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S.I. : CURRENT STATE-OF-THE-ART IN LASER ABLATION

A low-temperature limit for growth of ZnO nanowires by using of laser ablation processes

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Abstract

The contribution deals with growth of ZnO nanowires on metal catalysts by using of pulsed laser deposition and with the influence of growth temperature. The process of nanowires preparation comprised two technological steps—both were based on pulsed laser ablation processes: (1) production of metal nanoparticles by laser ablation in liquids and (2) pulsed laser deposition of ZnO nanowires by ablation of ZnO target on substrate with metal nanoparticles. Nanoparticles from various metals (Au, Ag, Ni, Cu, Al, Mg, Zn, Sn and BiSn alloy) were prepared by pulsed laser ablation at 1064 nm in deionised water. Colloids contained metal nanoparticles were applied on Si (100) substrates, and after drying, nanoparticles served as catalysts of VLS crystallisation. Temperatures in interval 600—200 °C were experimentally compared for the nanowires growth with applied ablation laser working at 248 nm. The lowest achieved temperature value for growth of ZnO nanowires was 425–450 °C. However, among applied metals Cu and Al nanoparticles only successfully catalysed ZnO nanowires at this temperature. Properties of prepared samples were investigated by scanning electron microscopy and photoluminescence. Experimental results revealed that along with the growth temperature, selection of proper metal catalyst is also important factor for nanowires crystallisation.

Keywords Zinc oxide · Nanowires · Nanoparticles · Directed growth · Pulsed laser ablation

1 Introduction

Semiconductor nanowires (NWs) are considered very interesting and perspective nanometre-scale structures. They can be controllably and predictably synthesised in single-crystal forms with all key parameters controlled, including chemical composition, diameter and length, doping and electronic properties, etc. Experimental and theoretical investigation of semiconductor NWs has more than 50 years long history if we consider the famous Wagner—Ellis paper [1]; however, main acceleration of published references is related to the last 10—15 years. Potential and yet successfully reported applications include wide speciality areas, for example sensors, electronic devices, photovoltaic cells, new design of electrical batteries, water splitting cells, biological interfaces and so on [2–6].

Generally, semiconductor NWs and zinc oxide as well can be prepared by a variety of very different methods (in vapour or liquid ambient medium); however, for purpose of this study we are focused on vapour phase growth methods and dominant nanocluster catalysed vapour–liquid–solid (VLS) growth mechanism. It is based on the presence of the seed crystal (the catalyst of the directional growth), which is in liquid state and has different chemical compositions than the final nanowire [7, 8]. Many different PVD and CVD deposition techniques are based on this principle, and different metals were used as the growth catalyst [2, 8]. Among them, pulsed laser deposition (PLD) proved its significant potential in ZnO NWs growth and plays an important role in experimental investigation in this speciality [9–13].

Unfortunately, the typically used temperatures are in the interval 700–1000 °C, and therefore, application of thermally sensitive materials in function of growth substrate or functional interfaces is disqualified. The lowest known published results have been reporting successful vapour deposition growth of ZnO NWs at 400—500 °C [14–19]. Reported

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methods substantially differed in deposition details. They varied from direct Zn evaporation [14, 16, 17] to MOCVD [19] or PLD methods [15]. Widely used organic materials or just lowering of energy consumption for cheap large area solar cells production need a deposition method for ZnO NWs at substantially lower temperatures.

The article deals with the experimental growth of ZnO nanowires by PLD, and the aim of presented experiments was the quest for the lowest possible temperature for successful growth of ZnO NWs and optimisation of main process. Also, along with reported experiments many different metals in function of catalyst of directional growth were compared.

2 Experimental

The abbreviation "VLS" (vapour–liquid–solid) suggests that the growth process consists of three stages and three different material states. In our experiments, we used an intense (pulsed) laser beam to produce ZnO vapours by ablating of a solid ZnO target. Absorption of such vapours in a melted metal nanodroplet forms a liquid metal–semiconductor alloy, and continuous incorporation of semiconductor material in the alloy through the vapour–liquid interface ultimately results in supersaturation of the semiconductor material. Such supersaturated state leads to precipitation of semiconductor and formation of a liquid–solid interface to achieve minimum free energy. Accordingly, the 1D crystal (nanowire) growth begins via transfer of the semiconductor material from supersaturated solution of the alloy droplet at the liquid–solid interface, which moves along with growth direction. The catalytic metal nanodroplet remains at the tip of evolved nanowire and defines the diameter of the nanowire [8].

Our experimental arrangement comprised two subsequent independent processes which were based on the pulsed laser ablation:

1. Preparation of metal catalytic nanoparticles as growth seeds.

Metal nanoparticles were prepared by the method of pulsed laser ablation in liquid [20]. The solid Nd:YAG pulsed

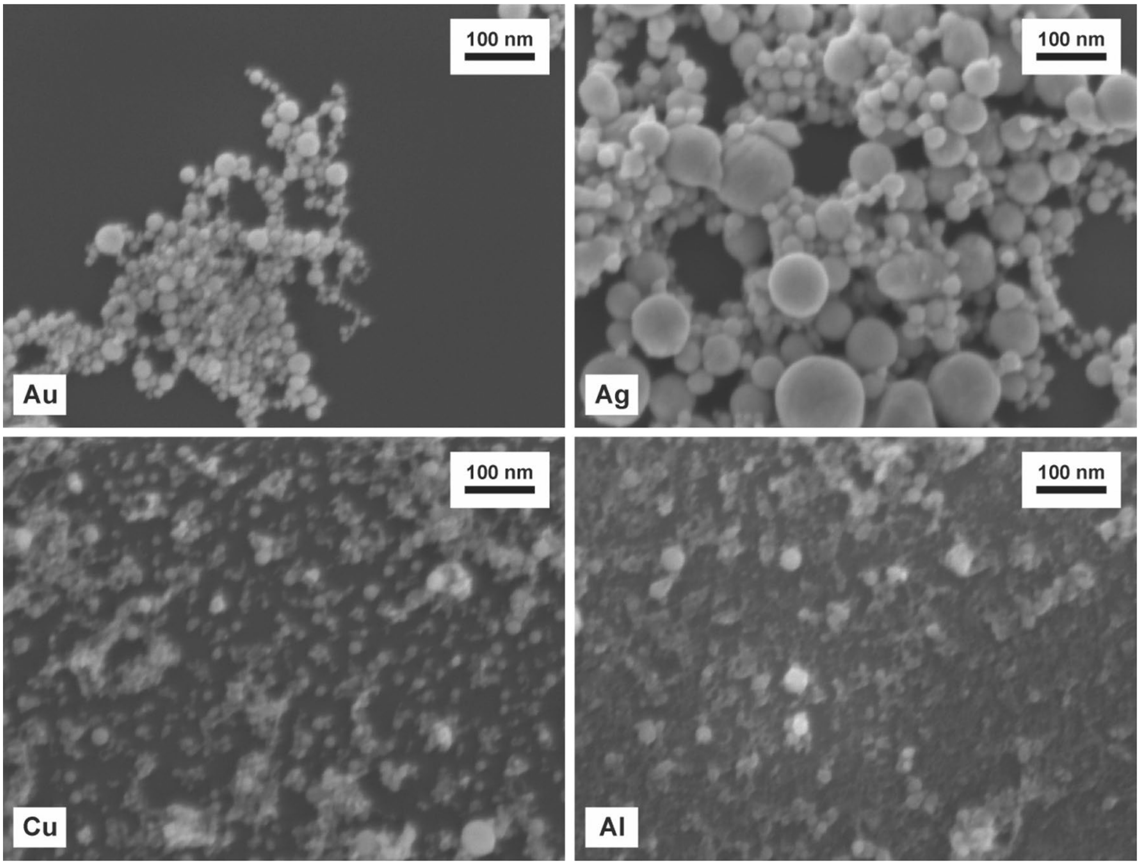

Fig. 1 Metal nanoparticles (prepared by laser ablation in deionised water) after drying on Si substrate before experimental growth of ZnO nanowires

Table 1 Properties of applied metal catalyst

Metal	Melting temperature (°C)	Crystallographic structure	Density (g cm^{-3})	Specific heat (J.g^{-1} K^{-1})	Latent heat (J g^{-1})
Au	1064	Cubic fcc	19.3	0.13	64.9
Cu	1083	Cubic fcc	8.96	0.38	205
Ag	961	Cubic fcc	10.5	0.24	103
Ni	1453	Cubic fcc	8.9	0.44	292
Al	660	Cubic fcc	2.7	0.9	396
Zn	420	Hexagonal hcp	7.14	0.39	112
Mg	650	Hexagonal hcp	1.74	1.02	358
Sn	232	Cubic fcc	7.3	0.21	59
Bi58Sn42	138	Cubic + rhombohedral	8.72	0.2	45

laser (Quanta Ray Pro 250 working at 1064 nm, 20 ns pulse length, 10 Hz) was used for the ablation of the metal target in deionised water. The resulting colloid containing metal nanoparticles was sprayed onto the substrate (Si (100) wafer) and subsequently dried. After evaporation of the water, a layer of metal nanoparticles was formed on the substrate surface. It should be noted that pure deionised water without any surfactant was used, and after drying of colloids, metal nanoparticles were unevenly distributed at the substrate surface (Fig. 1). However, such distribution is suitable for testing of ability to grow nanowires at applied temperatures. For better comparison of the effect of applied metals, nanoparticles from selected elements were simultaneously deposited on one shared substrate. Thus, deposition conditions were identical for compared metals at certain temperature. In this manner, experimentally were compared subsequent the possible catalytic metals: Au, Ag, Cu, Ni, Al, Mg, Zn, Sn and also binary alloy Bi58Sn42.

2. Growth of ZnO nanowires on substrate surface containing metal nanoparticles by using of pulsed laser deposition.

Target ablation was performed by an excimer laser (Compex Pro 205F, KrF, wavelength 248 nm, pulse length 20 ns) with a pulse energy of 120 mJ, and energy density at the target surface after focusing was varied in range of ~ 2.0–2.8 J cm^{-2}. The deposition process was run typically for 15 min (the total ablation pulses of 9,000, the pulse frequency of the laser 10 Hz). The deposition process (growth of nanowires) was carried out in a reaction chamber in atmosphere of pure Ar and pressures in range of 1–15 Pa. The main parameter was temperature which was varied from 600 to 200 °C. Other secondary optimised parameters were Ar pressure between 1 and 15 Pa and laser fluence from 2.0 to 2.8 J cm^{-2}.

Prepared samples were investigated by scanning electron microscope (SEM)—presence, morphology and dimension of NWs and their (photo)emission properties were investigated by photoluminescence measurements (PL).

3 Results and discussion

3.1 Preparation of metal catalytic nanoparticles as growth seeds

Gold, platinum and similar noble metals are the most frequently used as catalysts for VLS nanowires growth. An important condition for VLS growth is ZnO solubility in

Table 2 Growth of ZnO NWs in dependence of applied metal catalyst and deposition temperature

	Metal (catalyst)								
Temperature	Au	Ag	Cu	Ni	Al	Zn	Mg	Sn	BiSn
600 °C	P	G	E	P					
500 °C			E		E	N	G		
450 °C			E		E	N	G		
425° C			G		G	N			
400 °C	N	N	N		N	N			
300 °C								N	N
200 °C								N	N

E excellent, *G* good, *P* poor, *N* no NPs melted metal droplet with a certain upper concentration limit. Above it, a supersaturated state leads to precipitation of ZnO in solid form. According to proper thermal and concentration gradient, the precipitated matter crystallises in form of thin wire with a diameter corresponding to the metal nanoparticle diameter. The easiest way to asses proper combination “metal—ZnO” for VLS growth is application of binary phase diagrams. However, published databases do not provide diagrams for such unusual combination “metal—ZnO” and it is quite difficult theoretically to asses behaviour of investigated combinations. Moreover, published diagrams are defined for an equilibrium state while nanowires growth under referred experimental conditions works in highly nonequilibrium state. Therefore, the experimental approach played key role in presented results. The selected metals comprise traditionally used Au, Ag, Ni [2, 10, 21, 22] and other metals with relatively low melting temperatures. Also binary alloy BiSn (Bi 58 wt % / Sn 42 wt. %) with extremely low melting temperature (138 °C) was tested. List of applied metals and their properties summarises Table 1. It should be noted that the values given in the table are considered for “macro-volumes”, and the behaviour and properties of the nanoparticles may vary significantly for the nanoscale experiments [23–25].

Figure 1 compares the appearance of nanoparticles on the substrate surface after drying the colloid. The particles were approximately spherical in shape, and depending on the particular metal, their diameter ranged from units of nanometres to tens of nanometres. When depositing the colloid with nanoparticles, no procedure was used to prevent agglomeration of the particles, so that they formed irregular surface agglomerates in the micro-volume. Analysis by using of SEM revealed different agglomeration of selected metals. While Au and Ag formed distinctive globular nanoparticles with diameter in the range of 10–100 nm, Cu and Al nanoparticles do not exceed a diameter of 50 nm.

Distribution of nanoparticles was not an issue of performed experiments, and there was not applied any surfactant; therefore, nanoparticles are rather clustered. The main goal was to find out and experimentally obtain the behaviour of applied metals in process of ZnO nanowires synthesis.

3.2 Growth of ZnO nanowires on substrate surface containing metal nanoparticles by using of pulsed laser deposition

Table 2 summarises the results of nanowires growth depending on the used catalyst and the substrate deposition temperature. Initial experiments at 600 °C showed considerable differences in the efficiency of the applied metals. The analysis by SEM revealed that Cu nanoparticles exhibited the best catalysing effect comparing the population density and the length of grown nanowires.

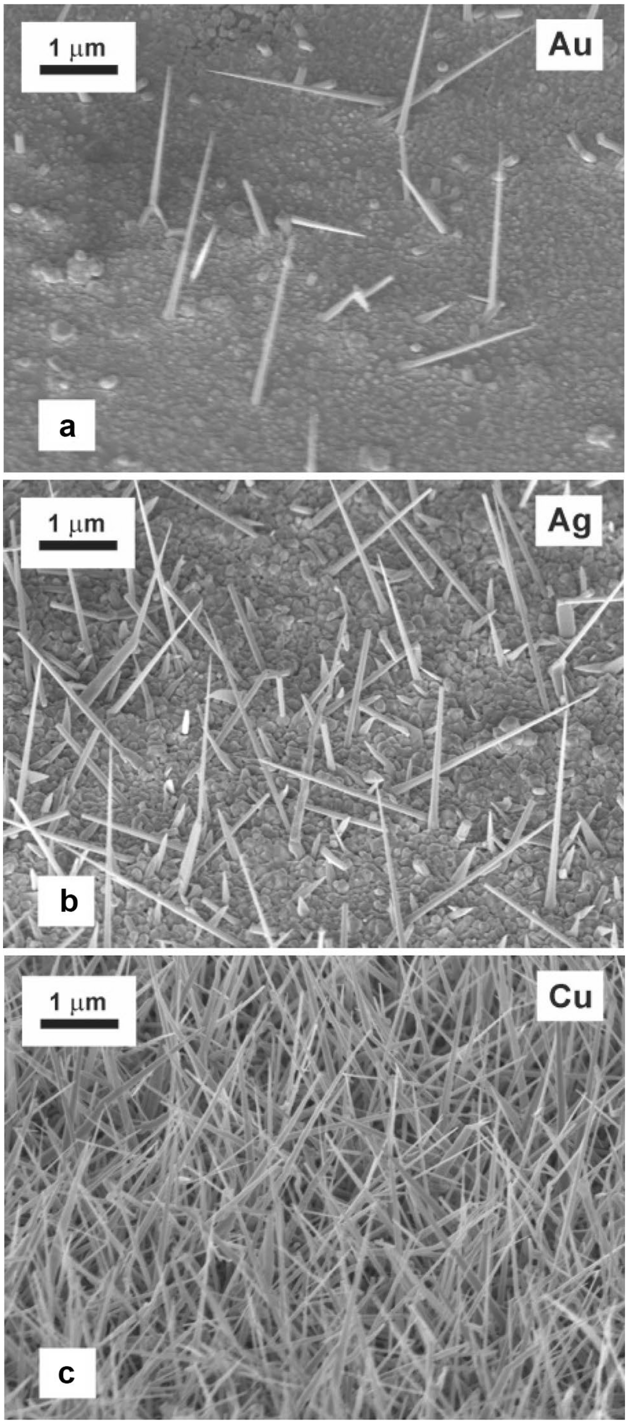

Fig. 2 ZnO nanowires grown at 600 °C (9000 pulses, 2.8 J.cm^{-2}, Ar 8 Pa) by using of different catalysts: **a** Au, **b** Ag, **c** Cu

Unlike with published results, the traditionally used Au catalyst probably needs higher temperature than 600 °C for improving of its efficiency. References in most cases refer to the successful use of Au as an effective catalyst for the

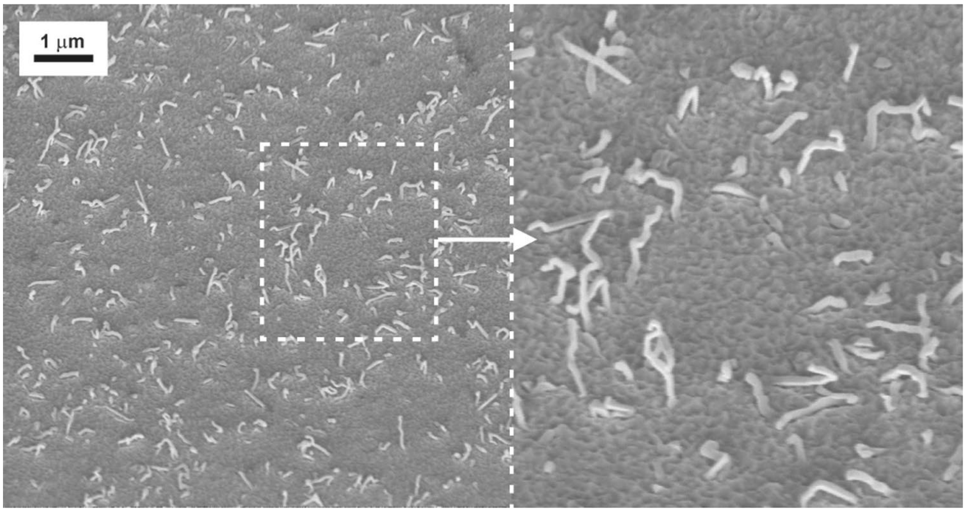

Fig. 3 ZnO nanowires grown at 400 °C (9000 pulses, 2.0 J. cm^{-2}, Ar 1 Pa) by using of Cu catalyst

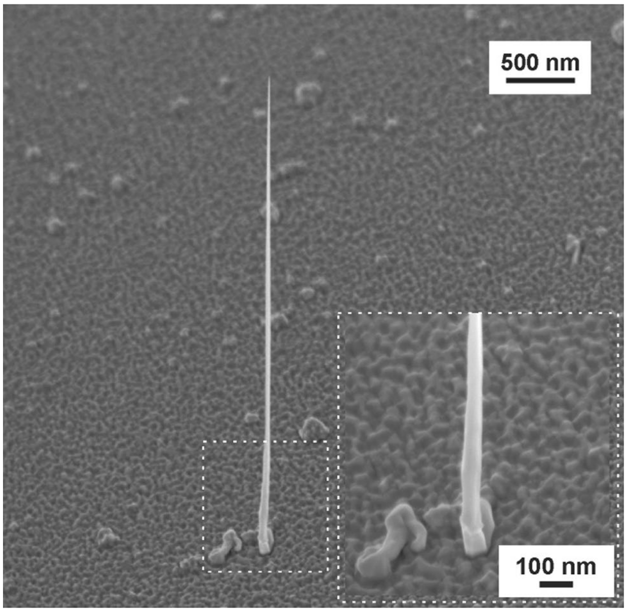

Fig. 4 An isolated ZnO nanowire on Si substrate (Al catalyst, 450 °C, 9000 pulses, 2.2 J.cm^{-2}, Ar 4 Pa)

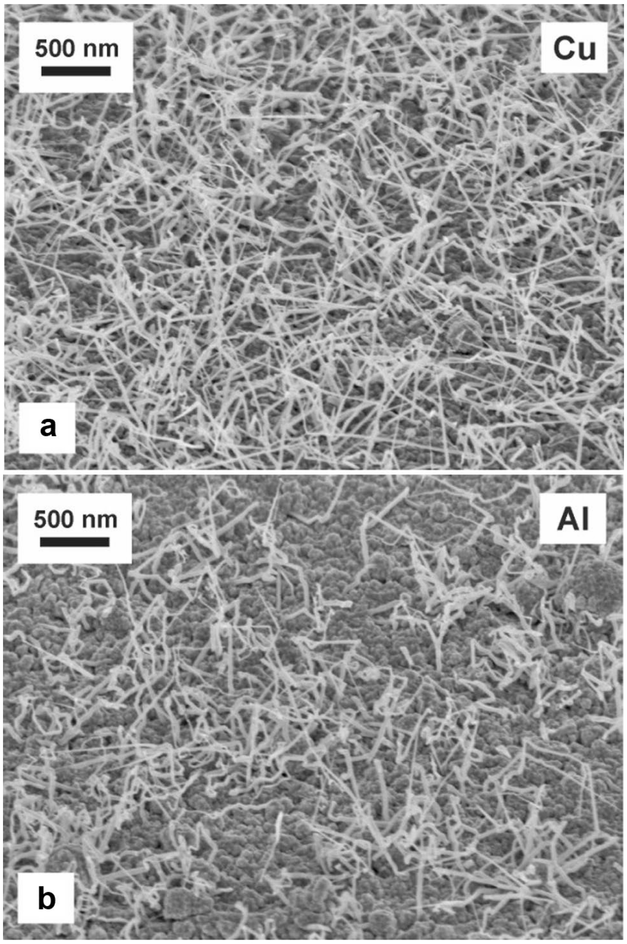

Fig. 5 ZnO nanowires grown at 425 °C (9000 pulses, 2.0 J.cm^{-2}, Ar 4 Pa) by using Cu catalyst **a** and Al **b**

growth of ZnO nanowires and semiconductor nanowires in general [10, 26, 27]. However, according to our experiments at 600 °C, the substantially lower efficiency of the Au nanoparticles was recorded compared to Cu and Ag catalyst (Fig. 2). Most likely, such temperature level was too low for efficient evolution of VLS growth process in Au-ZnO system [28]. References to the use of Cu as catalyst of nanowires growth are very rare [29], similarly Ag [21, 22] and Ni [22].

Other group of metals (Al, Mg, Zn) with lower melting points was used (in addition to successfully verified Cu) for depositions at temperatures below 600 °C. Among them, the Al only exhibited high catalytic efficiency for ZnO NWs growth. When the process temperature reached 400 °C, sporadic occurrence of NWs was recorded, however with short length (up to 1 microm) and strongly deformed containing kink parts (Fig. 3). At lower temperature below

Table 3 Growth of ZnO NWs at 400 °C in dependence of applied metal nanoparticles and deposition pressure and fluence

Metal	2.0 J cm^{-2}/8 Pa	3.8 J cm^{-2}/8 Pa	2.0 J cm^{-2}/1 Pa	2.0 J cm^{-2}/15 Pa
Cu	P	N	P	N
Al	N	N	N	N

E excellent, *G* good, *P* poor, *N* no NPs

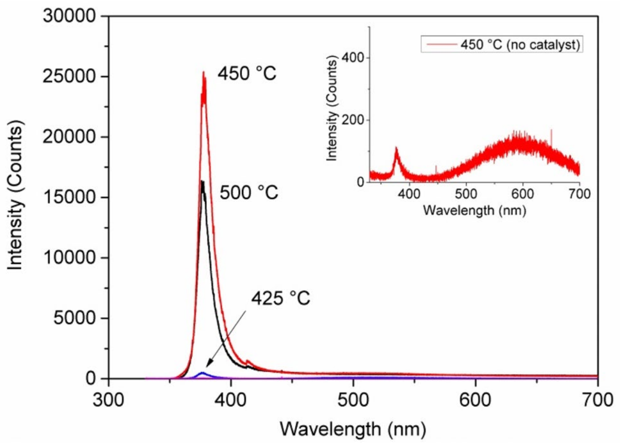

Fig. 6 Photoluminescence emission of ZnO NWs prepared on Cu NPs (HeCd pumping laser at 325 nm). Inset: a PL emission of polycrystalline ZnO deposited on the substrate surface without applied Cu nanoparticles

400 °C, no growth of NWs was recorded despite the use of low melting point metals.

Figure 4 shows an isolated nanowire prepared on Al catalyst at 450 °C. The resulted nanowires were randomly oriented, and according to applied composition of catalyst and deposition temperature, their typical length varied in order of micrometres. Usually, kinked parts indicate growth irregularities with the presence of structural defects [17]. In the temperature interval 600–450 °C, occurrence of such deformed nanowires was negligible in contrast to samples prepared at 425 and 400 °C (Figs. 3 and 5).

The optimisation of the secondary deposition parameters (Ar pressure, laser fluence) at 400 °C was focused on growth at Cu and Al catalyst. Investigation of prepared samples by SEM showed slight differences only, and the results in simplified form are shown in Table 3. We noticed that at low Ar pressure and laser fluence a positive impact on improving growth processes is observed. The final optimisation in temperature range 500–400 °C showed that 425 °C was the lowest temperature when substrates were successfully covered by dense population of ZnO nanowires (Fig. 5).

Room-temperature photoluminescence (PL) was measured with HeCd laser at 325 nm. All emission records consisted of an intense peak around 380 nm while the emission in visible region (450–700 nm) was negligible. Figure 6 shows comparison of PL spectra for ZnO nanowires grown by using of Cu nanoparticles. The inset is a PL emission of polycrystalline ZnO deposited on the substrate surface without applied Cu nanoparticles. Analysed PL spectra revealed substantially different properties of NWs crystallised at 425 °C unlike with their counterparts which were synthesised at higher temperatures (450–600 °C). Both compared PL spectra (450 vs. 425 °C) consisted of intense emission at around 380 nm which is attributed to the electron–hole annihilation; however, relative intensity of this peak was negligible for samples prepared at 425 °C. Samples prepared by using of Al nanoparticles exhibited similar behaviour. Such poor PL response for samples grown at 425 °C indicates the presence of imperfections in inner crystal structure and it is questionable to consider this result as successful growth. According to achieved results, it would be better to use the 450 °C level as the lowest temperature for successful growth of ZnO NWs, by applied metals which is in good accordance with published results [14, 15]. Comparison with published references suggests that there is a certain temperature level around 400–450 °C for crystallisation of ZnO in a form of nanowires as a result of VLS growth mechanism. Reported results vary in accordance with deposition conditions. Certain role plays the composition and the pressure of the growth ambient [17, 27, 30] or presence and the concentration of dopants in ZnO structure [15].

4 Conclusions

ZnO nanowires were deposited by PLD, and influence of deposition temperature was compared in interval 600–200 °C. Different metal nanoparticles (Ag, Au, Cu, Al, Mg, Zn, Sn) were applied for catalytic supported growth, and both Cu and Al exhibited the most efficient lowering of deposition temperature down to 450 °C. This temperature is still high for application with organic materials; however, the achieved results suggest that the selection of proper catalytic element can play an important role in synthesising of ZnO NWs at relatively low temperatures in comparison with traditionally published interval above 700 °C. The temperature level at 450 °C is still high for safe application of organic materials; however, it provides opportunity to combine ZnO nanowires with wide range of materials which are stable at this temperature.

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