Ag/GaN hybrid nanostructures for optoelectronics applications

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Abstract: A hybrid system consisting of Ag nanoparticles dispersed on GaN nanowall network (GaN NWN) exhibits its characteristic optical properties and electronic band structure. XPS studies of this system reveal the presence of a high density of surface charge carriers due to charge transfer between the conduction bands of GaN and Ag. Surface Enhanced Raman Spectroscopy (SERS) studies show that these surface modifications increase the density of hot spots and result in an enhanced Raman signal with an enhancement factor of $10^7$ and limit of detection of $10^{-10}$ M. Role of the optoelectronic properties of the substrate on the enhancement of SERS signal has been discussed.

Keywords: Ag nanoparticles; GaN nanowall network; Ag nanoparticles; SERS; XPS

1. Introduction
Nanostructures of metals in combination with semiconductor materials have emerged as promising materials in previous decade for various optoelectronic applications such as light emitting diodes [1,2], lasers and biomolecular sensing [3,4]. Size dependent tunability as well as coupling of their optoelectronic properties at nanoscale has led to miniaturization as well as novel devices with high efficiency and performance [5-7]. Metallic nanostructures possess large number of free electrons which can exhibit Surface Plasmon Resonance and can trap incident light to induce confinement effects especially in sub-wavelength dimensions [8]. These surface plasmons (SP) of metal nanostructures can be coupled with excitonic emission of semiconductor nanostructures to enhance their emission efficiency as well as rate of spontaneous photon emission. As per Okamoto et. al, in order to enable coupling of SP modes with radiated emission, large amount of area needs to be created on the surface of metals either by roughening or nanostructuring since it facilitates SPs with high momentum to lose their momentum which is essential for efficient photon extraction. Nanostructuring metals leads to Localized Surface Plasmon Resonance (LSPR) upon excitation with light which form ‘hotspots’ on the surface with enhanced electric field intensity. When a molecule is present in the vicinity of MNPs, scattering cross-section of Raman signal enhances upto $10^{15}$ times due to the creation of Plasmon-polaritons because of the interaction of photons with the surface free electrons [9-10]. The resonant frequency for localized SPRs (LSPR) for metallic nanoparticles (MNPs) depends on variety of factors like the size and shape of nanoparticles, interparticle distance, dielectric environment etc. [11]. Hybridizing these MNPs with semiconductors facilitates Plasmon-exciton interaction so that LSPRs can be tuned to utilize the metal-semiconductor hybrid system in biomolecular detection via Surface Enhanced Raman Spectroscopy (SERS) and enhancement of light emission from the semiconductor. A large number of metal-semiconductor hybrid materials have been studied to explore
the Plasmon-exciton interaction to employ them for solid state lighting and sensing applications. In the field of biomolecular sensing using SERS, a suitable substrate with high surface area with uniformly distribute metal nanoparticles can enhance the sensitivity and hence has been the focus of recent research. In addition, it has also been observed that underlying substrate also plays a very important role in SERS signal [12]. Various morphologies have been created to increase the surface area and density of hotspots such as roughened flat surfaces[13], colloidal nanoparticles[14-16], nanostructured islands [17] and films [18], porous substrates[19], tips[20], channels[21] etc using different techniques such as high energy ion beam irradiation, e-beam lithography, electroless deposition, etc. Various materials such as silicon[22], graphene[23], actinide embedded structures[24], GaN etc have been previously used as supporting substrates for distribution of nanoparticles to obtain SERS substrate. Of all these the combination of Ag and GaN hybrid nanomaterials have been recently explored to look at the Plasmon exciton interactions for solid state lighting and sensing applications using SERS. GaN being wide direct band gap material possesses a high chemical resistance, temperature and power capability and can be combined with In and Al to engineer the band gap. Surface roughened GaN has shown to improve the light extraction and porous or nanostructured GaN along with Ag has shown to improve SERS signals. But issues related to reproducibility, reusability, sensitivity which arise due to inhomogeneous distribution of metal nanoparticles, charge selectivity etc pose a serious challenge for their deployment for real-time applications.

Recently, we have developed a novel hybrid nanostructure of spherical Ag nanoparticles deposited on network of GaN nanowalls. Role of morphology and optoelectronic properties of the substrate on the optical and surface electronic properties of this hybrid material have been studied. SERS enhancement and limit of detection as a function of size of Ag nanoparticles and morphology of the GaN films has been reported.

2. Experimental details

GaN nanowall network were grown on c-plane sapphire using Plasma Assisted Molecular Beam Epitaxy (SVT associates, USA) at a base pressure of 3 x 10^{-11} Torr at 630 C for 3 hours. Temperature of Ga K-cell was maintained at 1000 C along with the nitrogen gas flowing at the rate of 4.5 sccm with RF forward power of 375W. Silver with two different coverage was deposited on both the samples using a physical vapour deposition with base pressure of 1 x 10^{-9} Torr. A quartz crystal microbalance (QCM) was used to monitor the thickness of the samples. All the samples were characterized by FESEM (Quanta 3D FEG, FEI, Netherlands) at 20kV. X-ray photoelectron spectroscopy (EAC 2000 SPHERA 547 spectrometer) with an X-ray spot diameter of 3-4 mm using Al K-alpha anode was used to study the electronic structure at the surface of these samples. The analyzer was placed normal to the surface of the samples and spectra were acquired with an analyzer pass-energy of 100eV for survey scans and 25eV for valence band scans. Raman spectra (inVia, Renishaw, UK) were recorded using a 532nm Nd:YAG solid state laser (~8mW power) in the 180° backscattering geometry, with a 2400/1800grooves/mm grating monochromator and Peltier-cooled CCD detector. 1μl of Rhodamine6G with concentrations varying from 10^{-4} to 10^{-10} M were drop-cast on the samples and Raman spectrum was acquired for 30s for SERS studies after drying them for one hour.

3. Results and discussion

Fig-1 a show the morphology of sharp tipped (<10nm) nanowall network (NWN) samples whose surface area is 80 to 100 times larger than that of GaN epilayer. The carrier concentration for NWN is 10^{20} cm^{-3}. Ag nanoparticles deposited for both the coverages show uniform distribution and average size of 13nm for fig-1b and 25 nm for fig-1c.

Rhodamine6G dye with concentrations varying from 10^{-4} M to 10^{-10} M was drop-cast on all the samples and the enhancement in the Raman signal is quantified by the enhancement factor (EF) calculations which show that 13nm Ag nanoparticles coated sharp-tipped GaNWN samples exhibits the highest enhancement factor of 10^{7} with limit of detection upto 10^{-10} M. The calculated enhancement factor for Ag-13nm/GaN sample for R6G analyte is 1 x 10^{7}. Corresponding raman spectra with reference to bare sharp-tipped GaN NWN is shown in fig-2. This interesting observation
led us to study that sample in comparison with bare NWN and epilayer to know the reason behind the observed enhanced Raman signal.

**Figure 1.** FESEM images of sharp tipped GaN nanowall network with a) sharp tips, b) 13nm Ag nanoparticles, c) 25nm Ag nanoparticles

**Figure 2.** Comparison of Raman spectra acquired for Sharp-tipped GaN NWN and Ag-13nm/GaN sample with R6G dye (10^{-4}M)

Fig-3 shows valence band and Ga 3d core level spectra for Sharp-tipped GaN NWN, 13nm Ag nanoparticles coated NWN and 25nm Ag nanoparticles coated samples compared with that of epilayer as acquired by XPS. It is clearly evident from the fig-2 that once the Ag nanoparticles are deposited extra states are occupied on the top of valence band thereby pushing the Fermi level towards the conduction band minima. Ga 3d core level shifts towards higher binding energy signifying a decrease in the surface band bending as shown in the band diagram (fig-4), and results in reduction of the barrier height and contact resistance. Interestingly, both the Ag nanoparticles coated samples possess an additional peak at -5.70 eV which are due to the degenerately occupied electron states in the conduction band. These observations indicate a charge transfer between GaN and Ag at the surface resulting in the increase in the number of surface electrons in the Ag/GaN hybrid system. The role of substrate in contributing to the surface free charges which can exhibit surface Plasmon resonance is the novel finding here which has never been studied or reported as per our knowledge.
Figure 3. Valence band and Ga3d core level spectra of GaN epilayer, Sharp-tipped GaN NWN, Ag 13nm/GaN acquired by X-ray Photoelectron Spectroscopy.

Figure 4. Schematic band structure of epilayer, GaN NWN and Ag-13nm/GaN

Fig-4 shows the schematic band structure of epilayer, GaN NWN and Ag-13nm/GaN derived from the valence band spectra of XPS (Fig-3) and photoluminescence studies. Since, the Fermi level lies close to the conduction band, all samples are n-type. In case of GaN NWN Fermi level merges with the conduction band minima (CBM), because of the large carrier concentration ($10^{20}$ cm$^{-3}$) on the surface. This is also due to the hybridized peaks shifting to the higher binding energy in NWN which results in shifting of the valence band maxima away from the Fermi level. In case of epilayer, Fermi level is 0.52eV lower than the CBM. After depositing 13nmAg nanoparticles on GaN NWN, the Fermi level shifts away from conduction band minimum compared to that of GaN NWN. Conduction band of the Ag deposited GaN NWN shows a clear broadening which is due to the charge transfer from GaN and Ag to the conduction band of Ag/GaN hybrid material, resulting in a peak at -5.6eV. This peak acts as additional surface free electrons of Ag/GaN material which exhibit the surface plasmon resonance upon illumination, thereby leading to the observed Raman signal enhancement.
The FDTD calculations shown in Figure 5 reveal that the SPR for the Ag nanoparticles lies closer to the wavelength of green laser used in the experiment resulting into higher enhancement. Densely packed Ag nanoparticles on GaN nanowalls will result in narrow gap region of intense electric field density often referred as “hot spots”. Analyte occupying such hot spots will give rise to intense Raman signals. High enhancement factor observed in 13 nm silver nanoparticles deposited on sharp tipped is due to presence of hot spots of high packing fraction of smaller nanoparticles on GaN nanowalls as seen in the FESEM images. These high density of hotspots are due to the presence of large carries on the surface as discussed in XPS results section.

4. Conclusions
A comparative study of different GaN NWN and Ag nanoparticles (13 and 25 nm) coated NWN has been done in order to look at the role of surface properties of Ag/GaN hybrid system in the enhancement of the SERS. XPS shows that GaN NWN with high carrier concentration (~10^{20} cm^{-3}) facilitates charge transfer to Ag/GaN conduction band caused due to surface band bending at the Ag/GaN interface. Enhancement factor of SERS signal is calculated to be 10^7 for Rhodhamine 6G analyte molecules. A large number of free electrons on the surface of Ag/GaN hybrid material, large surface area of GaN NWN and uniform distribution of hot spots, promote surface plasmon resonance leading to the observed enhancement. This work shows the potential of employing the Ag/GaN-NWN hybrid system for biochemical sensing applications using SERS.

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