Dispersion of resonant Raman peaks of CO and OH in SnO$_2$, Mo$_{1-x}$Fe$_x$O$_2$ thin films and SiO$_2$ bulk glass

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Abstract
Resonance Raman (RR) peaks of CO and OH stretching modes and their higher harmonics have been observed superimposed on the photoluminescence (PL) spectrum of SnO$_2$ thin films. Commercial fluorine doped SnO$_2$ thin films deposited by sputtering on glass and SnO$_2$ thin films deposited on Si by laser ablation have been studied. The dispersions of CO and OH stretching RR modes are $\sim$600 cm$^{-1}$ eV$^{-1}$ and 800 cm$^{-1}$ eV$^{-1}$, respectively. The dispersion of the third harmonic of the CO stretching mode is $\sim$2000 cm$^{-1}$ eV$^{-1}$. Similar dispersion of the RR peak of CO stretching modes and higher harmonics superimposed on PL spectra has been observed in Mo$_{1-x}$Fe$_x$O$_2$ thin films and SiO$_2$ bulk glass. Large dispersion of RR peaks seems to be a common property of oxides with impurities of CO and OH.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Photoluminescence (PL) studies are routinely used to characterize photonic materials. The use of oxide materials in bulk, thin film and nano-structure geometries has drawn the attention of many research groups for their uses in the ultraviolet (UV) and vacuum ultraviolet (VUV) ranges [1–5]. Wide band gap materials doped with rare earth ions (phosphors) find enormous application in plasma display panel (PDP) and lighting applications [2]. The application domain of these materials, however, depends on defect states, which could be either in bulk or at the surface of the sample. During the thin film processing of these oxide materials, the defects may be easily incorporated. In order to look into the nature of these defects, these wide band gap materials are also characterized by PL spectroscopy under UV and VUV excitation. Sharp resonance Raman (RR) peaks have been observed along with the PL spectra for some large band gap semiconductors [6–8]. Generally, PL measurements are done using a single energy excitation source and it is difficult to assign the exact origin of sharp superimposed peaks over PL bands as being due to RR or PL processes. The analysis of RR peaks due to impurities (intentional as well as unintentional) becomes important with excitation energies in the UV and VUV region in the case of wide band gap oxides, fluorides and oxyfluorides doped with rare earth ions. For example, in the case of SnO$_2$, sharp peaks superimposed on PL bands had been reported and the origin of these sharp peaks was ascribed to excitons and defects [9–11]. In this paper, we attempt to examine the origin of these sharp peaks by studying the PL spectra of different oxide systems, namely, SnO$_2$, Mo$_{1-x}$Fe$_x$O$_2$ thin films, bulk fused and ordinary SiO$_2$ glass. In our case, the incident energy is varied and it is concluded that the origin of these superimposed sharp peaks is due to the RR mechanism of CO and OH stretching modes and their higher harmonics. In single resonant Raman (SRR) spectroscopy, the energy of the incoming and scattered photon matches the transition energy of an allowed electronic transition and this increases the scattering cross-section. Details about the theory and experiments of SRR spectra are well documented and available in books and research papers [12, 13].
Another important feature of this study is the dispersion of resonance peaks with respect to excitation energy. The largest reported dispersion to date is of the D peak in the RR spectra of amorphous carbon and it is about 50 cm$^{-1}$ eV$^{-1}$ [14–17]. The dispersion of the D band has been explained using theoretical models of double resonant Raman (DRR) scattering [16, 17]. In DRR, the electron–phonon scattering makes a real transition in addition to incoming and outgoing resonances [16, 17]. We have observed dispersion of the order of 800 cm$^{-1}$ eV$^{-1}$ and 2000 cm$^{-1}$ eV$^{-1}$ for the stretching mode of OH and its third harmonic, respectively. Results of SnO$_2$, Mo$_{1−x}$Fe$_x$O$_2$ thin films, bulk fused and ordinary SiO$_2$ glass related to fundamental and higher harmonics of RR peaks and their dispersion with respect to incident energy are presented in this paper. Present results are discussed assuming triple resonant Raman (TRR) scattering. In TRR, the following processes (a) electronic excitation and recombination, (b) electron–lattice phonon transition and (c) electron–defect vibrational transition are in resonance. Initial studies of PL of LiTaO$_3$ thin films have also shown dispersion of the OH stretching mode of the same magnitude [18]. The aim of this paper is to show that the large dispersion of RR peaks seems to be a common property of oxides with impurities of CO and OH.

2. Experiment

Commercial SnO$_2$ thin films (doped with F) deposited by sputtering on glass and SnO$_2$ thin films deposited on Si by laser ablation have been used for PL study. The ceramic target used for SnO$_2$ film growth by pulsed laser ablation was prepared by the standard solid state reaction technique. A KrF excimer laser source ($\lambda = 248$ nm, pulse width = 20 ns) was used to ablate the target. The substrate was cleaned by the chemical method thoroughly and the chamber was evacuated at a base pressure of $2 \times 10^{-6}$ Torr before deposition. Depositions were performed at a substrate temperature of 700 °C and an oxygen partial pressure of $1 \times 10^{-4}$ Torr, while the target to substrate distance was 5 cm. The laser energy density and the pulse repetition rate were kept at 1.8 J cm$^{-2}$ and 10 Hz, respectively. The samples were cooled in the same pressure as used during the deposition, at the rate of 20 °C min$^{-1}$. Thicknesses of the films were 200 nm as determined using a Talystep profilometer. These thin films are polycrystalline. Mo$_{1−x}$Fe$_x$O$_2$ thin films were also deposited by laser ablation on sapphire substrates in a similar process. PL studies were carried out using an unpolarized excitation source as the incident ray. Outgoing scattered rays were recorded using back reflection geometry and spectra were recorded with an incremental step of 0.1 nm. The PL and RR spectral data were obtained using a spectrofluorometer (FluoroMax–3, Jobin Vyon). The background excitation source used for this purpose was a 150 W xenon, continuous output, ozone-free lamp. A calibrated photodiode and a R928P photomultiplier are used as excitation and emission detectors. All PL measurements have been done at room temperature in air. Excitation energies have been varied from 2.5 to 5 eV. RR measurements have been done on a PL experimental setup and spectra are recorded starting from wavelength 15 nm away from the excitation wavelength. Scattered light is measured for a shift energy of more than 1800 cm$^{-1}$. Hence, Raman scattering results for a shift energy of less than 1800 cm$^{-1}$ is not given in this manuscript. The normal Raman spectrum of SnO$_2$ thin films, measured on a Raman experimental setup, is similar to the published results in the literature [19].

3. Results and discussion

Emiroglu et al studied the vibrational modes of OH, CO, H$_2$O$^+$ and H$_2$O$^2_−$ attached to an SnO$_2$ powder surface by diffuse reflection infrared Fourier transform (DRIFT) spectroscopy [20]. Absorption peaks of OH related vibrational modes lie in the range 3400–3700 cm$^{-1}$. Vibrational modes of H$_2$O$^+$ and H$_2$O$^2_−$ attached to SnO$_2$ are in the range 2900–2850, 2250–2200, 1705–1660 and 1000–900 cm$^{-1}$. Adsorption of CO gives an absorption peak at 2200 cm$^{-1}$ [20]. Normal vibrational modes in H$_2$O are $\nu_1 = 3657$ cm$^{-1}$, $\nu_2 = 1595$ cm$^{-1}$ and $\nu_3 = 3756$ cm$^{-1}$, and in CO$_2$, these are $\nu_1 = 1340$ cm$^{-1}$, $\nu_2 = 667$ cm$^{-1}$ and $\nu_3 = 2350$ cm$^{-1}$ as given, in a book by Nakamoto [21].

Curves 1, 2 and 3 in figure 1(a) show PL spectra of F doped SnO$_2$ thin film deposited on glass, excited with monochromatic light from the xenon source of wavelengths 280 nm, 330 nm and 380 nm, respectively. The inset in figure 1(a) shows the normal transmission spectrum of SnO$_2$/glass thin film.
Encircled peaks in figure 1(a) are due to the noise of the experimental setup. The initial part of curve 1, figure 1(a), from 295 to 330 nm, is due to Rayleigh scattering. The broad peak from 340 to 410 nm is due to the sum of the band gap PL and PL from oxygen vacancies. The full width at half maximum (FWHM) of the band gap PL is 45 nm. The maximum of the band gap PL is in the range 365–380 nm. The optical band gap of SnO$_2$ at $T = 300$ K is $\sim 345$ nm (3.6 eV) and oxygen vacancies give PL near 390 nm [22, 23].

Intensities due to Rayleigh scattering for curves 2 and 3, in the range 350–450 nm, are more as the intensities of the excitation wavelengths increase for longer wavelengths. The intensities due to Rayleigh scattering and intensity due to band gap PL for curves 2 and 3, are mixed. There are some sharper peaks superimposed on the PL spectrum. The intensities of the superimposed peaks are maximum for the excitation wavelength 380 nm. Figure 1(b) shows curves 1, 2 and 3 of figure 1(a), as a function of shift energy with respect to energies of the incident light. It is known that the intensity of the RR peaks is maximum for the excitation energy equal to the sum of the band gap energy and the energy of the RR peak. In this condition, loss of energy to the lattice is minimum [12]. Let us concentrate on curve 3 of figure 1(b), as the excitation $\lambda = 380$ nm is near the maximum of the PL peak of SnO$_2$ thin film. The origins of the RR peaks, observed in this study, are assigned based on published DRIFT and FTIR results as given in table 1 [20, 21].

| Resonant peak positions (cm$^{-1}$) for SnO$_2$ for excitation of 380 nm | Possible modes of vibrations from published literature | Energy (cm$^{-1}$) | References |
|---|---|---|---|
| 2270 | CO stretching (adsorbed at the surface of SnO$_2$) | 2200, (2990–2850), (2250–2200), (1705–1660) (1000–900) | [20, 21] |
| 2270 | H$_2$O$^+$ (ions adsorbed at the surface of SnO$_2$) | Broad band at 2600 | [20] |
| 3440 and 3730 | OH (adsorbed at the surface of SnO$_2$) | 3655,3637,3602,3558 and 3479 | [20, 21] |
| 6970 | Third harmonic of CO stretching mode | 2270 CO stretching (adsorbed at the surface of SnO$_2$) | 2270 |
| 10252 | Third harmonic of OH stretching mode | | |

Table 1. Observed resonant Raman peaks for an SnO$_2$ thin film for excitation wavelength 380 nm and possible mode assignment by comparison with published results.

Of the CO and OH stretching modes are at different positions for curves 1, 2 and 3 in figure 1(b) due to dispersion. Similar results are observed for SnO$_2$ thin films deposited on the Si substrate by laser ablation deposition.

PL measurements were repeated on Mo$_{1-x}$Fe$_x$O$_2$ thin films, bulk fused quartz and ordinary glass slide. Curves 1 and 2 in figure 2(a) show PL intensity as a function of shift energy for fused quartz and ordinary glass, respectively, for incident wavelength of 360 nm. The sharp peak at 2445 ± 10 cm$^{-1}$ is present in both curves 1 and 2 in figure 2(a). However, the relative intensity of this peak in curve 2 is much smaller. The broad peak in the range 3000–5500 cm$^{-1}$ in curve 1 is absent in curve 2 of fused quartz. This broad peak in curve 1 of ordinary glass is due to impurities of OH and...
other complexes related to water [21]. Curves 1 and 2 in figure 2(b) show PL intensity as a function of shift energy for Mo1−x Fe2O5 thin film for incident wavelengths 375 nm and 350 nm, respectively. It is interesting to observe sharp peaks superimposed on PL spectra of these samples. Further, measurements were repeated for all samples by varying the incident wavelength from 260 to 450 nm to study the dispersion of RR peaks. Dispersions of the fundamental RR peak and its third harmonic are shown by curve 2.

Figure 3. The dispersion of RR peaks related to the fundamental (curve 1) stretching mode of CO and its third harmonic (curve 3). Symbols for three different samples SnO2 thin film, Mo1−x Fe2O5 thin film and ordinary SiO2 glass are squares, triangles and stars, respectively. The dispersion of the OH fundamental stretching mode is shown by curve 2.

Here, $E_i$ and $E_s$ are energies of incident and scattered photons, respectively, $l$ and $m$ are integers. $\hbar\omega_{\text{lattice}}$ is the energy absorbed by the lattice. $\hbar\omega$(CO, OH, ...) are energies of vibrational modes of CO, OH and their higher harmonics. It is well known in the case of RR scattering that when $E_i$ is slightly more than the energy of allowed absorption between energy levels, the loss of energy to the lattice ($\hbar\omega_{\text{lattice}}$) is minimum [12]. The difference between $E_i$ and $E_s$ is almost equal to $m\hbar\omega$(CO, OH, ...) when loss to the lattice is negligible. Now, let us look at the dispersion of the fundamental and third harmonic of the CO stretching mode in figure 2. The RR peak position of the fundamental CO stretching mode is varying from 1960 cm$^{-1}$ (for incident wavelength 450 nm) to 3360 cm$^{-1}$ (for incident wavelength 260 nm). If the actual energy of the CO fundamental stretching mode is $\sim$2200 cm$^{-1}$, then for the RR peak positions more than 2200 cm$^{-1}$, the difference is absorbed by the lattice and for the RR peak positions less than 2200 cm$^{-1}$ the difference is taken from the lattice. The reason for observing fundamental and its third harmonic and the absence of the second and the fourth, even harmonics can be understood with the help of vibrational energy levels of an asymmetric and anharmonic oscillator model for vibrations of CO and OH [20]. It is assumed that one atom (for example, O) is more rigidly attached to the lattice and another (for example, H) is relatively free. Transitions are allowed between symmetric and asymmetric wave-functions and vice versa. Transitions are not allowed between symmetric and symmetric and asymmetric and asymmetric wave-functions. Therefore, allowed transitions for $\Delta\nu = \pm 1, \pm 3$ etc will give odd harmonics and even harmonics are absent.

4. Conclusions

Superimposed sharp peaks on the PL spectra of SnO2, Mo1−x Fe2O5 thin films, bulk fused quartz and ordinary SiO2 glass are due to RR of vibrational modes of CO, OH and their higher odd harmonics. The dispersions of CO stretching RR modes are $\sim$600 cm$^{-1}$ eV$^{-1}$. The dispersion of the third harmonic of the CO stretching mode is $\sim$2000 cm$^{-1}$ eV$^{-1}$. The dispersion of RR peaks is the same for all samples irrespective of their crystalline structures. A detailed theoretical modelling is needed to explain the large dispersion of RR peaks related to fundamental stretching and higher odd harmonics of CO in oxide materials with these as impurities.

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