focusing of the pump laser beam on the sample would have resulted in the surface damage of the wafer samples.

The question arises whether the increase in the PDS signal amplitude is due to two- or multi-photon absorption processes occurring in the samples. In order to answer this question another experiment was carried out, in which a series of neutral density filters is used and placed in front of the dye laser aperture. The lens, L_1 , was fixed at a sharply focusing position found previously to keep the irradiated sample area constant. By gradually increasing the transmittance value of the neutral density filters in front of the aperture, more light flux from the pump laser was allowed to reach on the same area. Therefore, the photon density in this sample area was gradually increased proportionally to the transmittance value. These results are shown in Fig. 34. As seen from this figure, when the transmittance value of the neutral density filter used

Fig. 33: Effect of pump beam focusing on the PDS signal amplitude.

Fig. 34: Photon density dependence of PDS signal amplitude.

The focal point of the pump beam was (a) on the wafer surface and (b) 10 mm away from the surface. ($3 \times 10^{15} \text{ cm}^{-2} \text{ BF}_2^+$ -implanted silicon wafer was used as the sample.)

is small, the log-log plots between PDS signal amplitude and the photon density have a slope of 1.0 ± 0.3 . This linear behavior indicates that one-photon absorption dominantly occur in this photon density range. However, as the transmittance value is increased to a higher photon density range, the plot curves to a new slope of 2.5 ± 0.5 for the log-log plot in this photon density range. This result strongly suggests that the two- or possibly three-photon absorption processes take place in this high photon density range. This nonlinear absorption phenomenon has been observed with both B^+ and BF_2^+ -implanted silicon wafers. According to the optical sum rule the additional nonlinear absorption may further enlarge the differences in the total absorption coefficients between crystalline silicon and ion-implanted silicon wafers. The two- or multi-photon absorption is proportional to the square or multi-power of the light intensity of the pump laser, so that this kind of absorption process is significant when the laser power is high. It is clear from this result that one of the best experimental conditions is to use a pump laser of high irradiation power to take advantage of this enhanced absorption while remaining below the damage threshold at which surface destruction of a wafer sample begins to occur.

(d) PDS determination of implant dosages of silicon wafers

The pulsed PDS signals for crystalline silicon, B^+ - and BF_2^+ -implanted silicon wafers are similar. The signal amplitude reached a maximum value at a certain time delay after the firing of the pump laser, as shown in Fig. 35. First, The photodiode detector has a response time of about 50 ns which is much lesser than the rise time of the PDS signal. It, therefore, did not cause any significant delay of the PDS signal. Second, the deexcitation processes in the silicon crystal are electron-phonon scattering and electron-hole recombination, occurring on picosecond

Fig. 35: Typical pulsed PDS signal profile for ion-implanted Si wafers ($5 \times 10^{13} \text{ cm}^{-2} \text{ B}^+$ -implanted).

scale [129]. As well, the local thermodynamic equilibrium in silicon can be achieved in less than $1\mu\text{s}$. Hence, the signal delay is attributed to the slow heat transfer from the wafer sample to the air layer adjacent to the heated region on the sample surface to build up a gradient of refractive index in this air layer.

The background noise in PDS measurement originates from the following sources: laser noise (pointing and intensity fluctuations); electronic noise; and ambient or environmental noise (e.g., convection, turbulence, or mechanical vibrations) [3]. Among the above three categories of noise the laser noise is the most serious. The PDS signal is proportional to the deflection angle of the probe beam at the point where the focused pump beam creates the refractive index profile; any variations in the refractive index profile will result in noise. There are two ways in which the noise may be produced. The first is by variations in the spatial overlap between the probe and the pump beams – pointing errors from either laser will lead to noise. The second is by variations in the refractive index profile or temperature gradient. It is well known that pulsed lasers are characterized by poor pulse-to-pulse energy and mode stability. The pump laser used in our experiment has a nominal variation of 5% in its output energy. Obviously the refractive index profile or temperature gradient will follow this variation to the same extent which results in significant noise. A pinhole and an iris were respectively used in front of the probe laser and the pump laser apertures to alleviate the pointing errors from the two lasers. In addition, a boxcar averager was used to enhance the signal-to-noise ratio by taking the average of signals over 100 laser pulses.

Under the above experimental conditions the PDS signal amplitudes of B^+

and BF_2^+ -implanted silicon wafers were measured for various dosages. Their PDS signal amplitude were compared with that of crystalline silicon, and the data are plotted in accordance with Eq. (6–21). The relationship between the differences in the PDS signal amplitude and the implant dosages is shown in Fig. 35. The log–log plots have a linear portion in the dosage range of $5 \times 10^{12} - 3 \times 10^{15} \text{ cm}^{-2}$. As the dosage falls below $1 \times 10^{12} \text{ cm}^{-2}$, the PDS signal amplitude approaches the signal level for crystalline silicon and the difference in PDS signal amplitude between crystalline silicon and ion-implanted wafers is too small to be distinguished from the noise level (less than two times of the standard deviation of the noise level). Consequentially, it can be claimed that an implant dosage of $1 \times 10^{12} \text{ cm}^{-2}$ for B^+ and BF_2^+ is detectable.

Note that PDS methods are only sensitive to the defect density generated in ion-implantation process, but can not differentiate their chemical species. At the same implanting energy level a larger implant will produce more defects in the silicon substrate than a small implant does. As the B^+ is much smaller than Bi^+ , Fe^+ , and Tl^+ implants, fewer defects were generated by B^+ . Therefore, even though the detection limit in the present work appears to be similar to that in reference 112, the present PDS method is actually more sensitive as it can detect fewer defects per implanted ion. All the furnace-annealed silicon wafer samples have shown no PDS signals differentiable from that of the substrate. For annealed silicon wafers an infrared PDS technique is probably more suitable to detect the ion implantation effects in annealed silicon wafers as certain change still remains in the subgap and is detectable in infrared region even after annealing [99].

The slope u in Eq. (6–21), obtained from the linear portion of the curves in Fig. 36, are 0.21 ± 0.03 and 0.25 ± 0.03 for B^+ - and BF_2^+ -implanted silicon wafers, respectively. These two values can be compared with the several u values calculated.

Fig. 36: Log-Log plot between ΔV and N_i .
 (a) B^+ implant and (b) BF_2^+ implant.

(Each error bar represents the logarithm of one standard deviation from the mean obtained from the measurements on four sampling points.)

from the published data in the literature [111, 112, and 130] by using Eq. (6–21). In Table V the data in the last two rows are taken from doped semiconductor materials and used only for comparison. Generally, the u value may be used to characterize the formation of defects in the crystalline substrate for a given dopant. Despite the various differences in the experimental parameters used in the present and other cited works, some common trends can be extracted from the u value in Table V. First, for the same implant or dopant species, a large u value can be related to a high yield of defect generation in a substrate. Second, for the same substrate a large u value was a higher potential of an implant or a dopant to perturb the crystal lattice, which is related to the large mass or large size of an implant/dopant. However, there are many parameters which can affect the ion implantation process, such as the substrate lattice symmetry, implanting orientation, implanting–ion energy, and substrate temperature. The tensorial aspects of the ' u ' value may be better understood by making systematic investigation under specific experimental conditions.

Table V: Comparison of u values

Dopant	dose (ions cm ⁻²) or concentration (atoms cm ⁻³)	Substrate	Laser wave length (nm)	u	Reference
B ⁺	5x10 ¹² – 3x10 ¹⁵ (ions cm ⁻²)	c-Si	500	0.21 ± 0.03	this work
	1x10 ¹² – 1x10 ¹⁵ (ions cm ⁻²)	c-Si	514	0.22 ± 0.02	[94]
BF ₂ ⁺	5x10 ¹² – 3x10 ¹⁵ (ions cm ⁻²)	c-Si	500	0.26 ± 0.03	this work
In ⁺	2x10 ¹² – 5x10 ¹⁴ (ions cm ⁻²)	c-Si	514	0.8 ± 0.2	[111]
As	9.5x10 ¹⁸ – 4.6x10 ²⁰ (atoms cm ⁻³)	c-Si	500	1.28 ± 0.08	[130]
As	9.5x10 ¹⁸ – 4x10 ¹⁹ (atoms cm ⁻³)	c-Ge	1550	0.95 ± 0.07	[112]

(5) Conclusion

B^{+} and BF_2^{+} -implanted silicon wafers have been analysed by using the nonlinear PDS technique. A model is presented to relate the optical absorption coefficients, and hence the PDS signal amplitudes, to the implant doses. By focusing the pump laser beam to provide a high photon density below the damage threshold, a limiting dose of 1×10^{-12} ions cm^{-2} of either ion implant can be detected. These detection limits represent the best results ever reported for the two implants in crystalline silicon, thus justifying further development of this powerful nonlinear PDS technique.

Chapter 7

Conclusion

In analytical chemistry, sensitivity is one of the most important criteria for selecting an instrumental method. PTS techniques are preferential to conventional absorption spectrometry for trace analysis because they provide higher sensitivity for the determination of very low sample absorptions, in addition to the other attractive features mentioned earlier. It is worthy, therefore, to develop PTS techniques further. The development in laser technology and the improvement in electronic and optical component manufacturing will put new blood to photothermal spectroscopic studies.

The PAS technique has been developed for the past 20 years and is becoming mature now. Various kinds of applications can be found in literature, with the applications to solid opaque samples being the most significant. Comparing with other PTS techniques, the detector requirements are still the limiting factors in PAS applications. Only the sample with a size that can be accommodated in the gas-microphone PAS cell can be assessed, while the mechanical attachment of a piezoelectric transducer to a sample is not always convenient for routine analysis. Unless these problems are overcome by novel sample techniques, PAS will become less and less competitive against other PTS methods. The solid film sampling technique shown in Chapter 3 can be considered as one solution to the detector problems in that metal ions from a bulky water sample are extracted to form a small solid film sample for gas-microphone PAS measurement.

In contrast to PAS, the PDS technique is still in its developing stage. New

applications are appearing and there are many other possibilities remaining to be explored. PDS surface imaging, for instance, is becoming a very active research area at present for studying chemical adsorption and corrosion processes on an inhomogeneous sample surface. Since laser pulse can be made very short in duration ($< 10^{-9}$), pulsed-laser PDS has the capability of monitoring transient changes and intermediate products in kinetic studies.

By taking advantage of the high temperature coefficient of refractive index in liquids, PDS technique can be used to investigate interfacial phenomena between liquid and liquid or liquid and solid, in which many useful informations can be obtained to compensate the study by other methods.

As a spectroscopic technique, PDS can be used to investigate special quantum effect involved in the interaction between photon and matter. as shown in chapter 6, the nonlinear PDS technique developed for implant dose determination in silicon wafers is based on two- or possibly three-photon absorption processes.

All in all, rapid advancements in the further development and new applications of PDS technique can be anticipated for the next few years.

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APPENDIX 1:

Atomization Mechanisms of Barium Chloride and Barium Nitrate *

Several workers have investigated mechanisms in graphite furnace atomic absorption spectrometry (GFAAS) in order to understand the reactions involved and to approach the goal of interference-free analysis in GFAAS.

Different models have been proposed to explain atomization mechanisms in GFAAS. Campbell and Ottaway [1] proposed a thermodynamic model with which the appearance temperature of free atoms of the analyte in the vapour phase within the graphite furnace could be determined by calculating the temperature at which the standard free energy change (ΔG^0) for the reaction considered by them in GFAAS becomes negative, i.e., thermodynamically favorable for the considered reaction. Their method was successful for 18 elements out of the 27 elements investigated by them. By assuming that the atomic vapour temperature was equal to that of the graphite surface inside the furnace, Fuller [2–4] suggested a kinetic model for the formation of copper atoms in the Perkin–Elmer Heated Graphite Atomizer (HGA), model 70. Lvov et al. [5] proposed a macrokinetic model to explain the formation of analyte free atoms in GFAAS.

Sturgeon et al. [6] have proposed the following four main categories of atom formation in the commercial, semi-enclosed, tube type graphite atomizers:

- (1) Reduction of solid oxide by graphite surface:

* The work described in APPENDIX 1 of this thesis was done in the laboratory of Professor C. L. Chakrabarti under his direction and supervision.

(2) Thermal decomposition of solid oxide:

(3) Dissociation of oxide vapour:

(4) Dissociation of halide vapour:

(X is a halogen atom.)

As the applications and investigations in GFAAS became wider and deeper, the roles of carbon and oxygen in the atomization processes occurring in GFAAS have received more attentions and it has been recognized that the graphite furnace is a very complex system [7-9].

Many techniques were used to collect useful informations from graphite furnaces during atomization processes. Welz [10] introduced a useful experimental method to monitor the general change of an analyte in two consecutive thermal steps – charring and atomizing. Mass spectroscopy [11], molecular absorption spectroscopy [12], and X ray diffraction structure analysis [13] were also used to investigate the products of the atomization processes and to obtain evidences for the atomization

mechanisms.

On the atomization of barium oxide in a graphite furnace, Nagdaev et al. [14] and Jasim et al. [15] had different opinions. On the other hand, by using a mass spectrometer, Styris [16] monitored the products of the reactions that occurred in a graphite and a tantalum furnaces and proposed an atomization mechanism of barium chloride.

The atomization mechanisms of barium as the chloride and the nitrate have been the subject of the present study. Some of the experimental results revealed differences in the atomization mechanisms of barium chloride and barium nitrate.

Experimental

Equipment:

The Perkin–Elmer Atomic Absorption Spectrometer, model 5000, fitted with HGA 400 graphite furnace, was used to obtain the charring and atomization curves.

The Perkin–Elmer HGA 2100 graphite furnace with a laboratory made, electrical power supply was used. A barium hollow cathode lamp, manufactured by Perkin–Elmer Co. was used and was operated at the lamp current recommended by the manufacturer (25 mA). A Varian Techtron AA 5 monochromator with a laboratory–made detection system was used to study the molecular absorption spectrum of barium monochloride. A Deuterium hollow cathode lamp (Hamamatsu TV Co., Ltd, Japan) was used as the light source in the measurement of the molecular absorption spectrum of barium chloride.

The temperature of the graphite furnace was measured by using an automatic

optical pyrometer, series 1100 (Ircon Inc., Skokie, Illinois).

A Philips Automated Power Diffractometer, PW1050/81, equipped with a PW 1710 microprocessor was used for X-ray diffraction analysis.

Reagents, Solvents and Gases:

Argon of 99.995% purity was used both as the sheath gas and as the purge gas for the graphite furnace.

All chemicals used were of certified purity (> 99.9%).

Ultrapure water of resistivity 18.3 megohm-cm obtained directly from a Millipore Milli Q2 Water System (Millipore Corporation, Mississauga, Ontario, Canada) was used for the preparing solutions of standards and samples.

Results and Discussion

1. Charring and Atomization Curves:

The charring and atomization curves (Figs. 1 and 2) for the two barium compounds provide useful information on the thermal decomposition reactions of the barium compounds within the graphite furnace.

Barium chloride and barium nitrate were employed to obtain their charring and atomization curves. The 553.5 nm line of barium was used. The charring curves (the left hand side curves in Figs. 1 and 2) were drawn by plotting the barium absorbance obtained at the optimum atomization temperature as a function of the charring temperature. The atomization curves (the right-hand side curves in Figs. 1 and 2) were drawn by plotting the barium absorbance obtained at the optimum charring temperature

Fig. 1 : The charring and atomization curves of barium chloride.
2 ng Ba(II) was used each time.

Fig. 2 : The charring and atomization curves of barium nitrate.

4 ng Ba(II) was used each time.

as a function of the atomization temperature. By comparing the two figures, it was found that barium chloride could be charred upto about 1900 K without the loss of barium atoms (Fig. 1), whereas the loss of barium atoms occurred at a temperature above 1400 K (Fig. 2). Study of the charring curves of Figs. 1 and 2 shows that though for barium chloride (Fig. 1) the barium species begin to be lost from the analysis volume starting from the charring temperature of about 1900 K (probably as a result of formation of volatile species of barium), barium atoms are not formed until an atomization temperature of at least 2300 K is obtained, i.e., there is a gap of at least 400 K between the two temperatures, which should be attributable to the barium species (formed by thermal decomposition and/or other chemical reactions occurring at charring temperature > 1900 K) which are wholly or partly lost from the analysis volume. This is in sharp contrast with the charring curve of barium nitrate (Fig. 2), which shows that although the barium species begin to be lost from the analysis volume starting from the charring temperature of about 1400 K (probably as a result of formation of volatile species of barium), barium atoms are not formed until an atomization temperature of about 2300 K is attained, i.e., there is a gap of at least 900 K between the two temperatures, which should be attributable to the barium species (formed by thermal decomposition and/or other chemical reactions at charring temperature > 1300 K) which are wholly or partly lost from the analysis volume. Study of the atomization curves reveals that the atomization of barium increased rapidly with increasing atomization temperature in the case of barium chloride (Fig. 1); even at the highest atomization temperature possible (3170 K) with the apparatus, the absorbance was still increasing. This was in marked contrast to the atomization curve of barium nitrate (Fig. 2) which levelled off at about 2900 K. In Fig. 1, the atomization temperature employed was 3170 K for obtaining the charring curve, at

where κ and h are Boltzmann's and Planck's constants, respectively, and the quantities $\Delta G^{0\dagger}$, $\Delta S^{0\dagger}$ and $\Delta H^{0\dagger}$ are the free energy, the entropy and the enthalpy of activation, respectively. To a first approximation, the enthalpy of activation may be equated to the activation energy E_a for the reaction [21]. The equilibrium constant for the gas–condensed phase equilibrium, K_p , is related to the temperature through the well–known van't Hoff equation [22]:

$$\left[\frac{\delta \ln K_p}{\delta (1/T)} \right] = - \frac{\Delta H^0}{R} \quad (20)$$

where ΔH^0 is the standard enthalpy change accompanying the phase transition (reactants and products at unit fugacity). In the integrated form, using common logarithm, equation (20) may be written as

$$\log K_p = - \Delta H^0 / (2.3RT) + C \quad (21)$$

where C is an integration constant and ΔH^0 is assumed to be independent of temperature. Substituting Eqs. (19) and (21) into (18) one gets:

$$\begin{aligned} \log A_T &= - \frac{E_a + \Delta H^0}{2.3 RT} + \frac{\Delta S^{0\dagger}}{2.3 R} + \log \left(\frac{\kappa_a}{h} \frac{\alpha_s}{\kappa_d} \frac{\kappa T}{C} \right) \\ &= - \frac{E_a + \Delta H^0}{2.3 RT} + A_0 \end{aligned} \quad (22)$$

where A_0 stands for the sum of the last two terms of the previous equation. For highly endothermic reactions, such as atomization reaction in GFAAS, it is reasonable to make

and a slit width of 0.1 mm was used. D_2 lamp was used as the incident light source. The results are shown in Fig. 3. The appearance temperature of molecular absorption was confirmed by several measurements and found to be (1320 ± 50) K. The temperature which corresponds to the maximum peak absorption was (1850 ± 50) K. Barium chloride is a very stable chemical species and its boiling point is 1833 K [18]. As the appearance temperature of the molecular absorption is so low that the dissociation of $BaCl_2(g)$ could not occur, the absorption spectra were not due to $BaCl(g)$, but was probably due to $BaCl_2(g)$. The melting point of $BaCl_2$ is 1236 K [18], above which barium chloride ($BaCl_2$) will exist in the graphite furnace in the liquid state. The concentration of $BaCl_2$ in the vapour phase would be greatly increased as $BaCl_2$ turned from the solid into the liquid state within the graphite furnace. Therefore the molecular absorption may be produced by the $BaCl_2$ in the vapor phase. A phase equilibrium exists between the liquid and gas phases of $BaCl_2$. With increasing temperature, the concentration of $BaCl_2(g)$ would increase and therefore, higher absorption was obtained. This situation continued until the temperature reached 1833 K, the boiling point of $BaCl_2$. At the boiling point $BaCl_2(l)$ was rapidly evaporated into the vapor phase and there was no more $BaCl_2$ in the condensed phase. Therefore, there was no further supply of $BaCl_2$ from the condensed phase to the vapour phase to compensate for the loss of $BaCl_2(g)$, and from that temperature the concentration of $BaCl_2(g)$ began to decrease due to further loss. Experimentally one could observe the maximum molecular absorption occurring at about 1850 K when all the $BaCl_2(l)$ entered the vapour phase. At higher heating temperature, the analyte was lost either as $BaCl_2(g)$ or possibly as $BaCl(g)$ until the temperature (2300 K) was obtained, at which $BaCl(g)$ began to decompose to produce $Ba(g)$.

When a higher heating rate was used to raise the temperature of graphite

Fig. 3 : Molecular absorption spectra of barium chloride.

(a) heating rate = 1.25 K ms^{-1} , and (b) heating rate = 3.0 K ms^{-1} .

furnace, the molecular absorption signal was greatly reduced, as shown in Fig. 3b. This is a evidence that the absorbing species in the vapour phase had a lower concentration, therefore, the loss of the analyte as molecular species in the vapour phase before atomization was greatly reduced, which resulted in a higher atomic absorption signal in the atomization step. This is consistent with the result reported in literature [19].

The monotonic increase in the atomic absorption of barium (as the chloride) with increasing atomization temperature may be explained as follows. If one considered that free barium atoms were produced by the reaction (3), the atomization energy would be equal to the bonding energy of BaCl(g).

For reaction:

the thermodynamic equilibrium constant (K_{eq}) can be expressed as

$$K_{\text{eq}} = \frac{[\text{Ba(g)}] [\text{Cl}_2(\text{g})]^{0.5}}{[\text{BaCl(g)}]} = \frac{P_{\text{Ba}} [P_{\text{Cl}_2}]^{0.5}}{P_{\text{BaCl}}} \quad (4)$$

where P is the partial pressure of the species shown as the subscripts.

The dependence of the equilibrium constant, K_{eq} , on the atomization temperature, T(K), is given approximately by the following expression [20]

$$\log (K_{\text{eq}}) \approx -5040 \left(-\frac{D_0}{T} \right) \quad (5)$$

where D_0 is the dissociation energy and T is the absolute temperature.

From Eq. (5), one can find that K_{eq} becomes larger with increasing temperature (T), which means a higher vapor pressure for barium atoms in the vapour phase. Therefore, at higher atomization temperature more barium atoms were produced in the vapour phase and a higher atomic absorbance was measured.

3. Formation of free barium atoms from barium nitrate:

When barium nitrate was used as the analyte in GFAAS, the salt was first decomposed into barium oxide at the charring temperature 900 K [18]. With barium oxide in the graphite furnace, the following reactions are thermodynamically possible at various temperatures of the graphite furnace.

The thermodynamic feasibilities of these reactions were evaluated by calculating ΔG° values at specified temperatures, assuming the activity of the substances in the condensed phase as 1.

The calculation results show that barium carbide may formed by reaction (6) at charring temperature above 1400 K, and by reaction (9) at charring temperature of 1800 K. Barium carbide is a compound of low volatility; however, it has been found in the vapour phase within graphite furnaces (both vitrous carbon and pyrolytic graphite) at temperature above 1750 K by mass spectrometry [16]. The gradual decline on the charring curve for barium nitrate, started at the charring temperature 1400 K, may be

explained by the loss of barium carbide from the vapour phase.

The boiling point of barium is 1913 K [18]; however, at this temperature the atomic absorption signal of free barium atoms was not observed and there was little possibility that free barium atoms were produced from the evaporation or sublimation of metallic barium from its condensed phase. The appearance temperature of barium atoms in the vapour phase in the graphite furnace is about 2300 K, corresponding to the decomposition temperature of barium oxide.

For the reaction:

The equilibrium constant, K_{eq} , can be expressed as

$$K_{\text{eq}} = \frac{[\text{Ba(g)}] [\text{O}_2\text{(g)}]^{0.5}}{[\text{BaO(g)}]} = \frac{P_{\text{Ba}} [P_{\text{O}_2}]^{0.5}}{P_{\text{BaO}}} \quad (11)$$

where P is the partial pressure of the species shown as subscripts.

At first glance, the equilibrium constant, K_{eq} , increased with increasing temperature [in Eq. (5)], so more barium atoms should have been produced in the vapor phase according to Eq.(11). However, the partial pressure of oxygen, which is not only from the decomposition of BaO but mainly depends on the oxygen as impurity in the purge gas, has a large effect on the production of free barium atoms. According to the thermodynamic equilibrium calculation, the partial pressure of oxygen in the graphite furnace increased with increasing atomization temperature [8]. The increasing partial pressure of oxygen in the graphite furnace would suppress the decomposition of BaO in

the vapour phase according to Eq. (11). Therefore, the increase in the atomization temperature favours the decomposition of BaO, whereas, on the other hand, the increase in atomization temperature also resulted in a increase in the partial pressure of oxygen that would suppress the decomposition of BaO. When these two effects were balanced at a temperature, the yield of free barium atoms in the furnace did not changed with increasing atomization temperature. Therefore, one observed that the atomic absorption of barium did not increase with the increase in atomization temperature continuously.

4. X-ray diffraction analysis:

In order to investigate the reaction products due to thermal decomposition in the charring stage, X-ray diffraction analysis was carried out. 1000 – 2000 μg each of barium as barium nitrate and barium chloride were charred under different thermal programs on graphite platforms, and then the graphite platforms were sent to the X-ray diffraction analysis laboratory for the identification of the species. Although the sensitivity of X-ray diffraction structure analysis is much less than that of GFAAS, the results could be used as an indirect evidence for deriving atomization mechanism. With barium chloride as the analyte, no barium oxide was found on the graphite platform after charring, which meant that there was no hydrolysis of barium chloride during charring stage. With barium nitrate as the analyte, barium oxide and barium carbide were both found on the graphite platforms after charring at 1500 K. It is probable that the formation of barium carbide was responsible for the loss of barium in the charring stage above 1400 K.

5. Activation energies for atomization:

Determination of the activation energy, E_a , which characterizes the rate-determining step, is an important method used to verify the detailed pathways for atomization. The activation energies for atomization of barium chloride and barium nitrate were obtained by using the following method proposed by Sturgeon et al. [6].

Consider the most general atomization reaction:

If the final step in the atomization process is characterized by a unimolecular rate constant κ_1 , then the rate of production of $\text{M}_{(g)}$ at any temperature is given by :

$$\frac{d[\text{P}_{\text{M(g)}}]}{dt} = \kappa_1 \text{P}_{\text{MO(g)}} = \kappa_1 K_p \alpha_s \quad (13)$$

where $K_p = \text{P}_{\text{MO(g)}}/\alpha_s$, α_s is the activity of the condensed phase on the surface of the graphite furnace, and P is the partial pressure denoted by the subscript of P.

Metal vapour is lost from the analytical volume by processes which are largely diffusional in nature in the absence of purge gas. The net rate of appearance of metal vapour is given by the following equation:

$$\frac{d[\text{P}_{\text{M(g)}}]}{dt} = \kappa_1 K_p \alpha_s - R_d \quad (14)$$

where R_d is the diffusional loss rate of metal vapour from the furnace. It may be approximated by a simple first order process; hence,

$$R_d = \kappa_d P_{M(g)} \quad (15)$$

in which κ_d is the (slightly temperature dependent) rate constant for loss of vapour. During a short period when α_s is nearly constant, a steady-state is achieved (at each temperature) in which the number density of all species no longer changed with time, that is,

$$\frac{d[P_{M(g)}]}{dt} = 0 = \kappa_i K_p \alpha_s - \kappa_d P_{M(g)} \quad (16)$$

which upon rearrangement yields:

$$P_{M(g)} = (\kappa_i K_p \alpha_s) / \kappa_d \quad (17)$$

In atomic absorption spectrometry, the measured absorbance is directly proportional to the concentration of atomic vapour; hence,

$$A_T = \kappa_a P_{M(g)} = (\kappa_a \kappa_i K_p \alpha_s) / \kappa_d \quad (18)$$

where A_T is the absorbance by metal vapour at any temperature T and κ_a is a proportionality constant relating absorbance to metal vapour concentration. According to transition state theory, the rate constant κ_i can be formulated in thermodynamic terms by introducing the standard free energy change for the reaction:

$$\kappa_i = \frac{\kappa T}{h} e^{-(\Delta G^{0\dagger}/RT)} = \left(\frac{\kappa T}{h}\right) e^{(\Delta S^{0\dagger}/RT)} e^{-(\Delta H^{0\dagger}/RT)} \quad (19)$$

where κ and h are Boltzmann's and Planck's constants, respectively, and the quantities $\Delta G^{0\dagger}$, $\Delta S^{0\dagger}$ and $\Delta H^{0\dagger}$ are the free energy, the entropy and the enthalpy of activation, respectively. To a first approximation, the enthalpy of activation may be equated to the activation energy E_a for the reaction [21]. The equilibrium constant for the gas–condensed phase equilibrium, K_p , is related to the temperature through the well-known van't Hoff equation [22]:

$$\left[\frac{\delta \ln K_p}{\delta (1/T)} \right] = - \frac{\Delta H^0}{R} \quad (20)$$

where ΔH^0 is the standard enthalpy change accompanying the phase transition (reactants and products at unit fugacity). In the integrated form, using common logarithm, equation (20) may be written as

$$\log K_p = - \Delta H^0 / (2.3RT) + C \quad (21)$$

where C is an integration constant and ΔH^0 is assumed to be independent of temperature. Substituting Eqs. (19) and (21) into (18) one gets:

$$\begin{aligned} \log A_T &= - \frac{E_a + \Delta H^0}{2.3 RT} + \frac{\Delta S^{0\dagger}}{2.3 R} + \log \left(\frac{\kappa_a}{h} \frac{\alpha_s}{\kappa_d} \frac{T^C}{\kappa_d} \right) \\ &= - \frac{E_a + \Delta H^0}{2.3 RT} + A_0 \end{aligned} \quad (22)$$

where A_0 stands for the sum of the last two terms of the previous equation. For highly endothermic reactions, such as atomization reaction in GFAAS, it is reasonable to make

the following approximation:

$$\log A_T = -\frac{E_a}{2.3 RT} + A_0 \quad (23)$$

A plot of the logarithm of absorbance (A_T) against the reciprocal of absolute temperature should result in a straight line of negative slope, which can be used to calculate the activation energy (slope = $-\frac{E_a}{2.3 R}$)

The experimental values for activation energies obtained from Figs. 4 and 5 were $109 \pm 5 \text{ kcal mol}^{-1}$ for the analyte barium chloride and $134 \pm 7 \text{ kcal mol}^{-1}$ for the analyte barium nitrate. The experimental value for activation energy of barium chloride agrees well with the bond dissociation energy ($106 \pm 2 \text{ kcal mol}^{-1}$) of BaCl(g) reported in literature [18] and the experimental value for activation energy of barium nitrate agrees well with that of BaO(g) , ($133.5 \pm 1.3 \text{ kcal mol}^{-1}$) reported in literature [18]. The uncertainty in our experimental values represents one standard deviation of replicate measurements.

Fig. 4 : Arrhenius plot for barium as the chloride, atomized in HGA-400 furnace.
Heating rate = 1.25 K ms^{-1} .

Fig. 5: Arrhenius plot for barium as the nitrate, atomized in HGA-400 furnace.
Heating rate = 1.25 K ms^{-1} .

6. Proposed mechanisms for atomization

Mechanisms of Atomization of Barium Chloride

Temperature(K)	Reactions and Species in graphite furnace
1240	$\text{BaCl}_2(\text{s}) \rightleftharpoons \text{BaCl}_2(\text{l})$
1360–1850	$\text{BaCl}_2(\text{l}) \rightleftharpoons \text{BaCl}_2(\text{g})$
$1900 < T < 2300$	$\text{BaCl}_2(\text{g})$ is lost.
≥ 2300	$\text{BaCl}_2(\text{g}) = \text{BaCl}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g})$ $\text{BaCl}(\text{g}) = \text{Ba}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g})$

Mechanisms of Atomization of Barium Nitrate

Temperature (K)	Reactions and Species in graphite furnace
900	$\text{Ba}(\text{NO}_3)_2(\text{s}) = \text{BaO}(\text{s}) + 2\text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
> 1400	$\text{BaO}(\text{s}) + 3 \text{C}(\text{s}) = \text{BaC}_2(\text{s}) + \text{CO}(\text{g})$ $\text{BaC}_2(\text{s}) \rightleftharpoons \text{BaC}_2(\text{g})$
$1400 < T < 2300$	$\text{BaC}_2(\text{g})$ is lost.
2190	$\text{BaO}(\text{s}) \rightleftharpoons \text{BaO}(\text{l})$
≥ 2300	$\text{BaO}(\text{l}) \rightleftharpoons \text{BaO}(\text{g})$ $\text{BaO}(\text{g}) = \text{Ba}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

Conclusion

The mechanism of atomization of barium chloride is different from that of barium nitrate. Barium chloride is preferable to barium nitrate as the analyte because of its simpler atomization mechanism and higher sensitivity in GFAAS analysis.

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Faculty of Graduate Studies and Research
Department of Chemistry
Ph.D. Thesis Examination
Wednesday, May 31, 1989 at 10:00 a.m.
Room 115 Steacie Building

CANDIDATE:

Runde Guo
M.Sc. (Changchun Institute of Applied Chemistry,
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ppm, which is much higher than the range of Cu(II) concentration usually found in aqueous environmental samples.

When water samples contain significant amounts of Ag(I), Au(III), Hg(II) or Pt(II) ions, these ions can be separated from Pd(II) by adopting the methods described by Marczenko et al [67].

Tap water was used as the sample for the determination of its Pd(II) content by the present PAS method. The concentration of Pd(II) in tap water, however, was found to be below the detection limit of the method, i.e., less than 0.04 ppb. In a separate experiment, the recovery of 200 ng of Pd(II) added to 100 mL of tap water (which corresponded to 100 ng of Pd(II) in the solid film sample) averaged 96% in three replicate determinations.

(4) Conclusion

A technique has been developed to automatically prepare solid film samples for the PAS determination of trace amounts of Pd(II) in water samples after extraction with 0.005% dithizone solution in CCl_4 . The PAS method can be used to determine Pd(II) at a concentration of 0.04 ppb in an aqueous solution. Apparently there are still two approaches for improving the detection limit: (a) using a more powerful laser than the present 17-mW instrument as the excitation source and (b) employing a complexing agent that either forms a Pd(II) complex of higher molar absorptivity or permits a higher preconcentration factor than 100 in the extraction process.