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Plasmonic Crystals and Nanophotonic Sensing Devices

T. A. Kelf[1], Y. Sugawara[2], R.M. Cole[3], N.M.B. Perney[3], J.J. Baumberg[3], M.E. Abdelsalam[4] and P.N. Bartlett[4]

[1]Department of Applied Physics, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628.
[2]Analysis Technology Center, FUJIFILM Corporation. Nakanuma 210, Minamiashigara-shi, 250-0193
[3]School of Physics and Astronomy, University of Southampton, Southampton, SO17 1BJ, UK
[4]School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

1. Introduction

The field of plasmonics has drawn a growing interest in recent years due to its ability to bridge the length scales of optical and electronic phenomena. At one end of this scale the ability to convert light into surface plasmons provides the possibilities for smaller scale optical circuitry, while at the other extreme plasmonics provides the tools to detect and study single molecules.

Before either goal can be fully realized a full understanding of both the surface plasmons themselves and their interactions with both light and molecules must be attained. Towards these goals we have been studying the fundamentals of plasmonic systems as well as how molecules can interact with these communal electron oscillations.

2. Samples

To investigate the full potential of nano-structured systems two different approaches have been utilized.

The first uses a natural lithographic process of electroplating through an array of self-assembled microspheres. This approach is both quick and cheap and provides great flexibility over the precise surface geometry as both the dish diameters and depths can be precisely controlled from sample to sample.

The second approach employs a lithographic procedure to produce precise arrays of square and circular nano-pits in a silicon wafer. This technique allows absolute control over the pit shape as well as the array spacing and geometry. After production gold is sputtered over the surface to create plasmon active surfaces.

3. Plasmonic Properties

By measuring the angle resolved spectral absorption of different plasmonic crystals an understanding of the complex energetics can be build up. It is found that essentially two different forms of plasmon exist, as depicted in figure 1. The first are free to propagate over the crystals surface, and so scatter strongly due to the structuring. This forms Bragg surface modes with symmetries equal to those of the initial array. The plasmons, termed Bragg plasmons, are thus delocalised and have energies that are dependent on both the sample orientation and the angle of the incident light, as shown in figure 1a. Through assuming a weak-scattering approximation these plasmons can be accurately modelled, as indicated by the solid lines. The second type of plasmon is trapped within the structured pits or dishes. These are termed localized plasmons and have energies completely independent of the incident angle but are strongly dependent on the size and shape of the confining region. Figure 1b shows the typical dispersion of a localised plasmon, and indicated by the dashed line.

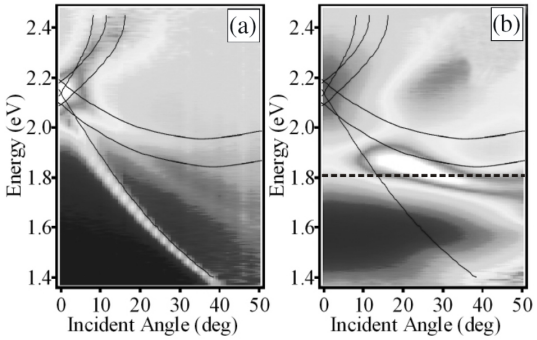

Figure 1. Angle resolved absorption spectrum, grey scale from no absorption (black) to full absorption (white), for (a) Bragg plasmon on a thin structured film and (b) Localized plasmon within a nearly encapsulated void. Solid lines show theoretical Bragg dispersion, dashed line indicated localized plasmon.

The two types of plasmon have radically different dispersions and so behave like completely different entities. By tuning the angle of excitation and surface geometry it is possible to bring the energies of the different modes into coincidence. Under these conditions strong coupling between the different plasmon modes occurs and the modes split into new mixed states[1]. This provides further control over the exact electric field distributions and energy flow over the surface, which is of critical importance for the development of plasmon based applications.

4. Plasmonic Interactions with Organic Molecules

An intrinsic property of surface plasmons is that as quasiparticles they are partly optical and partly coherent electron oscillations. This can be effectively utilized to enhance the coupling between an optical field and single molecules.

To demonstrate the strength of this effect we have explored the interactions between plasmons and an organic semiconductor self-assembled from a cyanine dye. The dye is drop cast onto a plasmon active surface,

where it forms a thin J-aggregated film characterized by a molecular exciton state at 1.85eV. Again, through the tuning of void sizes and incident angles it is found that this exciton interacts strongly with both Bragg and Localized plasmons. In both cases interactions are within the strong coupling regime, most clearly depicted in figure 2.

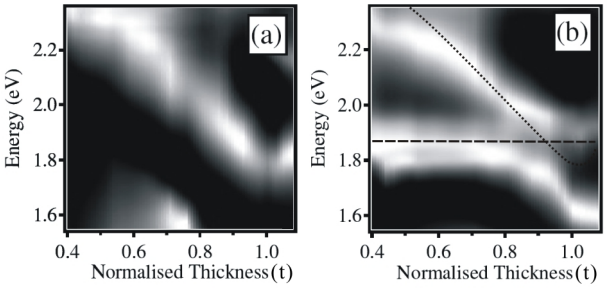

Figure 2. Thickness dependence of optical absorption spectrum from plasmonic crystals at normal incident, sample is graded in thickness from a flat surface, t=0, to an array of fully encapsulated voids, t=1. (a) Without a J-aggregate film. (b) With a J-aggregate film.

Here, a sample has been produced with a spatial variation in the thickness (t) of the gold film. This means the surface geometry smoothly changes from shallow dishes (t≈0.1) through to truncated spherical cavities (t=0.5) and then encapsulated voids (t=1)[1,2]. This causes a drop in the energy of the localized plasmon mode due to a change in plasmon confinement (fig 2a). The application of the J-aggregate layer creates a strong absorption feature at 1.85eV (fig 2b, dashed line) due to the exciton mode. As can also clearly be seen, the dispersion of the localized plasmon is modified by the exciton mode and an anticrossing is observed with a Rabi splitting of 230meV - the original localized plasmon dispersion is indicated with the dotted line[2]. We also observe that the plasmon modes enhance and extend the wavelength range of the dye fluorescence. This shows that plasmon active surfaces hold great potential for modifying and enhancing material properties to pave the way for new optically active devices. Further to this, a more direct application of such surfaces is in the detection of trace levels of complex molecules through the process of enhanced Raman scattering.

Raman scattering is a powerful tool for molecular identification since every molecule possesses a unique 'fingerprint'. Unfortunately Raman scattering is a weak process, and so is rarely used outside the laboratory. The use of plasmons to generate enormous local electric fields gives the ability to boost this coupling and bring Raman scattering up to usable signals.

Figure 3a shows the reflectivity plot of a plasmonic crystal which has been coated in a monolayer of benzene thiol. Due to the trace level of the molecules and their small optical cross-section, this has no observable effect on the absorption spectrum. However, when one of the Bragg plasmons is directly pumped with a more powerful infrared laser, as indicated by the white cross, and the Raman scattered light is viewed using a high-sensitivity photodetector, we find an enormous enhancement in the Raman scattered light from the thiol molecules as shown in figure 3b. Here the horizontal bands correspond to Raman transitions of the thiol molecule. Not only does the surface act to reproducibly enhance the scattering cross-section by 3 million times, but it also imprints the plasmonic dispersion into the signal[3]. This provides direct information about the enhancement process, useful for further optimisation, but also opens the way for direct molecular fingerprinting as the surface acts to both enhance the signal and spatially resolve the generated Raman light.

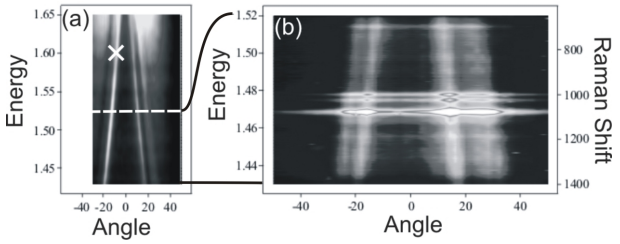

Figure 3. (a) Angle dependent absorption spectrum of a Bragg plasmon. (b) Raman scattered signal from the region indicated, white cross makes pump laser angle and photon energy.

Using photolithographically produced nano-pits, the precise dimension of nanoscale voids can be exactly controlled and so it is easier to optimise the different parameters, such as pit depth, spacing and size, to produce the maximum enhancement for a given molecule and pump wavelength[4]. This project has allowed for the commercialisation of viable Enhanced Raman sensing technologies by the UK spin-out company Mesophotonics, which now sells a range of molecular sensing systems and is currently exploring the potential to utilize this technique in areas as diverse as mass clinical trials and homeland security.

5. Conclusions.

Plasmon active surface provide the grounds for the investigation of many interesting experiments. With the addition of molecules to the nano-patterned surfaces a whole new area of experimentation is opened up, and one which has already begun to show commercial value. Through furthering of the current understandings, the way is paved for many more possible applications such as plasmonic lasers and more advanced molecular sensing devices.

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