Simulation of the photonic nanojet effect for Raman scattering enhancement in the diagnostics of oxide films

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Abstract. In this paper, by means of numerical simulations in the COMSOL Multiphysics software it's demonstrated that Raman scattering enhancement can be achieved for the diagnosis of metal oxide films using spherical particles made of barium titanate with a 10-micron diameter sphere. The formation of photonic nanojet in the sphere/film/substrate system at different radiation wavelengths and microsphere refractive index, film, and substrate was studied. The optimal interval of the particle refractive index is n≈1.8-2 was determined, at which the gain occurs directly at the particle/film interface. It is shown that for the UV wavelength range of wavelengths and film thicknesses from 50 to 200 nm, the gain is maximum. For ZnO and PZT films in the perovskite phase, sapphire and quartz are preferred as the substrate material, while for PZT in the pyrochlore phase, sapphire is preferred.

1. Introduction
Raman spectroscopy is a method of molecular spectroscopy based on inelastic light scattering in a substance. It can be used to obtain information about the chemical composition and phase transition of the material under study. Due to the small cross-sections of the interaction, the Raman signal is extremely weak and difficult to separate from the much stronger Rayleigh scattering signal [1]. The analysis of nano-sized objects, such as nanoparticles, biomolecules, and proteins, is challenging due to the low intensity of Raman scattering and the small sample size. Various approaches are used to increase the Raman signal, one of them being the photonic nanojet (PNJ) effect. If you illuminate a spherical particle that is larger than the incident radiation wavelength with a well-chosen refractive index, the particle behaves like a microlens, focusing light into" jets " of sub-wavelength length that come out of the shadow surface of microsphere. For a spherical particle, the PNJ is formed within a narrow line (transverse size of the order \( \lambda / 3 \)), while its propagation to the depth (lateral size) it can be stretched to a distance greater than \( \lambda \), depending on the refractive index of the medium and the substrate on which the sphere is placed [2,3]. The inhomogeneity of the refractive index at the interface between the particle and the sample leads to a change in the electromagnetic field distribution, including an increase in its localization. Therefore, Raman scattering can be amplified, since it strongly depends on the magnitude of the electromagnetic field [4,5]. Compared to traditional approaches such as surface-enhanced Raman light scattering (SERS), Raman microsphere-enhanced spectroscopy may be advantageous due to the ease of sample preparation, particle position control, and microsphere size control [6]. In [6], an increase in Raman scattering was demonstrated due to the use.
of nanostructures on silicon dioxide particles. It is shown that the most effective amplification occurs when the particle diameter is equal to the size of the incident radiation spot. In [7], the Raman scattering amplification using individual polystyrene microspheres was investigated. It was also found that the maximum gain occurs when the sphere is approximately equal to the size of the incident beam.

The Raman spectroscopy method can be used to study metal oxide films. At present, metal oxide films are both scientific and practical interest [8,9,10,11], since their application is possible in a wide field of optoelectronics both in the form of layers in film heterostructures [12] and in the form of composite systems [9,13]. Zinc oxide films are used as conductive transparent and barrier layers in optoelectronics, in particular, in solar energy [11,14], the conductive and optical properties of the films are modified by doping and special surface treatment [15]. Lead zirconate-titanate films are characterized by a wide variability of properties, including refractive index, which are determined by the composition [16] and can crystallize in different phases [14,17], which differ in refractive indices. The limitations of using the Raman spectroscopy method in the study of metal oxide films are associated with small sample thicknesses, and, as a result, small Raman scattering signals. Signal amplification is possible with a local increase in the incident radiation intensity, which can be realized when the PNJ is formed on the surface of the film.

In this paper, the possibility of amplifying Raman scattering using dielectric microspheres for the diagnostics of thin metal oxide films of zinc oxide and lead zirconate-titanate (PZT) in the perovskite phase and the pyrochlore phase is theoretically investigated.

2. Methods and materials

The possibility of amplifying Raman scattering using microspheres was investigated by numerical simulation in the COMSOL Multiphysics software. The physical model consisted of five components: an incident plane wave, the environment (air), a spherical particle, a film, and a substrate. The direction of propagation of the plane wave is perpendicular to the film surface. Schematically, the physical model is shown in figure 1.

![Figure 1. Schematic physical model in COMSOL Multiphysics software.](image)

Barium titanate (BaTiO3) was selected for the microsphere material. Medium – air (n0 = 1). The choice is determined by the dependence of the PNJ size on the particle refractive index. Previous calculations showed that if the refractive index is less than 1.8, the PNJ begins to move away from the shadow surface of the particle and extends in length, and if it is more than 2.1, the PNJ moves inside the particle. Therefore, the optimal range is 1.8 > n > 2 BaTiO3 has a refractive index of 1.9, so it is excellent for simulation the effects that occur behind the particle surface at the boundary with the studied film.

The substrate on which the sample is placed can strongly affect the light holding and propagation of the nanostructure, as demonstrated in [18]. Therefore, three different materials, such as sapphire
(n=1.77), quartz (n=1.46), sitall (n=1.53), were used as substrates to choose the most effective combination.

In this work, a plane wave was modelled, the wavefront width is equal to the sphere diameter. The sphere diameter is 10 microns. The PNJ effect was achieved by focusing a plane wave through a microsphere. The radiation intensity profiles were calculated along the x-axis at the boundary of the sphere and the film (figure 1), the maximum and average radiation intensity values were determined over the entire depth of the film, as well as the geometric dimensions of the PNJ in the lateral (n) and transverse (R_t) directions. The parameters R_n and R_t are the full width at the half maximum (FWHM) of the PNJ intensity peak in the sections along z and x, respectively, passing through the point of maximum intensity. The simulation was carried out in a wide wavelengths range to select the best value at which the maximum gain in the sample will be achieved. It is assumed that the value of the PNJ radiation intensity is a measure of the Raman signal amplification.

3. Results and Discussion

Figure 2 shows graphs of the dependence of the average and maximum field intensity in the ZnO film on the wavelength. At this thickness, we can assume that the value is the same across the entire depth of the film. It can be seen that for different variants of the substrate and the film thickness, the intensity is maximum in the UV region of the spectrum, and it decreases with increasing wavelength.

According to figure 2, 248 nm wavelength can be chosen for the study of the film in practice, for example, the radiation of an excimer laser (KrF). It is also possible to use radiation with 350-380 nm wavelengths and 470 nm for the visible range (there are peaks at the graph in these areas). For other PZT films, the peaks are observed in the same ranges.

![Figure 2](image_url)

Figure 2. The value of the light intensity in the ZnO film depending on the light source wavelength. Film thickness: (a) 100 nm; (b) 500 nm. Substrate – sitall.

![Figure 3](image_url)

Figure 3 - Dependence of the (a) average and (b) maximum radiation intensity on the film thickness. Substrate – sitall.
Figure 4. Field intensity distribution along the x-axis: (a) BaTiO3/ZnO/sitall $d_{film} = 100$ nm (b) $d_{film} = 500$ nm. (c) BaTiO3/PZT (perovskite)/sitall $d_{film} = 100$ nm (d) $d_{film} = 500$ nm, (e) BaTiO3/PZT (pyrochlore)/Al2O3 $d_{film} = 100$ nm, (f) $d_{film} = 500$ nm. Radiation wavelength – 248 nm.

Graphs of the dependence of the light intensity on the sample thickness are shown in Figure 3. The samples under study: ZnO and PZT films in the perovskite phase and pyrochlore phase were placed on sital substrates, and the film thickness varied from 50 nm to 700 nm.

It’s found that for the PZT in the perovskite phase, the dependence is almost linear, while the PZT in the pyrochlore phase and zinc oxide have well defined peaks. For zinc oxide, it is 200, 450 and 500 nm, for PZT in the pyrochlore phase – 200 nm, 450 and 650 nm. In general, we see a tendency to decrease in intensity with increasing film thickness due to absorption within the film.

Table 1. Full width at half-maximum (FWHM) for various film/substrate combinations, radiation wavelength-248 nm.

| Film material | Substrate material | $R_n$ (FWHM), um | $R_n$ (FWHM), um | $R_n$ (FWHM), um | $R_n$ (FWHM), um |
|---------------|-------------------|------------------|------------------|------------------|------------------|
| ZnO           | Sapphire          | 0.140            | 1.046            | 0.139            | 1.157            |
|               | Quartz            | 0.142            | 0.979            | 0.142            | 1.153            |
|               | Sitall            | 0.120            | 0.880            | 0.132            | 1.021            |
| PZT (perovskite) | Sapphire   | 0.135            | 1.101            | 0.143            | 1.237            |
|               | Quartz            | 0.129            | 0.928            | 0.123            | 1.261            |
|               | Sitall            | 0.127            | 0.884            | 0.134            | 1.022            |
| PZT (pyrochlore) | Sapphire   | 0.141            | 0.883            | 0.151            | 1.166            |
|               | Quartz            | 0.168            | 0.936            | 0.152            | 1.069            |
|               | Sitall            | 0.144            | 1.025            | 0.146            | 1.139            |

Table 1 shows the results of calculating the main geometric characteristics of the PNJ – "length" $R_n$ (lateral size) and "width" $R_r$ (transverse size). The PNJ formation for films with 100 and 500 nm thickness was considered. According to Figure 2, maximum increase in intensity was expected on the
film with \( d = 100 \) nm, and therefore the values of \( R \) and \( n \) should be less than at \( d = 500 \) nm. The maximum increase was observed on the sitall substrate for zinc oxide films and PZT in the perovskite phase, but it is small relative to another substrates 2–3%. For the PZT film, the pyrochlore phase is the highest intensity achieved on a sitall substrate. So, by selection, it was possible to identify the most effective combination of film and substrate.

The increase in intensity at the particle-film interface was considered in more detail. Figure 4 shows the radiation intensity distribution along the x-axis for each case of maximum gain. The position of the particle and the thin film is schematically marked. The intensity peak is located at the boundary between the particle and the film. Also, the peak intensity is shown on the field strength distribution at the point of contact of the particle with the sample along the y axis. This shows that the amplification occurs directly in the sample, which means that the Raman scattering can be enhanced. After the peak, the gain decreases.

4. Conclusions
In this paper, it was demonstrated by means of numerical simulations that it is possible to achieve Raman scattering amplification using microspheres for the diagnostics of metal oxide thin films. The formation of photonic nanojet in air at different radiation wavelengths, the microsphere refractive index and diameter, and the film refractive index are studied. It was found that to enhance Raman scattering by microspheres, it is necessary to choose the refractive index of the particles in the range \( n \approx 1.8–2.0 \). Then the gain occurs directly at the particle / film boundary. Also, it is necessary to choose the relevant wavelength. It was determined for all test samples that it is best to use the UV range wavelength and the optimal film thickness is 50-200 nm. For ZnO and PZT (pyrochlore phase) films, intensity peaks are observed also in the 450–500 nm thickness range. As a substrate for sample deposition, sitall and quartz can be used for ZnO and PZT films in the perovskite phase. For PZT in the pyrochlore phase, the gain is maximum if one uses the sapphire substrate.

Thus, with the correct choice of the radiation wavelength, the microsphere refractive index, the film refractive index and thickness, it is possible to effectively increase the intensity of the field inside the film. This method is easy to prepare and implement, cost-effective, and can provide field amplification for Raman scattering detection.

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References
[1] Darafsheh A 2021 Photonic nanojets and their applications, *J. Phys. Photonics* 3 6678-6690
[2] Yang H, Trouillon R, Huszka G, Gijs M A 2016 Super-resolution imaging of a dielectric microsphere is governed by the waist of its photonic nanojet *Nano Lett.* 16 4862–4870
[3] Chen Z, Taflove A, Backman V 2004 Photonic nanojet enhancement of backscattering of light by nanoparticles: a potential novel visible-light ultramicroscopy technique *Opt. Express.*12 12141220
[4] Du C L, Kasim J, You Y M 2011 Enhancement of Raman scattering by individual dielectric microspheres *J. Raman Spectrosc.* 47 42145–42148
[5] Das G M, Laha R, Dantham V R 2016 Photonic nanojet-mediated SERS technique for enhancing the Raman scattering of a few molecules *J. Raman Spectrosc.* 47895–900.
[6] Yi K J, Wang H, Lu H, Yang Y F 2007 Enhanced Raman scattering by self-assembled silica spherical microparticles. *Appl. Phys.* 47 42145–42148
[7] Du C L, Kasim J, You Y M, Shi D N and Shen Z X 2011Enhancement of Raman scattering by individual dielectric microspheres *J. Raman Spectrosc.* 42 145-146
[8] Afanasjev V P, Mukhin N V, Redka D N 2017 Surface Modification of ZnO by Plasma and Laser Treatment *Ferroelectrics* 508 1 124–129

[9] Afanas'ev V P, Vorotilov K A, Mukhin N V 2016 Effect of the Synthesis conditions on the Properties of Polycrystalline Films of Lead Zincate Titanate of Non-Stoichiometric Composition *Glass Physics and Chemistry* 42 3 295–301

[10] Mukhin N V 2014 Diffusion model of intrinsic defects in lead zirconate titanate films on heat treatment in air *Glass Physics and Chemistry* 40 2 238–242

[11] Evseenkov A S, Tarasov S A, Lamkin I A, Solomonov A V and Kurin S Y 2015 The efficiency of UV LEDs based on GAN/ALGAN heterostructures *Proceedings of the 2015 IEEE North West Russia Section Young Researchers* 27-29

[12] Mukhin N V 2016 Investigation of the formation kinetics of grain boundary inclusions of lead oxide in lead zirconate-titanate films *Glass Physics and Chemistry* 42 1 64–69

[13] Afanasjev V P, Chigirev D A, Mukhin N V and Petrov A A 2019 Formation and properties of PZT-PbO thin heterophase films *Ferroelectrics* 496 1 170–176

[14] Redka D N, Mukhin N V, Zakharov I G 2016 Variations in Optical and Structural Properties of Zinc Oxide Films after Laser Processing *Technical Physics* 61 11 1744–1746

[15] Agafonova D S and other 2018 Phases in Polycrystalline Films of Ferroelectric Oxides of the Perovskite- Type on the Basis of Bi2SrTa2O9 and Pb (Zr,Ti)O3 *Glass Physics and Chemistry* 44 1 15-20

[16] Iakovlev A and other 2019 Laser surface modification of ZnO for solar converters *Proceedings of SPIE* 10062 100621F

[17] Mukhin, N, Chigirev, D, Bakhchova, L and Tumarkin, A 2019 Microstructure and properties of PZT films with different PbO content-ionic mechanism of built-in fields formation *Materials* 12 18 2926

[18] Dantham V R, Bisht P B, Namboodiri C K R 2018 Enhancement of Raman scattering by two orders of magnitude using photonic nanojet of a microsphere *J. Appl. Phys.* 109 103103