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Enhancement of Raman scattering by two orders of magnitude using photonic nanojet of a microsphere

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The enhancement of Raman signal is observed on excitation through a single microsphere. The dependence of the enhancement ratio (ER) on various parameters viz., numerical aperture (NA) of the microscopic objective lens, pump wavelength, size and refractive index of the microsphere has been studied. The enhancement has been explained due to interaction of the increased field of the photonic nanojet emerging from the single microsphere. The photonic nanojet induced ER of Raman peaks of silicon wafer and cadmium ditelluride is reported here. It is observed for the first time that by suitable selection of the experimental parameters, it is possible to enhance the Raman signal by approximately two orders of magnitude. © *2011 American Institute of Physics*. [doi:10.1063/1.3590156]

I. INTRODUCTION

Raman spectroscopy can be used to obtain the information on the chemical composition and phase transition of the material under investigation. The intensity of the Raman frequency of a molecular vibration is linearly proportional to the concentration of the specific molecule and its cross section.[1] Due to small interactive cross sections, the Raman scattering signal is extremely weak. Several mechanisms such as surface-enhanced Raman scattering,[2] tip enhanced Raman scattering,[3] shell-isolated nanoparticle-enhanced Raman spectroscopy,[4] and resonance Raman scattering[1] are being used for improving the Raman scattering signal.

The Raman scattering signal can also be enhanced by the photonic nanojet emerging from the single microparticles. Theoretical studies[5,6] on photonic nanojet have been carried out for plane and Gaussian beam excitations, respectively. By using closely packed spherical silica microparticles, Yi *et al*.[7] have achieved an enhancement factor of 6 in the Raman scattering. With the single polystyrene microspheres, Du *et al*.[8] have observed enhancement factor of 11 in the Raman scattering peak of silicon wafer. During the experiment on variation of the size of the single microspheres,[9] we noticed that this enhancement depends upon the pump wavelength, the refractive index of the microsphere and the collection objects. In the present study, therefore we report the variation in the enhancement factors of Raman peaks of silicon wafer and cadmium ditelluride ($CdTe_2$) thin films due to these parameters. It is observed for the first time that by suitable selection of the experimental parameters, it is possible to enhance the Raman signal by approximately 2 orders of magnitude.

II. EXPERIMENTAL

The $CdTe_2$ thin film was deposited on the slide glass from the cadmium telluride (CdTe) bulk by using a thermal evaporation unit (Hind High Vacuum Company, Bangalore) at a vacuum of 9×10^{-5} mbar. The silica (Duke Scientific Corp.) and barium titanate ($BaTiO_3$) (Mo-sci. Corp.) microspheres were used as received. A few microspheres were transferred to a silicon wafer/$CdTe_2$ thin film for the spectral measurement.

Raman spectra of substrate (silicon wafer/$CdTe_2$ film) were recorded by using a Raman spectrometer (Jobin Yvon, model HR-300) equipped with a He-Ne laser (632.8 nm) and an Ar^+ laser (488 nm). The excitation laser with a Gaussian profile was focused on the substrate through a single microsphere by using a $10\times$ (NA = 0.25) microscopic objective lens as shown in Fig. 1. The Raman scattering signal was collected in the backscattering geometry, and was guided to a Peltier-cooled CCD (DV420 A-OE-324) detector. A 3 cm^{-1} resolution (with a grating of 600 grooves/mm) in the Raman shift has been used to record these spectra. The laser power used to irradiate the sample was measured at the laser head and was kept at 20 mW for all the measurements. The exposure time was kept as 5 s for each measurement. The Raman peak of silicon wafer at 521 cm^{-1} was also used to calibrate the spectrometer.

III. THEORETICAL ASPECTS

The total electric field in the photonic nanojet emerging from a single dielectric particle (Fig. 2) due to the plane wave excitation is given by[10]

$$\mathbf{E}_{jet}(\mathbf{r}) = \mathbf{E}_{inc}(\mathbf{r}) + \mathbf{E}_{sca}(\mathbf{r}), \quad (1)$$

where $\mathbf{r}$ is the radial distance. $\mathbf{E}_{inc}(\mathbf{r})$ and $\mathbf{E}_{sca}(\mathbf{r})$, respectively, are the incident and scattered wave fields given by

$$\mathbf{E}_{inc}(\mathbf{r}) = \sum_{n=1}^{\infty} i^n\{(2n+1)/[n(n+1)]\}[\mathbf{M}^{(1)}_{o\,ln}(\mathbf{r}) - i\mathbf{N}^{(1)}_{e\,ln}(\mathbf{r})], \quad (2)$$

$$\mathbf{E}_{sca}(\mathbf{r}) = \sum_{n=1}^{\infty} i^n\{(2n+1)/[n(n+1)]\}[ia_n\mathbf{N}^{(3)}_{e\,ln}(\mathbf{r}) - b_n\mathbf{M}^{(3)}_{o\,ln}(\mathbf{r})], \quad (3)$$

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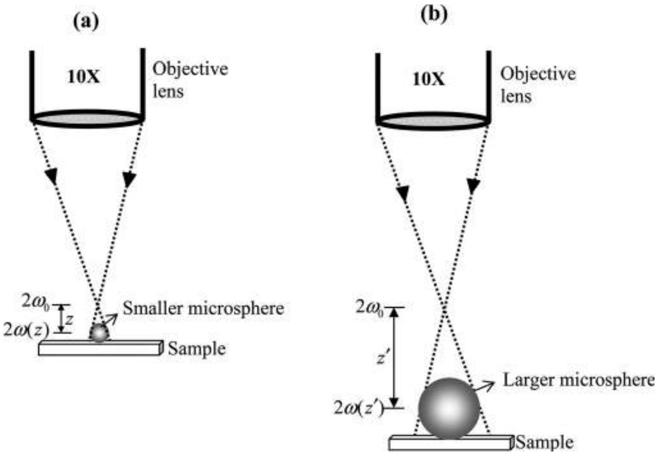

FIG. 1. The schematic of the experimental setup for enhancement of Raman scattering signal of the sample with (a) smaller and (b) larger microsphere. Here, $2\omega_0$ is the beam diameter at the focal point. $2\omega(z)$ and $2\omega(z')$ are the beam diameters at the distances z and z', respectively.

where $\mathbf{M}_{o\,\ln}$ and $\mathbf{N}_{e\,\ln}$ are the vector spherical harmonics. The superscripts (1) and (3) appended to the vector spherical harmonics denote the spherical Bessel and Hankel functions, respectively. a_n and b_n are the scattering coefficients and are the function of refractive index of the sphere (n_{sphere}) relative to the surrounding medium and the size parameter (x). The size parameter is given by

$$x = 2\pi a n_{\text{med}}/\lambda, \tag{4}$$

where a is the radius of the sphere. λ is the wavelength of the light and n_{med} is the refractive index of the surrounding medium.

IV. RESULTS AND DISCUSSION

A. Enhancement of Raman scattering signal for silicon wafer

The silicon wafer was selected for the present study as a standard sample. It is well known that the silicon wafer has a sharp peak at 521 cm^{-1} assigned as the first order transverse optical (TO) mode.[11]

1. *Effect of microsphere diameter*

The Raman spectra of silicon wafer were recorded by exciting through the single silica microspheres. However, without keeping the microsphere in the field of view, the obtained spectrum is weak as seen by the comparison of the two spectra in panel A of Fig. 3. For a silica microsphere of ~ diameter 36 μm, the Raman signal enhances by about 16 times. This indicates that the electric field is well confined to the surface of the silicon wafer in a nanometer-scale region. Since the Raman scattering signal is strongly dependent on the electric field, it is enhanced due to the strong localization of the electric field. This is due to the photonic nanojet emerging from the single microsphere due to the Gaussian beam excitation. The photonic nanojets,[5] can be created with small (radius $\approx \lambda$) as well as with large (radius $> 20\lambda$) microspheres.[12]

Panel B shows the Raman spectrum of silicon wafer on excitation through a single silica microsphere of diameter ~10 μm. Along with the TO mode of silicon, several sharp peaks appear in the lower and higher Raman shift region. These peaks are known as whispering gallery modes (WGMs) of the microsphere.[9]

The value of the enhancement ratio (ER) of the Raman intensity was calculated for different microspheres. This was done by taking the ratio of the Raman intensity of the sample with excitation through a single microsphere to that with the direct excitation (without a microsphere). It can be seen that the ER increases with the microsphere diameter (panel C). In the present case, the maximum ER (~16) is obtained for the microsphere of diameter ~36 μm. This is obtained by placing the microsphere at a distance of 0.11 mm away from the focus point as shown in the Fig. 1. At this distance, the beam waist can be estimated follows.

The Gaussian beam waist [$\omega(z)$] at a distance (z) is given by[13]

$$\omega(z) = \omega_0\left[1 + \left(\lambda z/\pi\omega_0^2\right)^2\right]^{1/2}, \tag{5}$$

where the minimum beam waist (ω_0) at focus is given by[14]

$$\omega_0 = 0.61\lambda/\text{NA}. \tag{6}$$

At a distance of 0.11 mm, the beam diameter incident on the microsphere is estimated to be 29.2 μm. It can be seen that the microsphere diameter (36 μm) is within an error of 23% of this estimate. It is also observed that the ER decreases on moving the sample from the focus point toward the objective lens.

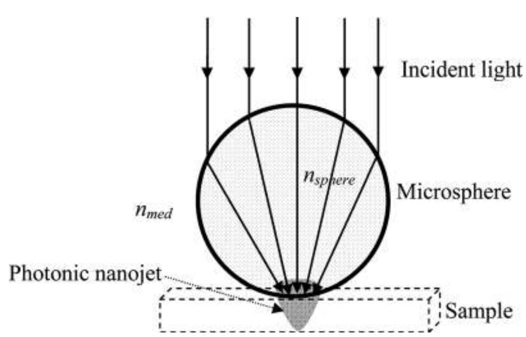

FIG. 2. Schematic of the photonic nanojet emerging from a single microsphere.

2. *Effect of refractive index of the microsphere (n_{sphere})*

The electric field in the photonic nanojet depends on the refractive index of the microsphere [Eqs. (1)–(4)]. In order to see the effect of refractive index of the microsphere, the Raman spectra of silicon wafer were also recorded by exciting through the larger refractive index ($n_{\text{sphere}} = 2.1$) microsphere of $BaTiO_3$. The observed values of ER with silica and $BaTiO_3$ microspheres of two different sizes are shown in the Table I. It can be seen that the ER values with the $BaTiO_3$ microspheres are lower than those of silica. This is due to the fact that the electric field strength in the photonic nanojet

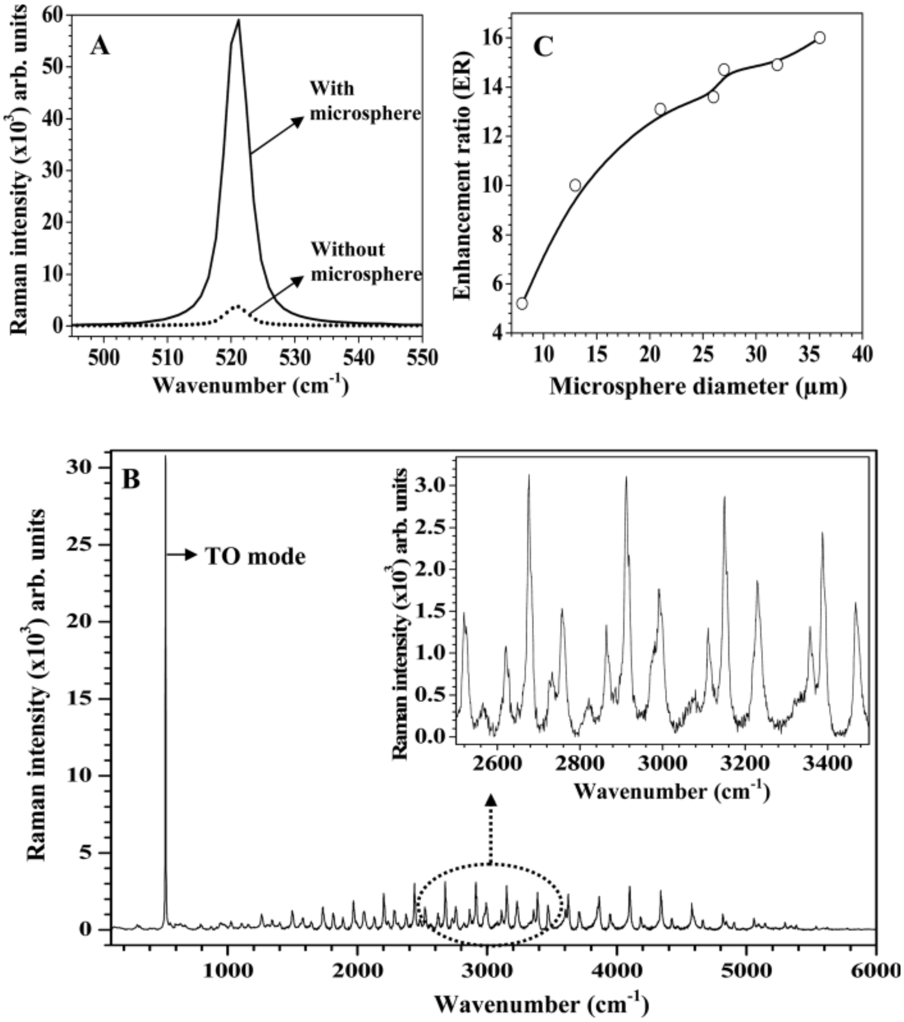

FIG. 3. (A) Enhancement of Raman intensity of the 521 cm^{-1} peak of silicon wafer (with microsphere of diameter $\sim$36 μm). Typical Raman spectrum of silicon wafer on exciting through a single silica microsphere of diameter $\sim$10 μm (B). The inset shows an expanded region of the spectrum showing WGMs. Panel C shows the ER obtained with single silica microspheres.

decreases on increasing the refractive index of the microparticle[5] and is lower in $BaTiO_3$ microsphere.

3. Effect of pump wavelength (λ)

Along with the refractive index, the electric field in the photonic nanojet also depends upon the pump wavelength. The Raman spectra of silicon wafer were also recorded on exciting with 488 nm. Obtained values of ER are shown in the Table II. It can be seen that the ER values increase on decreasing the λ. This observation can be understood as follows. In the case of excitation of a dielectric microsphere by a Gaussian beam of wavelength λ, the effective volume of the photonic nanojet beyond the microsphere is given by[6]

$$0.6(\lambda/n_{\mathrm{med}})^3. \tag{7}$$

Therefore, the photonic nanojet due to 488 nm confines into a smaller volume beyond the microsphere as compared to that with 632.8 nm. Due to stronger confinement of light, the electric field in the photonic nanojet increases more in the case of 488 nm excitation resulting in more enhancement.

B. Enhancement of Raman scattering signal for $CdTe_2$ thin film

To confirm the obtained results with the standard sample of silicon, we studied the thin film of $CdTe_2$ as another example. The Raman spectra of the thin film obtained with the excitation wavelength of 632.8 nm are shown in Fig. 4.

TABLE I. Dependence of ER of TO mode of the silicon on the refractive index of the microsphere.

	ER	
Diameter (μm)	Silica ($n_{\mathrm{sphere}} = 1.45$)	$BaTiO_3$ ($n_{\mathrm{sphere}} = 2.1$)
13	10	6
36	16	14

TABLE II. Excitation wavelength dependence of ER of TO mode of silicon for $BaTiO_3$ microsphere.

	ER	
Diameter (μm)	$\lambda = 632.8$ nm	$\lambda = 488$ nm
13	6	14
36	14	32

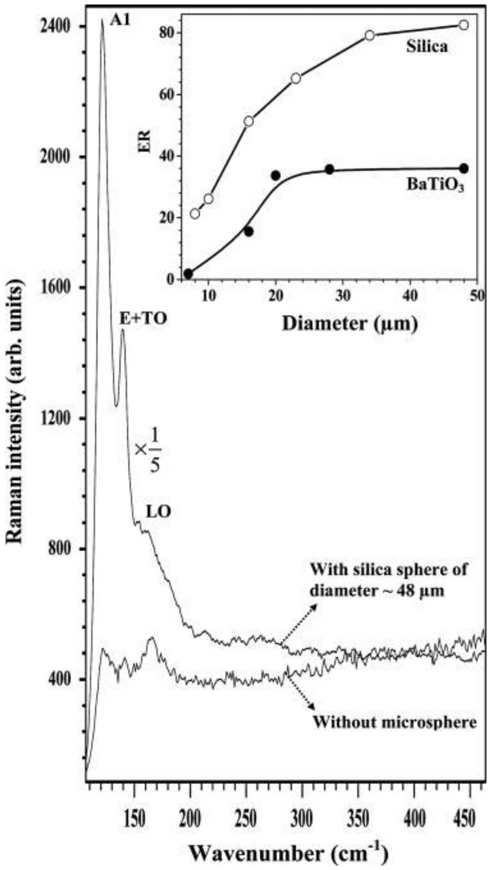

FIG. 4. Raman spectra of $CdTe_2$ thin film obtained with the excitation wavelength of 632.8 nm through the 10 × lens. Inset shows the obtained ER of the A1 peak with the different microspheres.

There exist three peaks at 123, 141, and 164 cm^{-1} in the spectra. The peak locations match well with those reported in the literature.[15] The first peak (123 cm^{-1}) is due to the A1 symmetry phonon (peak labeled as A1). The second peak (141 cm^{-1}) is due to both the pure tellurium phase (E) and the transverse optical phonon (TO) of the CdTe lattice (peak labeled as E + TO). The third peak (164 cm^{-1}) is the characteristic of the CdTe phase and is due to lattice vibrations along the (110) and (111) crystallographic directions [the longitudinal-optical phonon (LO)].

As mentioned in the experimental section, the thin film is grown from the thermal evaporation of the bulk CdTe. The intensity of the LO peak obtained with the direct excitation (without microsphere) is higher than that of the remaining peaks. This has been considered as the Raman signature of the $CdTe_2$ phase. The transition takes place from CdTe to $CdTe_2$ phase depending upon the deposition conditions. On excitation of the film through the single microsphere, Raman peaks become more intense considerably. However, the enhanced intensity of the LO peak is lower as compared to the other peaks. This is due to decomposition of the $CdTe_2$ compound into two more stable phases namely CdTe and Te on increasing the incident irradiation power.[15]

The ERs of the A1 peak obtained with silica and $BaTiO_3$ microspheres are shown in the inset of Fig. 4. It is to be noted that the ER increases with the microsphere diameter in both the cases. However, the observed ER for $BaTiO_3$ microspheres is lower as compared to that with the silica microspheres. For example, the larger silica microsphere (48 μm) gives an ER value of 83 while it is 35 for the $BaTiO_3$ microsphere of same size. The lower value of ER is due to the higher refractive index of $BaTiO_3$ microspheres (vide supra Table I).

The Raman spectra of silicon and $CdTe_2$ by exciting through silica microspheres were also recorded with the help of 50 × (NA = 0.75) objective lens. In contrast to the case of 10 × objective lens, the value of ER increases on decreasing the microsphere diameter from 48 to 8 μm due to the tightly focusing of light. However, the obtained ER with 50 × objective lens is 4 times smaller than that with the 10 × objective lens.

V. CONCLUSIONS

The intensity of the Raman peaks of silicon wafer and $CdTe_2$ thin film are enhanced with the excitation through the single microspheres. The maximum ER of the silicon wafer and $CdTe_2$ thin film is found to be ~16 and 83, respectively. The ER values are found to decrease on increasing the refractive index of the microspheres. ER value depends on the matching the excitation spot size with that of the microsphere. Excitation with lower wavelengths results in higher ER values. An application of this study is to record the weak Raman signals, thereby improve the efficiency of the Raman based sensors.

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