Plasmon Coupled Nanophotonic Devices Based on Encapsulated 2-D Silver Nanoparticle Arrays

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ABSTRACT

Ordered and encapsulated 2-D arrays of silver nanoparticles have been fabricated for applications as reliable, durable, reproducible, and high sensitivity sensors and photoconductors based on plasmon resonance enhanced local electromagnetic fields. Silver nanopartilces are encapsulated by anodic aluminum oxide or atomically thin graphene to isolate silver from adverse environmental effects. In this paper, fabrication process of the sensor and its applications to SERS detection of adenine molecures and wavelength dependent photoconductive sensing of light are presented. This structure combines excellent intrinsic performance of silver plasmon resonance and the effective isolation of silver from harsh environments by encapsulation to achieve high performance and long-term reliability.

Keywords: nanoparticles, alumina, graphene, plasmon, SERS, adenine

1 INTRODUCTION

Solid-state plasma oscillation, known as plasmon resonnance, is among powerful funcions of nano-scale structure of materials. When electrons in a metal nanoparticles are accelerated by an electromagnetic (EM) wave, such as light illumination, electrons drift back and forth under the influence of time-varying electric field. The maximum absorption of EM power occurs when the frequency of the EM wave matches the resonant oscillation frequency of electrons in the metal particles. Charge separation within individual nanoparticles driven by the EM wave creates strong local charge-induced EM field originating from charges on or near the surface of metal nanopartilces. When the distance between nanoparticles is short, tunneling of hot electrons occur from one nanoparticle to the other. Electron transport through the dielectric between nanopartilces induces photocurrent which makes the nanostructure including metal nanoparticles a wavelength selective photoconductor. The strong local electromagnetic field also enhances Raman scattering in molecular structures and enables surface enhanced Raman scattering with very high enhancement factors making originally non-detactble low concentration of molecules easy to be detected and identified.

Among the best performing metal nanopartilces for devices based on plasmon resonance, silver is the popular choice. However, silver is reactive to environments with deteriorating performance with exposure time. Therefore, a environmentally compatible and durable protective layer to cover and protect silver nanoparticles is desirable and being studied by research groups. Because the strong local electric field originating from charges on or near the surface of nanoparticles attenuateds rapidly with the distance from the nanoparticles, the protection layer must be very thin and chemically and phsically robust. For photoconductivity applications, the protection layer can not be too electrically conductive in the dark because it will produce too much dark current. For surface enhanced Raman scattering (SERS) applications, the protection layer should not weaken the local plasmon induced electric field. Electrochemically anodized and atomic layer deposited aluminum oxide, and other dielectric thin films have been studied. Atomically thin graphene sheet is also a perspective candidate ultra-thin film for application as a protection layer over silver nanoparticles. In this paper, SERS and photoconductivity applicatoins of silver nanoparticles protected by anodic alumina or graphene encapsulation layers are discussed.

Surface-enhanced Raman spectroscopy (SERS) is an effective optical diagnostic tool for chemical and biomolecular sensing [1-4]. Silver nanoparticles for SERS are in the form of either colloidal solution or deposited on a solid substrates [5, 6]. The strength of local strong electric field induced by surface plasmon resonance and distribution of “hot spots” (spots with very strong electric fields) among silver nanoparticles depend on size, shape, inter-distance, and ambient dielectrics [7-13].

For photoconductivity aplications, two electrodes are deposited on the dielectric protection layer for detecting photocurrent when the dielectric spacer between those two electrodes can not stop the flow of electrical current between them. Light illumination of the area between these two electrodes causes the resistance between two electrodes to fall.

We synthesize silver nanoparticles electrochemically inside nanochannels of anodic aluminium and use the thickness controllable alumina barrier layer at the bottom as an encapsulation layer for silver. Atomically thin graphene sheets are also used to cover silver nanoparticles by thermally evaporating silver on the surface of silicon dioxide, followed by thermal annealing, to form silver nanoparticles on the surface of silicon dioxide. For SERS,

the analyte molecules are placed on top of the barrier layer used for protection.

2 EXPERIMENTAL RESULTS AND DISCUSSION

Well-ordered arrays of Ag nanoparticles are electrodeposited and encapsulated inside AAO nanochannels as shown in Fig. 1 [14-15]. After the left over aluminum is etched away, the exposed AAO barrier layer at the bottom of nanochannels as shown in Figure 2 serves as a protection dielectric layer for the encapsulated silver.

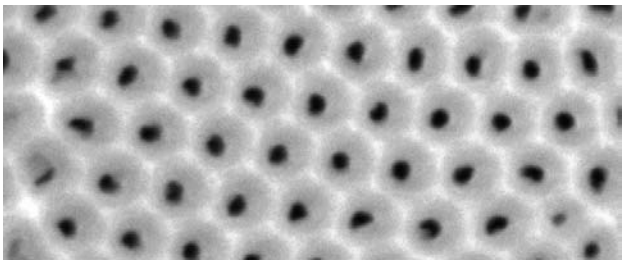

Figure 1. An AAO substrate showing ordered nanochannels.

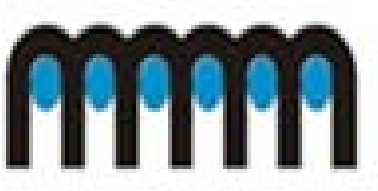

Figure 2. Schematic diagram showing electro-deposited silver (marked in blue) at the bottom of AAO channels after the left-over aluminum has been etched away to expose the residual alumina barrier layer (marked in black).

Two tungsten electrodes are sputter coated on the AAO barrier layer for measuring photo induced electrical current when a DC voltage is applied between two electrodes. Photoconductivity as a function of the wavelength of the illuminating light is found to be consistent with the wavelength dependent absorption by plasmon resonance of silver nanoparticles as shown in Figure 3. This structure acts as a two-dimensional photoconductor, which might find applications in optoelectronic sensors and integrated photonic and optoelectronic circuits [14].

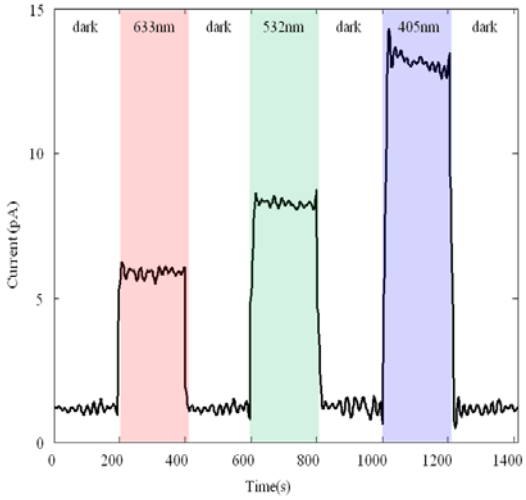

Figure 3. Photocurrent in an AAO protected silver nanoparticles array. Light illumination by 633nm, 532nm, and 405nm is turned on and off sequentially.

The Ag-AAO structure has also been demonstrated as an excellent SERS detector because they have high density of Ag nanoparticles with uniform distribution. The SERS substrate exhibits outstanding SERS reproducibility and a high enhancement factor of greater than 10^6 for probing adenine molecules [16].

The channel diameter and the distance between channels of AAO can be controlled by process parameters. When this is combined with the convenient electrochemical deposition of Ag to fabricate the Ag-AAO structure, an inexpensive manufacturing process is developed without needing vacuum processes nor high-temperature treatments. These advantages are believed to make this structure very useful for many applications.

When the AAO barrier layer is further etched chemically to become thinner, the attenuation of plasmon induced strong local electric field is reduced and improved plasmon resonance effects are achieved. However, the thickness of the AAO barrier layer is not exactly the same across a large surface and the etch rate of the barrier layer by chemical etching can also vary due to environmental factors. These facts make it difficult to control the final thickness of the AAO barrier layer after chemical etching down to 1nm or less.

Single-layer graphene is a one-atom thick carbon film of the same structure of one layer of graphite. It is proven to be stable physically and chemically in the ambient environments [17-21]. We have grown single-layer graphene by means of thermal CVD in methane and hydrogen at temperatures around 1000^{o}C at sub-Torr pressures on copper foils. Single layer-graphene is transferred, after chemically etching copper completely, to cover silver nanoparticles formed on a substrate as a protection layer. A Raman spectrum for a single-layer graphene is shown in Figure 4. Raman spectra of adenine and other molecules are examined using this graphene covered silver nanoparticles to exhibit the characteristics

Raman peaks. The characteristic peak of adenine at 734cm^{-1} could not be detected when adenine is applied to a silicon dioxide substrate. This peak is clearly seen when silver nanoparticles covered by a single-layer graphene is used as the SERS substrate as shown in Figure 5.

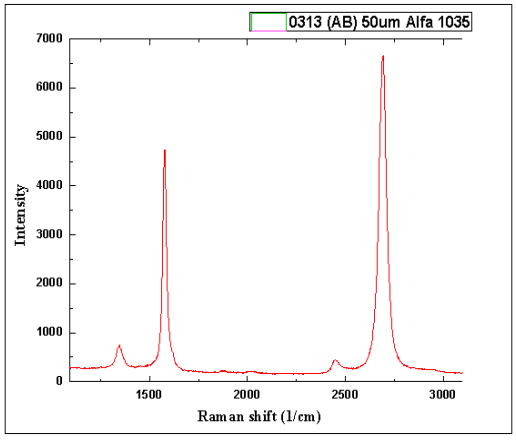

Fig. 3. Raman spectrum of a single-layer graphene grown by thermal CVD.

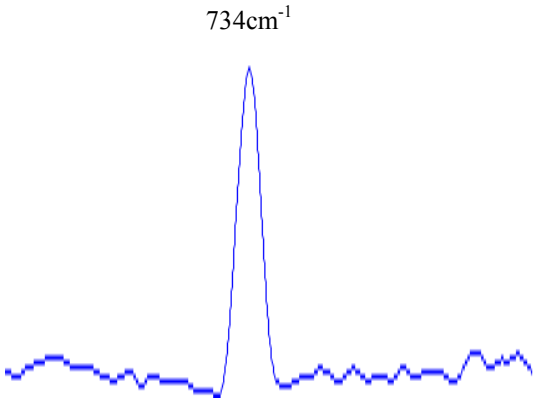

Fig. 4. Characteristic Raman peak of adenine molecules at 734cm^{-1} excited by 532nm laser for adenine on silver nanoparticles which are covered by a single-layer graphene. Silver nanoparticles are formed on silicon dioxide. For adenine applied directly on silicon dioxde without silver and graphene, no signal is detected.

3 CONCLUSIONS

Two-dimensional arrays of silver nanoparticles electrodeposited at the borrom of AAO nanochannels and a silver thin film thermally evaporated on silicon dioxide followed by annealing are protected by AAO barrier layers and sinlge-layer graphene, respectively, against adverse environmental effects. Photoconductors and SERS applications of such structures have been demonstrated.

We gratefully acknowledge the support from Taiwan National Science Council via grants 96-2221-E-006-286-MY3, 99-2120-M-006-004 and 99-2911-I-006-504.

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