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SYNTHESIS OF CORE/SHELL CuO-ZnO NANOPARTICLES AND THEIR SECOND-HARMONIC GENERATION PERFORMANCE

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The present paper presents the method for obtaining core/shell CuO-ZnO nanoparticles and nanocoatings by using a commercially available vacuum coating system. Initially generated Cu-Zn core/shell nanoparticles have been oxidised with a highly reactive atomic oxygen beam. Second-harmonic generation has been observed in the obtained samples. The dependence of second-harmonic intensity on the wavelength of the exciting radiation is shown in the paper.

Keywords: *core-shell nanoparticles, second harmonic generation.*

1. INTRODUCTION

At present, core/shell nanomaterial systems of semiconductors have become an object of in-depth research due to their interesting properties, because compared to other kinds of systems they have various advantages and prospects for their application are wide as well [1]–[3].

Though ZnO and CuO, both separately and in various compounds, are semiconductors that are studied most extensively, the systems of CuO-ZnO nanoparticles and nano-coatings, in general, have been researched comparatively little despite the fact that their practical application is forecasted to be wide, for instance, sensing applications [4]–[6], photocatalysis [7]–[9] etc.

The mixed systems of zinc oxide and copper oxide have been explored as powders [10], [11], thin coatings [12], [13], nano-size structures [14]; however, nanosize core/shell structures of these materials have not been reported yet.

The search for methods of synthesising semiconductor nanoparticles still continues, and it is of great importance from both fundamental and practical aspects. We present method of synthesis of Cu_2O shielded with ZnO_2 nanoparticles alloy, where commercially available vacuum equipment is employed. It is being proved that using active oxygen it is also possible to oxidise shielded metallic nanoparticles and thereby obtain a functional coating of semiconductor nanoparticles.

It is reported [15], [16] that optical second-harmonic generation (SHG) may

be used in research on various low-dimensional structures with nanometer size, for instance: nano-crystals, nanowires, quantum-dots, quantum-wells etc. At present, such systems are being intensively explored and they are promising for SHG studies. The research on ZnO nanostructures, e.g., nano-threads, non-linear optical properties (NLO) is being conducted very actively [17], [18]; both practical and theoretical studies of different nanoparticles and nanostructures are carried out [19]–[21], yet SHG measurements of nanosize core/shell CuO-ZnO systems are not known to the authors.

2. EXPERIMENTAL METHODS

For generation of nanoparticles we use a commercially available system Nanosys500 (Mantis Deposition Ltd.) equipped with NanoGenTrio, core-shell coater and MesoQ high-mass quadrupole spectrometer and filter. In this system, nanoparticles are produced by a "terminated gas condensation" method [22], [23].

Before the deposition of the nanoparticles, the system pressure has been set at 1×10^{-8} Torr. The nanoparticles have been deposited onto a glass substrate; formation has been controlled by the quadrupole mass spectrometer. Cu nanoparticles (average size of about 3 nm max) have been generated and shielded with Zn alloy by core-shell coater; maximum total particle size – 5.5 nm. Sputtering parameters – Argon gas is flown into the volume around the magnetron at a rate of 50 sccm for Cu and 40 sccm for Zn, the power of Cu target has been kept at 5 W, Zn target – 7 W and the sputtering time – 12 h. Before and after landing onto a glass substrate, nanoparticles have been oxidised with a highly reactive atomic oxygen beam (O_2 flow – 2 sccm) generated by RF plasma source.

The crystal structure of samples has been determined by using X-ray diffraction (XRD); particle size distribution has been obtained by using small angle X-ray diffraction (SAXD). Patterns of the samples have been recorded by a RIGAKU SmartLab Xray diffractometer using CuKα radiation. General morphology and thickness of coating have been characterised by AFM (NX10, Park).

Titan-sapphire (Ti:Al2O3) femtosecond laser CHAMELEON ULTRA (180 fsec pulse width, 80 MHz repetition rate, k – 690– 1040 nm) used in a unified complex with microscope LEICA has allowed measurements of transmitted and reflected light intensity with an opportunity to decompose the reflected signal with respect to its wavelengths (k-scanning) as described in reference [24].

3. RESULTS

Growth rate of coating has been below the detection limit of the crystal monitor, after sputtering of 12 hours total thickness of coating estimated by AFM has accounted for125 nm.

Q-2Q x-ray scans have been analysed by PDXL2 (Rigaku) software. Due to the thickness and weak crystallisation of the alloy, a comparatively weak and wide diffraction maximum has been obtained (Fig. 1); however, after respective simulations, we can conclusively state that it corresponds to several merged Cu_2O and ZnO_2

maxima, the broad peak at about 23° of the 2θ in pattern has been ascribed to the amorphous phase diffraction.

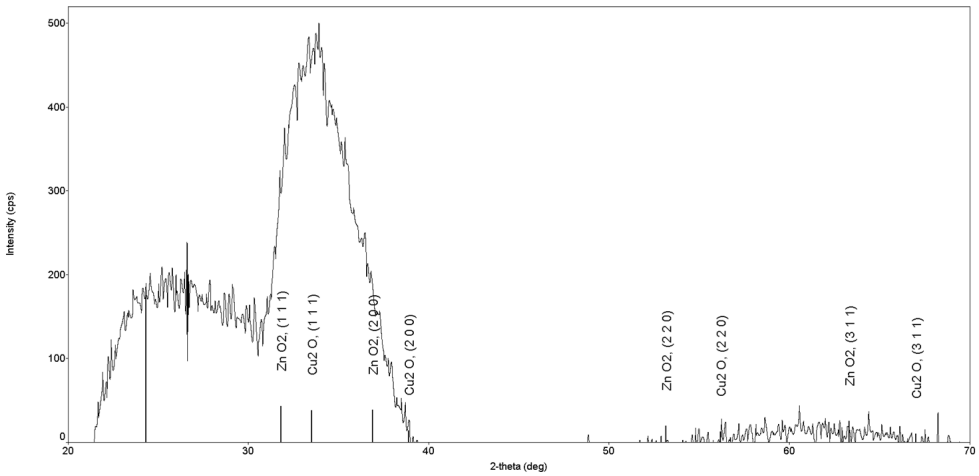

Fig. 1. XRD pattern of Cu_2O/ZnO_2 nanoparticle alloy and peaks of respective phases.

Figure 2a shows that nanoparticles on the surface of the sample join bigger formations, while XRD and SAXD analyses testify to the fact that particles maintain their initial structure.

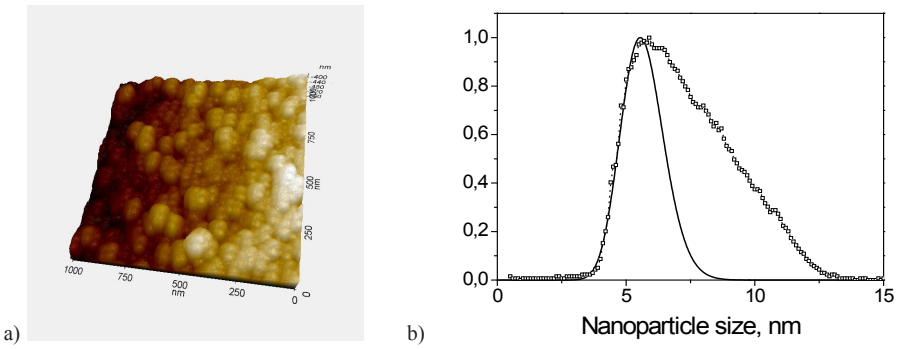

Fig. 2. a) AFM picture of sample surface; b) - Normalised nanoparticle size distribution, - modelled from SAXD, -□- quadrupole mass spectrometer data.

Particle distribution from SAXD data has been modelled by NanoSolver (Rigaku) software. Normalised modelled distribution data and data obtained by a quadrupole mass spectrometer are compared in Fig. 2b.

Due to the thinness of the obtained coating, no measurements of optical properties have been possible, yet the illumination of the sample with powerful femtosecond laser radiation leads to the appearance of second-harmonic generation (SHG) (Fig. 3a). All observed SHG peaks have been approximately the same FWHM

~ 10 nm. Intensity of second-harmonic (SH) depends on wavelength of the exciting radiation and reaches its maximum at approximately 890 nm (Fig. 3b).

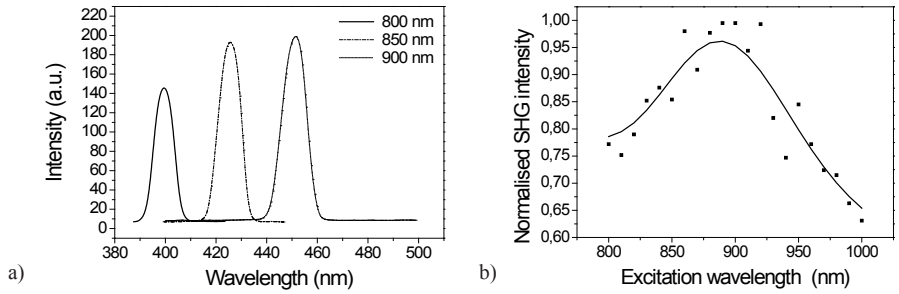

Fig. 3. a) Emission spectra of Cu-ZnO nanoparticles excited by intense femtosecond pulses at different wavelengths, measured with Q=90°. The excitation area is about $5x10^{-2}$ mm^2 (225x225 μm) and the excitation intensity is 7.5 kW/cm2. b) Normalised second-harmonic intensity vs the excitation wavelength. The excitation area is about $5x10^{-2}$ mm^2 (225x225 μm) and the excitation intensity is 7.5 kW/cm^2.

The question whether the SH signal is generated by separate particles or whether it is done by several clusters of particles observed by AFM (Fig. 2a) remains still open.

4. CONCLUSIONS

By using commercially available coating systems, it is possible to generate nanoparticles and nano-coatings of core/shell oxides. On the substrate, retaining their initial size of about 4–6 nm, nanoparticles form amalgamations of a bigger size – clusters of nanoparticles indicated by AFM and XRD measurements. The illumination of a thin ZnO-CuO core-shell coating with femtosecond laser radiation also leads to the generation of the second-harmonic signal with the maximum at approximately 890 nm in the intensity dependence on the wavelength curve.

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KODOLS/ČAULA CuO-ZnO NANODAĻIŅU SINTĒZE UN TO SPĒJA ĢENERĒT OTRĀS HARMONIKAS SIGNĀLU.

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Kopsavilkums

Darbā tiek demonstrēta metode kodols/čaula CuO-ZnO nanodaļiņu un nanopārklājumu sintēzei, izmantojot komerciāli pieejamu vakuuma pārklājumu sistēmu. Sākotnēji sintezētās Cu-Zn kodolš/čaula nanodaļiņas tika oksidētas ar aktīva skābekļa plūsmu. Iegūtajos paraugos tika novērota otrās harmonikas signāla ģenerēšanās. Ir parādīta otrās harmonikas signāla intensitātes atkarība no ierosinošā starojuma viļņa garuma.

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