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## Modelling the Localized Surface Plasmon Resonance of Nanoclusters of Group III Metals and Semimetallic Antimony

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*Surface plasmon resonance in metal nanodroplets formed by droplet epitaxy was studied numerically. Metals compatible with molecular beam epitaxy and semimetallic antimony are shown to be effective for plasmonic applications in infrared region. The resonance position can be controlled by varying the droplet size. The increase in the effective droplet size results in the linear redshift of the resonance wavelength. The nanodroplet parameters needed to match a particular quantum dot emission can be found.*

*Keywords: plasmon resonance, discrete dipole approximation, metal droplet, plasmonic nanoantenna.*

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### Introduction

One of the challenges in modern nanotechnology is to increase efficiency and control of optical properties of quantum emitters. Quantum dots (QDs) have received much attention because they are key elements of diverse advanced devices such as single photon source. An efficient approach is to use metal nanoparticles as nanoantennas for QDs. It is well known that under the effect of light the oscillations of the electron density near the metal-dielectric interface can be excited in the form of localized surface plasmons. The plasmon resonant frequencies are determined by the geometry and the material of a particle and they can vary in a wide range. The local enhancement of the plasmon electrical field near the particle increases the rate of spontaneous recombination in the QD due to the Purcell effect [1]. Therefore, the coupling of the QD with a metal particle increases the efficiency of the emitter.

This approach brings additional advantages to control QDs properties. Precise control of the resonator parameters and the design of the plasmon modes allow one to tune the wavelength of the QD ensemble. It also allows for decreasing significantly the size of devices based on QDs as the plasmon wavelength is smaller than the light wavelength.

To realize the coupling a metal particle should be placed close to a QD. The most common method is lithography when nanoscale gold stripes are placed on the surface of a sample with self-organized QDs. While the precise location of the patterned gold particles can be achieved, the distance between the QD and the gold particle varies and, therefore careful selection of the QD-metal pair is required. Moreover, as gold is not compatible with molecular beam epitaxy (MBE) technique the opportunities of this method to produce more complicated structures are substantially limited.

The alternative approach is to produce metal particles in self-assembled mode that should be more efficient to control the distance between a particle and a QD. The initial stage of droplet epitaxy is a promising technique of QD fabrication based on preliminary formation of metal

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droplets on the substrate [2] and thus it can be used for metal droplet fabrication. It is known that if QDs layers are grown close enough they tend to align vertically and form stacks. The alignment is caused by the distribution of elastic tension in the matrix. The substitution of an upper layer of QDs with droplets should lead to the same self-alignment, i.e., the formation of a droplet just over a QD. Despite of random position of the pair such approach fixes the distance between QD and droplet and, therefore allows controlling their interaction precisely by adjusting the buffer layer thickness. The important advantage of this method is the full compatibility with the MBE technique used for QD growth.

However, the self-alignment of hybrid pair implies the substitution of gold with one of materials available in MBE machine. Apart from low losses, the extensive exploiting of gold for surface plasmon resonance based detectors is due to its chemical inertness which is of great importance for biosensors. QD emitters are free of such limitations and any of the available metals (In, Ga, Al, Sb) can be considered as a candidate for plasmon structures. It was recently reported that indium was successfully used for plasmon applications in IR range [3].

To control the system design we start with simulation and investigate a metal nanostructure numerically. We focus on the influence of material and size of the metal particle on the absorption spectra. We consider our approach as a practical way to design plasmon modes for the application in QD coupling.

## 1. Methods

The problem of plasmon modes in the sphere was analytically solved by Mie in 1920s. The exact solutions are also known for some specific geometries, namely, for the infinite cylinder [4] and for the spheroid [5]. Therefore, some approximation is required to model optical properties of particles with other geometries like droplets. Discrete dipole approximation (DDA) is a powerful tool for numerical simulations with a number of target parameters. In DDA a droplet is replaced by an array of point dipoles. The electromagnetic scattering problem for an incident periodic wave interacting with this array can be solved quite precisely [6]. Therefore, any shape can be modelled providing the interdipole distance being small enough in order to describe the shape features. The polarizabilities of the dipoles are determined by the material dielectric constants. The target size is defined by the effective radius of a sphere with an equivalent volume  $a_{eff}$ . The output of DDA simulations used in this work is the efficiency of the nanostructure absorption  $Q_{abs}$  defined as the absorption cross section normalized to the geometrical cross section  $Q_{abs} = C_{abs}/\pi \cdot a_{eff}^2$ .

To model a droplet the geometrical parameters experimentally obtained by atomic force microscopy (AFM) measurements in our previous investigation were used [7]. The typical droplet was set as a part of the sphere with the aspect ratio of droplet height to radius equals to 0.25. This parameter was varied to study geometrical dependencies. An example of the droplet consisting of 118000 dipoles is presented in Fig. 1. In what follows the incidence angle between the droplet symmetry axis and a light wave vector was set to be  $45^\circ$  unless specified otherwise. The incident light was linearly polarized with the electric field either parallel to the droplet base (TE polarization) or in the incidence plane (TM polarization).

## 2. Results and discussion

The first important issue when MBE compatibility is desired is how the metal of plasmonic structure influences the resonance position and shape. It was mentioned that indium might be effectively used for plasmonics in the infrared region despite of high losses. However, to our knowledge the indium application has never been studied. The spectra for droplets consisting of metals available in the MBE technology (namely, indium, aluminium and antimony) were simulated. The droplet effective radius was set to be 40 nm, resulting in the height of 21 nm and

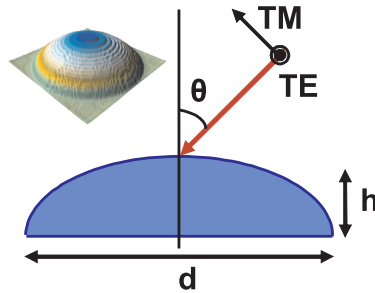


Fig. 1. A schematic droplet model used for simulations

the diameter of 170 nm. The spectra were also simulated for a larger droplet with the effective radius of 80 nm ( $h = 42$  nm and  $d = 340$  nm). A gold droplet was considered as a reference because gold is the most common metal for plasmonics.

The results of numerical experiment for various droplet materials are shown in Fig. 2. One can see that for the smaller droplet the amplitude of the main dipole peak of indium droplet absorption is about 70% of the gold absorption peak one and its width is larger. With the increase of the droplet size the situation changes and the absorption of the droplets of the group III metals exceeds that of the gold droplet. The widths of absorption peaks remain larger because of higher losses.

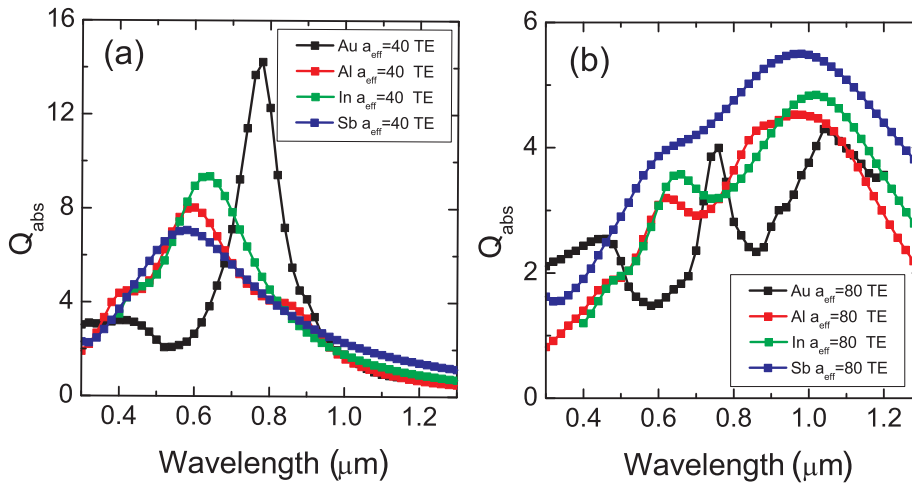


Fig. 2. Absorption spectra depending on droplet material. Droplet sizes are: a)  $a_{eff} = 40$  nm,  $h = 21$  nm,  $d = 170$  nm; b)  $a_{eff} = 80$  nm,  $h = 42$  nm,  $d = 340$  nm

It is interesting to note that the highest absorption is observed for the droplet consisting of antimony that is known to be semimetallic. To our knowledge antimony is not used so far for plasmonic applications. Our simulations show new perspectives of this material in the field of plasmonics. Therefore, numerical experiments prove that the group III metals are promising materials for the coupling with QDs in infra-red wavelength region. Combined with the MBE compatibility they bring obvious improvement to the technological procedure.

It is well known, that the droplet geometry and size influence the resonance significantly. Therefore, the droplet size might give an instrument to tune a resonance position. To implement such approach substrate temperature or metal amount can be used [8]. The absorption spectra

simulated for the indium droplet with the size varying in the range of  $a_{eff} = 30 \dots 100$  nm are presented in Fig. 3. Here  $a_{eff}$  is used as a convenient scaling parameter while corresponding

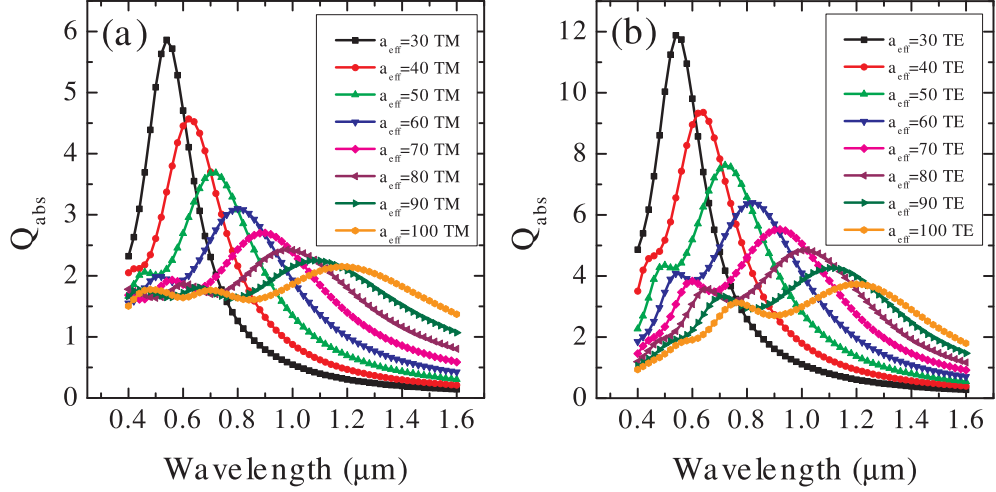


Fig. 3. Absorption spectra for an indium droplet with following effective radii  $a_{eff}$ , heights  $h$  and diameters  $d$  (all sizes are given in nm):  $a_{eff} = 30$   $h = 16$   $d = 128$ ,  $a_{eff} = 40$   $h = 21$   $d = 170$ ,  $a_{eff} = 50$   $h = 27$   $d = 213$ ,  $a_{eff} = 60$   $h = 32$   $d = 256$ ,  $a_{eff} = 70$   $h = 37$   $d = 300$ ,  $a_{eff} = 80$   $h = 43$   $d = 340$ ,  $a_{eff} = 90$   $h = 48$   $d = 384$ ,  $a_{eff} = 100$   $h = 53$   $d = 427$ . Spectra for TM and TE polarizations are shown in (a) and (b), respectively

heights and diameters are indicated in the figure caption. The results shown in Fig. 3 demonstrate that the droplet size influences absorption peaks dramatically. The peak corresponding to the dipole mode dominates in the spectra but starting with  $a_{eff} = 40$  nm a pronounced quadrupole mode peak appears in the spectra and with the further size increase a new peak arises. In the studied size range the dipole peak position can be shifted from 500 nm to 1.2  $\mu\text{m}$ . The dependence of the dipole and quadrupole modes of surface plasmon resonance (SPR) on the effective radius as the characteristic size is presented in Fig. 4. It appears that the position

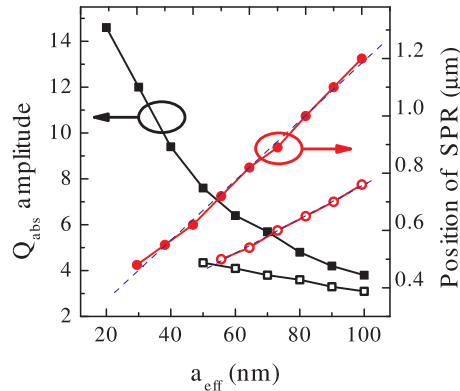


Fig. 4. The dependences of the dipole (closed symbols) and quadrupole (open symbols) modes of SPR position and  $Q_{abs}$  amplitude on  $a_{eff}$ . For the SPR position dependence the linear approximation is shown (dashed line)

of SPR linearly redshifts as the effective radius increases. The observed relation is in good agreement with the experimental and theoretical analysis for ellipsoids [9] and nanorods [10, 11] made of noble metals. In addition, the absorption amplitude demonstrates the decrease of the absorption efficiency close to  $1/R$ . As MBE allows controlling the substrate temperature and the amount of deposited material with high precision, plasmon resonances could be designed according to the QD requirements.

The spectra corresponding to large droplets in Fig. 3 exhibit few peaks that we attribute to dipole and quadrupole modes. The structure of plasmon modes is known to be determined by the droplet geometry. Normally two well defined axes are present and, therefore longitudinal and transverse plasmon modes (LM and TM, respectively) can be easily separated. The droplet shape that was described before implies that the main contribution is provided by the polarized charges distribution in the droplet base. However, the surface curvature can also affect the modes.

To analyze multipole SPR modes that we observed for large droplets more thoroughly we focus on the indium droplet with  $a_{eff} = 80$  nm as the spectrum of this droplet contains all the features of interest. The series of spectra for the different incidence angle  $\theta = 15, 45, 60$  and  $75^\circ$  and for both light polarizations were simulated. The results are presented in Fig. 5.

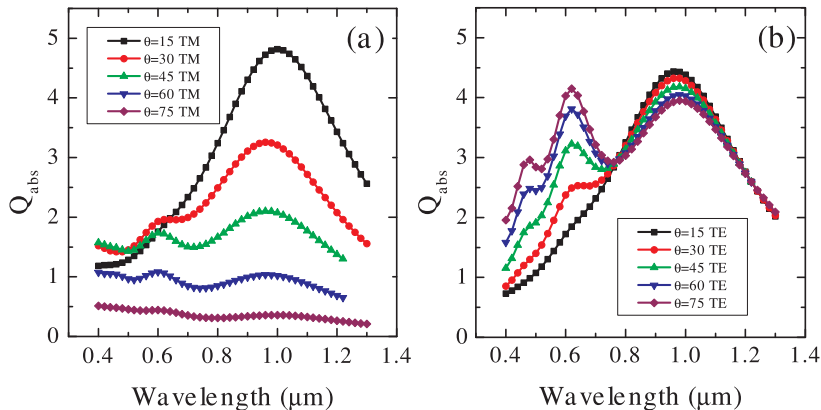


Fig. 5. Absorption spectra for In droplet with  $a_{eff} = 80$  nm for different incidence angles  $\theta$  and for TM (a) and TE (b) polarizations

The spectra in Fig. 5 demonstrate few distinguished resonances. Their origin and properties are important for the understanding of plasmon polariton in droplets. It can be seen that the peaks behave differently for TE and TM light. Angular dependences were simulated for selected wavelengths of 0.48, 0.62 and  $1 \mu\text{m}$  to investigate the structure of corresponding plasmon modes.

Fig. 6 clearly demonstrates the difference between the resonances that correspond to different plasmonic modes. The absorption for the resonance at  $1 \mu\text{m}$  decreases slightly with the increase of the incident angle up to  $90^\circ$  for TE light but drops to nearly zero for TM polarization. The behavior of TM absorption is proportional to  $\cos^2 \theta$  that simply describes the intensity of electric field projected to the droplet base. Therefore, this mode corresponds mostly to the charge redistribution in the plane of the droplet base.

The absorption of TM waves for 0.48 and  $0.62 \mu\text{m}$  demonstrates the behavior typical for conventional surface plasmon polariton (SPP) and presents peaks sensitive to the incident angle. It can be interpreted as mixing of transverse and longitudinal modes resulting in the peak evolution with the increase of the electric field projection to the droplet axis. The absorption of TE waves increases monotonically with the increase of the angle of incidence and reaches its maximum at the angle  $\theta = 90^\circ$ .

The presence of a few distinguished resonances within the MNP suggests a new type of

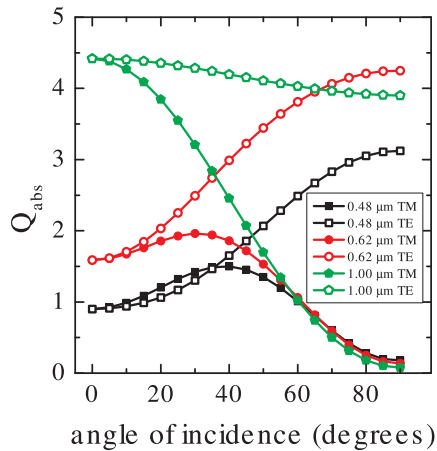


Fig. 6. Angular dependencies of absorption spectra for wavelengths of incident light of 0.48, 0.62 and 1  $\mu\text{m}$

plasmonic antenna with different channels. When the only resonance is used for both effective excitation of a quantum emitter and for the enhancement of the radiated signal [12] it is complicated to separate the weak signal from the pumping and scattered light. With a few multipolar modes one can tune, for example, the dipole mode to the emission band of a QD and use a pumping wavelength that is resonant with a quadrupole mode. Therefore, pumping and the signal use different channels providing a high signal-to-noise ratio. The obtained polarization dependences demonstrate a significant difference between TE and TM light. This can be used to increase the selectivity. For instance, for an incidence angle  $\theta = 75^\circ$  (see Fig. 6), the TE and TM wave absorptions at two wavelengths differ by a factor of 16. Thus the polarization control brings new opportunities for the development of a highly selective antenna.

### 3. Conclusions

Surface plasmon resonance in metal droplets produced by droplet MBE was studied numerically. It is shown that the metals compatible with conventional MBE setup can be effectively used to obtain resonance peaks in infrared region. Droplet size has a clear impact on the resonance positions and with the effective size increase the resonance position is linearly shifted to infrared region. Within the droplet size range used for simulations the peak is shifted from 500 to 1200 nm that makes the droplet size an effective parameter to tune the plasmon resonance in droplets. The incident angle dependence of the absorption spectra allow us to assume that while the charge redistribution in the droplet base is the main cause of the plasmon mode formation the curved upper surface of a droplet also influences plasmon modes. Using the simulation results the set of nanodroplet parameters needed to match particular QD resonance can be found.

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## Моделирование локализованного поверхностного плазмонного резонанса в нанокластерах металлов III группы и полуметаллической сурьме

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Численно изучен поверхностный плазмонный резонанс в металлических нанокластерах, полученных с помощью нанокпельной эпитаксии. Показано, что металлы, совместимые с методом молекулярно-лучевой эпитаксии (МЛЭ), и полуметалл сурьма могут эффективно применяться в плазмонных приложениях в инфракрасном диапазоне. Положением резонанса можно управлять, изменяя размер капли, причем с увеличением эффективного размера резонанс линейно смещается в длинноволновую сторону. Метод позволяет найти параметры капель для подстройки под излучение квантовых точек.

Ключевые слова: плазмонный резонанс, приближение дискретных диполей, металлическая капля, плазмонная антенна.