2D Colloidal Crystals based SERS Sensors for NH₃ Detection

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Abstract—**This work demonstrates Au Nanoparticles (NPs) decorated onto partial embedded PS 2D colloidal crystals embedded in the flexible PDMS matrix by RF-sputtering technique for surface enhanced Raman spectroscopy (SERS) NH₃ sensor. The surface morphology and optical properties of Au NPs decorated over 2D PS colloidal crystals (CC) on flexible substrate is investigated by scanning electron microscopy (SEM) and UV-visible spectroscopy. The sensitivity of the Au NPs/ 2D CC/PDMS system for NH₃ detection is investigated by the SERS techniques. A significant increase in the SERS intensity is observed as a function of NH₃ concentration from 100 to 1000 ppm for the synthesized sensors system. The noticeable change in the SERS intensity with the exposure of the NH₃ gas is attributed to the change in the electric near-field due to the Au NPs aggregation or distance as well as change in the dielectric of the surrounding medium. The SERS intensity exhibit a dependence on the change in refractive index/dielectric constant by NH₃ gas molecules, and are linked to coupling effects between surface plasmon resonance (SPR) on the corrugated Au NPs islands and the hot spot formed by 2D PS CC assembly. The proposed Au NPs/ 2D CC/PDMS sensor system is capable for single molecule detection of gaseous precursors.**

Index Terms—**2D PS colloidal crystals, Au NPs, self-assembly, PDMS, SERS**

I. INTRODUCTION

DETECTION of toxic or harmful gases such as ammonia (NH₃) has been become an essential issue for the environmental safety, disease diagnostics, and industrial products manufacturing/monitoring [1] [2]. Additionally, ammonium nitrate present in explosives, gradually decomposes to release traces of ammonia [3]. It is, therefore essential to detect NH₃ concentrations towards air quality improvement and to prevent the fatal accidents [4] [5]. The traditional gas sensors based on semiconducting oxides materials show excellent performance in terms of sensitivity, but usually operate only at high temperature ($\sim$ 200–600 ^{o}C), which raises several issues such as high power consumption, high temperature set up and other safety related issues [6]. These restrictions have motivated researchers to fabricate gas sensors which can operate at room temperature. In order to meet the requirements of industry and other applications oriented fields fascinated towards the utilization of surface enhanced Raman spectroscopy (SERS) based sensors and proven it as a promising alternative to time-consuming laboratory techniques. The principle of operation is quite simple, conversion of chemical changes around plasmonic crystal into optical signal.

Typically, SERS effect occurs when a group of chemical/biological species molecules are adsorbed onto electron rich, rough surface of metal alike Au, Ag, or Pt [7].

Afterwards its characteristics Raman signal gets enhanced in many orders by the surface plasmons excitation available on
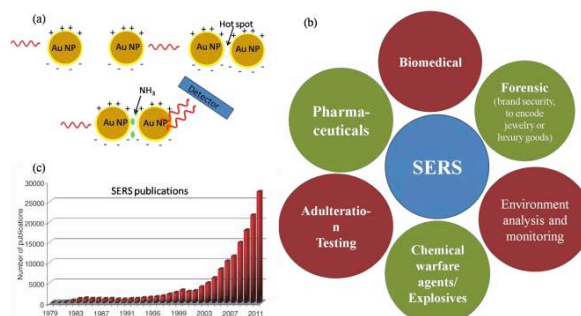

Fig. 1. (a) SERS excitation mechanism, (b) SERS sensor applications in different area and (c) SERS research current progress.

the nanoparticles (NPs) surfaces and hot spot formation when two or more plasmonic NPs are brought closely together [8] [9].

To achieve an effective SERS, analytes must be adsorbed to suitable nanostructures that support surface plasmon excitation [10] – [15]. The gas sensing response of SERS based sensors have several advantages (unique vibrational spectra, no dye needed, tenability, economic) than conventional sensors although SERS sensors research is still in its nascent stage.

Therefore, the wide applications of SERS in various fields of sensors/detection technology are shown in Fig.1. There is a growing need to find a suitable alternative reproducible cost effective NH₃ gas sensor with high throughput, large area, integrated onto flexible surfaces, in order to prevent the fatal accidents. Thus, 2D polystyrene (PS) colloidal crystals (CC) template partially embedded in polydimethylsiloxane (PDMS) matrix, having source of surface plasmon resonance (SPR), Au NPs of tunable size onto their surface, is one of the most promising solution.

Therefore, the present work address to the fabrication of self-assembly based 2D PS CC monolayer array, having the plasmonic Au NPs onto their surface and partial embedded in the flexible PDMS substrates are proposed and is explore for SERS NH₃ gas sensor applications.

II. EXPERIMENTAL

The surface contamination on silicon wafers were removed by dipping and ultrasonic in isopropyl alcohol (IPA) for 10 min followed by rising with DI water for 1 min. after that substrate are dipped in piranha solution 3:1, (H_2SO_4:H_2O_2) at room temperature for 10 min, and by rinsing repeatedly with DI water. Next, the standard RCA treatment (5:1:1 (H_2O:NH_4OH:H_2O_2)) at 70-80 ^{o}C for 10min is given to substrate and again rinse with the DI water in order to make Si wafer hydrophilic by addition of –OH group. The substrates were dried in nitrogen jet stream. After this 200 nm PS colloidal solution is prepared in methanol (1:4) and were spin coated on cleaned silicon substrate with 800 rpm for 45
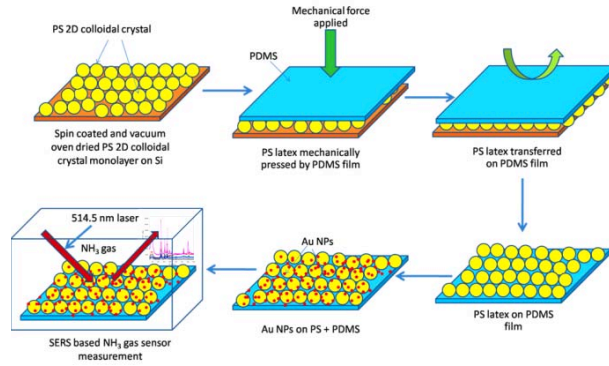
Fig. 2. Schematic of flexible sensors fabrication process flow and NH₃ chemisorptions on Au NPs deposited on PS colloidal crystal partial embedded in flexible PDMS elastomer.

Fig. 3. FESEM images of well orderly hexagonal patterns of Au NPs decorated 200 nm PS colloidal crystals partially embedded in flexible PDMS substrate. The inset shows the corresponding enlarge image of Au NPs decorated 200 nm PS colloidal crystal embedded in flexible PDMS.

second to form the self assembled 2D colloidal crystal monolayer. The PS CC monolayer is then transferred to the PDMS substrate by mechanical pressing as shown in Fig. 2.

After that Au NPs were deposited on the PS colloidal crystal monolayer by the RF magnetron sputtering with sputtering time of 15 seconds. Colloidal crystal based gas sensors were characterized by Varian Cary 50 UV-visible spectrophotometer, field emission scanning electron microscope (FESEM) SUPRA™ 40 Carl Zeiss. The NH₃ gas sensing properties of the as prepared sensor was studied by exposing with the different concentration of the NH₃, and measuring Raman spectra with a WiTec CRM200 confocal Raman system with a 100× objective lens (NA 0.95) under backscattering configuration.

III. RESULTS AND DISCUSSION

The Au NPs decorated 2D colloidal crystal NH₃ gas sensor is characterized by UV-visible, FESEM and Raman spectroscopy. Fig. 3 shows the FESEM images of well ordered hexagonally patterns of 200 nm PS 2D CC decorated with Au NPs on PDMS substrate. The inset in Fig. 3 shows enlarge image of the Au NPs decorated hexagonally patterned 200 nm PS 2D CC on flexible PDMS substrate. It is clear from the SEM images that the monolayer of PS 2D CC is uniformly distributed on the flexible PDMS substrate. The hexagonally arranged monolayer of partially embedded 2D PS CC form voids of ~25 nm as shown in Fig. 3.

The NH₃ molecule was adsorbed to Au NPs PS sensor system by exposing the sensor system to NH₃ gas flow. Fig. 4 shows, the UV-visible spectrum of Au NPs exposed to the NH₃ gas precursors, deposited on the partial embedded, 2D CC surfaces. The UV-Visible spectrum have the plasmon adsorption peak at 474 and 533 nm respectively are typical Au NPs signature peaks, with a certain distortion due to different shape and size. The band at lower energy or longer wavelength in (686 and 729 nm) absorption spectra are also observed which is due to aggregates formed by Au NPs agglomerations on NH₃ exposure.

As a result of Au NPs agglomeration, the shape of the UV-Vis spectra becomes broader and the plasmons band becomes
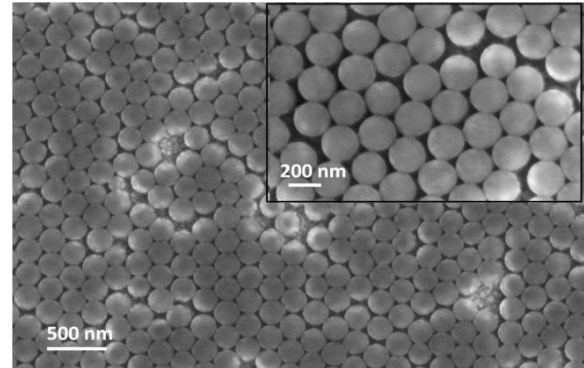
asymmetrical [16]-[18].

The SERS is a result of electromagnetic enhancement due to the surface plasmons excitation onto Au NPs surfaces deposited on top of partially embedded, PS, 2D CC in the PDMS substrate. The void between the Au NPs deposited on the PS CC result in the formation of hot spot and leads to enhancement of the SERS intensity.
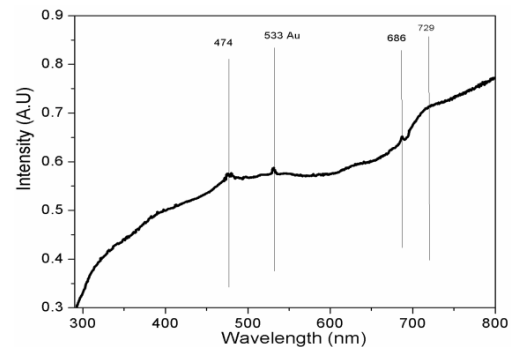

Fig. 4. UV-visible spectrum of Au NPs decorated 2D colloidal crystal embedded in PDMS substrate with NH₃ exposure

The SERS excitation spectrum for NH₃ gas adsorbed onto proposed Au NPs containing 2D PS CC flexible systems are shown in Fig. 5. At resonance the effective electric field (E_c) experienced by adsorbed gaseous precursors onto plasmonic flexible systems are perceived to a great extent larger than the actual applied field. It is an account of a considerable contribution of Au NPs local field existed in the voids of 2D PS CC. In addition to this the effectual SERS of proposed flexible systems are also depend upon size of 2D PS colloidal crystal, NPs size, and excitation wavelengths [16] [19] [20]. Besides this the SERS intensity enhancement is a function of radiation damping, and the effective field (E_c) decreases as $1/r^3$ away from Au NPs surfaces [16] [21]. Thus, for SERS sensing the NH₃ molecules need not to be in the direct contact with the SERS active surfaces, but it can be detected anywhere within the vicinity of polarizing local field of NPs and voids [21].

The SERS spectra of the sensor system in Fig. 5 the signature peaks at 160, 189, 491, 615, 689, 713, 790, 864,
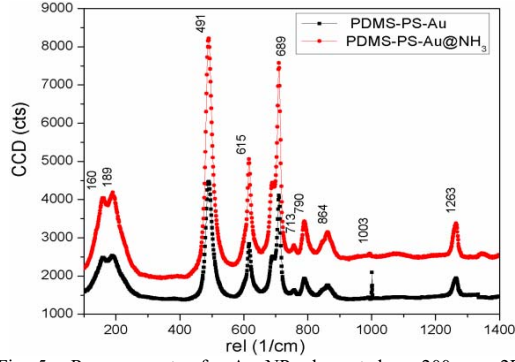
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Fig. 5. Raman spectra for Au NPs decorated on 200 nm, 2D colloidal crystals flexible sensor with and without NH_3 gaseous environment.

Fig. 6. Sensor signal (SERS enhancement factor) variation with NH_3 concentrations for Au NPs/ 2D CC/PDMS sensor system.

1003, and 1263 cm^{-1} ($\bar{v}$) respectively, represent to polystyrene (PS) which are in accordance with the reported value in literature [22]. The peaks located at 689, 864 cm^{-1} ($\bar{v}$) corresponds to the B_2 symmetry and the peaks at 615, 1003, 1263 cm^{-1} ($\bar{v}$) are for B_1 symmetry of polystyrene. The NH_3 adsorption on polystyrene results in Au–N SERS interaction and shows their prominent signature at 491 cm^{-1} ($\bar{v}$). The Au–N stretch interaction of NH_3 contributes in enhancement of the SERS intensity at 491 cm^{-1} ($\bar{v}$) for the NH_3 exposure as shown in Fig. 5 [23]. The significant enhancement of SERS intensity at 491 cm^{-1} ($\bar{v}$) (Fig. 4) for NH_3 gaseous precursor is result of Au–N stretch mode, respectively. Thus SERS intensity for Au NPs on 2D CC have reference value 4415 CCD(cts) and increases to 8362 CCD (cts), for NH_3 gaseous exposure, respectively. There is a noticeable increase in SERS intensity of 3947 CCD (cts) result by NH_3 exposure. Alongside, the other spectral peaks perceived at 1263 cm^{-1} ($\bar{v}$) in the Fig. 5 may be as a result of formation degradation product from PS with the irradiation of excitation laser. Likewise, the band around 160 and 189 cm^{-1} belongs to Au–S–C bending modes, it point outs towards the sulphate terminated 2D PS CC used in this study [24].

The variation in SERS intensity for the in Au NPs decorated 2D PS Colloidal Crystal on flexible PDMS substrate is explained by SERS enhancement factor (G), which is given by following relation [16].

$$G = [(1 + 2g)(1 + 2g_o)]^2 \qquad (1)$$

$$g = \frac{(n^2-1)}{(n^2+2)} \ and \ g_o = \frac{(n_o^2-1)}{(n_o^2+2)} \qquad (2)$$

Where, n_o and n are the refractive indices of the medium for the incident and scattering radiation at frequency ω_o and ω. The dielectric constant κ is related to refractive index m as $\kappa=n^2$.

The SERS enhancement factor depends upon the n and κ of the medium [25]. It indicates that as NH_3 molecule approaches the Au NPs on the surface of the 2D CC on the flexible PDMS the dielectric constant/refractive index around the Au NPs changes which result in the SERS intensity enhancement. The sensor signal (SERS enhancement factor) variation with different NH_3 gas concentration exposed to Au NPs decorated
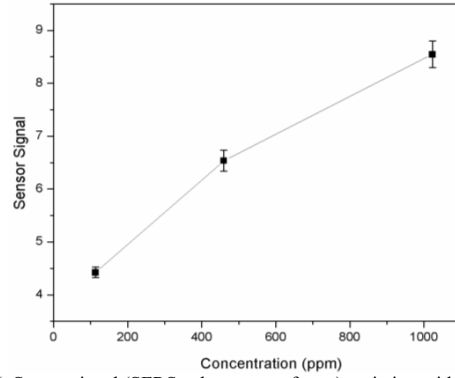
2D PS CC on PDMS substrate as shown in Fig. 5. The Sensor signal (EF) is estimated using expression [26] [27]:

$$EF = \frac{I_{SERS}}{I_{RS}} \frac{P_{RS}T_{RS}}{P_{SERS}T_{SERS}} \qquad (3)$$

Where I_{SERS} & I_{RS} are the SERS intensity and Raman intensity, P_{RS} is the laser power for Raman measurement, P_{SERS} is the laser power for SERS measurement, T_{RS} is the data acquisition time of Raman measurement, T_{SERS} is the data acquisition time for the SERS measurement. From Fig. 6 sensor signal increases with the concentration of NH_3 gas precursor. The adsorption of the NH_3 gas molecules to the 2D, PS CC may also result a agglomeration/densification of Au NPs due to swelling/de-swelling of the 2D, PS, CC on PDMS substrate [28]. This process of de-swelling and densification results a considerable variation in the inter-particles distance of Au NPs onto 2D, PS CC, concentrate more charges near inter-particle junction which results a "hot spot" formation and exceptionally enhancement in the SERS signal [29].

IV. CONCLUSIONS

The present work, investigated the Au NPs decorated onto partially embedded 2D PS colloidal crystal on flexible PDMS elastomer for NH_3 gas sensing application. The surface morphology, decoration of 2D CC and sensing signals, after the exposure of the gases NH_3 is characterized with SEM, UV-Visible spectroscopy and Raman spectroscopic techniques. It observed that 2D CC closely packed in hexagonal arrangement and the SERS intensity variation indicated that the sensor signal depend upon void between the Au NPs coated PS colloidal crystal. The SERS intensity exhibit a dependence on the change in refractive index/dielectric constant caused by NH_3 gas molecule and are linked to coupling effects between SPRs on the corrugated Au NPs islands and the hot spot formed by 2D PS CC assembly. The Au NPs/ 2D CC/PDMS sensor system can be used for single molecule detection of gaseous precursors.

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