# Agent Reactive Modulated Optical Reflector for Hazardous Agent Detection

A. E. Kovalev[*], M. G. Bray[**], T. S. Mayer[***], and D. H. Werner[****]

*Pennsylvania State University, University Park, PA, USA, Email: axk46@psu.edu
**Pennsylvania State University, University Park, PA, USA, Email: mgb144@psu.edu
***Pennsylvania State University, University Park, PA, USA, Email: tsm2@psu.edu
***Pennsylvania State University, University Park, PA, USA, Email: dhw@psu.edu

## ABSTRACT

Early detection of chemical and biological agents from standoff distances has significant practical importance. The Agent Reactive Modulated Optical Reflector (ARMOR) approach described in this paper has the potential to provide a long-range eye safe detection solution by producing an extremely large change in the near infrared (NIR) reflection from micrometer to centimeter-scale devices with exposure to a wide range of chemical agents, toxic industrial chemicals (TICs), and volatile organic compounds (VOCs). The ARMOR is based on a Salisbury Screen Absorber (SSA) extended to the NIR range. We fabricated and characterized device prototypes that exhibited more than a 20 dB difference in reflection contrast following a 2 sec exposure to 2000 ppm of HCl vapor.

*Keywords*: standoff, infrared, sensor, hazardous

## 1 INTRODUCTION

There is growing interest in standoff detection of chemical and biological agents [1] at optical and NIR wavelengths. With passive techniques, the detector evaluates the signal from the object and compares the radiation from the object to that from the background. The source of the radiation is the object itself or other natural sources. The standard detection scheme for the passive sensing is IR spectroscopy [2]. With active sensing, the object or area is illuminated by an auxiliary beam. The active detection methods that are commonly used include laser induced breakdown spectroscopy, Raman spectroscopy, laser induced fluorescence, and variations of these approaches [3].

In each of these methods, the detected signal intensity drops with a decrease in the analyte vapor concentration. This makes detection of the dilute vapors difficult, especially at long standoff distances. In this paper, we describe a new ARMOR sensor platform that has the potential to provide long-range standoff detection of analyte vapor mixtures at low concentrations and volumes. The intensity of the detected signal will depend on the number of sensing elements per unit volume, and the concentration of the vapor will determine the response time.

## 2 PRINCIPLE OF OPERATION

The ARMOR sensor is based on the SSA as shown on the Figure 1. The classical SSA consists of a thin resistive layer of material with a sheet resistance $R_s = 377$ $\Omega/\square$, a dielectric spacer with thickness equal to one quarter of the wavelength at the center of the absorption band, and a metal layer. At normal incidence, the SSA that has an infinitely thin resistive layer provides complete absorption of the incident light at the center wavelength. An increase in the reflection will be observed if the thickness of the resistive layer is not negligibly small in comparison to the wavelength within the layer.



Figure 1. The classical Salisbury Screen Absorber design.

Modulating the sheet resistance of the topmost resistive layer of the SSA with exposure to the analyte vapor gives a large change in the reflected signal from the surface. In the two limiting cases, where the resistive layer is either nearly insulating or metallic, the surface will completely reflect the incident light. In the first case, this occurs by strong reflection from the backing metal layer, while in the second case the reflection is from the top highly conductive layer. It can be shown that -3 dB refection for normal incidence will occur when the thin resistive layer has $R_s$ equal to 60 or 2200 $\Omega/\square$. Thus, the reflection from the SSA can vary greatly even if the sheet resistance of the top layer changes only by several times.

A sheet resistance in the range of 100's $\Omega/\square$ at NIR frequencies can be obtained using many materials including conducting polymers. For example, the IR conductivity of conducting polymers such as polyaniline ranges from 100-1000 S/cm, which means that the resistive layer can have thickness < 100 nm. In addition, polyaniline can change its NIR conductivity by several orders of magnitude in the presence of bases or acids [4].

## 3 EXPERIMENTAL

### 3.1 Fabrication

The operation of the ARMOR sensor platform was demonstrated by fabricating and characterizing the optical response of prototype devices that had an active area of 1 x 1 cm$^2$. The devices were fabricated by depositing a 150-nm thick gold reflecting layer onto a silicon handle wafer. A silicon nitride (Si$_3$N$_4$) dielectric layer was deposited on top of the Au reflecting layer at 300°C using inductively coupled plasma enhanced chemical vapor deposition (ICP-PECVD). The Si$_3$N$_4$ film thickness and refractive index (~1.8) were measured using a Woollam M-2000® spectroscopic ellipsometer. The topmost polyaniline conductive polymer layer was deposited by spin casting directly over the Si$_3$N$_4$ dielectric layer.

The highly conductive polyaniline films were obtained following standard protocols for combining 10-camphorsulfonic acid (10-CSA)/m-cresol [5]. All of the chemicals were purchased from Sigma-Aldrich Co. Specifically, 200 mg of polyaniline emeraldine base powder (molecular weight ~100,000) and 200 mg of 10-CSA powder were separately dissolved in 10 ml of m-cresol and stirred for about an hour. The solutions were mixed together and were stirred for 12 hours. The resulting mixture was centrifuged to separate the large sediments.

The polyaniline solution was spin coated on the Si$_3$N$_4$ layer at 1000 rpm for 1 min. After spinning, the devices were immediately placed on a hot plate at a temperature of 100°C and baked for 1 min to evaporate the solvent. Then the devices were washed for about 1 min in a weak solution of ammonia in acetone to de-dope the polyaniline thin film. This process was also used to fabricate large numbers of 100×100 μm$^2$ ARMOR chaff elements for aerial dispersion. A dark field optical microscope image of these chaff elements is shown in the Figure 2. This fabrication process is compatible with high throughput manufacturing techniques used in back-end semiconductor processes as well as larger-format antireflection coatings.
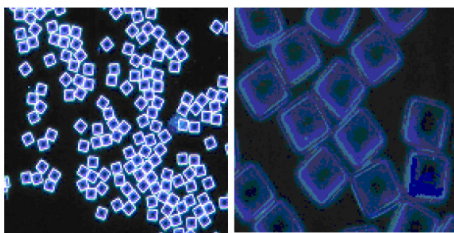


Figure 2. Dark field optical microscope images of fabricated 25 × 25 μm$^2$ ARMOR elements.

### 3.2 Measurements

The sensitivity and the response time of the devices were measured by exposing the ARMOR sensor to 2000 ppm HCl acid vapor (the lowest lethal concentration for humans is 1300 ppm in 30 min). Figure 3 shows the measured reflected signal before and after exposure to the HCl vapor. When the device is exposed to the HCl vapor, the polyaniline resistive layer undergoes a transformation from an insulating (high impedance) to a conducting state (~ 377 Ω) and the reflectance changes from –1 dB to –25 dB at the design wavelength of 1.5 μm. The device responded in < 2 sec following exposure to 2000 ppm of HCl vapor.
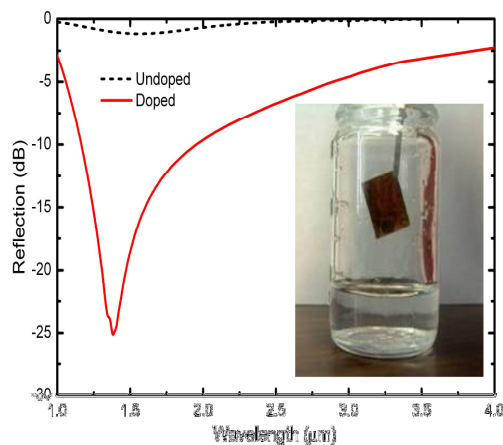


Figure 3. Plot of reflected power vs wavelength. The ARMOR was exposed to 2000 ppm of HCl vapor for 2 sec. Black dashed line corresponds to the spectrum before exposure, while the red solid line follows exposure. Inset: Device exposed to vapor from 24% water HCl solution.

## 4 CONCLUSIONS

The ARMOR platform has the potential to monitor the presence of chemical vapors from long-range standoff distances. The devices undergo a transition from the highly reflective to the highly absorbing state at a 1.5$\mu m$ detection wavelength with exposure to HCl vapor. The NIR reflected power changed by > 20 dB at the detection wavelength, which corresponds to more than a 99% change in the reflected signal.

### ACNOLEDGEMENTS

### REFERENCES

[1] "Chemical and Biological Standoff Detection III", ed. by J. O. Jensenand and J.-M. Thériault, SPIE 5995, 2005.
[2] H. Lovie, *et al.,* SPIE, 575, 96, 2005.
[3] R. M. Measures, "Laser Remote Sensing, Fundamentals and Applications", Krieger Publishing, 1992.
[4] U.-W. Grummt, *et al.* Anal. Chem. Acta., *357*, 253, 1997.

[5] A.G. MacDiarmid and A.J. Epstein. Synth. Met., *65*, 103, 1994.