The continued interest in ZnO-based materials in the low dimensional regime is based on the highly sought-after properties in optoelectronics such as wide bandgap of 3.37 eV, large excitonic binding energy of 60 meV and size dependent optical and electronic properties. One of the developing area during the last few years is the improving of the near band gap emission of ZnO with a use of different plasmonic materials, at the beginning noble metals, and then aluminum, which is more convenient for commercialization. Raman scattering also attracts attention because it characterizes the internal properties of material, phonon modes, and electron-phonon interactions. The studies of the resonant Raman enhancement of ZnO are limited due to the high energy of the interband electronic transitions, which implies the excitation in the UV region. Aluminum has a favorable dielectric constant value to sustain localized surface plasmon resonances in deep-UV-vis region. In this work, we report on enhancement of the ZnO nanocrystals Raman scattering with a use of aluminum nanostructures. We design the system of coupled Al nanocylinders of elliptical shape that have collective plasmonic modes in the UV spectral range corresponding to the intrinsic interband excitation and emission of ZnO nanocrystals.

Fig. 1. Extinction spectra of the Al array (two polarizations) without (a) and with (b) overlying layer of ZnO. There are measurements for the polarizations along the short and long axis of the elliptical cylinders and reference spectrum of the ZnO nanocrystals layer. Corresponding numerical simulation for all measurements (c, d). In the right panel the SEM microscopy of the elliptical nanoparticles and its schematic illustration are shown.

Fig. 3 Raman spectra of ZnO seed layer on Al nanocylinders and on a reference glass substrate.

In the extinction spectrum of the Al nanoparticles covered with ZnO layer two modes appear (Fig. 1). These two modes show hybridized character. According to charge distribution calculations, the mode at 370 nm looks like the mode $D_0Q_0H_0$, where the $D_0$, $Q_0$, $H_0$ are the initial dipolar, quadrupolar and hexapolar modes.

The photoluminescence spectra of ZnO feature the peak at 385 nm, which corresponds to the near band emission of ZnO. We compare the fluorescence signal from the system with and without the additional peak in the extinction. For the nanoparticles 192x102 nm the photoluminescence enhancement factor was 9.7 times, for the nanoparticles 170x102 nm it was 5.4 times (Fig. 4).

Resonant Raman spectrum of the ZnO nanocrystals on Al nanostructures features an intense peak at 570 cm$^{-1}$, which corresponds to the optical phonon Al (LO), and sequential peaks at 1140 cm$^{-1}$, then 1710 cm$^{-1}$, which are the LO overtones (Fig. 3).

Fig. 2 The extinction maps depending on superstrate refractive index for round cylinders d=102 nm (a), for elliptical cylinders 192x102 nm (b); the extinction maps depending on the long axis size for n=1 (c) and layer of ZnO (d). Diffractive orders are marked with white lines.

Fig. 4. Photoluminescence spectra of ZnO seed layer on array of Al nanocylinders of two sizes 192x102 and 170x102, and on reference glass substrate. Inset shows the extinction spectra of two arrays.