# Ozone Sensing Properties of $NbO_2$ Thin Films for Health and Safety Applications

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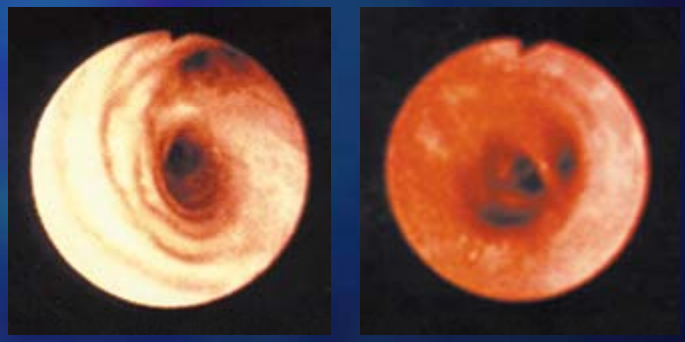
# Introduction

- Ozone ($O_3$) measurement for air quality monitoring and atmospheric research is largely carried out by spectroscopic (Figure 1) or electrochemical methods [1].
  - These techniques are very accurate and sensitive to atmospheric ozone concentrations but require expensive equipment as well as a high degree of expertise for correct operation and subsequent data interpretation [2].
- Since ozone has very low allowable limits of < 100ppb (Table 1), very high sensitivities and selectivity are required to avoid cross – interference with other oxidizing gases, such as, $NO_2$, $SO_2$ and $Cl_2$, which normally occur at much higher concentrations [3].

Figure 1. Mass Spectrometer

# Introduction

- Ozone has been classified as a dangerous pollutant by regulatory bodies around the world
- Ozone can have serious adverse effects on human heath, in both the immediate and long term
  - Immediate effects include coughing, wheezing, difficulty breathing, pain when breathing, airway inflammation, aggravated asthma or other respiratory diseases, increased susceptibility to respiratory infection.
  - Long term effects include accelerated aging of the lungs, diminished lung capacity, decreased lung function, aggravated asthma, bronchitis and emphysema.
- Ozone can inflame the lining of the lungs. Figures 2(a) and (b) illustrate a healthy lung airway (a) and an inflamed lung airway after exposure to ozone (b).



(a) (b)

# Table 1. Effect of Ozone on Human Health

| Ozone Concentration (ppm) | Effect on human health |
|---|---|
| 0.001 | Too small to accurately measure. Considered to be harmless |
| 0.003 – 0.010 | Can be detected by the average person |
| 0.040 | Maximum limit of emissions for household devices |
| 0.100 | Human exposure should not exceed 8 hours per day |
| 0.300 | Causes nasal and throat irritation for short exposure periods |
| 0.500 – 2.00 | Causes nausea, headache and chest pain |
| 5.00 – 25.00 | Dangerous to health, maximum exposure time of 2 hours |
| 25.00 + | Immediately hazardous to human life |

# Introduction

- Recently, a great deal of research has been directed toward the development of small dimensional gas sensors for practical applications ranging from toxic gas detection to manufacturing process monitoring [3].
- Using metal oxides has many advantages such as simplicity in device structure, low cost of fabrication, robustness in practical applications and adaptability to a wide range of reducing and/or oxidizing gases.
- The gas detection technique is primarily based on a change in the electrical resistance of the semi-conducting metal oxide layer.
- Most of the current metal oxide gas sensors on the market operate at elevated temperatures from 200 – 600 C.
- Therefore room temperature operation is a very desirable characteristic and offers many advantages such as reduced fabrication and operating cost.

# Niobium Oxide

- Niobium Oxide has been extensively studied due its broad range of applications [4]. It is widely used in catalysts, gas sensors, electrochromic devices and optical fibres.
- Particular attention has been focussed on the use of niobium oxide as an oxygen sensor, where its conductivity decreases when oxygen partial pressure is increased [5].
- Among the niobium oxides $Nb_2O_5$ is gaining popularity for gas detection applications and is a very promising material for the development of integrated gas sensors.
- Table 2 shows a range of Niobium oxide based gas sensors currently being utilized for the detection of a number of gases, also shown are operating temperatures and response times for each sensor.

# Table 2. Niobium Oxide Based Gas Sensors

| Material | Target Gas | Operating Temperature | Detection Limits | Response Time | Refs. |
|---|---|---|---|---|---|
| $Nb_2O_5$ | CO, $NH_3$ | 450 – 500 | 100 – 1000 ppm | ~ 3min | [6] |
| $Nb_2O_5$ | $NH_3$ | 500 | 100 – 1000 ppm | ~ 4min | [7] |
| $Nb_2O_5$ | $C_2H_5OH$ | 500 | 2.1 % | < 1min | [8] |
| $Nb_2O_5$ | $NH_3$, CO | 400 – 500 | 100 – 1000 ppm | ~ 4min | [9] |
| $Nb_2O_3$ | DMA, TMA, $NH_3$ | 300 – 640 | - | - | [10] |

# Coating System

- An Edwards E306A Coating System (Figure 3) was used for the fabrication of the sensor electrodes and oxide layer via the Vacuum Thermal Evaporation (VTE) process.
- The system contains an Edwards FTM5 quartz crystal to monitor the rate of deposition and the film thickness
  - The mass deposited on the crystal surface during the evaporation process alters the natural frequency of vibration of the crystal, from which the deposition rate and thickness can be determined.
- The Edwards Coating System is also equipped with a 550 – Watt rotary pump and an E040 diffusion pump capable of achieving a vacuum of $6.5 \times 10^{-7}$ mbar with the assistance of a liquid nitrogen trap facility.

Figure 3. Edwards E306A Coating System

# Sensor Preparation

- Interdigitated structures (IDS) are commonly used as a basis for gas sensitive layers [11].
  - The advantage of sensors based on this structure is the simple and cheap fabrication process and the ability to use the sensor in a wide range of applications without crucial changes to the sensor design [12].
- The IDS is an arrangement of two comb electrodes interlocked into each other.
- For the electrical properties measurements, copper (Cu) electrodes were manufactured on the substrate via the thermal evaporation technique.
  - A Cu layer was first deposited on the substrate, the Cu layer was then coated with photoresist (Az5214) and allowed to cure in air for 24 hours before partial exposure to UV light in order to trace the desired electrode pattern, after the exposure the substrate was placed in a developer solution and then rinsed in cool water before being placed in the etching solution (SEMO 3207 fine etch crystals) which reveals the IDS electrode pattern. Finally the substrate was re-exposed to UV and developed for a further 20 – 30 seconds to remove the excess photoresist.

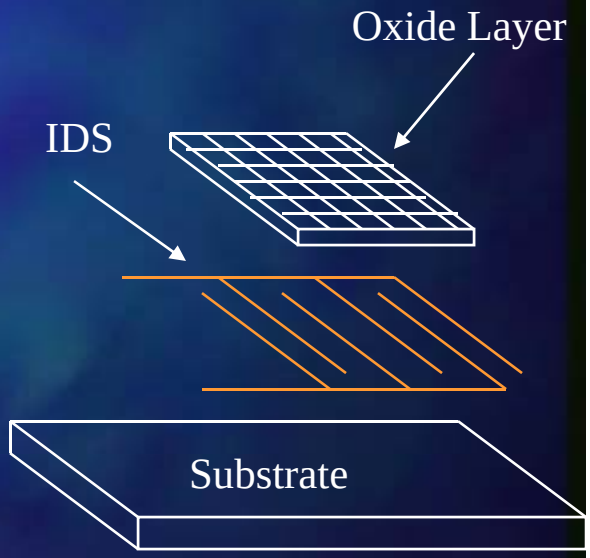



Figure 4. Sensor Structure

# Sensor Preparation

- The deposition of the thin metal oxide layer was performed via the vacuum thermal evaporation technique.
- Niobium oxide ($NbO_2$) was placed in a modified tungsten boat and heated under high vacuum conditions ($6 \times 10^{-7}$ mbar).
- Current was passed through the tungsten boat until the desired evaporation rate was reached
- The vapour phase was condensed on the substrate which was placed directly above the evaporation source.
- Once the desired thickness was reached the current flowing through the boat was switched off and the process stopped.
- During the evaporation the substrate was held constant at a temperature of 300 C.
- The sensing layer was deposited over the IDS structure in a rectangular patter covering an area of 2mm x 3mm.
- The substrate was allowed to cool to room temperature before being exposed to atmospheric conditions.

# Experimental Procedure

- The test chamber consists of a Teflon base covered by a detachable Teflon structure containing inlet and outlet valves, allowing the gas to flow directly over the sensing layer.
  - The flow rate was controlled via a mass flow controller and during testing was held constant at a rate of 0.25l/min. The temperature inside the test chamber was also held constant at room temperature.
- Ozone was generated by pumping oxygen through a quartz tube under exposure from a UV lamp.
  - Ozone concentration was controlled by the oxygen flow rate and via a metal shutter enclosing the UV lamp.
- The ozone concentration was calibrated with a UV analyzer.
- A thurlby multimeter was used to measure and record the variations in resistance of the sensor on exposure to ozone
  - Readings were automatically recorded over short time durations

# Optical Properties

- The analysis of the optical absorption spectra has been one of the most important productive tools for understanding and developing the theory of the electronic structure of amorphous materials.
  - In general, thin films prepared via the thermal evaporation technique are amorphous.
- The optical energy gaps $E_{OPT}$ for as-deposited and exposed to ozone films were determined from the high absorption regions of the fundamental edges using the Mott and Davis model [13].

$$\alpha(v)h\,v = B(h\,v - E_{OPT})^{n}$$

- Figure 5 shows the plots of the optical absorbance spectra at UV-Vis wavelength range for the thermally evaporated $NbO_2$ film.
  - As-deposited and exposed to 3 ppm of ozone for 1 and 2 hours.

# Optical Properties

- It can be seen from Figure 5 that no appreciable changes in the optical properties were recorded in the wavelength range from 300nm – 340nm.
- While from 340nm – 1000nm the effect of ozone exposure manifested itself as a change in the optical density of the metal oxide film.
  - The greatest effect was seen after exposure for 1 hour with the effect decreasing with continuous exposure.

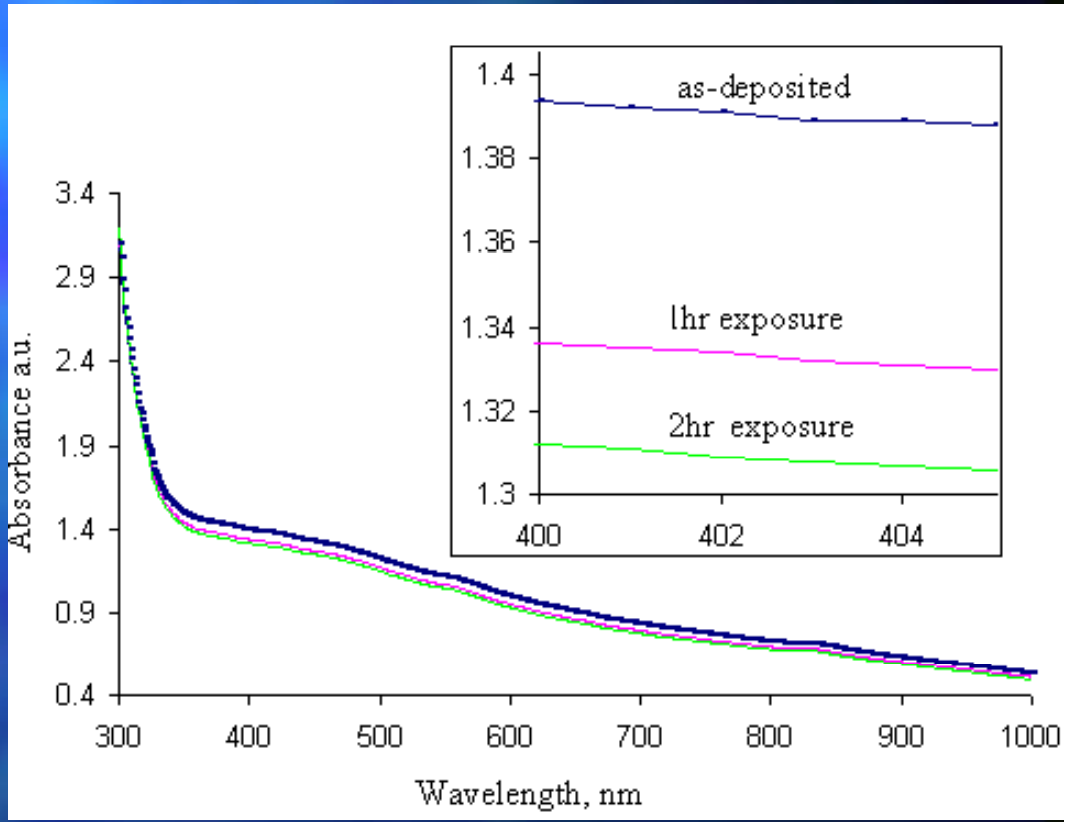



Figure 5. Optical absorbance spectra for 120 nm of $NbO_2$ for as-deposited, 1 and 2 hour ozone exposure

# Optical Properties

- The change in the optical density is associated with the changes in the optical band gap, as can be seen from Figure 6.
- Using the Mott and Davis Theory [13], the estimated optical band gap for the as-deposited film was 3.66 and increased to approximately 3.68 after the film was exposed to 3 ppm of ozone for 1 hour.

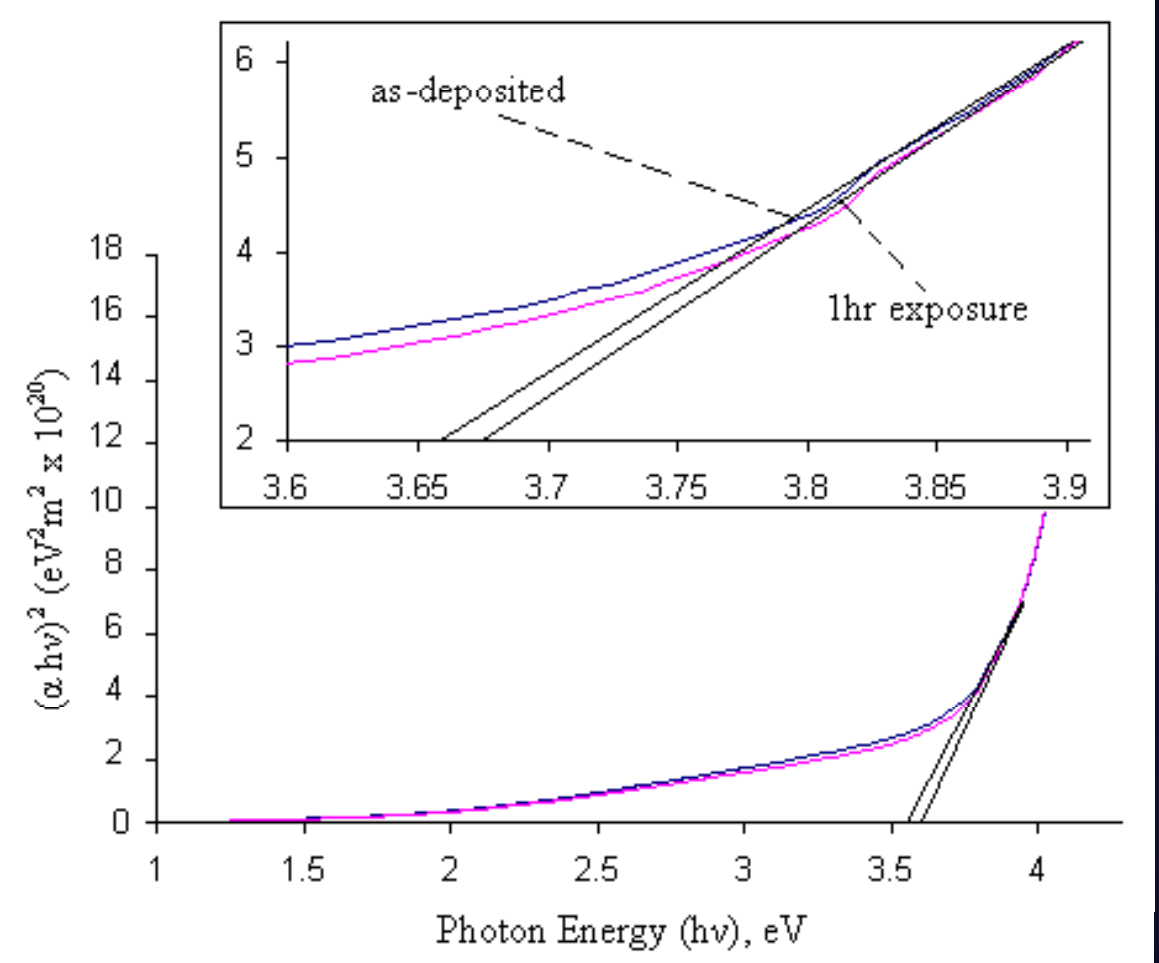



Figure 6. Plots of $(\alpha h\nu)^2$ versus photon energy h u for as–deposited and exposed to ozone for 1hour

# Sensor Performance

- The principal detection process is the change of the oxygen concentration at the surface of the metal oxide, which is caused by the adsorption and heterogeneous catalytic reaction of oxidizing and reducing gaseous species [5].
- There is a finite density of electron donors and/or acceptors bound to the surface of the semiconducting oxide.
  - The electron donors/acceptors cause the formation of surface states followed by an exchange of electrons within the interior of the semiconductor thus forming a space charge layer close to the surface. By changing the surface concentration of these donors/acceptors, the conductance of the space charge region can be modulated.
- The result is that n-type oxides increase their resistance when oxidizing gases are present and decrease resistance when reducing gases are present.
  - In contrast to n-type, p-type oxides decrease resistance for oxidizing gases and increase resistance for reducing gases.

# Sensor Performance

- Sensor response was calculated using the following relationship: $R_{TAR}/R_{REF}$, where $R_{TAR}$ is the measured resistance upon exposure to 240 ppb ozone and $R_{REF}$ is the measured resistance prior to ozone injection.
- Figure 7 illustrates the response of a 120 nm sensing layer deposited at a rate of 10–12nm/sec to environmentally relevant ozone concentrations (240 ppb)
- The sensor responds well to 240 ppb ozone, however, the recovery of the sensor is poor and it fails to return to baseline resistance.

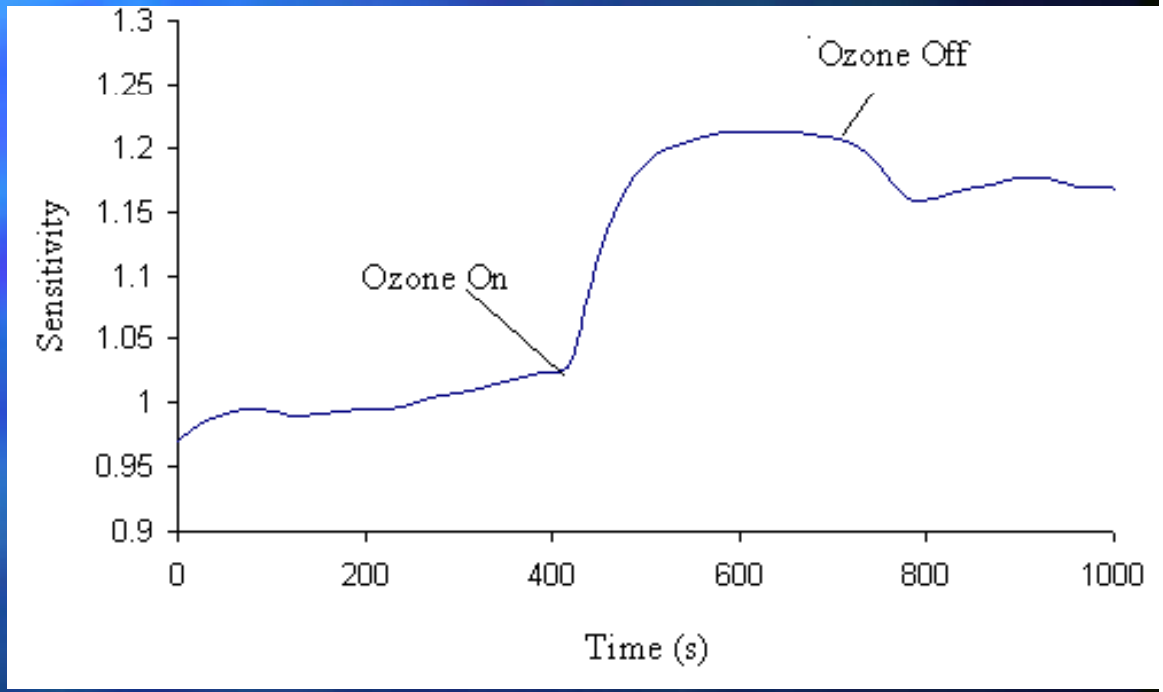



Figure 7. Response curve of 120nm $NbO_2$ sensing layer to 240ppb ozone

# Sensor Performance

- Figure 8 illustrates the response of a 70 nm thick sensing layer deposited at a rate of 10 – 12 nm/sec at a pressure of 5 x10 $^{-6}$ mbar.
- The sensitivity of the device is greatly increased by reducing the thickness of the sensing layer.
  - Reducing thickness from 120 nm to 70 nm results in a 30% increase in response to 240 ppb ozone.
- It is suggested that strongly oxidizing gases immediately interact with the outermost layer of the film, producing a resistivity change.
- This effect will influence the conductance of a thin film layer more than that of a thicker film.

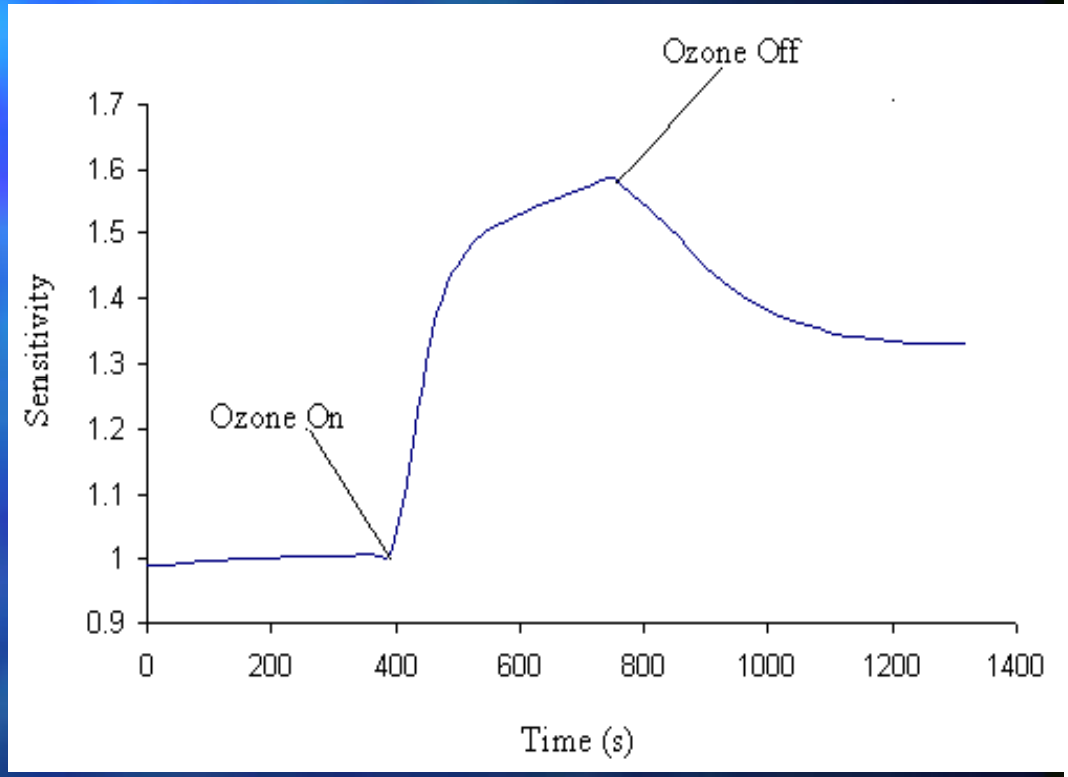



Figure 8. Response curve of 70nm $NbO_2$ sensing layer to 240ppb ozone

# Conclusions

- This work has shown that thin films of $NbO_2$ are very promising candidates for use as real time ozone sensors.
- Thin films of $NbO_2$ were prepared using the Vacuum Thermal Evaporation Technique (VTE).
  - In general thin film sensors respond very easily towards strongly oxidizing gases.
- These films were found to be sensitive to environmentally relevant ozone concentrations (in the ppb region) while operating at room temperature.
- Most of the current metal oxide based ozone sensors operate at elevated temperatures.
- Room temperature operation offers many advantages over elevated temperature operation such as; reduced fabrication costs, reduced operation costs, reduced power consumption, and ease of implementation into portable/handheld devices

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# Thank You


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