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Anil Kumar Pal, D. Bharathi Mohan

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SERS Enhancement, Sensitivity and Homogeneity Studies on Bi-metallic Ag-Cu Films through Tuning of Broad Band SPR towards Red Region

Anil Kumar Pal and D. Bharathi Mohan*
Department of Physics, School of Physical, Chemical and Applied Sciences,
Pondicherry University, R.V. Nagar, Kalapet, Puducherry-605014

E-mail: anilpal.physics@gmail.com; *d.bharathimohan@gmail.com

Abstract: The objective of this work is to obtain a strong and a broad visible surface plasmon resonance (SPR) and also to tune the wavelength towards red region in thermally evaporated bimetal Ag-Cu film which will act as relatively sensitive surface enhanced Raman spectroscopy (SERS) substrate for the application in bio molecule detection. For the optimization, the morphological property including surface roughness, number-particle density, size distribution and inter-particle distances were altered through varying Cu content in Ag-Cu and temperature by vacuum thermal annealing. The effective dielectric constant of Ag-Cu films is studied from theoretical simulation using extended Maxwell garnet method demonstrating a strong plasmonic character as compared to pure Ag and Cu films. The elemental composition and the surface oxidation states of Ag-Cu film are probed through X-ray photoelectron spectroscopy (XPS). SERS study of RhG molecules exhibit higher enhancement factor for $Ag_{0.75}Cu_{0.25}$ film (annealed at 100 °C) as compared to pure Ag and Cu by the factor of 1.6 and 50 respectively and congruently the limit of detection was found to be 10^{-9} M. The higher SERS homogeneity with the least standard deviation of 18% on RhG molecules was studied through Raman mapping and bar plot. A broad and visible SPR band optimized towards red region on $Ag_{0.75}Cu_{0.25}$film may improve the sensitivity of bio-molecules detection.

Keywords: thin films, vapour deposition, optical properties, atomic force microscope, inelastic light scattering, optical spectroscopy, photoelectron spectroscopy, scanning electron microscope.

1. Introduction

Ag nanoparticles (NPs) play a vital role in the field of plasmonics and most importantly towards surface enhanced Raman spectroscopy (SERS). Many scientists developed SERS substrates using Ag and Au nanostructures and detected various biological molecules at lower concentration [1-6]. So far, Au nanostructure is dominantly used in all commercial optical, chemical and bio sensor applications due its excellent plasmonic and oxidation resistant characters [7-8]. Ag nanostructure enhances SPR when it is prepared with nanotriangle and cube shapes due to the formation of large number of hotspots [9]. Apart from enhancing solely SPR by increasing number of hot spots and it is also very important to tune SPR towards red region so that Raman scattering become highly sensitive for the detection of probe molecules as it is always very strong near infra-red (NIR) region [10]. Hence, the main key factor to increase the SERS efficiency of any probe molecules is to increase the SPR strength of nanostructure in red region for which many researchers change the shape of nanoparticle with the right tuning of particle size distributions. Among Si, Ag, Au, Pt, Pd, Cu and Al, Ag reserves more advantages over SPR tuning across the entire visible-near IR range because of its larger quality factor, oscillator strength and modal volume [11]. The commercially available SERS substrates are very expensive because they are mostly made from either Si or Au. Therefore, it is currently very important to find another material which can reduce the cost of SERS substrate, however at the same time it is also very challenging to maintain the SERS enhancement factor. Recently, A. K. Pal et al prepared Ag films with thickness ranging from 5 nm to 60 nm and then annealed at different temperature in order to tune SPR to the NIR region however, it was not possible to maintain the same SPR strength instead it disappears with inhomogeneous broadening due to increase in surface roughness and the formation of oxide phase [12]. Ultra-thin Ag films prepared by thermal evaporation technique helped to reproduce Ag nanostructure based SERS substrate for the detection of RhG of 10^{-6} M concentration [13]. Nanosculptured Ag films prepared by thermal evaporation with glancing angle deposition technique has been reported to be good SERS sensors [14-