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Characterization of Gold Coating on Nanostructured CR39 Polymer as SERS Sensor

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Abstract: The development of highly sensitive sensors has become an efficient field of research. In this work, an ArF Excimer laser of 193 nm with a maximum pulse energy of 275 mJ, 15 ns pulse duration and a repetition rate of 1 Hz is utilized to form a Laser Induced Periodic Surface Structures (LIPSS) of three different morphologies (nanochains, contours, grooves) on surface of CR39 polymer at a fluence range above the ablation threshold (250 mJ/cm^2). The laser ablated polymer surface is then Surface Enhanced Raman Scattering (SERS) activated by deposition of a gold layer of 30 nm thickness. The capability of the produced substrate for surface enhanced Raman scattering is evaluated through thiophenol as an analyte molecule. It is observed that the Laser Induced Periodic Surface Structures of grooves like nanostructures coated with 30 nm gold layer gives a best enhancement factor in the range from 0.9*10^8 to 2*10^8 which is suitable for a single- molecule sensitivity.

Keywords: LIPSS, CR39, SERS sensor, Thiophenol.

Introduction

A highly sensitive detection of biological and chemical species is significant in a wide range of technological and scientific fields [1, 2]. SERS is considered being a highly promising technique for the development of new sensors. This technique combines the huge number of data that can be acquired from Raman spectrum with a high sensitivity accomplished through the amplification of signals that is realized when the molecules of interest are at or near surface of a nanometer- sized noble metallic structures [3]. As a result, the weak Raman signal is enhanced by many order of magnitude and leads to prominent sensitivities that reach the limit of detecting a single molecule and enable SERS substrates for use in enormous biological inspections, sensor or environmental analysis [4-7]. Since the discovery of SERS effect, many fabrication techniques of SERS substrate have been developed in order to achieve a high SERS enhancement Factor (EF). The SERS enhancement factor (EF) is determined by comparing both the SERS and normal Raman scattering (RS) intensity [8].

$$EF = \frac{I_{SERS}}{I_{RS}} \frac{N_{vol}}{N_{SERS}} \qquad (1)$$

Where N_{vol} the average is molecular number in the scattering volume and N_{SERS} is the number of adsorbed molecules on the optically probed SERS substrate. Among such techniques, Laser nanostructuring of polymeric materials followed by coating with noble metallic nanoparticles have attracted significant interest. They exploit the polymer substrate excellent properties (low cost, mechanical flexibility, enhanced durability and light weight) compared with more rigid substrates in coincide with quite distinctive

properties of nanostructured metals [9]. M.A D Jesus et al [10], studied the efficiency of Electron Beam Lithography (EBL) fabricated various nanostructures of negative tone photoresist (ma-N2403) directly coated by 25 nm films of Ag and Au for SERS. Xin Liu et al [11], investigated the ability of laser-assisted replication to fabricate SERS substrates consisting of arrays of gold-coated cyclic olefin copolymer nanopillars. Recently, Esther Rebollar et al. [12] reported on another technique which results in formation of Laser Induced Periodic Surface Structure for fabrication of SERS substrate. Excimer laser represents a leading technology which can be used for this purpose and that is due to its capability to process surfaces only within the sub micrometer scale without any damage to the bulk of the material. In polymers, this is possible which is due to the fact that most of it shows a high absorption for UV light and have low heat conduction properties [13]. Allyl diglycol carbonate (ADC) or CR39 polymer is a thermoset plastic polymer distinguished by being hard, infusible and insoluble in all solvents [14]. It has various applications in many fields and technologies. One of the most important application is in nuclear physics [15].
Here, we report an effective fabrication method for SERS substrate through surface nanostructuring of CR39 polymer using ArF Excimer laser ablation followed by coating with gold nanoparticles.

Experimental work

A 193 nm Excimer laser (Lambda Physik, LPX 220i) is utilized for inducing Periodic Surface Structure (LIPSS) on surface of CR39 polymer of 1 mm thickness. The ArF laser produces a pulses of 15 nsec. with a repetition rate of 1 Hz at an output energy of 275 mJ. The produced nanostructured substrates are cleaned using ultrasonic water and dried in ambient condition. Then, a quorum high resolution turbomolecular-pumped coating system (Q150T ES) is utilized to deposit a gold (99.99% purity, Quorum Technologies) layer onto the nanostructured polymer surface to produce a SERS substrate. Atomic Force Microscopy (AFM) images are obtained using Angstrom advanced (A3000). For SERS characterization, thiophenol (TP) (C6H6S) (99%, sigma-Aldrich) with a molecular weight of 110.19 g/mol and a density of 1.08 g/cm^3 is chosen as an analyte molecule. In order to measure SERS signal, the molecules of analyte must deposit on the surface of SERS substrate, as close as possible to the hot spots molecules. Consequently, a drop of 100 µl solution of thiophenol diluted in ethanol (100%, Hayman specialty products) is poured onto SERS substrate and dried in air. Typically, 100 nM, 100 µM and 100 mM concentrations of thiophenol solution in ethanol followed by rinse with ethanol to remove unbound molecules. Raman spectra are recorded with a Holmarc (HO-ED-S06) laser Raman spectrometer equipped with 40mW Diode Pumped Solid State (DPSS) laser at a wavelength of 532 nm. Raman spectra are acquired in a 90◦ scattering with an objective of 0.09 Numerical aperture (NA). The average of spectra is measured at three random locations on the SERS substrate for each concentration of thiophenol.

Results and discussion

LIPSS formation

The treated areas above ablation threshold (> 250 mJ/cm^2) present major morphological changes as shown by AFM images presented in Figure 1 (a) – (c) at 1200 laser pulses with a fluence of 300, 750 and 1250 mJ/cm^2 respectively.

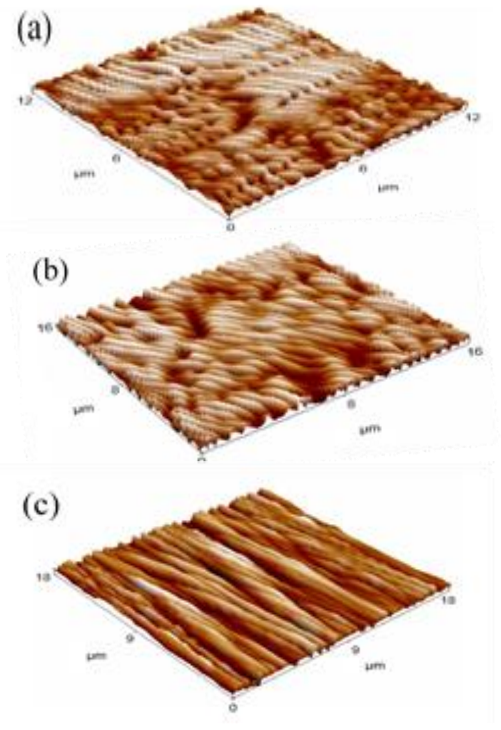

Fig. 1: AFM images of irradiated CR39 samples at 1200 laser pulses with a fluence of a) 300mJ/cm2, b) 750 mJ/cm2, c) 1250 mJ/cm2.

In particular, the morphology comprised of three types of laser induced periodic surface structures (LIPSS), entangled nanochains microstructures at low energy dose (2.4 – 150 J/cm^2) and contours having a progressively increasing radius with energy dose at moderate level (200 - 500 J/cm^2) then the grooves patterns are gradually aligned at energy dose > 500 J/cm^2. It is worth emphasizing that these surface structures are formed at the crater bottom of the CR39 sample. Regarding the mechanism of LIPSS formation, it is commonly accepted that the interference between the incident laser beam and the surface- scattered wave play an important role [16,17] and this interfacing resulting in a modulated distribution of the energy on the surface. For polymers, some authors have been proposed that the modulated energy disposal on the surface induces a similarly modulated substrate heating [16, 18]. For CR39 polymers, the subsequent gradients of temperature allow diffusion of polymeric chains and, as consequence, entangled nanochains microstructures is evolved on the polymer surface. After repeated cycles of heating and cooling, accumulation of polymer motion leads to the formation of grooves pattern, due to increasing number of pulses.

SERS characterization

The SERS enhancing properties of nanostructured CR-39 polymer surface coated with 30 nm gold (Au) metal layer have been tested using Thiophenol (TP) as a probe molecule. TP is used as a model system, which has widely been studied to evaluate the conductivity between metallic electrodes and the body of conjugated molecules [19]. The Raman spectrum of the supplied TP liquid in a cuvette and the spectrum of a drop of TP poured onto unirradiated CR39 substrate and dried in air substrate is shown in Figure 2.

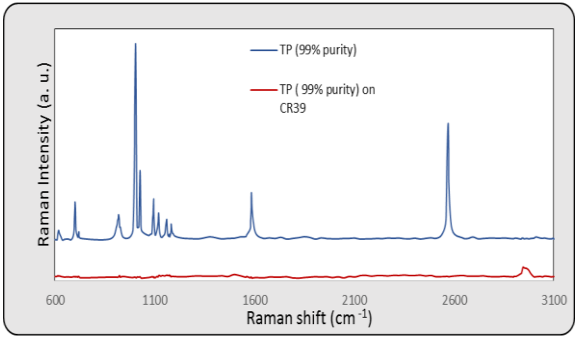

Fig. 2: Raman spectra of Thiophenol (TP) (99% purity) in liquid and on CR39 substrate. The spectrum has been shifted vertically for clarification.

The spectrum of TP exhibits the characteristic bands that belonged to its molecular vibrations [20, 21]. For the TP poured on the surface of CR39 sample, no Raman signal of TP is recognized and only a band in 2945 cm^{-1} that attributed to CR39 sample is detected [22].

Self- assembled monolayers of pure and functionalized alkylthiols on metals, especially on gold, have been practically investigated [23-25]. At the molecular level, these systems have facilitated investigations and added extensive fundaments insight to this field. This approach is used here to generate a monolayer of thiophenol (TP) to estimate the SERS activity of the produced substrate. In particular, the interaction of TP with gold surface causes variations in the Raman bands of the TP in terms of frequency shift and change of relative intensity or disappearance of some of the bands with respect to the spectrum of the solution which is related to the surface enhancement mechanism and molecular orientation [26-28]. Most prominently, bands recognized in the spectrum of TP liquid at 918 and 2570 cm^{-1} that ascribed to the stretching and binding vibrations of the S-H bond respectively disappeared in the spectrum of gold coated nanostructured CR39 substrates. This observation suggests that TP is chemisorbed dissociatively on the substrate surface by rupture of the S-H bond as mercaptide ($C_6 H_5S^-$) [20, 29]. This effect, together with the intensity enhanced of bands shifted from 1094 to 1074 cm^{-1} and from 1584 to 1572 cm^{-1} (Figure 2 blue line with Figure 3), belonged to a change of the adsorbed molecules environment, gives supporting evidence of the bonding of TP anion to the gold surface through the sulfur atom, indicating the formation of a monolayer at the surface [20].

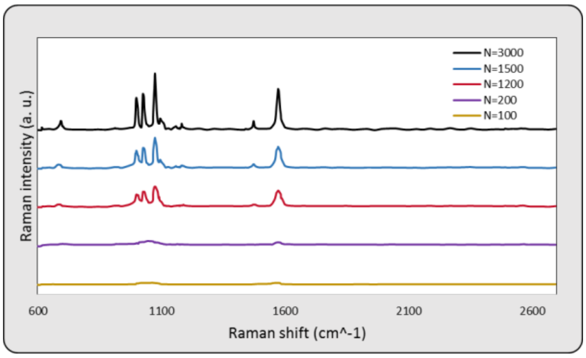

Fig. 3: SERS spectra for TP at a concentration of 100 µM on 30 nm gold coated irradiated CR39 substrate with 650 mJ/cm2 at 100, 200, 1200, 1500 and 3000 laser pulses respectively. Spectra have been consecutively shifted vertically for clarification.

Figure 3 compares the Raman spectra obtained for a TP (100µM concentration) acquired on 30 nm gold coated irradiated CR39 substrates with 650 mJ/cm^2 at 100, 200, 1200, 1500 and 3000 laser pulses respectively. As expected, the SERS intensity is dramatically improved due to the existence of LIPSS on polymer substrate underlying the gold layer and this enhancement depends on the variation of the morphology of polymer substrate. It has been reported that gold nanoparticles coating nanostructured polymer film that prepared by spin coating on silicon wafer enhanced the Raman signal many order of magnitude while a negligible Raman signal is obtained for TP concentration of 9 M on silicon wafer [9]. The enhancement of the Raman signal can be attributed to the electromagnetic enhancement mechanism which is direct consequence of hot spots created by agglomeration of the deposited gold nanoparticles [30]. The SERS enhancement factor is determined by using equation (1). To estimate values of signal intensity for both SERS (I_{SERS}) and normal Raman scattering (I_{RS}), the SERS intensity of the strongest TP band at 1074 cm^{-1} is compared with the corresponding band measured from liquid TP, as proposed [31]. For normal Raman measurement, the number of contributing molecules (N_{vol}) is calculated by determining the number of molecules situated in the focal volume which is about 4.74*10^{21} molecules. For SERS measurement, the number of molecules contributing is calculated by estimating the number of molecules in the focal spot, which is about 0.86*10^{14} molecules for 100 µM concentration of TP. The Enhancement Factors of SERS substrates for TP at 100 µM concentration are compared on different LIPSS morphology that produced using ArF laser pulses and coated with gold Figure 4.

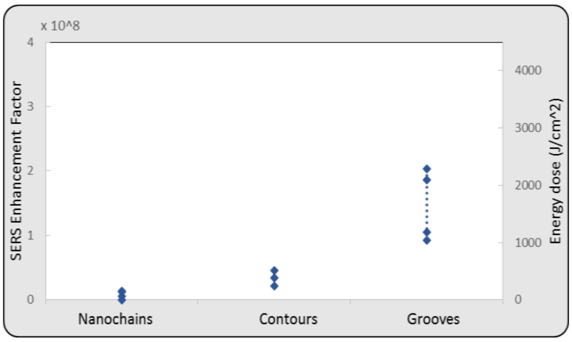

Fig. 4: Enhancement factor of SERS substrate for TP at a concentration of 100 µM on 30 nm gold coating as a function of LIPSS morphology.

The SERS equation calculate the EF by comparing the normal Raman scattering and SERS signal counts for the number of contributed molecules. When measuring the normal Raman signal from a solution, an acceptable accurate speculation of the total number of contributing molecules is made through calculation of the system focal volume. However, for SERS signal, it is quite challenging to find the exact number of molecules that adsorbed on the nanostructured surface. Instead, a speculation of a number of contributing molecules that might suit into the focal plane is utilized. Nevertheless, for the goal of completeness, the EF for SERS substrate is speculated and the highest obtained values are recorded for LIPSS of grooves like structure. It is found to be in the range from 0.9*10^8 to 2*10^8 which is four times greater than that reported for gold coated LIPSS that generated on thin PTT film upon 193 nm ArF laser irradiation [12]. A comprehensive study on SERS enhancement factor demonstrated that the EF needed is 10^7 for a single- molecules sensitivity [32].

Conclusion

LIPSS formed on surface of CR39 polymers followed by coating with gold layer is an appropriate substrate for SERS. The adjustment of surface morphology provide an effective means to maximize the sensitivity of the produced substrate so that it can be used for detection of ultra trace amounts of an analyte.

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تشخيص تركيب البوليمر النانوي نوع CR39 المطلي بالذهب كمتحسس لسطوح رامان المحسنه

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الخلاصة :ان تطور المتحسسات عالية الحساسية اصبحت من المجالات الفعالة للبحوث. في هذا العمل, ليزر الاكسيمر 193 نانومتر مع اعلى طاقة نبضة 275 ملي جول, 15 نانوثانية زمن نبضة ومعدل تكرارية 1 هيرتز قد تم استخدامه لتكوين تراكيب سطحية دورية محتثة بالليزر وبثلاثة اشكال مختلفة (السلاسل النانوية, الشكل المحيطي, الاخاديد) على سطح البوليمر بكثافة طاقة فوق عتبة الاستئصال (250 ملي جول/سم^2). ان سطح البوليمر المستئصل بالليزر تم تفعليه كمحسن سطح في تشتيت رامان من خلال ترسيب طبقة من الذهب بسمك 30 نانومتر. ان كفاءة السطح المنتج كمحسن سطح في تشتيت رامان قد تم تقييمها من خلال الثايوفينول كجزيئة محللة. وقد لوحظ ان التراكيب السطحية الدورية المحتثة بالليزر ذو الشكل الاخدودي والمطلية بسمك 30 نانومتر من الذهب اعطى افضل معامل تحسين بحدود $0.9*10^8$ الى $2*10^8$ وهو مناسب لكشف جزيئة منفردة.