

FINAL REPORT

“SERS RAMAN SENSOR BASED ON DIAMETER-MODULATED SAPPHIRE FIBER”

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EXECUTIVE SUMMARY

Surface enhanced Raman scattering(SERS) has been observed using a sapphire fiber coated with gold nano-islands for the first time. The effect was found to be much weaker than what was observed with a similar fiber coated with silver nanoparticles. Diameter-modulated sapphire fibers have been successfully fabricated on a laser heated pedestal growth system. Such fibers have been found to give a modest increase in the collection efficiency of induced emission. However, the slow response of the SERS effect makes it unsuitable for process control applications.

The objective of this Phase I project was to examine the feasibility of fabricating a Surface Enhanced Raman Scattering(SERS) probe from a diameter-modulated sapphire fiber coated with Au nanoparticles. The rationale for using this combination is that both sapphire and gold are highly resistant to harsh chemicals, and thus hold promise as components for a practical probe. The idea of diameter modulation as a signal enhancement mechanism came from our earlier observation that the fluorescence from a dye coupled into a sapphire fiber with random diameter modulation can be almost as strong from the side as from the end. It was envisioned that the proposed SERS probe may find use in process control in the chemical industry.

There were two main components to this project. First, experiments were performed to identify the best way to coat sapphire fiber with Au nanoparticles. The procedures investigated were dipping the fiber in a colloidal suspension of Au nanoparticles and coating the fiber with a thin film of gold followed by heat treatment to form Au nano-islands. The second part was to develop a technique for growing sapphire fibers with periodic diameter modulation and then assess the extent of signal enhancement by collecting light from the side as well as the end of the fiber.

To check the adequacy of the Raman spectroscopic system we assembled , it was decided to use a probe coated with Ag nanoparticles

first, since the latter is known to produce a larger enhancement than Au nanoparticles.[1] The colloidal Ag was prepared as follows. First, 27mg of AgNO_3 was combined with 150ml of DI water in a flask, which was then topped with a condenser. The mixture was heated on a hot plate set at 300°C while being stirred. When the mixture came to a boil, 30mg of trisodium citrate dissolved in 3ml of DI water was added. After heating for another 90 min, the hot plate was turned off and the colloidal Ag was allowed to cool to room temperature while being stirred.

To immobilize the Ag nanoparticles on the probe, one end of a polished 300um sapphire fiber was first sonicated in acetone for 10min. It was further cleaned by soaking in 0.1mg/ml solution of KMnO_4 in H_2SO_4 for 1hr. After a thorough rinsing in DI water, the cleaned fiber was dipped in 2% v/v APTMS(3-aminopropyl trimethoxysilane) solution with 95% ethanol and 5% DI water for 5min. After rinsing with ethanol, the probe was allowed to dry in air for 24hrs. Then following further rinsing with methanol and DI water, the probe was dipped into freshly prepared colloidal Ag for 24 hrs. The Ag nanoparticle coated probe was finally stored in DI water for later use. An SEM image of a sapphire fiber coated with Ag nanoparticles is shown in Fig.1. Charging effects limited the resolution of the image, but it can be seen that the particles were no larger than about 100nm. Also, it is seen that the coverage is only on the order of 1%.

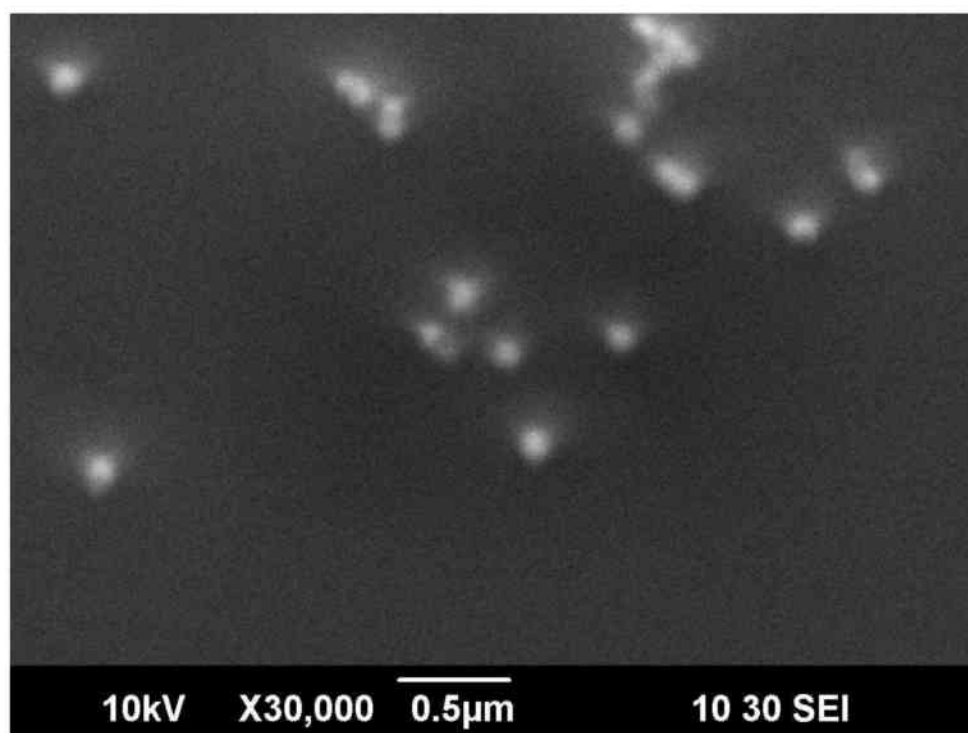


Fig. 1

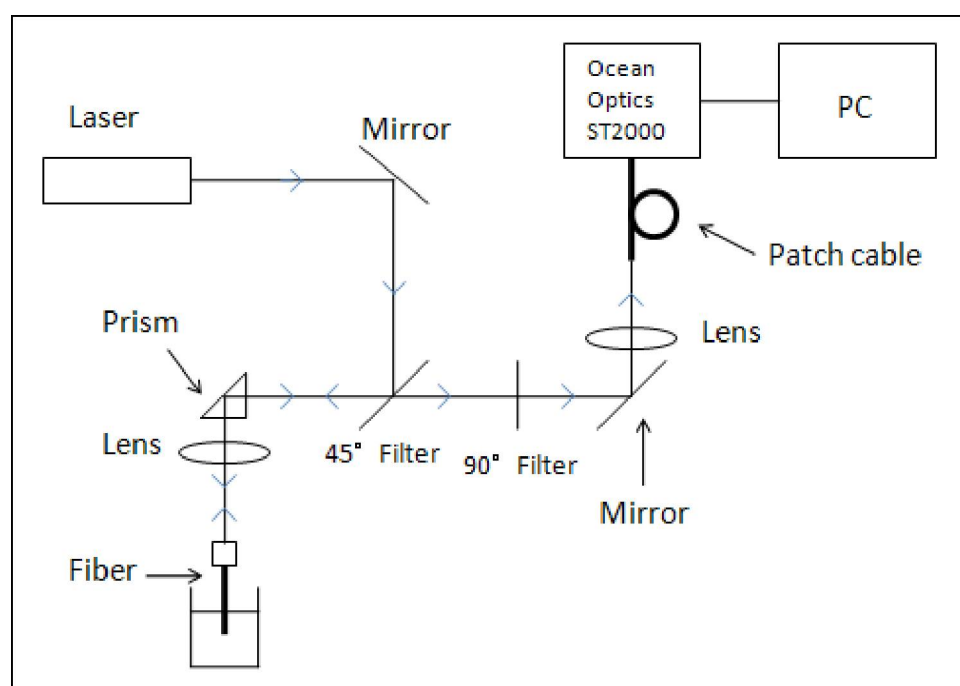


Fig. 2

A schematic of the experimental set-up used in the Raman

measurements is shown in Fig.2. All the sapphire fiber probes used had diameters and lengths of approximately 300 μ m and 5cm. The laser used for the probe coated with Ag nanoparticles had a wavelength of 532nm and an output power of 6mw. Both the 45° and 90° filters were long-pass edge filters which blocked the laser wavelength and passed those approximately 300 cm^{-1} or more to the red of that of the laser. The sample used was 10^{-8} M R6G in water. The emission spectra from the probe are shown in Fig.3. The lower and upper traces correspond to immersion in the dye solution for 2 and 10hrs respectively. The broad peak covering the entire range shown is due to fluorescence from the dye. The two outer peaks of the triplet narrow peaks on the left are due to Raman scattering in the sapphire fiber with shifts of 417 cm^{-1} and 750 cm^{-1} . The middle one of the triplet as well as all the peaks on the right are SERS signals from the dye. The Raman shifts obtained match closely those reported in the literature.[1][2][3] It is seen that all the Raman peaks due to R6G nearly double with the additional soaking of 8hrs. The fluorescence signal also increases somewhat, to a much lesser degree, presumably as a result of adsorption of dye molecules on the uncoated part of the fiber's end. The slight increase in the sapphire Raman peaks can be explained by resonant reflection of the pump light by adsorbed dye molecules on the uncoated part of the fiber's end.

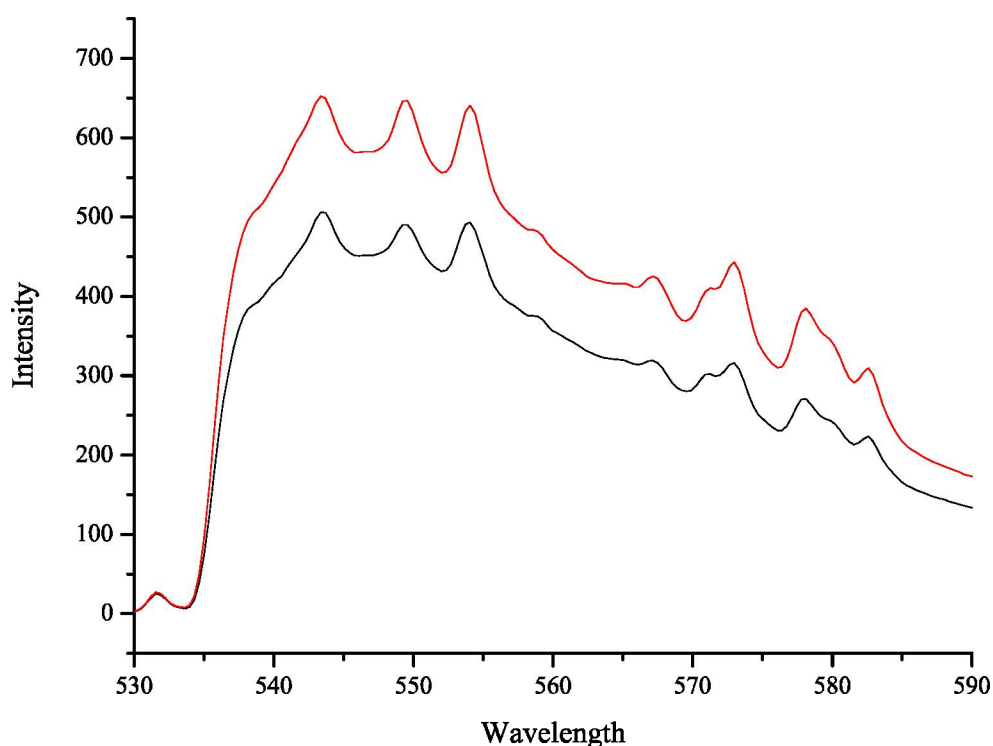


Fig. 3

Following this preliminary work, we proceeded to characterize probes coated with Au nanoparticles. Two kinds of commercial colloidal Au nanoparticles, with diameter centered at 5nm and 73nm, were tried. The immobilization procedure used was the same as that for Ag nanoparticles. The coverage obtained, however, was only 0.01-0.1%. Evidently, the greater chemical inertness of Au nanoparticles made their adsorption on sapphire more difficult. When the emission spectra from these probes in 10^{-8} M R6G were analyzed, no Raman peaks were discernable. The strong fluorescence signal from the dye precluded the use of samples with higher concentrations.

We then turned our attention to the preparation of probes covered with Au nano-islands. Gold films with thickness of 15nm and 30nm were evaporated onto the ends of polished 300um sapphire fibers. The coated fibers were then heated in an Ar atmosphere to temperatures of 500°C, 600°C, and 700°C using a cycling profile of 1hr ramp-up, 2hrs at maximum temperature, and 1hr of ramp-down. An example of the heat treated probe is shown in Fig. 4. The experimental arrangement used to evaluate these nano-island-coated films was the same as described before, except the source was changed to a 633nm He-Ne laser with an output power of 5mw (and the edge filters replaced to correspond to that wavelength), in order to avoid the strong fluorescence from the dye.

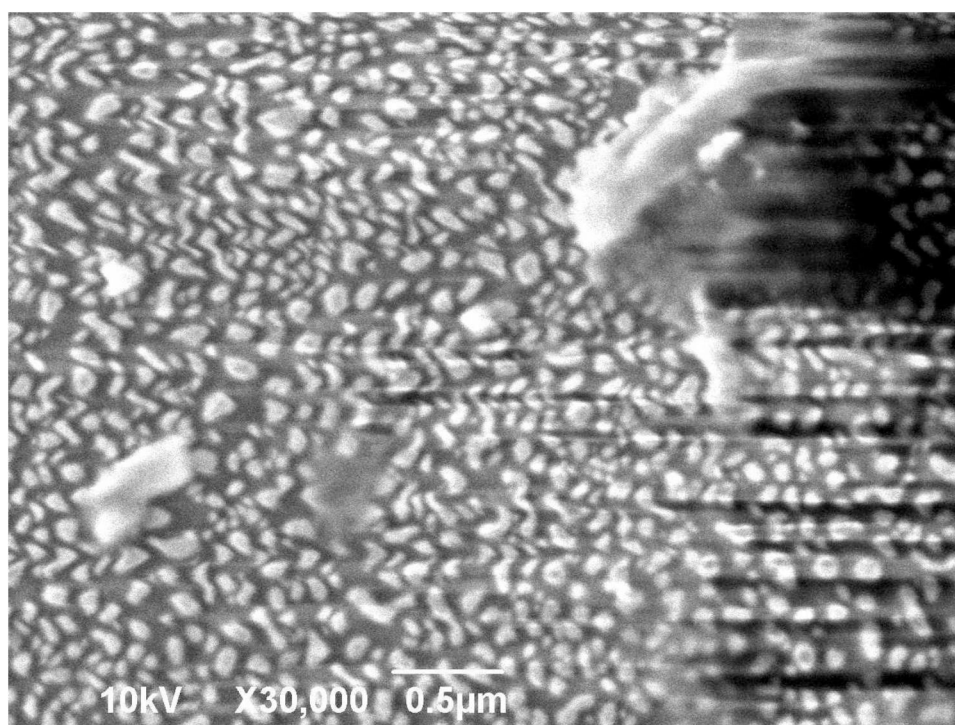


Fig. 4

Raman signals from the R6G dye solution was not noticeable until

the concentration was increased to 10^{-2}M . The data obtained from a fiber with a 15nm coating of Au heat treated at 700°C are shown in Fig. 5. From bottom to top, the traces correspond to the probe in air, a few minutes after immersion in the dye, and 12hrs later. As before, the two peaks on the left are from Raman scattering in the fiber. The peaks at 694nm and 706nm on the right are due to plasma lines from the He-Ne laser. It can be seen that between these two lines three distinct peaks developed between the time immediately after immersion of the probe in the dye and 12hrs later. It is also seen that the 694nm peak has grown substantially during that time. Indeed, when the spectrum taken in air is subtracted from those taken in the dye, a prominent peak is revealed as shown in Fig. 6. In fact, this peak corresponds to the dominant 1370cm^{-1} Raman line that has been observed in all earlier studies.

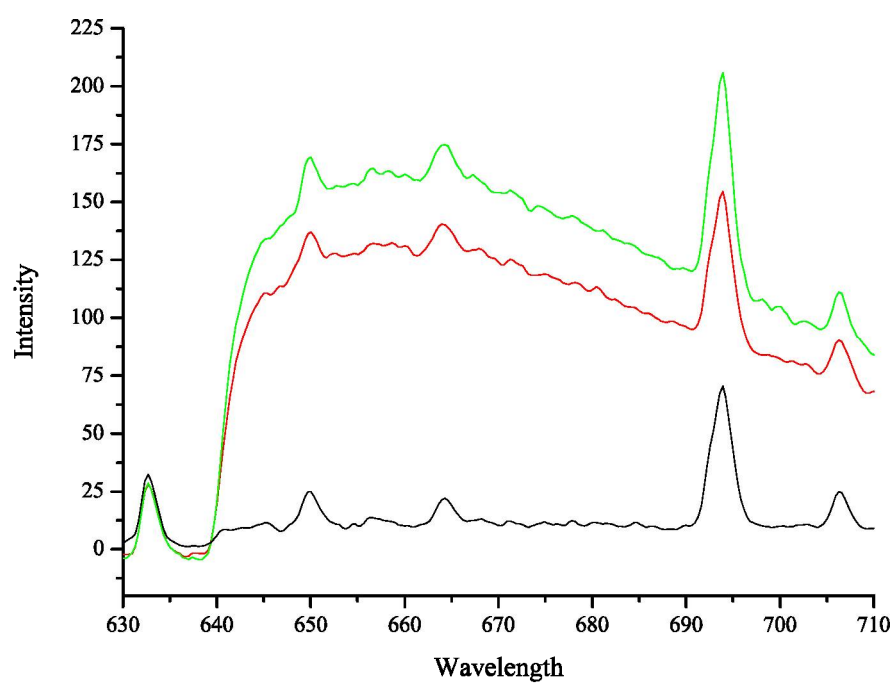


Fig. 5

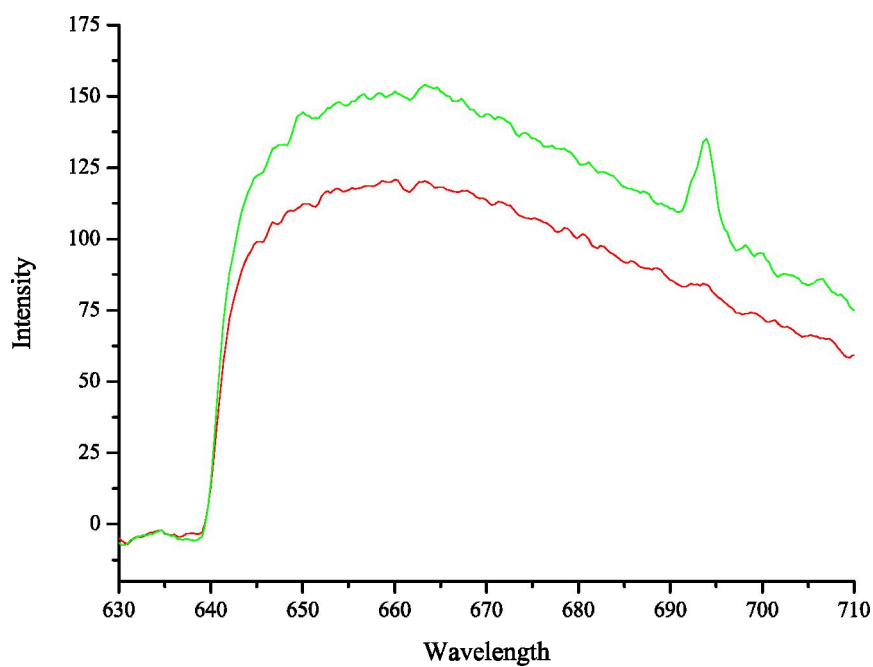


Fig. 6

Concurrent with the SERS investigations, the growth of sapphire

fibers with diameter modulation was underway using MMI's laser heated pedestal growth system. It was found that the lag time between programmed and actual tapers dictates a modulation period of at least 4mm, largely independent of the growth speed. Also, in order to have a pronounced modulation, one must effect a periodic variation in the temperature of the molten zone through modulating the power of the laser along with the programmed diameter reduction ratio. One period of a fiber with the deepest modulation we were able to achieve is shown in Fig. 7, indicating a maximum diameter of 300um and a minimum diameter of 240um.

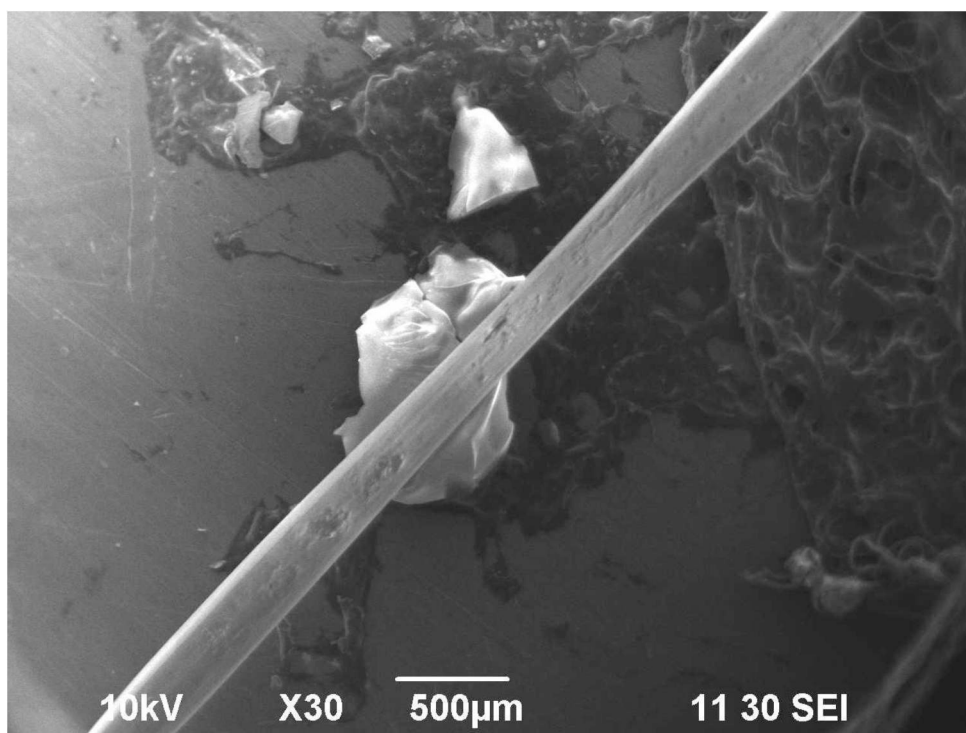


Fig. 7

To study the effect of side coupling in a modulated sapphire fiber, the change in fluorescence signal with increasing number of periods

immersed in the dye was measured. The results are shown in Fig. 8. It is seen that with each additional period immersed, the signal increased by approximately 15%.

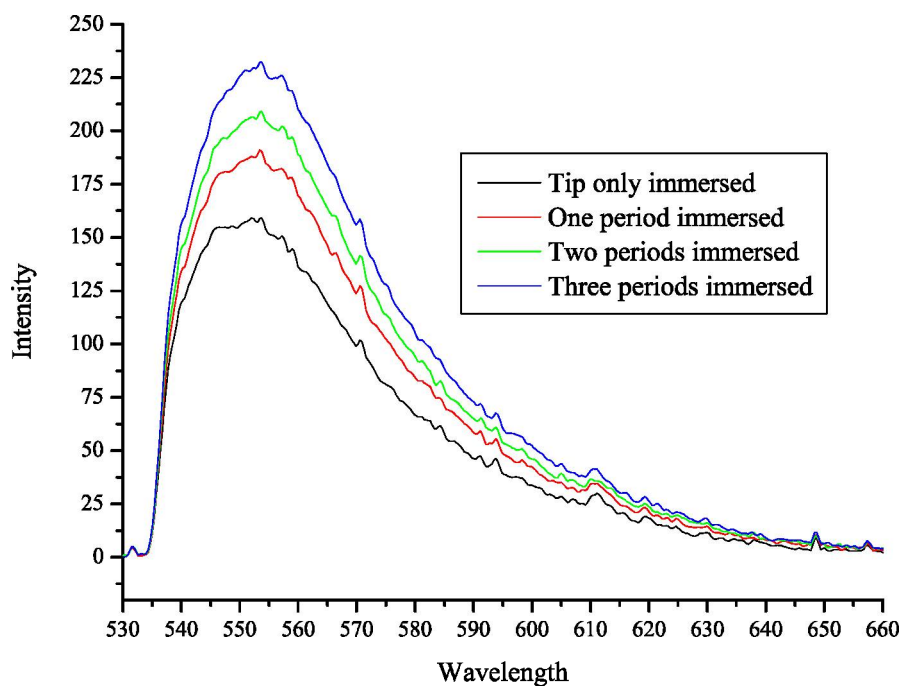


Fig. 8

In conclusion, in this Phase I project we have demonstrated the enhancement of the collection efficiency of a fiber-optic emission probe through side coupling as a result of diameter modulation. We have also observed for the first time the SERS effect using a Au nano-island-coated sapphire fiber. However, the response of the effect was found to be exceedingly slow. This makes such a sensor impractical for chemical process control applications.

References:

- [1]A. M. Schwartzberg, C. D. Grant, A. Wolcott, C. E. Talley, T. R. Huser,
R.Bogomolni, and J. Z. Zhang. J. Phys. Chem. B 108, 19191(2004).
- [2]A. Lucotti and G. Zerbi. Sensors and Actuators B 121, 356(2007).
- [3]L. Maya, C. E. Vallet, and Y. H. Lee. J. Vac. Sci. Technol. A 15, 238(1997).