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Laser power influence on Raman spectra of ZnO(Co) nanoparticles

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ABSTRACT

Influence of laser power on nanocrystalline samples of ZnO(Co) prepared by commonly used wet chemistry method followed by calcination was investigated. Previous confirmation of the existence of ZnO and Co_3O_4 phases was based on the X-ray diffraction measurements. Here we report the experimental spectra of non-resonant Raman scattering in the range between 100 cm^{-1} and 1600 cm^{-1}, for a series of samples irradiated with four different laser power densities. The laser power density has different influence on relative intensity of peaks that belong to ZnO phase than on those corresponding to Co_3O_4 phase. Both peak types show characteristic broadening and red shift toward lower frequencies. The laser power densities used in our study did not cause thermal destruction in any of the investigated samples. Laser-induced local heating effects in samples caused formation of cobalt dimers on the surface of Co_3O_4.

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1. Introduction

ZnO with its wide direct band gap of 3.37 eV and large binding energy of 60 meV at room temperature is a material suitable for use in a wide variety of next-generation applications, such as in the low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films or gas sensors. Alloys of ZnO with 3d transition metals (Mn, Ni, Co, etc.) have attracted much attention due to their room temperature ferromagnetism fitting for spintronic applications. Nanostructured semiconductors exhibit novel electronic, mechanical, optical and vibrational properties which are a consequence of surface and quantum confinement effects. Good knowledge of vibrational properties of ZnO nanostructures is essential for understanding transport properties and phonon interaction with free carriers, both of which have great impact on the performance of ZnO-based optoelectronic devices. A method often used in the explanation of these processes is Raman scattering [1–4].

Raman scattering has been proven to be powerful, sensitive, non-destructive and rapid technique to characterize and study vibrational and optical properties of band gap semiconductor crystals, thin films, micro and nanostructures, both pure and doped. The parameters of a Raman mode, for example, frequency and linewidth, provide the basic information on the sample quality, specific aspects of lattice dynamics such as isotopic effects and phonon lifetimes [5], position of doping ions in the host lattice, as well as on the presence of impurities which are undetectable by X-ray analysis [6]. The evolution of these parameters with temperature is also important due to its influence on practical application of the investigated material. Consequently, Raman spectroscopy is a method of choice for many studies [4], and is used in our study of ZnO doped with CoO, as well as.

The wurtzite-type semiconductor, ZnO, belongs to the space group $C_{6\upsilon}^4$ with two formula units per primitive cell, where all atoms occupy $C_{3\upsilon}$ sites. The Raman active zone-center optical phonons, predicted by the group theory are A_1, E_1, and $2E_2$. The phonons of A_1 and E_1 symmetry modes are polar phonons and hence, exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) vibrations because of the macroscopic electric field associated with the LO phonons. On the other hand nonpolar and Raman active phonon modes with symmetry E_2 have two frequencies: E_2^{high} associated with oxygen atoms and E_2^{low} associated with Zn sublattice [7].

In crystals of reduced dimensionality, shifts and broadenings of some peaks in the Raman spectra may occur with respect to their positions and widths in the spectra corresponding to bulk ZnO. In their work on ZnO nanocrystals some authors attribute the origin of these changes to confinement effects [8–12], others claim that the shifts are due to local heating rather than spatial confinement

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[1,13], whereas some indicate that the phonon localization by defects can be a mechanism for phonon peak shifts in Raman spectra [1].

Temperature dependence of Raman spectra has attracted significant attention and has been widely studied. These studies go in two directions. In the first approach temperature change is applied to the whole sample, mainly in the temperature range from 80 to 750 or 800 K in pure ZnO or in ZnCoO ternary alloy [4,5]. In the other line of studies temperature increase in samples is produced locally by employment of local laser heating effects. Most often, the focus was on pure ZnO either to study the influence of local laser heating effects [1] or to avoid it [13]. In all the cases increase in temperature produced redshift and broadening of the peaks.

The purpose of our experimental study is to study samples in the wide range of Co concentration: below, above and close to the solubility limit as well as to get further insight into the influence of laser power on both the behavior of the dopants in the ZnO lattice and the heating induced effects.

2. Samples and characterization

Many of transition metal ions have a low solubility limit in Diluted Magnetic Oxides (DMO) [14,15]. In the literature various values of solubility limit of Co ions in ZnO were reported. The highest values are reported for samples prepared by the non-equilibrium growth techniques such as pulsed laser deposition (PLD) or ion implantation [16]. The high value, about 40 at%, was reported by Kim et al. [17] for films prepared by PLD technique. Prellier et al. studied films prepared by this method and revealed that the c-lattice parameters in ZnO:Co obeys Vegard law until 10 at% of [18]. A strong phase separation tendency towards Co_3O_4 was observed for films prepared by metal-organic deposition with $x > 5$ at% [19]. For bulk samples, it was reported that the solubility limit was about 10 at% [20]. It was observed that solubility threshold was 15 at% in nanoalloys [21]. For samples prepared by sol–gel and RF sputtering techniques the forming of Co nanoclusters was observed for $x > 12$ at% [22]. All the cited results are in terms of atomic percent (at%) of Co. In our study we have use weight percent of CoO (wt%).

The experiments were performed on samples obtained by wet chemical method followed by calcination. A mixture of cobalt and zinc hydroxides was obtained by adding the ammonia solution or 2 M solution of KOH to the 20% solution of the proper amounts of $Zn(NO_3) \cdot 6H_2O$ and $Co(NO_3) \cdot 4H_2O$ in water. The obtained hydroxides were filtered, dried at 70 °C and calcinated at 300 °C for one hour. Nanopowders obtained in this way were pressed into indium panel.

Table 2
Phase composition and mean crystallite sizes.

wt% of CoO	ZnO [nm]	Co_3O_4 [nm]
5	156	55
10	118	50
20	57	21
30	101	30
40	80	17
50	43	21
60	–	14
70	–	15
80	–	21
90	–	25
95	–	20

This method allowed us to obtain series of nano-sized ZnO samples with nominal concentration of CoO ranging from 5% to 95%. The real chemical composition (solubility of Co in ZnO) of the samples was determined using the ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) technique (Optima 5300 DV, Perkin Elmer). The real wt% values of Co and Zn are gathered in Table 1. The results of micro-Raman spectroscopy we are about to present correspond to the most representative samples.

The morphology of samples was investigated using scanning electron microscope (SEM) followed by the phase composition of the samples determined by the X-ray diffraction (XRD) (CoKα radiation, X'Pert Philips) [7]. Here we emphasize that XRD analysis reveals presence only of ZnO and Co_3O_4 phases. Using the Scherrer's formula [23], the mean crystallite size $\tilde{a}$ in the prepared samples was determined to be between 43 and 156 nm for ZnO phases and from 14 to 55 nm for Co_3O_4 phases. The phase compositions as well as the mean crystallite sizes obtained with XRD are gathered in Table 2. The crystalline size of ZnO, generally, decreases with the increase in the content of CoO, while the crystallite size of the second phase, i.e., of Co_3O_4, does not have monotonous dependence. The XRD spectra has not been taken after laser irradiation of sample surfaces; therefore, we were unable to observe the influence of laser irradiation on XRD spectra.

The relative change in crystallite size of Co_3O_4 phase is smaller than the change corresponding to ZnO phase. For samples with CoO content of 60% and more, althought the presence of ZnO phase was registered, the results obtained for its crystallite size are unreliable and are therefore notshown in Table 2.

All samples were analyzed and those with the most prominent changes are chosen to discuss the influence of dopant concentration and laser power used for sample irradiation.

Table 1
The real wt% values of Co and Zn.

Intentional chemical composition		Real chemical composition					
CoO [wt%]	ZnO [wt%]	Co [ppm]	Zn [ppm]	Co [wt%]	Zn [wt%]	Co_3O_4 [wt%]	ZnO [wt%]
5	95	1.00	18.60	4.02	74.85	5.48	93.27
10	90	1.76	17.44	7.14	70.61	9.73	87.99
20	80	3.37	15.85	13.43	63.02	18.29	78.53
30	70	5.13	13.82	20.46	55.06	27.85	68.61
40	60	6.53	12.02	26.40	48.56	35.94	60.52
50	50	8.39	9.71	33.83	39.18	46.07	48.83
60	40	9.07	8.65	36.51	34.83	49.72	43.40
70	30	11.13	7.24	44.34	28.85	60.37	35.95
80	20	13.00	5.26	52.74	21.34	71.81	26.59
90	10	15.96	2.44	64.56	9.64	87.90	12.01
95	5	16.82	1.05	67.96	4.25	92.53	5.297

The real chemical composition of the samples was determined using the ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) technique (Optima 5300 DV, Perkin Elmer). The real wt% values of Co and Zn are gathered in Table 1.

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