

# Surface-enhanced Raman spectroscopy of semiconductor nanostructures

A.G. Milekhin<sup>a,b,c</sup>, L.L. Sveshnikova<sup>a</sup>, T.A. Duda<sup>a</sup>, N.A. Yeryukov<sup>a,b,\*</sup>, E.E. Rodyakina<sup>a,b</sup>, A.K. Gutakovskii<sup>a</sup>, S.A. Batsanov<sup>a</sup>, A.V. Latyshev<sup>a,b</sup>, D.R.T. Zahn<sup>c</sup>

<sup>a</sup> Institute of Semiconductor Physics, Lavrentjev avenue 13, 630090 Novosibirsk, Russia

<sup>b</sup> Novosibirsk State University, Pirogova street 2, 630090 Novosibirsk, Russia

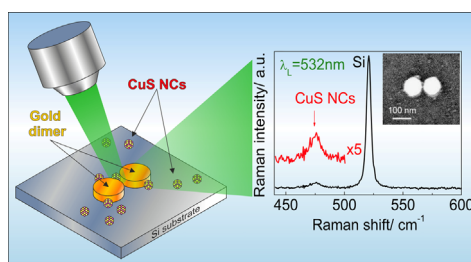
<sup>c</sup> Institut für Physik, Technische Universität Chemnitz, D–09107, Chemnitz, Germany

## HIGHLIGHTS

- SERS by confined optical phonons in CdS, CuS and ZnO nanocrystals was observed.
- SERS by surface optical phonons in Ga(Al)N and ZnO nanostructures was demonstrated.
- SERS by a few CuS nanocrystals in the vicinity of a single gold dimer was probed.

## GRAPHICAL ABSTRACT

SERS by optical phonons in few CuS NCs placed in the vicinity of Au dimer.



## ARTICLE INFO

### Article history:

Received 10 June 2015

Received in revised form

11 August 2015

Accepted 8 September 2015

Available online 16 September 2015

### Keywords:

Raman scattering

SERS

Nanostructures

Localized plasmon resonance

Phonons.

## ABSTRACT

We review our recent results concerning surface-enhanced Raman scattering (SERS) by confined optical and surface optical phonons in semiconductor nanostructures including CdS, CuS, GaN, and ZnO nanocrystals, GaN and ZnO nanorods, and AlN nanowires. Enhancement of Raman scattering by confined optical phonons as well as appearance of new Raman modes with the frequencies different from those in ZnO bulk attributed to surface optical modes is observed in a series of nanostructures having different morphology located in the vicinity of metal nanoclusters (Ag, Au, and Pt). Assignment of surface optical modes is based on calculations performed in the frame of the dielectric continuum model. It is established that SERS by phonons has a resonant character. A maximal enhancement by optical phonons as high as 730 is achieved for CdS nanocrystals in double resonant conditions at the coincidence of laser energy with that of electronic transitions in semiconductor nanocrystals and localized surface plasmon resonance in metal nanoclusters. Even a higher enhancement is observed for SERS by surface optical modes in ZnO nanocrystals (above  $10^4$ ). Surface enhanced Raman scattering is used for studying phonon spectrum in nanocrystal ensembles with an ultra-low areal density on metal plasmonic nanostructures.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Raman scattering is one of the most effective optical methods of studying vibrational spectrum of bulk semiconductors, thin films and nanostructures such as superlattices, nanowires, nanorods, and nanocrystals (NCs) or quantum dots [1]. Investigations

\* Corresponding author at: Institute of Semiconductor Physics, Lavrentjev avenue 13, 630090 Novosibirsk, Russia. Fax: +7 383 333 27 71.

E-mail address: [yeryukov@isp.nsc.ru](mailto:yeryukov@isp.nsc.ru) (N.A. Yeryukov).

of Raman scattering by phonons in semiconductor nanostructures (in the first turn, in superlattices) allowed experimental discovering of new physical effects including confinement of acoustic and optical phonons [1–5], folding of acoustic phonons [5], and renormalization of interface modes [6,7].

As a rule, experimental Raman study of nanostructures is limited by their low Raman cross-section because of the vanishing space size of the nanostructures (particularly, NCs). It is possible partially to overcome this limitation e.g. by using a large number of the layer sequences in superlattices or a thicker layer containing NCs or at the expense of formation of nanostructure ensembles with a higher areal density. However, the most interest is caused by single nanostructures due to large set of quantized phonon modes predicted theoretically. The frequencies of the confined modes depend on the structural parameters of nanostructures such as the size and the shape of NCs, diameter of nanowires *etc.* [6,8]. Experimental observation of these modes is a challenge while nanostructures (e.g. NCs) have inhomogeneous size and shape. This inhomogeneity prevents observation of a fine structure of the spectra of confined and interface optical phonon modes in nanostructure ensembles. The observed Raman phonon scattering spectra reveal the only broad feature which is a superposition of Raman phonon replicas of NCs having different size and shape. Therefore, investigation of principal mechanisms of phonon spectrum formation in a single nanostructure is substantially limited.

Several approaches can be used to enhance the phonon response in Raman spectra. One of the widely used approaches is the resonant Raman scattering for which the nanostructures under investigation are excited with the energy close or equal to that of optical electronic transitions in the nanostructures. Resonant Raman spectroscopy leads to increasing Raman scattering by optical phonons by about 3 orders of magnitude [9,10]. It was recently shown that resonant Raman spectroscopy allows the phonon response from ensemble of NCs with a low areal density down to 10 NCs/ $\mu\text{m}^2$  to be measured using a micro-Raman setup [11].

Surface-enhanced Raman scattering (SERS) is considered as an alternative approach for studying a phonon spectrum of semiconductor nanostructures. To observe SERS effect, semiconductor nanostructures should be either grown on special substrates with nanostructural metal surfaces or placed in the vicinity of metal nanoclusters.

Traditionally SERS is used for studying vibrational spectra in organic substances [12] with a low concentration down to a single molecule [13] and demonstrates the Raman enhancement up to  $10^{14}$ . Despite no principal physical limitations for SERS by phonons in semiconductor inorganic nanostructures take place, its experimental evidence was found only recently [14].

Even though SERS effect was discovered almost 40 years ago [15] the SERS enhancement mechanisms are still under debates. It was established that at least two mechanisms, electromagnetic and chemical, contribute separately or simultaneously to SERS enhancement. Electromagnetic mechanism shows itself in drastic enhancement of local electromagnetic field  $E$  in the vicinity of heterogeneities of metal surfaces or metal nanoclusters when the energy of electromagnetic field of the incident light coincides with that of localized surface plasmons (LSPs) [16]. SERS intensity is proportional to  $E^4$  and SERS enhancement factor is determined mostly by metal type, morphology of the metal surfaces or metal nanoclusters, and dielectric function of surrounding medium.

A variety of metals such as Pt, Cu, Li, Al, *etc.* were also shown to reveal SERS enhancement [17]. However, commonly, Ag and Au are used for formation of metal nanoclusters in SERS experiments while their LSP resonance (LSPR) energies are located in visible spectral range for which a number of excitation sources (lasers)

with various wavelengths can be applied. Choice of metal for SERS experiments (even between Ag and Au) is ambiguous and depends on materials under investigation, experimental conditions, *etc.* On the one hand, Ag provides a maximal Raman enhancement, while Au possesses the lowest imaginary part of complex refractive index  $n$  among metals [17]. On the other hand, Ag is not stable enough under ambient conditions and reacts with  $\text{H}_2\text{S}$  from atmosphere forming  $\text{Ag}_2\text{S}$  shell over Ag nanoclusters, that results in decreasing enhancement factor. Therefore, inert Au having the lower enhancement factor is often used in numerous applications.

Structural parameters of metal nanoclusters including nanocluster size, shape, their size dispersion and concentration is another crucial factor which governs SERS enhancement while it determines the energy of LSPR.

Since LSPR energy depends, in general, on a large set of structural parameters of metal nanoclusters, the calculation of LSPR energy for real nanoclusters is still a challenge. Therefore, this value is derived as a rule from optical absorption [18–20] or dark-field spectroscopy [21,22] experiments.

Optical properties of metal nanostructures with nanoclusters having spherical, triangular, pentagonal, tetrahedral *etc.* shape were investigated in detail [18]. In particular, it was established that increasing size of spherical nanoclusters causes a red shift of LSPR energy [19] which in its turn depends on refractive index of a surrounding medium [20,23]. However, optical absorption experiments require fabrication of metal nanostructures on transparent substrates that limits the application of this method. Dark-field spectroscopy and ellipsometry despite their relative complexity are free from this limitation and were also used to characterize plasmonic nanostructures [18,24].

One of the experimental approaches to observe SERS by organic materials is to use solid substrates covered with metal nanoclusters prepared by vacuum deposition [25] or liquid chemistry [26,27] followed by further deposition of the organic layer. An obvious disadvantage of the approach is a stochastic size and shape distribution of metal nanoclusters leading to a broadening of the LSPR, therefore reducing the intensity of the SERS signal. From this point of view, the SERS substrates containing ordered, size- and shape-controlled reproducible metal nanocluster arrays which can be fabricated by means of nanolithography are most preferable for SERS experiments.

Despite, numerous studies of SERS in organic and biological materials were carried out, the SERS effect by phonon modes in semiconductor nanostructures remains poorly known.

As it was already established, several semiconductor nanostructures demonstrate SERS by phonons. Honma et al. have demonstrated SERS effect by longitudinal optical (LO) phonons of CdS in Ag–CdS nanostructural composite particles in solution [28]. Suh and Lee reported on SERS by CdS nanowires deposited electrochemically into the pores of anodic aluminum oxide, where silver has been predeposited [29]. R.Venugopal et al. [30] have investigated SERS by CdSe nanobelts with off- and near-resonant excitations. Hugall et al. [31] have observed a resonant SERS enhancement by LO phonons of CdSe in core–shell CdSe/ZnS NCs deposited on commercially available nanostructured Au substrates. Later, SERS effect by LO phonons in CdSe in CdSe/ZnS NCs was realized on non-ordered nanostructured Ag surfaces [32]. Very recently, Lee et al. [33] have reported on observation of SERS by the surface optical (SO) and LO phonon mode in CdSe core and the transverse optical (TO) phonon mode in ZnS shell of core–shell CdSe/ZnS NCs attached to the surface of Au nanowire.

Enhancement of Raman scattering by LO phonons was observed in Au–ZnO NC nanocomposites [34] and ZnO–Au core–shells [35] excited near the resonance with the interband electronic transitions in ZnO NCs. Anomalously enhanced Raman scattering by LO phonons in nanostructured epitaxial GaN and ZnO

Download English Version:

<https://daneshyari.com/en/article/1543932>

Download Persian Version:

<https://daneshyari.com/article/1543932>

[Daneshyari.com](https://daneshyari.com)