Fano resonance in dual-disk ring plasmonic nanostructures

Lifang Niu,1,2 Jing Bo Zhang,1,2,* Yuan Hsing Fu,1,2 Shripad Kulkarni,1 and Boris Luk’yanchuk1

1 Data Storage Institute, Agency for Science, Technology and Research
5 Engineering Dr 1, off Kent Ridge Crescent, National University of Singapore, 117608, Singapore
These authors have equal contribution
1 zhang_jingbo@dsi.a-star.edu.sg

Abstract: A dual-disk ring (DDR) structure with broken symmetry and weakly dissipating material, silver, is proposed to achieve Fano resonance in visible wavelength range. Symmetry breaking of a metallic ring is realized by placing two disks inside the ring. The excitation of the Fano resonance is interpreted in terms of coupling of the ring and the dual-disk plasmonic modes. The potential of using an array of such DDR nanostructures as a biochemical sensor is evaluated with the figure of merit (FOM). Based on our design and simulation, arrays with DDR structures are fabricated and the Fano resonance peak is observed in visible wavelength range of extinction spectra of individual silver DDR nanostructures.

©2011 Optical Society of America

OCIS codes: (260.5740) Resonance; (240.6680) Surface plasmons; (220.0220) Optical design and fabrication; (220.4241) Nanostructure fabrication; (160.4760) Optical properties.

References and links
4. F. Hao, Y. Sonnefraud, P. Van Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, “Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance,” Nano Lett. 8(11), 3983–3988 (2008).

1. Introduction
Fano resonance in nanoscale plasmonic nanostructures could have many promising applications in both biological and physical sciences [1-2]. One significant application among them is a platform for ultrasensitive refractive index based biosensing and surface enhanced molecular sensing. The basic idea for such a platform was discussed a few years ago [3-4], however, there are some unresolved problems. First, majority of previously suggested structures have pronounced Fano resonance peaks in the near IR range of spectra, while for
many practical applications it is preferred or necessary to achieve a sensitive spectral response located in visible range. Second, one needs a device with higher refractive index sensitivity, for example, compared to plasmonic refractive index sensor [5] with conventional Lorentz-shaped plasmon resonance. The third problem is related to fabrication challenges. It is simpler to tune desirable properties precisely with 2D structure fabricated by lithographic methods [6-7] compared to e.g. core shell structures with broken symmetry [8-9] or other 3D plasmonic nanostructures.

This paper elaborates on our newly proposed design, fabrication and characterization work of a dual-disk ring (DDR) silver nanostructure to achieve a Fano resonance with its spectral response feature located in visible range. The spatial and spectral tunability of the Fano resonance incurred in such a DDR structure has been explored by finite difference time domain (FDTD) electrodynamics calculations in order to examine the electric field distribution and spectral assignments of extinction peaks and their relative strength. Experimentally, electron beam lithography (EBL) was employed to fabricate DDR structures on quartz substrates. Cost effective batch duplication was also performed with nanoimprinting lithography (NIL). The optical spectra of the structures were characterized by dark field light scattering measurement. Optical responses of the proposed nanostructures to a change of both bulk and interfacial refractive index were also calculated and analyzed.

2. Design and computation approach

Fano resonance is an interference result of two excitation modes thus intrinsically more sensitive to wavelength or environmental refractive index changes. Therefore it will be very promising to make use of the Fano resonance as the sensing mechanism. On the other hand, with working spectral features in visible optical range has always been a fond or preferred target in many applications of plasmonics and metamaterials.

We propose one broken-symmetry dual-disk ring (DDR) nanostructure model to bring the Fano resonance spectral feature to less than 800 nm. Symmetry breaking of a metallic ring is achieved by placing two disks inside the ring. Considering the easiness of generating a pronounced extinction peak with Fano resonance arisen from weakly dissipated material, silver (Ag) is selected as the plasmonic material throughout this study.

Figures 1(a) and 1(b) illustrate the model of DDR nanostructure, whose geometry is characterized by 5 parameters: the inner and outer radii \( r_1 \) and \( r_2 \) of the ring, the identical radius \( R \) of the two disks, the gap \( g \) between the ring and the near edge of each disk, and the thickness \( t \) of the metal layer, which is equivalent to the height of the disks and the ring.

In order to obtain desired resonance peak and maximum local field enhancement in visible range, structure dimension has been manipulated by fine tuning certain geometric parameters to meet our requirements and in the same time to compromise with the critical limit on nano fabrication side. To investigate the spatial and spectral tunability of DDR and thus to find the optimum geometry for the best sensing functionality, finite difference time domain (FDTD, Lumerical FDTD Solutions) electrodynamics calculations have been performed to examine firstly the electric field distribution and enhancement, and secondly extinction peak locations in the spectrum and their relative intensity strength. In all calculation model, the DDR
structure lies on a glass substrate (SiO$_2$ with reflective index of 1.456), which occupies semi filling space under DDR structures. Optical responses of the proposed nano structures to a change of both bulk and interfacial refractive index were also calculated and analyzed. Evaluation of the performance of the potential resonance-based sensor was quantified using the figure of merit (FOM) [10], the commonly used parameter to specify various sensors.

We start by investigating the extinction spectrum of a typical silver DDR structure as shown in Fig. 2(a), and its electric field distribution diagrams at resonance peaks of 557 nm, 684 nm and 1589 nm respectively as shown in Fig. 2(b). The optical properties of the silver DDR can be explained as a hybrid among the two silver disks and the silver ring. Qualitatively, the spectral response of such structures can be modeled by a system of coupled oscillators [2]. In Fig. 2(a), the broad resonance peak at the wavelength of 557 nm represents the high energy, anti-bonding mode combining of ring dipole and disk dipole. The high resonance peak at the wavelength of 1589 nm is the low energy bonding mode coupled from the ring dipole and the disk dipole. The Fano resonance peak at wavelength of 684 nm arises from coupling between the subradiant octupolar mode of the ring and the superradiant dipole mode of the disks, which is observed from the electric field distribution in the middle of Fig. 2(b). It is different from the situation of a single-disk ring nanostructure with broken symmetry [4], where Fano resonance arises due to interference of dipole (disk) and quadrupole (ring) modes.

![Fig. 2. (a) Extinction spectrum for silver (Ag) dual-disk ring (DDR) on a silica substrate with $r_1 = 146$ nm, $r_2 = 120$ nm, $R = 44$ nm and $g = 10$ nm; (b) The left electric field distribution at the wavelength of 557 nm represents the anti-bonding mode combining of ring dipole and disk dipole; the middle plot at the wavelength of 684 nm represents the coupling of ring octupolar mode and disks dipole mode, resulting in a Fano resonance; the right at the wavelength of 1589 nm represents the bonding mode from the ring dipole and the disk dipole.](image)

In Fig. 3, a series of FDTD computations of spectra are presented to illustrate the effects of varying the geometric parameters of DDR. Figure 3(a) shows the effects of decreasing the gap $g$ between the ring and the near edge of disks. For a given ring and disks, when the gap gets smaller, the stronger interaction between the ring and disks results in increased spectral intensity of the Fano resonance as well as red-shift of the resonance peaks. Figure 3(b) shows that if all other parameters keep the same, with increasing of the disk size, the peak position of the Fano resonance is red shifted and the profile of the peak is broadened. Figure 3(c) shows the effects of changing the outer radius of the ring, $r_1$, while keep the inner radius $r_2$ of the ring, the radius of the disks $R$, and gap $g$ disk as constants. The Fano resonance peak and the superradiant dipole mode peak are blue shifted and the peak value of the Fano resonance increases largely. Effect of polarization orientation is shown in Fig. 3(d). Electric field polarization parallel to x-axis (the axis passing through the centers of the two disks) gives rise to a slightly more red and higher peak value of the Fano resonance. Both x polarization and y polarization irradiations generate the octupolar ring mode plasmonic resonance.

It is proved that via varying the geometric parameters, both the intensity and the spectral position of the resonance peak can be manipulated. With selection of silver, a weakly dissipated metallic material, such a DDR structure allows for greater enhancement of octupolar mode and sustains pronounced Fano resonances in visible range.
Fig. 3. Extinction spectra for silver (Ag) dual-disk ring (DDR) structures (a) with \( r_1 = 146 \text{ nm}, \) \( r_2 = 120 \text{ nm}, R = 44 \text{ nm}\) and \( n = 1 \) as a function of the gap for: \( g = 6 \text{ nm}, \) \( 10 \text{ nm}\) and \( 14 \text{ nm}; \) (b) with \( r_1 = 146 \text{ nm}, r_2 = 120 \text{ nm}, \) and \( g = 10 \text{ nm}\) as a function of the disk size \( R \) for: \( R = 44 \text{ nm}, \) \( 48 \text{ nm}\) and \( 52 \text{ nm}; \) (c) with \( r_2 = 120 \text{ nm}, R = 44 \text{ nm}, \) and \( g = 10 \text{ nm}\) as a function of ring outer radius \( r_1 \) for: \( r_1 = 146 \text{ nm}, 140 \text{ nm}\) and \( 134 \text{ nm}; \) (d) with \( r_1 = 146 \text{ nm}, r_2 = 120 \text{ nm}, R = 44 \text{ nm}\) and \( g = 10 \text{ nm}\) as a function of irradiation polarization along: x-axis (the axis passing through the centers of the two disks) polarization and y-axis polarization. Inset: electric field distribution for Fano resonance peak with the irradiation light at x and y polarizations respectively.

Giving that the plasmonic property of this Fano resonance is strongly influenced by the refractive index of the surrounding bulk medium or by the presence of a thin layer of dielectric materials in the vicinity of the nanofeature, the DDR structure may serve as a sensing unit with high sensitivity. In Fig. 4(a), we compare the extinction spectra of a DDR structure with complete dielectric filling (vacuum or dielectrics occupies the semi filling space over glass substrate excluded DDR structure) of three different media \( (n = 1, 1.25\text{ and } 1.33)\) respectively. The spectra clearly show large red-shifts of the Fano resonance. The wavelength position of the Fano peak as a function of the refractive index of surrounding medium at different DDR gaps were examined and the results are compared in the inset of Fig. 4(a). The predicted refractive index sensitivity from these calculations for a DDR structure with a gap of 14, 10, and 6 nm are 0.78, 0.80, and 0.83 eV/RIU, respectively. The values are close to the previously reported 1.17 eV/RIU for aluminum (Al) triangle nanoparticles [5]. However Al structures can be practically used just in ultrahigh vacuum. The calculated sensitivity values also indicate that when the surrounding medium is changed, the smaller gap gives rise to a bigger Fano resonance energy change and thus higher refractive index sensitivity. We use the figure of merit (FOM) to evaluate the performance of the Ag DDR sensor with respect to a change of the surrounding medium. Full width of the Fano resonance is taken as the energy difference between the peak and the lower-left dip. The calculated FOM is 8.00, 7.32 and 6.81 for corresponding gaps of 6 nm, 10 nm and 14 nm respectively. For gaps of 6 nm and 10 nm, The FOM values are close to the previously
reported 8.34 for the Fano resonance of a nonconcentric gold disk/ring cavity (NCRDC) nanostructure where the Fano resonance lies in NIR range [4].

Dielectric material attached to the plasmonic metal surface is also expected to have a strong influence on the spectral position. In Fig. 4(b), we evaluate the application of such a system for the detection of molecular recognition or binding, which typically involves the thickness change with an additional thin dielectric film close to the metal surface. The sensing characteristics under such conditions are expected to be influenced by the local surface electromagnetic field intensity and the homogeneity of the decay of the field away from the surface. Simulations were performed for the situations of without and with an additional dielectric film covering the metal nanostructure at thickness of 2 and 4 nm respectively under the same condition of $n = 1.45$. The additional dielectric thin layers with 2 and 4 nm thickness give rise to a Fano peak position shift of 26 nm and 48 nm respectively. It clearly displays potency of the immediate plasmonic response of DDR structure to enhance the optical biosensor's sensitivity.

Fig. 4. Refractive index sensitivity for dual-disk ring (DDR) structures. (a) Spectra of structures with $r_1 = 146$ nm, $r_2 = 120$ nm, $R = 44$ nm and $g = 10$ nm for surrounding media with different refractive index, at $n = 1, 1.25$ and 1.33. Inset: wavelength shift of the Fano resonance peaks for surrounding media with different refractive index at gaps of 6 nm, 10 nm and 14 nm. (b) Spectra of structures with $r_1 = 146$ nm, $r_2 = 120$ nm, $R = 44$ nm and $g = 10$ nm, as a function of the thickness of an additional dielectric coating, at 0 nm, 2 nm and 4 nm respectively. The upper inset depicts the manner of the dielectric capping layer binding onto the top surface and the side wall of a nanodisk and the lower inset depicts a bare nanodisk (equivalent to a capping layer with zero thickness).

2. Experiment and characterization

Since the arisen plasmons are extremely sensitive to the shapes of structures, significant efforts on precise control over the structure morphology and a narrow size distribution of individual nanofeatures are crucial obtaining a sharp plasmon spectrum from a single Ag DDR nanostructure as well as from one array of Ag DDR nanostructures. Electron beam lithography (EBL) and corresponding nano processes were used to fabricate the DDR molds and nano imprinting lithography (NIL) was used to duplicate the DDR nanostructures onto sputtered Ag film on substrates with the concern of economical fabrication of future sensors.

In our experiments, quartz (silicon dioxide) was used as the mold material. Firstly, 10 nm chromium (Cr) layer was sputtered onto a 1 inch × 1 inch quartz substrate. On top of the Cr layer, a 70 nm thin film of a negative-tone electron-sensitive resist, hydrogen silsesquioxane (HSQ) was spin-coated and the coated sample was baked at 180 °C for 5 minutes. The DDR array was then written by with the EBL system (Elonix 100kV system). After exposure and development to define the desired pattern, the Cr film at areas without protection of the HSG was removed by ion milling to create a metal mask. Then the nanostructure was transferred down to the quartz substrate by reactive ion etching (RIE), which selectively etched away the quartz material in the unmasked region. Etching depth was about 80 nm. The Cr metal mask
was removed from the quartz substrate by dipping the substrate into Cr etchant solution. By this way, the quartz mold with protrusion features was prepared as a hard master mode for nano imprinting lithography (NIL).

Similarly, the mold can also be generated with 60 nm thick Ag film instead of Cr. The advantage of using Cr film is for its very good adhesion to quartz and stability over a long period upon formation of a thin protective oxide layer of a few atoms. While using Ag film for molds during the long cycle of geometrical optimization, one can use the Ag DDR array directly for spectroscopic characterization and thus guide geometrical modifications rapidly.

Displayed in Fig. 5(a) is the scanning electron microscopy (SEM) image (JEOL JSM7401F) of an array of the Ag DDR nanostructures fabricated by EBL and corresponding nanoprocess. The inset is an enlarged SEM image with the magnification of 230 k. For this array of DDR, the gap is 10 nm, the two disks are with \( R = 44 \text{ nm} \) and \( r_1 \) and \( r_2 \) being 146 nm and 120 nm respectively. The charge-up effect occurred at the bottom surface of the dielectric material (quartz here) causes the small gap \( g \) invisible from SEM images. However, the set of four dark field images in Fig. 5(b), taken with one true color air-cooled charged coupled device (CCD) (Q Image) attached to an inverted Nikon microscope (Nikon Ti-U), proves that the Ag DDR structures with the narrow gaps of 10 and 15 nm respectively are fabricated successfully. The slightly changed color distinguish arrays with the identical values of \( r_1 = 147 \text{ nm}, \ r_2 = 133 \text{ nm}, \) and (I) \( R = 40 \text{ nm}, \ g = 10, \) (II) \( R = 40 \text{ nm}, \ g = 15 \text{ nm}, \) (III) \( R = 43 \text{ nm}, \ g = 15 \text{ nm}, \) (IV) \( R = 38 \text{ nm}, \ g = 15 \text{ nm}, \) respectively.

Two-step nano imprinting process was used to transfer the nanostructures on the mold to a layer of 60 nm Ag film deposited on quartz substrate. On top of the Ag film, a layer of 70 nm polymer, a UV resistant named STU 90, was spin-coated as a target substrate for nano imprint. In the first thermal imprint step an inverted intermediate polymer mold (IPS) was copied from the quartz master mold. The printing time was 180 seconds at 160 °C with an imprinting pressure of 30 bars. In the second imprint step a simultaneous thermal and UV process was employed to transfer the IPS pattern to the target substrate. The printing time was 60 seconds at 65 °C using a printing pressure of 30 bars, followed by a UV cure for 6 seconds. By this way, the polymer layer with protrusion features was fabricated on top of Ag film. After an etching process with ion milling, the areas in the Ag film protected by those protrusion features were retained and the nano structure was totally transferred onto the Ag film on surface of the quartz substrate. The residual layer of polymer left on top of the imprinted features was removed by Oxygen plasma RIE stripper right before the
nanostructures were optically characterized. Samples with nanopatterned Ag surface are kept in airtight tubes filled with nitrogen gas.

Experimental spectrum of a single Ag DDR nanostructure was obtained using the dark-field illumination mode of the same inverted microscope (Nikon Ti-U) together with a spectrometer (Andor SR-303i) and attached 400 × 1600 pixel EMCCD (Andor Newton). The white light from the halogen lamp of the microscope was focused by a dark-field condenser before being applied to excite the structures on sample. The scattered light was collected with a 100X oil immersion objective lens (NA 0.5-1.25, Nikon) and fed into the spectrometer attached to one port of microscope. A color camera was also attached to another port of the microscope to collect optical images of the scattering pattern in dark field illumination mode. The scattering spectra were measured over the wavelength range of 450-850 nm.

Figure 6(a) shows simulation spectrum of a DDR nanostructure with \( r_1 = 175 \) nm, \( r_2 = 130 \) nm, \( R = 54 \) nm and \( g = 15 \) nm respectively, while the measured optical spectrum of a single Ag DDR structure with the same set of nominated parameters, are found in Fig. 6(b), where the solid curve was obtained by moving average of measurement data. The experiment shows a comparatively good fit with the simulated spectrum, apart from a spectral broadening and peak shifting, which may due to the roughness of the top surface as well as the side wall of the fabricated structure. The redshift of the peak may also due to the residual polymer left on top of the DDR structure after RIE process. The effect was calculated in Fig. 4(b), where additional few nanometer dielectrics capped on metallic nanostructure leads redshift of the Fano peak. The peak position in Figs. 6(a) and 6(b) are 568 nm and 623 nm, respectively, which still located in visible wavelength range. In biochemical sensor application, the peak will be a reference of the bare sensor device.

3. Conclusion

We propose a symmetry broken dual-disk ring (DDR) plasmonic nanostructure with the weakly dissipating material of silver to realize the Fano resonance in visible wavelength range. The octupolar mode resonance of the ring interacts with the dipole mode of the disks to generate the asymmetric spectral feature of Fano resonance. Simulation analyses show large spectral tunability of the shape and position of the Fano resonance by varying geometric parameters. The sensitivity is high considered the visible working wavelength range. The figure of merit (FOM) of the DDR structure also indicates comparatively high performance, in the visible wavelength range, to the refractive index of surrounding medium as well as to the local refractive index change. Based on design and simulation, arrays of the DDR structures are fabricated and the Fano resonance is repeated observed in spectrum of a single DDR nanostructure. This silver DDR structure has potential to be developed to a promising
platform for ultrasensitive refractive index sensitive biosensing or for surface enhanced molecular sensing with the shift of Fano resonance within the visible range. Further work on biomolecule conjugation to the functionalized surface of the silver nanostructure array and characterization of sensing performance could lead the current study to a feasible biosensor.

Acknowledgment

We acknowledge the financial support by Joint Council (JOC) grant (JCOAG03-FG04-2009) and Science and Engineering Research Council (SERC) grant (No 102 152 0018) of Agency for Science, Technology and Research (A*STAR).