Photoacoustic Surface Plasmon for the Detection of Nicotine.

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Photoacoustic spectroscopy (PA) in combination with the surface plasmon (SP) generated by attenuated total reflection (ATR) in Ag film has been employed as a sensor for selective detection of nicotine. The active material for the interaction with nicotine is a thin film of dioctyl phthalate (DOP) with nicotine-tetraphenylborate deposited on the Ag film to form nicotinum-tetraphenylborate. The angular scan for PA-ATR spectra shows a shift of the SP maximum coupling angle and a broadening of the Lorentzian line shape, due to the interaction of nicotine molecules with the active layer.

Introduction:

Recently, surface plasmon SP sensors has played an important role in the development of sensor technology. The development of chemical sensors for selective detection of analytes using SP is considered an important result in modern science. The combined photoacoustic PA spectroscopy with SP generated by attenuated total reflection ATR sensor offers a sensitive monitoring system for environmental testing of nicotine as a polluting agent[1]. Nicotine is the most abundant and potent pharmacological agent in tobacco smoke, it has a sedative effect and may eventually induce cancer diseases. The detection of nicotine has great relevance for health and clean environment [2],[3]. The SP is normally generated in Ag film via a prism coupler in a Kretschmann configuration [4]. PA spectroscopy is an excellent method for the study of non-radiative relaxation of surface plasmons in thin Ag film. The basic idea of the method is to place the SP sample to be investigated in a closed cell containing a gas or air and a sensitive microphone. The non-radiative transitions of SP is transferred as a heat to the gas in the cell. Since the SP is modulated by the chopper, the gas heating produces a pressure fluctuation within the cell which can be detected by the microphone as acoustic signal. This combined technique is termed PA-ATR spectroscopy and the generated signal is thus capable of probing directly non-radiative relaxations of surface plasmons occurring in thin Ag film, i.e., measuring the thermalized part of the generated SP. The PA generated signal S_{PA} can be expressed as[5]

$$S_{PA} = \alpha I_o A(\theta_i) \quad (1)$$

where I_o is the part of the incident laser power generating the SP, $A(\theta_i)$ is a function representing the angular scan, and α is just a constant, that depends on the environment in the cell, the sensitivity of the microphone and the chopping frequency. Consequently, the resulting S_{PA} signal has the same Lorentzian shape as a function of the angle of incidence θ_i in the prism, since it measures the damping of a generated surface plasmons that follow the Lorentzian shape. The dispersion relation for, the simplest case, surface plasmon propagating along the interface of the metal/air film is given by[6]

$$K_{sp} = (\omega/c)[(\varepsilon_m(\omega)\varepsilon_a)/(\varepsilon_m(\omega)+\varepsilon_a]^{1/2} \quad (2)$$

where K_{sp} is the complex SP wave vector, ω is angular frequency, c is the velocity of light, $\varepsilon_m(\omega)$ is the complex dielectric constant of the metal, ε_a is the dielectric constant of the ambient (~1).We have employed the PA-ATR technique as a tool for sensing the presence of nicotine gas.To carry out this detection, a thin add layer has to be deposited on the SP active Ag film that constituted the window of the PA cell.The deposition of the add layer to the Ag

film leads to a more complex dispersion relation of the generated SP. In this case, one has to use more detailed expressions that describe the coupling of SP in the case of four medium configuration (prism-metal-add layer-air), a wave vector K_T has to be added to the above simple case, and is given by[7]:

$$\mathbf{K_T} = \mathbf{i}\left(\frac{2\pi\, \mathbf{d}_l}{\lambda}\right)\left(\frac{\omega}{\mathbf{c}}\right)\left(\frac{\varepsilon_\mathbf{m}}{\varepsilon_\mathbf{m}+1}\right)^2 \frac{1}{(\varepsilon_\mathbf{m})^{1/2}(\varepsilon_\mathbf{m}-1)}\left(\varepsilon_l + \frac{\varepsilon_\mathbf{m}}{\varepsilon_l} - \varepsilon_\mathbf{m} - 1\right) \quad (3)$$

this added wave vector is proportional to the thickness of the slab d_l , and represent the perturbation due to the transition layer, ε_l is the dielectric constant of the add layer and λ is the wavelength of light in vacuum.

Experimental:

The PA cell consisting of a metal frame and an electrit microphone is shown in Fig (1). The angular scan PA-ATR spectroscopy was carried out to observe the resonance angle θ_{ATR} in Kretschmann configuration. The metal film at the base of the glass prism is placed into the PA cell at the center of a turntable of a converted x-ray (θ-2θ) diffractometer. The (θ-2θ) turntable has an angular resolution of 0.001^o. The chopped TM polarized laser incident on the PA cell produces periodically heat by the non-radiative relaxation of excited SP. Therefore, a periodic variation of the gas pressure in the sealed PA cell is produced, which can be detected by a sensitive microphone. The PA-ATR signal was measured by synchronized heterodyning techniques using the optical chopper and lock-in amplifier whose output is connected to PC- computer. The Ag films are of thickness (42.5±0.5 nm) and deposited at a rate of evaporation 1 nm/s to obtain a relatively smooth film [8]. The TM polarized radiation was incident from Ar^+ laser on the prism at four different wavelengths 457.9nm,472.7nm,488nm and 5145nm were used in these investigations. Poly(vinyl-chloride) (PVC) was dissolved in dioctyl phthalate (DOP) with nicotine-tetraphenylborate to constitute the membrane to be deposited on the metal film, which is selectively sensitive to nicotine [$C_{10}H_{14}N_2$]. Such a membrane is expected to interact with nicotine to form nicotinum-tetraphenylborate ion-pair $[C_{10}H_{14}N_2H]^+$, $[C_{24}H_{20}B]^-$ [9]. The actual weights used were 68.2 mg of PVC, 124 mg of the solvent mediator DOP and 2.9 mg of. nicotine-tetraphenylborate, then a sufficient amount of tetrahydrofurane (THF) was added and mixed to obtain a transparent solution. An amount of $4x10^{-2}$ml of this solution was dropped onto the Ag film and the THF was allowed to evaporate at room temperature leaving a membrane of nicotine-tetraphenylborate trapped in a PVC matrix of nearly 300 nm thickness. The nicotine smoke is then entered inside the PA cell .

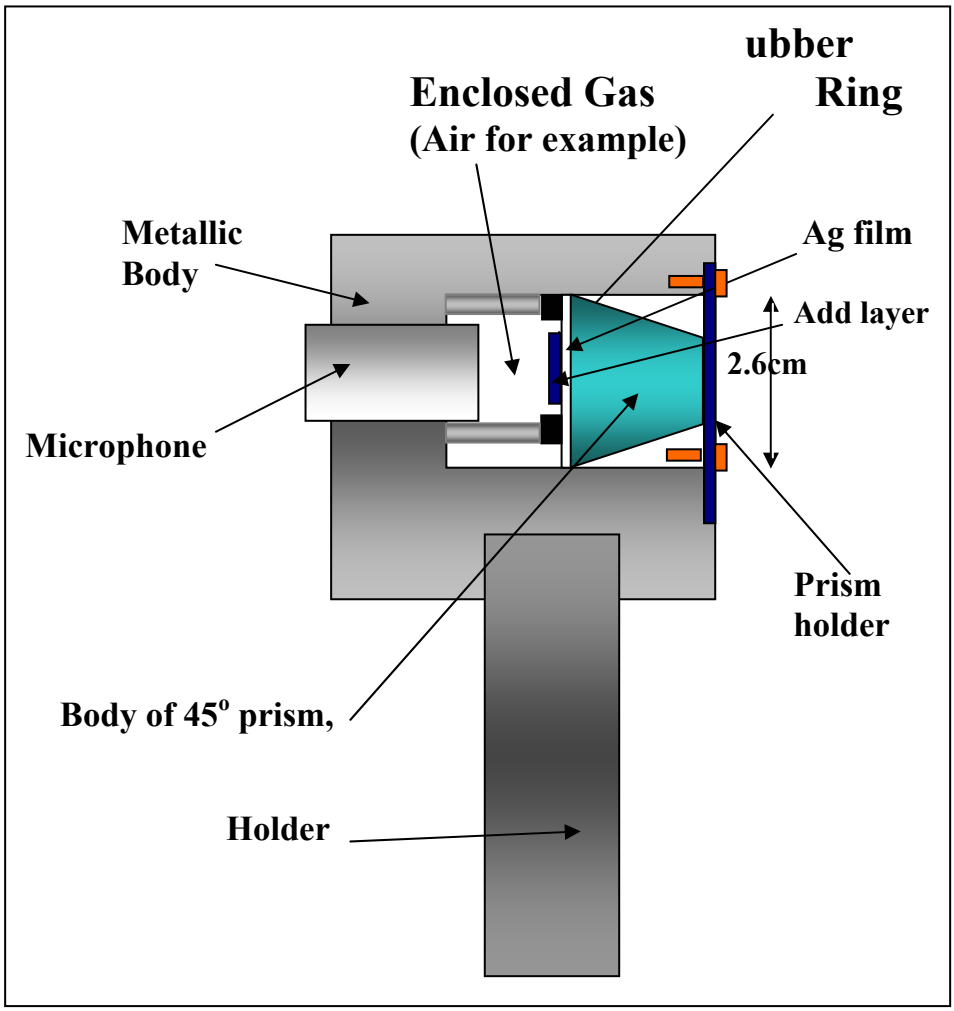

Fig. (1): Block diagram for PA-ATR Cell

Results and Discussions:

The angular PA-ATR spectrum of pure Ag film with thickness 42.5 ±0.5nm is presented in Fig (2) using TM-polarized light for four different wavelengths 457.9, 472.7, 488, and 514.5 nm. The PA spectrum shows a Lorentzian shape as a function of θ_i through the prism larger than the critical angle $\theta_c(41.3^o)$. On adding the nicotine-tetraphenylborate, it is observed that there is an angular shift in the resonance angle i.e., the change in the SP wave vector due to the presence of this unexposed add layer.In Fig (3), the angular scan for PA-ATR is shown, where the wavelength λ_i is 457.9 nm, the coupling angle is shifted from (46.21^o) to a larger value (46.65). The resonance half

width increases from a value (0.74^o) to a value (1.04^o). The calculated real part of the dielectric constant ε'_1 of this membrane is (3.55). The exposure of the film to the nicotine gas causes the coupling angle $\theta_{PA\text{-}ATR}$ to shift to a higher value (47.21^o) and a change in the amplitude of the peak. Furthermore there is an increase in the half width of PA-ATR peak to (1.68^o) due to the increase of the damping processes. The angular shfit shows a change due to the perturbation caused by the addition of the selectively sensitive layer (nicotine-tetraphenylborate). While the half width plays a significant role as an extremely sensitive and to the condition of the surface in characterizing the surface. The corresponding PA-ATR angular scan for the different wavelengths 472.7nm, 488nm and 514.5nm are shown in Fig(4), Fig(5), and Fig(6) repectively. The calculated values for the optical parameters for the add layer before and after exposure to nicotine gas are shown in Table (1).

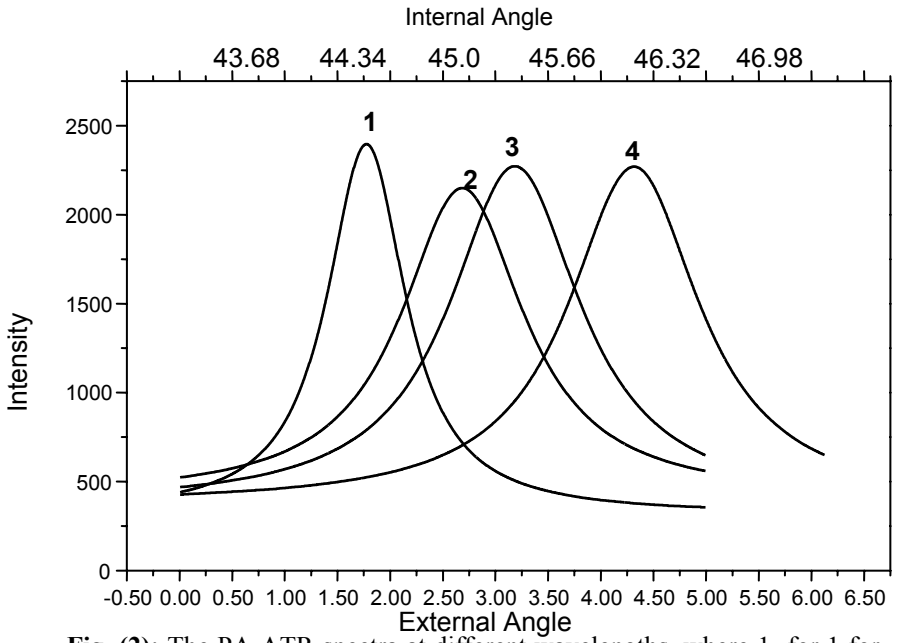

Fig. (2): The PA-ATR spectra at different wavelengths, where 1 for 1 for λ = 514.5 nm, 2 for λ = 488.0 nm, 3 for λ = 472.7 nm and 4 for λ = 457.9 nm.

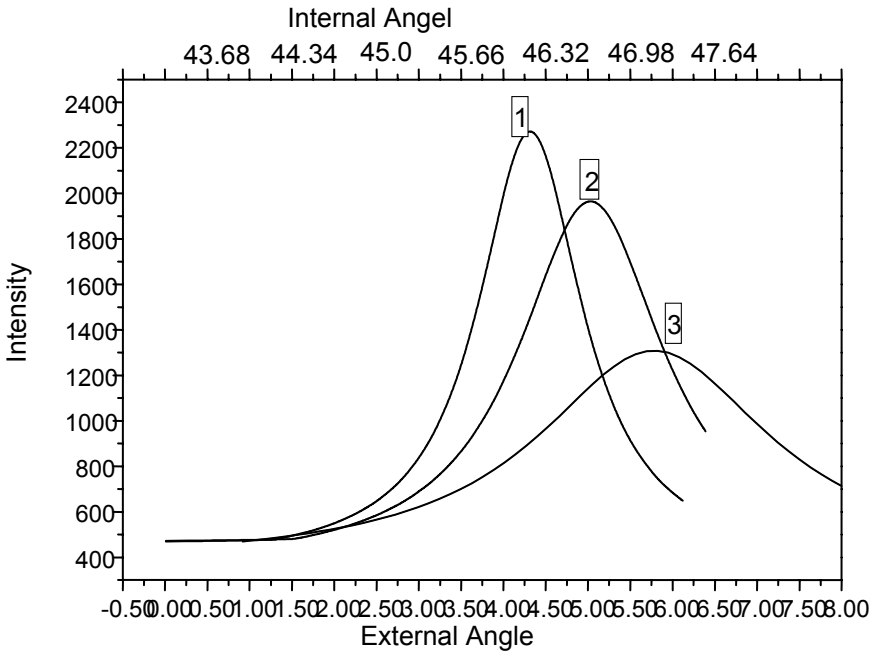

Fig. (3): The PA-ATR spectra at wavelength λ_i= 457.9 nm 1 is for the pure Ag, 2 for Ag + add layer (before exposure), and 3 after exposure.

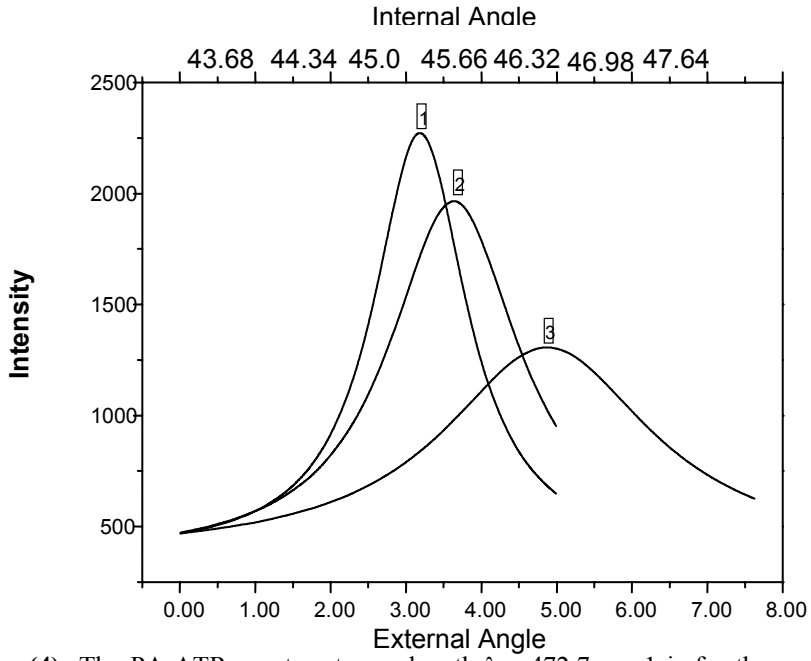

Fig. (4): The PA-ATR spectra at wavelength λ_i= 472.7 nm 1 is for the pure Ag, 2 for Ag + add layer (before exposure), and 3 after exposure.

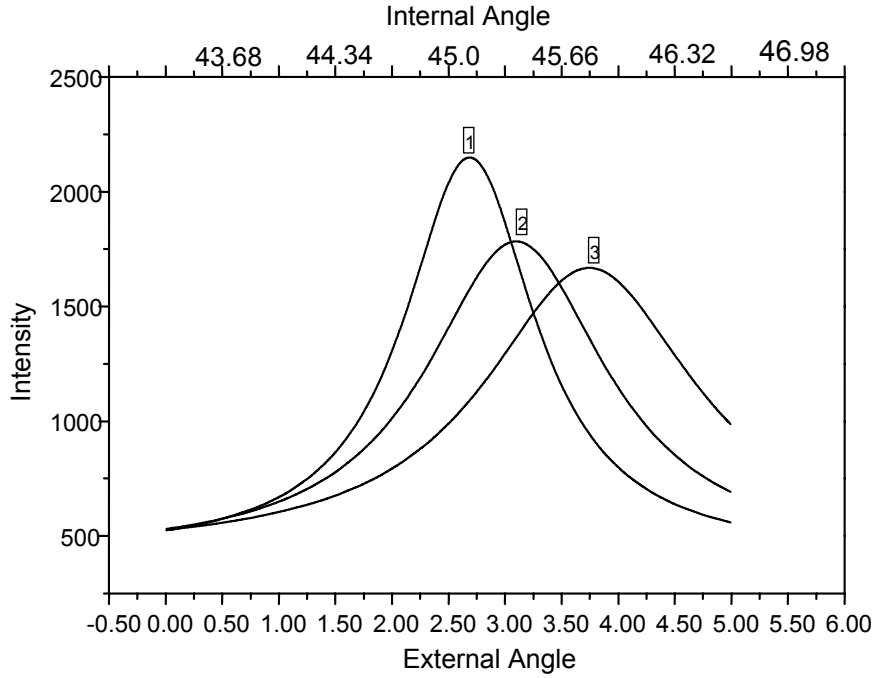

Fig. (5): The PA-ATR spectra at wavelength λ_i= 488 nm 1 is for the pure Ag ,2 for Ag + add layer (before exposure), and 3 after exposure.

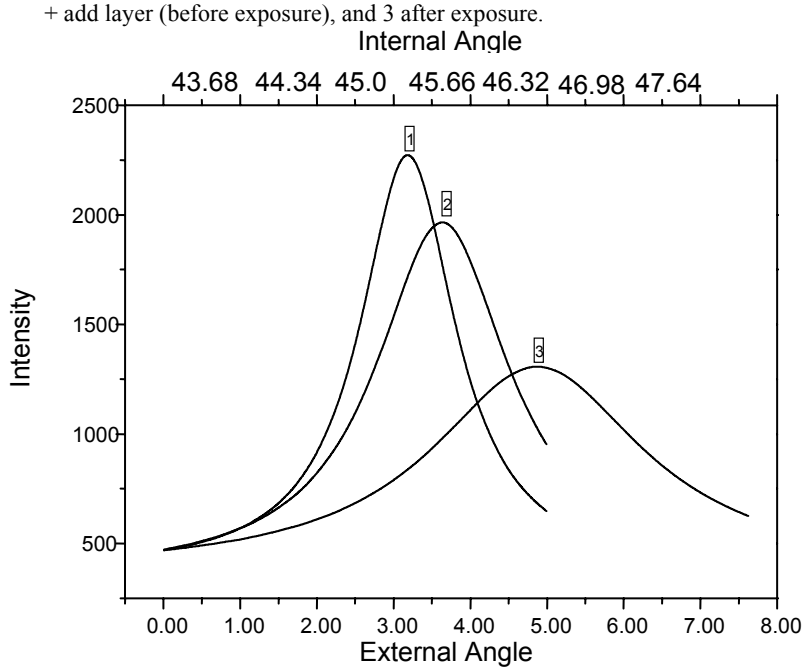

Fig. (6): The PA-ATR spectra at wavelength λ_i= 514.5 nm 1 is for the pure Ag, 2 for Ag + add layer (before exposure), and 3 after exposure.

Table (1): The optical parameters before and after exposure to nicotine gas

Add layer	λ nm	θ_{PA-ATR} ±0.05°	K' ±0.001x10^5 (cm)$^{-1}$	ε'_{Ag} ±0.469	ε'_l ±0.0417
Before	457.9	46.65	1.511	-6.125	3.5499
After		47.21	1.532		3.5190
Before	472.7	45.74	1.442	-7.042	3.6808
After		46.56	1.462		3.6422
Before	488.0	45.39	1.388	-7.555	3.7235
After		46.12	1.406		3.6845
Before	514.5	44.80	1.304	-8.786	3.5646
After		45.37	1.316		3.5210

From the above results and discussions one may conclude that the PA-ATR sensor for nicotine using (nicotine-tetraphenylborate)as a selectively sensing layer is comparable with the data produced by the SP resonance ATR technique. The technique also enabled us to determine the dielectric constant of the sensing layer before and after passing the nicotine gas. The PA-ATR sensor can be manufactured as a portable, foolproof device that is inexpensive and selectively sensitive to nicotine.

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