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Design and fabrication of silicon oxynitride based evanescent optical waveguide sensor for rapid detection of adulteration in petrol

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Abstract

In this paper we report on the design and fabrication of an Evanescent Optical Waveguide Sensor (EOWS) using silicon oxynitride (SiON) as the core layer on silica-silicon wafer and its implementation for rapid detection of adulterant traces in pure petrol incorporating composite planar waveguide geometry. The embedded waveguide of length ~ 10,000 μm and core width ~ 50 μm was fabricated using standard Plasma Enhanced Chemical Vapour Deposition (PECVD) technologies and Reactive Ion Etching (RIE) technique. The main aim of this work is to encompass an abrupt choice to the time-consuming existing adulteration detection methods which generally requires some time to give the consequence. Using Simple Effective Index Method (SEIM), the theoretical predictions and experimental results at wavelength 632.8 nm are analyzed and presented, which demonstrated that the sensitivity of the proposed EOWS is ~40 times more than that of the existing planar waveguide sensors and also 20 times more than that of asymmetric waveguide structure thereby allowing rapid detection of adulterant traces in pure petrol without involving the use of chemicals. It is found that the sensor structure is polarization independent and advantages include high sensitivity, easy fabrication and more importantly, requirement of very minimal amount of sample volume for detecting adulteration.

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Keywords: Adulteration; Evanescent waveguide; Optical sensor; Waveguide sensitivity; Simple Effective Index Method

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1. Introduction

Sensors based on integrated optic waveguide technology have received considerable attention in the recent years finding prospective applications in environmental monitoring, pharmacology and medicine [1], providing good compactness, immunity to electromagnetic interferences (E.I), high sensitivity and high compatibility with fiber optic networks. The principle of operation depends on the evanescent field of the guided mode that interacts with the sample (analyte) to be detected and essentially senses the changes in refractive index of the cladding/sensing layer. Although fiber optic sensor has shown all these advantages, it is not much promising with respect to efficiency and miniaturization. Although efforts have been made in the recent years to design and develop evanescent field optical sensors [2], it is seen that the precise sensing requires perfect modelling and design of the waveguide structure in which one has to consider the surrounding sensing region of the waveguide sensor accurately for enhancement of sensitivity. Adulteration of petroleum products is a major setback in developing country like India. Skyrocketing prices of petroleum product is not the only worry that the consumers are facing with, but the issue is the purity. Even after paying a good price for them, the rampant practise of adulteration of petroleum product has overwhelmed the Indian market. According to a report released in 2001 by the central pollution control board, Delhi our country is losing at least Rs. 10,000 crores annually because of fuel adulteration, but lately this figure has been estimated at over Rs. 30,000 crores which includes diversion of PDS kerosene and damages to vehicles as stated by Mishra et al. (2008) [3]. Roy (1999) [4] developed a technique for detection/estimation of adulteration of petrol/diesel by kerosene using optical fiber sensor.

In this paper, we illustrate the design and fabrication of silicon oxynitride (SiON) based Evanescent Optical Waveguide Sensor (EOWS) for the detection of adulteration in petrol using a mathematical model based on sinusoidal mode Simple Effective Index Method (SEIM). It is found that the theoretical predictions are in good agreement with the results obtained experimentally. The sensor is highly sensitive even for very low percentage of adulteration in petrol. More importantly, this optical waveguide based sensor developed requires very minimal amount of sample volume for its detection and further the sensor can be easily integrated with fiber optic network.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>n</td>
<td>refractive index of the medium</td>
</tr>
<tr>
<td>$N_{\text{eff}}$</td>
<td>effective refractive index</td>
</tr>
<tr>
<td>c</td>
<td>velocity of light in free space</td>
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### Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$\alpha, \gamma, \delta$</td>
<td>waveguide parameter</td>
</tr>
<tr>
<td>$\beta$</td>
<td>propagation constant</td>
</tr>
<tr>
<td>$\omega$</td>
<td>frequency</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>permeability in free space</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>permittivity in free space</td>
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### Subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
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<tbody>
<tr>
<td>C</td>
<td>core</td>
</tr>
<tr>
<td>S</td>
<td>sensing region</td>
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</table>

1.1. Composition of petroleum and prone to adulteration

Petrol, kerosene and high speed diesel (sub-product obtained from the fractional distillation of petroleum) is a mixture of organic volatile compounds, mainly hydrocarbons (83-87% of carbon and 11-15% of hydrogen) [5-7]. The petroleum fraction for petrol, kerosene and diesel is shown in Table 1.
The hydrocarbons present in the petroleum are divided into two main classes. Open chain or aliphatic compounds: comprising of n-paraffins series (CₙH₂ₙ-2), isoparaffin series (CₙH₂ₙ₊₂), olefin series (CₙH₂ₙ), ring compounds comprising of Naphthalene (C₁₀H₈) (derivative of cyclopentane and cyclohexane) and aromatic series or benzene series.

Adulteration takes its levy both in terms of the air pollution and loss in tax revenue and the primary cause of adulteration of petroleum products is the voracity fueled by differential tax system. The large price differences of petrol, kerosene and diesel have led to severe problem [8-12]. Although the government of India has given some specifications through the Bureau of Indian Standards (BIS) [13]; but in the recent years, due to the high demand and good price of petrol, it is very much prone to adulteration. With increasing consumption of petrol and diesel, people deliberately add cheaper products like kerosene [14-15] in venture to lift profit margins that results in sternly knocking down the automotive engines and thereby, decreasing the performance and boosting the environmental pollution. Adulteration is financially unattractive when less than (10%) while more than 30% [16] without doubt is likely to be detected by the user from the degradation of the performance of the engine caused by the adulterated fuel. The oil companies adds antiknock compounds like Tetra Ethyl Lead (TEL), (CH₃CH₂)₄Pb to increase the antiknocking property as reported by http://en.citizendium.org/wiki [17].

\[ 4\text{CH}_3\text{CH}_2\text{Cl} + 4\text{NaPb} \rightarrow (\text{CH}_3\text{CH}_2)_4\text{Pb} + 4\text{NaCl} + 3\text{Pb} \]  

(1)

Adulteration lead to increased tailpipe emission of hydrocarbons (HCs), carbon monoxide (CO), oxides of nitrogen (NOX), particulate emissions (PM₁₀, SPM) and emissions of air toxins such as benzene, methylbenzene and polyaromatic hydrocarbons which are well known carcinogenic compounds.

1.2. Methods for estimation of petroleum adulteration

Over the past it is seen that different methods and standards involving determination of physical and chemical properties are carried out for detection of adulterated petroleum products. As adulteration occurs mainly at some point of product delivery between refineries and fuel stations, this has endeavoured researchers to find procedures and techniques for detecting the adulteration level in order to prevent it from reaching the public. The American Society for Testing and Materials International (ASTM International) has developed and documented test methods for its detection including petroleum products. But such methods endure from limitations in terms of accuracy and sensitivity. Although different tests namely Density test (ASTM D4052), Evaporation test (ASTM D3810), Distillation test (ASTM D86), Chemical Marker test, Gas Chromatography (GC) may be used to determine the adulteration; however these methods are not suitable in the context that: (a) For density measurement of the fuel, ASTM D4052 requires expensive instruments like Hydrometers and digital densitometers and need a controlled environment, the overall sensitivity of this method is rather poor, (b) ASTM D3810, which is a laboratory based method, (c) ASTM D86 measurement process is time consuming, (d) requirement of an user friendly equipment in GC for interpretation of the result. In addition, there are other methods like ultrasonic techniques [9], titration techniques [10-11], optical technique [12] but the above mentioned methods endure from limitations in terms of accuracy and sensitivity to determine the adulteration levels.
In the present work an attempt was made to address the problem by the design and fabrication of an Evanescent Optical Waveguide Sensor (EOWS) of length ~10,000 μm and core width ~50 μm incorporating composite planar waveguide geometry. Using silicon oxynitride (SiON) as the core (guiding) layer, the proposed sensor was adapted for rapid detection of adulterant traces in pure petrol using kerosene and diesel as the adulterant with high waveguide sensitivity ~4.1. The adulteration is defined as the percentage (v/v) of kerosene and diesel in petrol.

2. Adulteration detection using Evanescent Optical Waveguide Sensor (EOWS)-A new method

2.1. Design and working principle

We consider a waveguide structure as depicted in Fig. 1 consisting of a guiding (core) layer of Silicon Oxynitride (SiON) [Refractive Index (R.I), \( n_c=1.46 \)], deposited on silica-on-silicon substrate and sensing region of refractive index, \( n_s \), as a cladding and an outside medium (air) with refractive index \( n_{air} \) that is less than R.I of core.

The refractive index profile of the waveguide structure (as shown in the Fig. 2.) is given by:

\[
n(x) = \begin{cases} 
    n_c & ; \quad 0 \leq x \leq x_1 \\
    n_s & ; \quad x_1 < x \leq x_2 \\
    n_{air} & ; \quad x > x_2
\end{cases} \tag{2}
\]

where \( x_1 = \) half width of core and \( x_2-x_1 = \) sensing region width.

The starting point for the analysis of the three layered embedded waveguide sensor structure as illustrated in Fig. 1, is the Maxwell’s equations [18] with an \( \exp[i(\omega t-\beta z)] \) dependence of the electric and magnetic field vectors and the wave equation is obtained as:

\[
\frac{d^2 E_y}{dx^2} + \left[k_0^2 n^2(x) - \beta^2\right]E_y(x) = 0 \tag{3}
\]

where

\[
k_0 = \omega \left(\mu_0 \varepsilon_0\right)^{1/2} = \frac{\omega}{c}
\]

Light propagation is described by an “Effective Index Method”, \( N_{eff} \) of the waveguide, which is related to the propagation constant \( \beta \) of guided modes in the waveguide as:

\[
\left(N_{eff}\right) = \frac{\beta}{k_0} \tag{4}
\]
Fig. 1. 3D view of the planar optical waveguide sensor with sensing region placed on the top of silica on silicon substrate.

Fig. 2. xz plane view of the waveguide core showing the refractive index profile.
The change of the refractive index of the cladding layer results in the change in effective refractive index of the modes propagating in the waveguide sensor structure. Based on the Simple Effective Index Method (SEIM) [19], the following dispersion relation [20-21] corresponding to the TE mode of the waveguide is obtained as:

\[
\alpha_x x_1 = m \pi + \text{Cot}^{-1} \left( \frac{\cosh \alpha_x x_2 + \left( \frac{\gamma(C)}{\alpha_2} \right) \sinh \alpha_x x_2}{\alpha_1 \left( \frac{1}{\gamma(C)} - \frac{1}{\alpha_2} \right) \sinh \alpha_x x_2} \right)
\]

(5)

where \(\gamma(C) = \sqrt{\beta^2 - k_0^2 n_s^2(C)}\)

and \(n_s(C)\) is the refractive index of sensing region depending on concentration \(C\) of the adulterant.

The most important quantity when speaking about optical sensing is the power flow inside the different layer of the optical waveguide. The sensitivity of the sensor is critically dependent on the fraction of total power propagating inside the core of the waveguide. From the dispersion relation, given by Eq. (5), after some tricky mathematical calculations, the following expression for the estimation of normalized power remaining inside the waveguide core along the z-axis is obtained as:

\[
W(z) = W'(0) e^{-2\gamma(C)z}
\]

(6)

where

\[
W'(0) = \left( \frac{0.0018}{n_s(C) - 1.3315} \right) W(0) ; \quad W(0) = \left( \frac{k^2 \pi^2}{\Gamma(C)^2} \right)
\]

\[
\Gamma(C) = \frac{4 \alpha_x x_2 \gamma_x (x_2 - x_1)}{\beta_x x_2 \delta(C) x_2 (1 + \gamma_x x_1)}
\]

\[
\alpha_x = \sqrt{k_0^2 n_s^2 - \beta_x^2}, \quad \gamma_x = \sqrt{\beta_x^2 - k_0^2 n_s^2(C)}, \quad \beta_x = \sqrt{k_0^2 n_s^2 - \alpha_x^2}
\]

\[
\delta(C) = \sqrt{\alpha_1^2 + \gamma(C)^2}
\]

2.2. Sensitivity response

From the dispersion relation given by Eq. (5), the waveguide sensitivity \(S_w\) (i.e. the rate of change of effective refractive index \(N\) with respect to refractive index \(n_s\) of the sensing medium) is obtained as:

\[
S_w = \frac{\delta}{\delta n_s(C)} \left( \frac{\beta}{k_0} \right)
\]

(7)
The sensitivity of the proposed waveguide sensor is analyzed for detection of adulteration in pure petrol using kerosene and diesel as the adulterant. Fig. 3 shows the sensitivity of the waveguide sensor versus core refractive index ($n_c = 1.45$) for different core width ($2x_1$) of the waveguide. It is seen that sensitivity increases slightly with increase of $n_c$ and independent of waveguide core thickness. This is because the sensing area does not increase with increase of $n_c$ and $x_1$. Further it is found that the sensitivity is enhanced by ~40 times more than that of the existing planar waveguide sensors [22] and also 20 times more than that of asymmetric waveguide structure [23].

![Image](image.png)

**Fig. 3.** Waveguide sensitivity versus $n_c$ of the proposed waveguide structure with different core width ($2x_1$).

### 2.3. Fabrication and experimental results

Herein reported work, application of silicon oxynitride (SiON) as the waveguide material was mainly provoked by its excellent optical properties such as high transparency, good stability and adjustable refractive index (i.e. refractive index of SiON can be easily adjusted over a large range, i.e., between 1.45 ($\text{SiO}_2$)–2.0 ($\text{Si}_3\text{N}_4$)). This offers the litheness in choosing the refractive index of this material for designers of integrated optical devices.

The waveguide sensor structure was fabricated on thermally oxidized $<100>$ Si wafers. The embedded SiON waveguide core of width ~50 μm was deposited by plasma enhanced chemical vapour deposition (PECVD) and the refractive index was tailored by controlling different gas concentrations (SiH$_4$, N$_2$O, and NH$_3$). The waveguide patterns are transferred by standard photolithography, developed and etched by reactive ion etching (RIE) using CF$_4$ and O$_2$. Fig. 4 shows the SEM image of sensor planar waveguide of length ~10000 μm. The fabricated planar waveguide was placed inside a cylindrical enclosure (CE) with efficient butt couplings between the input fiber to waveguide sensor and waveguide to output coupling fiber to reduce the fiber/waveguide coupling losses during our experimental work.
To detect petrol adulteration, the designed and fabricated waveguide sensor using SiON technology with core refractive index 1.46 was housed within a cylindrical enclosure (CE) as shown in Fig. 5. Light from a He-Ne laser of wavelength 632.8 nm was focused onto the sensor using focusing lens by means of optical fiber and the output signal from the waveguide sensor is guided by an optical fiber for detection of the same to the optical detector placed at the other end. The normalized powers $W(z)/W(0)$ for detecting the adulteration have been measured using the experimental setup as shown in Fig. 5, where $W(0)$ is measured with distilled water in the sensing region.

At first the designed sensor was placed inside the cylindrical enclosure (CE) having planar waveguide inside and then validated its characteristic by measuring the normalized powers using distilled water (DI) as reference solution. The length of the waveguide within the CE is unclad such that the waveguide is directly in contact with the analyte that is, the adulterated sample under test (cladding/sensing layer). The output signal is measured from the other end of the sensor using an optical power meter. The refractive indices of petrol, kerosene and diesel as measured using an Abbe refractometer are found to be 1.419, 1.436 and 1.461 respectively. Fig. 6 shows the measured normalized power versus kerosene concentration for petrol-kerosene and petrol-diesel-kerosene determining the concentration of adulterant in petrol.
3. Conclusion

In this paper, the design and fabrication of an evanescent optical waveguide sensor (EOWS) with high sensitivity using a mathematical model based on sinusoidal mode simple effective index method (SEIM) was reported for rapid detection of adulteration in pure petrol. The theoretical results are in good agreement with the results obtained experimentally. Owing to its enhanced accuracy (up to three decimal) and high waveguide sensitivity of ~4.1 compared to the earlier reported works [22-23], the proposed waveguide sensor allows spot determination of adulteration in pure petrol without involving the use of chemicals. Advantages include high sensitivity, easy fabrication and more importantly, requirement of very minimal sample volume for detecting adulteration.

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