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Influences of oxygen vacancies on the enhanced nonlinear optical properties of confined ZnO quantum dots

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ABSTRACT

Confining ZnO quantum dots (QDs) into a solid state matrix to form nanocomposite materials is an important mean to design nonlinear optical devices. In this paper, ZnO confined in Al_2O_3 matrix are synthesized by pulsed laser deposition method and rapid thermal annealing technique. The substantial oxygen vacancies are generated in the N_2-annealed ZnO QDs. Magnetic measurements illustrate that the ferromagnetic nature of ZnO QDs confined in Al_2O_3 matrix can be due to the oxygen vacancies. The determined two-photon absorption in N_2-annealed ZnO QDs is an instantaneous nonlinear process and is enhanced almost 2 times compared to that of O_2-annealed ZnO QDs. The enhancement of optical nonlinearities achieved in confined ZnO QDs with substantial oxygen vacancies is important for the practical applications of ZnO nanostructures in such as optical limiting devices and all-optical switching elements.

1. Introduction

Metal oxide nanostructures have attracted considerable interests in many areas of material sciences, physics and chemistry owing to their fascinating properties [1,2]. Among them, ZnO has emerged as a promising optoelectronic material due to its large exciton binding energy of 60 m eV, and wide band gap of 3.3 eV [3]. Attributed to these distinctive properties, ZnO nanostructures such as Zno films [4–6], doped ZnO films [7,8], ZnO/PMMA nanocomposite [9], ZnO/Cu_2O heterojunction solar cells [10], ZnO nanorods [11] etc. exhibit attractive nonlinear optical properties that make them ideal candidates for nonlinear optical based devices. More recently, the functionalization of graphene oxide (GO) with ZnO quantum dots (QDs) is expected to improve the optical nonlinearity. In comparison with ZnO QDs, ZnO/GO composites exhibit larger two-photon absorption (2PA) coefficient [12]. However, ZnO/GO hybrid was prepared by solution precipitation and hydrothermal method, which is unfavorable for the nano-device applications. Confining the ZnO QDs into a solid state matrix to form nanocomposite materials may be a useful mean to design nonlinear optical devices.

It is well known that the magnetic, optical and optoelectronic properties of ZnO nanostructures are significantly influenced by defects [13,14]. The defects in ZnO nanostructures can significantly modify the chemical and physical properties, which can be reflected in nonlinear optical measurements. The tremendous possibilities offered by ZnO nanostructures in terms of altering their electronic structure using defect engineering widen their scope in nonlinear optical applications. A better understanding of the impact of defects on the nonlinear optical properties of ZnO nanostructures can help one to gain efficient control to design and fabricate new devices for optoelectronic applications. Generally, the defect levels in ZnO are categorized into four types, namely, oxygen vacancies and zinc vacancies which are generally surface defects, and interstitials (Zn and O) and anti-sites which exist in the bulk of the material [14]. Oxygen vacancies are intrinsic defects in ZnO, which are easily generated during crystal growth processing [15]. Specifically, oxygen vacancies-related issues are of particular interest for ZnO. Currently, it is generally accepted that the oxygen vacancies play central role in determining the physical and chemical properties of ZnO.

Therefore in this article, through systematic measurements

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conducted along with microscopic and spectroscopic characterization, we explore the effects of oxygen vacancies on the nonlinear optical properties of confined ZnO QDs. These studies are further corroborated by measurements of other independent properties such as magnetization. The enhancement of optical nonlinearities can be achieved in confined ZnO QDs with substantial oxygen vacancies, which is important for the practical applications of ZnO nanostructures in such as optical limiting devices and all-optical switching elements.

2. Experimental

ZnO QDs confined in Al_2O_3 matrix were fabricated using pulsed laser deposition (PLD) method and rapid thermal annealing (RTA) technique. Briefly, a KrF pulsed laser beam of 248 nm wavelength with frequency of 10 Hz was used to ablate the target in an ultra-high vacuum chamber. The targets to be laser ablated consisting of one piece of high purity (99.99%) Al_2O_3 round target (of about 40 mm in diameter) and a square piece of high purity (99.99%) ZnO target (of about 8 mm in length) were prepared. The deposition and growth of the film on the Si substrate were carried out in a high vacuum system with a background pressure of about 1×10^{-7} Torr, with the substrate at room temperature. After deposition, the thin film was subjected to a RTA process at 600 °C for 300 s in N_2 and O_2 ambient, respectively. The deposited film structure was examined using high-resolution transmission electron microscope (HRTEM) with a JEOL 2010 microscope working at 200 kV. The TEM electron diffraction pattern was matched against a simulated diffraction pattern for ZnO generated using a TEM simulator Java electron microscopy simulation (JEMS) software [16,17]. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos Axis Ultra DLD spectrometer employing Al K_α radiation. The binding energies were corrected for samples charging by referencing the C1s peak visible at 285 eV. Raman spectroscopy measurements were carried out with a HORIBA Jobin-Yvon Labram HR, using an excitation wavelength 514 nm. The quantum design physical properties measurement system (PPMS) with a vibrating sample magnetometer (VSM) option was used to investigate the magnetic field and temperature dependence of the magnetic moment of the deposited sample. Magnetization measurements as a function of temperature of the deposited sample were carried out, combining zero-field-cooling (ZFC) and field-cooling (FC) routines with an applied magnetic field of 100 Oe in the temperature range from 5 K to 300 K. The hysteresis loops, M (H), were measured at different temperatures to determine the temperature dependence of the magnetic properties of the deposited sample. The room-temperature nonlinear optical properties of N_2-annealed and O_2-annealed ZnO QDs were investigated at the wavelength of 400 nm with standard Z-scan and pump-probe techniques, respectively [18]. The femtosecond laser pulses were produced using an optical parametric amplifier (TOPAS, USF-UV2), which was pumped with a Ti:Sapphire regenerative amplifier system (Spectra-Physics, Spitfire ACE-35F-2KXP, Maitai SP and Empower 30). The pulse repetition rate was 2 kHz and the minimum beam waist was about 15 μm. It should be noted that the laser-induced damage occurs at excitation irradiances (before the sample surface) of ~500 GW/cm^2 (or ~60 mJ/cm^2) or higher [19]. All the nonlinear optical measurements reported here are performed with excitation irradiances below the damage threshold. The Z-scan experimental results were repeatable when the excitation irradiance was decreased back to the previous lower values, which indicated that the excitation irradiance was below the damage threshold. Moreover, the thermal effects become pronounced when the laser repetition rate is high enough (mega Hertz) or the pulse width is long enough (pico- or nano seconds) to produce heat accumulation [20]. In this paper, the 400-nm laser with pulse width of 35 fs and pulse repetition rate of 2 kHz was used to perform the nonlinear absorption measurements on the thin films with ZnO QDs confined in amorphous Al_2O_3 matrix. Thus, the contribution of thermal effect induced by the laser pulses can be neglected. It should be also noted here that the pure amorphous Al_2O_3 matrix annealed in N_2 and O_2 ambient were also respectively examined under the same conditions with N_2-

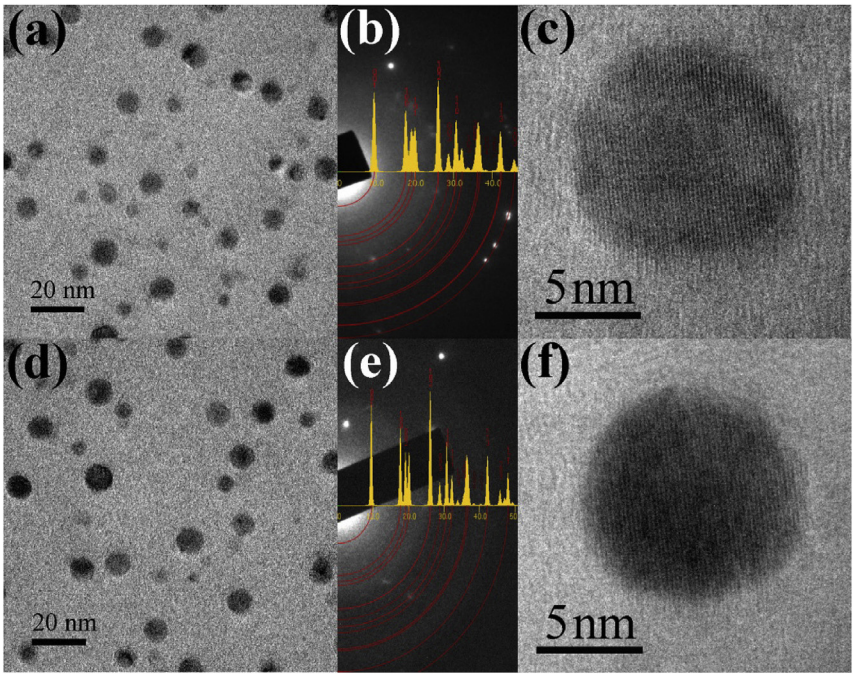

Fig. 1. (a) TEM image of N_2-annealed ZnO QDs confined in Al_2O_3 matrix; (b) electron diffraction pattern of N_2-annealed ZnO QDs; (c) HRTEM image of a single N_2-annealed ZnO QD; (d) TEM image of O_2-annealed ZnO QDs confined in Al_2O_3 matrix; (e) electron diffraction pattern of O_2-annealed ZnO QDs; (f) HRTEM image of a single O_2-annealed ZnO QD.