Sensing and Bio-Sensing Research 11 (2016) 37–44

Contents lists available at ScienceDirect

Sensing and Bio-Sensing Research

journal homepage: www.elsevier.com/locate/sbsr

# Gold nanoparticles encapsulated in a soda-lime glass substrate for plasmonic temperature sensing

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ARTICLE INFO

*Article history:*
Received 14 March 2016
Received in revised form 7 October 2016
Accepted 11 October 2016
Available online xxxx

*Keywords:*
Localized surface plasmon resonance
Au nanoparticle
Pure temperature sensing
Fully encapsulation

ABSTRACT

We present a study on the temperature response of the plasmon peak of gold nanoparticles (AuNPs) completely encapsulated in soda-lime glass for temperatures ranging from 298 K to 723 K and in ambient pressure air, Ar and aqueous environments. The observed peak position changed with temperature in a linear manner, as expected from the theoretical model also presented in this study. The linear character was upheld in different gaseous environments of inert Ar and ambient air, as well as in both pure deionized water and acidic water. The consistent expected dependence provided proof of the versatility of the encapsulated AuNPs and their robustness to be able to withstand both high temperature and high acidity and still retain their sensing capability.



## 1. Introduction

Sensors that rely on the principle of localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs) have gained popularity in chemical and biological applications due to its tenability, label-free sensing, and sensitivity [1–5]. Extensive studies on the ability for LSPR-based sensors to operate at high temperatures have already been established [6], but no pure temperature sensor has been developed. The temperature effect of noble metal NPs has been studied [6,7], but these studies are normally done with NPs embedded in porous silica matrix, which will not be able to isolate a chemical effect in ambient environments.

The plasmonic properties of AuNPs are sensitive to changes in temperature due to three effects: 1) electron-phonon scattering in the NP, 2) thermal expansion of the NP, and 3) temperature dependence of the dielectric permittivity of the host matrix [6,7]. From the Drude model (Eq. (1)), the peak frequency of the plasmon peak position, Ω, is shown to be strongly influenced by the free electron density of the NPs (N / R [3]), where N is the number of free electrons and R is the radius of the NPs. Ω is also influenced by e, the elementary charge, $\varepsilon_m$ the dielectric function of the matrix surrounding the NPs, $\chi^{ib1}$ (the real part) the interband transition dependence of the dielectric function of the NPs, γ the damping constant, $m_e$ the electron mass and $\varepsilon_o$ the vacuum permittivity [8].

$$\Omega = \sqrt{\frac{Ne^2}{(1+2\varepsilon_m+\chi^{ib1})m_e 4\pi\varepsilon_o R^3} - \gamma^2} \quad (1)$$

The damping constant is given by

$$\gamma = \gamma_\infty(T) + A\frac{V_F}{R} \quad (2)$$

where $\gamma_\infty$ is the size-independent damping constant resulting from the scattering of electron with electron, phonon, and lattice defects, A is a theory-dependent parameter detailing the scattering process, and $V_F$ is the Fermi velocity in bulk metal ($1.29 \times 10^8$ cm/s for gold). For changes in the peak position of the plasmon resonance, a change in the size of the NP due to thermal expansion will reduce the free electron density of the NP, thus, causing a red shift in the plasmon band towards longer wavelengths. Electron-phonon scattering and changes in the dielectric permittivity are also affected by an increase in temperature but cause only minor shifts towards redder wavelengths of the plasmon band. The full width at half maximum (FWHM) of the plasmon band is also affected by an increase in temperature and generally broadens as a result, with electron-phonon scattering being the dominant contribution in the increasing FWHM with temperature. This theory was proven to

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http://dx.doi.org/10.1016/j.sbsr.2016.10.003

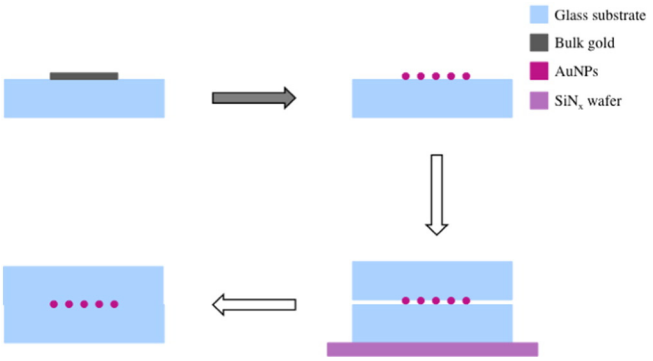


**Fig. 1.** Fabrication process for the embedded sample.

hold under experimental testing with AuNPs of various sizes in a silica matrix [7].

Theoretically, both temperature and chemical effects influence the LSPR properties of AuNPs. Composition of the surrounding environment will cause shifts in the peak position of the Au plasmon peak, a principle that has been traditionally used for plasmonic chemical sensing at high-temperatures [6,9]. By eliminating this chemical effect, a pure temperature measurement can be created that relies on this popular LSPR-based sensing mechanism. Isolation of the AuNPs from ambient environments by fully embedding the particles in a glass matrix can prevent chemical effects on the NPs, allowing for the development of a pure temperature sensor that can be used in different environments [6].

## 2. Experimental

Two samples of AuNPs embedded in glass were prepared to study the temperature dependence of the LSPR of Au. One sample was a shallow-embedded sample of AuNPs in a 1-mm thick piece of soda-lime-silica glass and the other sample was a deep-embedded sample of AuNPs sandwiched between two pieces of the same type of glass. A 5 nm-thick Au thin film was thermally evaporated onto the glass and then annealed at 400 °C for 10 min to form the AuNPs on the surface. To create either the shallow-embedded or the deep-embedded AuNPs, the sample was further annealed at a higher temperature without or with being placed with another piece of 1-mm thick soda-lime glass. The pieces were annealed on a $SiN_x$ coated silicon wafer at 660 °C, well above the glass transition temperature of 540 °C for soda-lime glass, for 6 h in static air. This allowed the AuNPs to sink into the glass or made the pieces of glass fuse together, trapping or sealing the AuNPs inside as shown in Fig. 1 for the deep-embedded AuNPs sample. The sample was then cooled at a rate of 1 °C/min to 400 °C, 1.5 °C/min to 200 °C, and, finally, natural cooling to 25 °C.

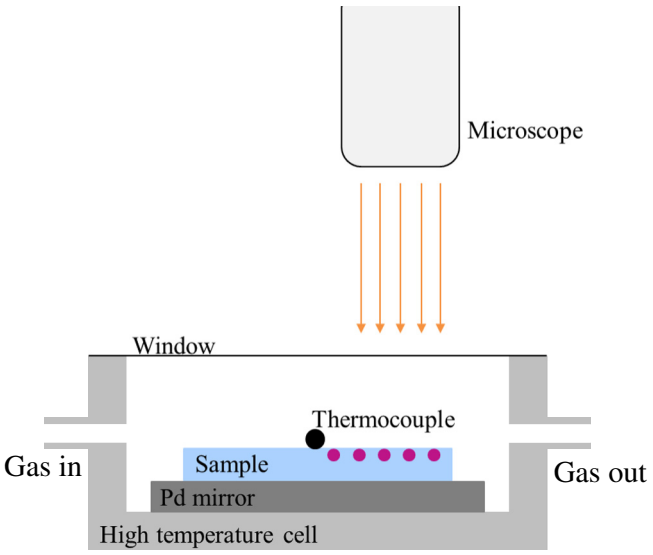


**Fig. 3.** Schematic diagram of set up for reflection tests.

The embedded glass samples were first used to investigate the AuNP's temperature dependence in transmission mode. The sample was mounted on a Macor holder and placed into a quartz flow tube as shown in Fig. 2. In this setup two detectors are used to monitor sensing signal and light source stability for real time correction, respectively. Tests were done by exposing the sample to both air and Ar at different temperatures ranging from room temperature to 450 °C (far below the glass transition point), taking a spectrum of the NPs every 10 s. At the highest temperature, the gas flow was switched to 1% $H_2$ in air to test for chemical inertness.

For reflectance mode measurements, the deep-embedded sample was too thick to achieve focus in the small high temperature cell so the shallow-embedded sample had to be used. The sample was placed onto a Pd mirror in the high temperature cell as seen in Fig. 3. A thermocouple was directly mounted on the sample surface to ensure accurate temperature reading near the AuNPs for better curve fitting. Reflected light was collected by a microscope objective and then detected using an Ocean Optics UV–vis spectrometer. The sample was tested in 5% $O_2$ in Ar at temperatures ranging from room temperature to 350 °C for 1 h at each temperature step, like the tests in transmission mode, a spectrum of the sample was taken every 10 s.

Finally, testing of the temperature dependence of the plasmonic properties of AuNPs was done in water. For this experiment, the sample was placed between a quartz window and a reflector. The sample and reflector were suspended from a tube and allowed to be submerged in water. The window provided a barrier between water and the inside

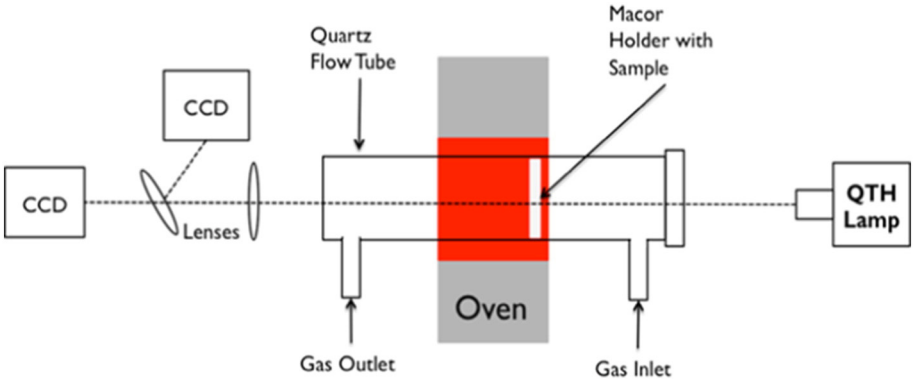


**Fig. 2.** Schematic diagram of set up for transmission tests.