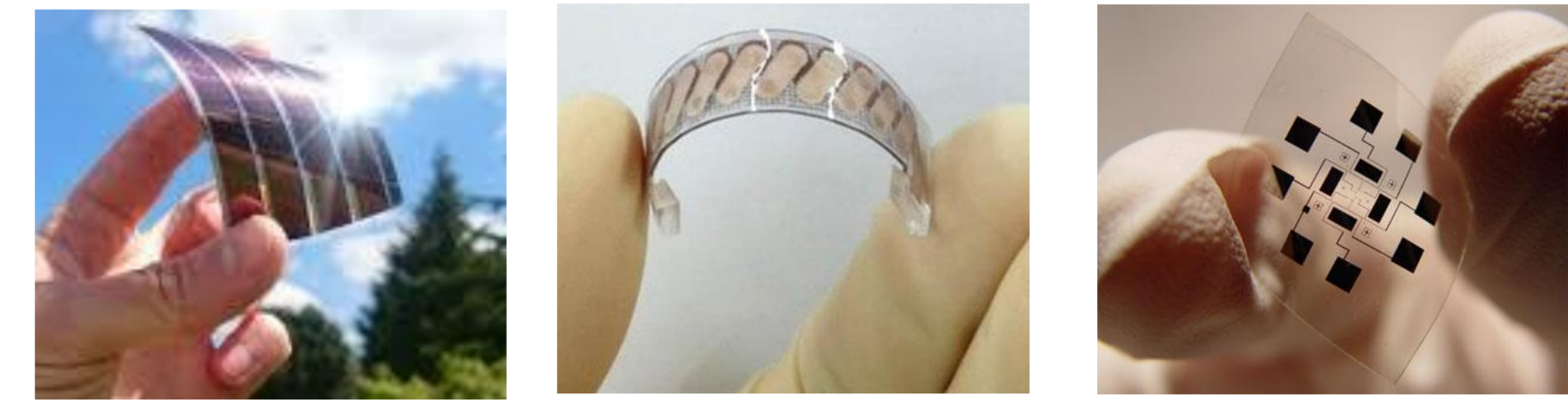


Motivation

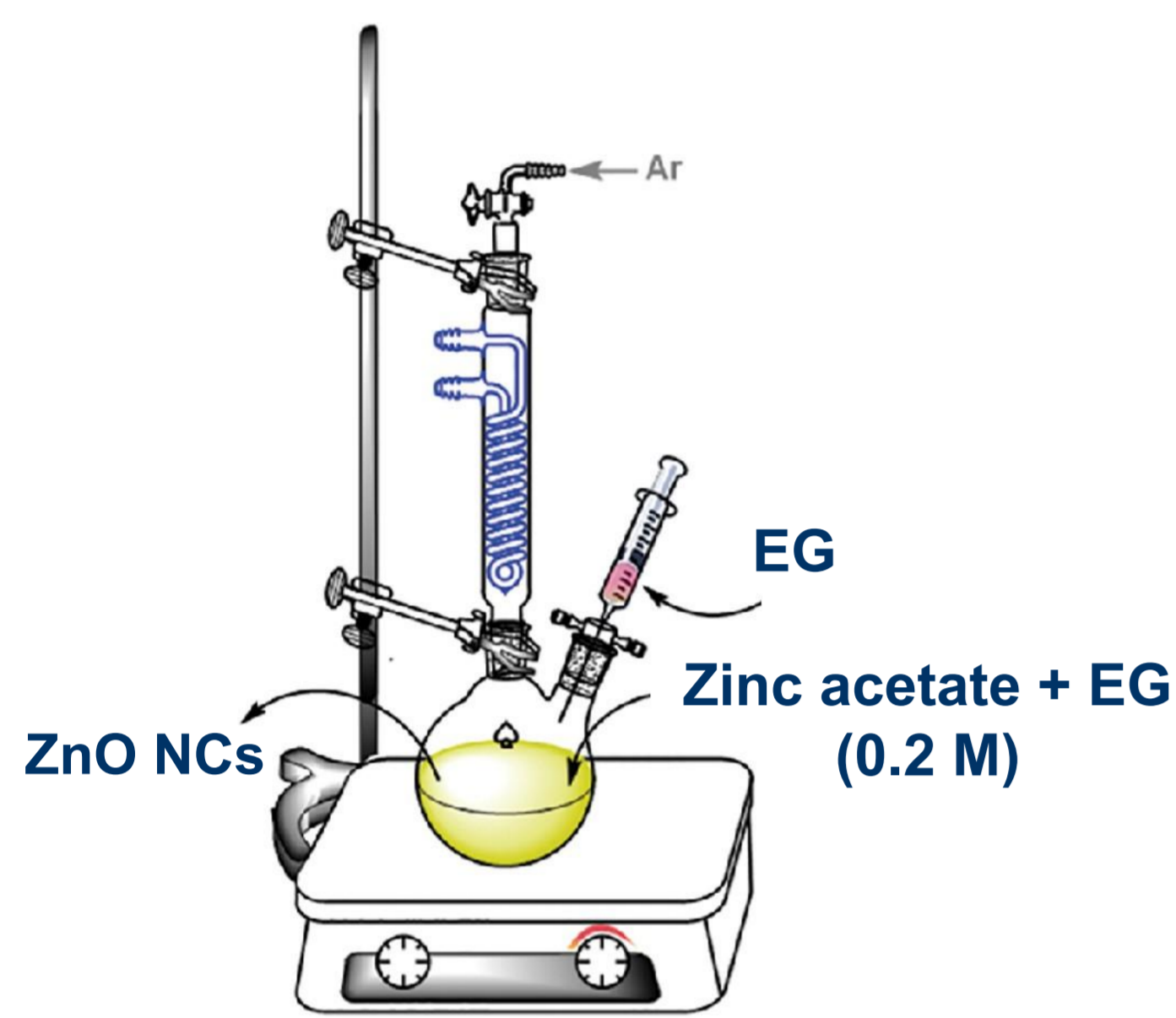
- Era of modern flexible microelectronic devices, particularly flexible solar cells, thermoelectric generators and sensors;
- Functional elements based on ZnO semiconductor material due to excellent physico-chemical properties are widely used in development of microelectronic devices;
- Nanoink spray printing approach to develop flexible ZnO films are low-cost, versatile, scalable allowing to design functional elements with programmed fundamental properties;
- Functional and performance features (e.g. energy conversion efficiency, sensitivity, stability, reproducibility) of flexible ZnO based microelectronic devices are strongly related to fundamental properties (crystal structure, phase and chemical composition, substructural and optical properties).



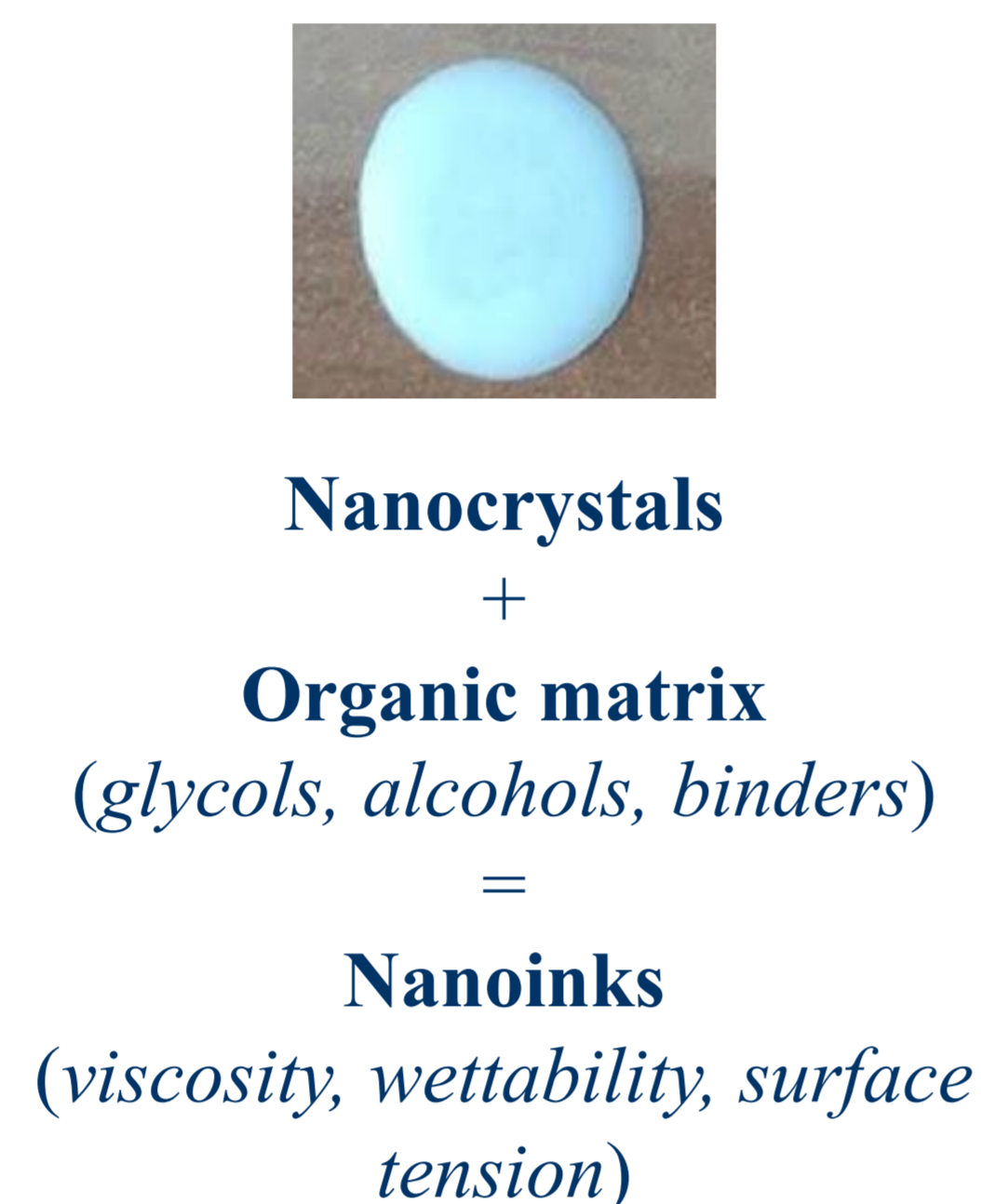
World class flexible solar cell, thermoelectric generator and sensor

Steps to develop flexible ZnO films

Nanocrystal synthesis



Nanoink formation

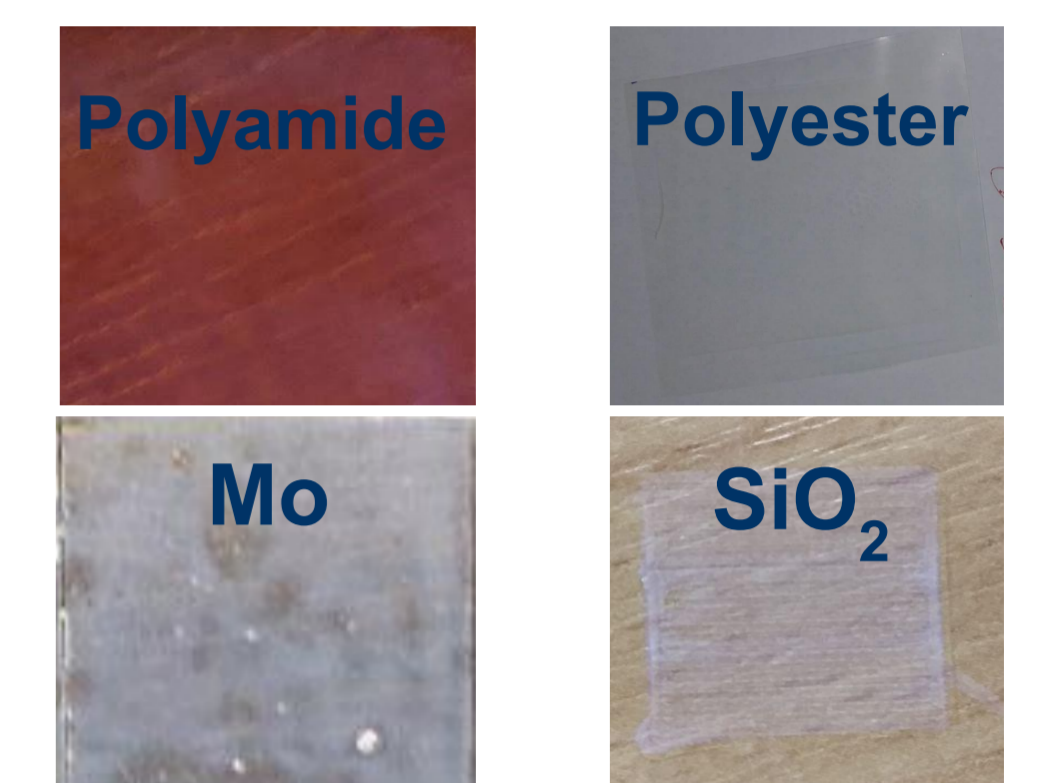


Spray printing



- Spraying parameters:**
- Air conditions;
 - Polyamide substrate (8 x 8 cm);
 - 150 °C substrate temperature;
 - 20 printing cycles (spraying - 3 s, pause - 5 s);
 - Annealing at 200-400 °C for 10-60 min in Ar atm.

Functional elements



ZnO films onto flexible (polyamide, polyester) and rigid (Mo, SiO₂) substrates.

Fundamental properties of flexible ZnO films

Structure and substructure

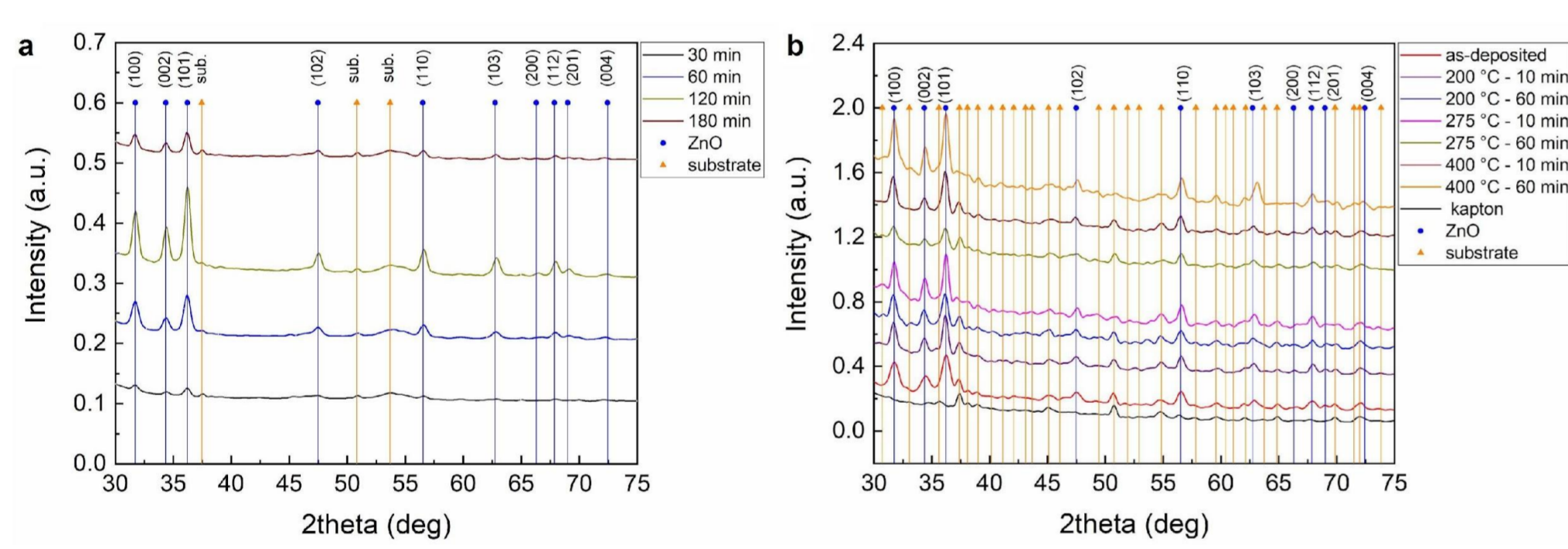


Fig. 1. XRD patterns from synthesized ZnO nanocrystals at the different growth time (blue vertical lines correspond to ZnO; orange vertical lines correspond to polyester substrate) (a) and XRD patterns from deposited and annealed ZnO films at the different temperature and time (blue vertical lines correspond to ZnO; orange vertical lines correspond to polyamide substrate) (b).

Morphology and chemical composition

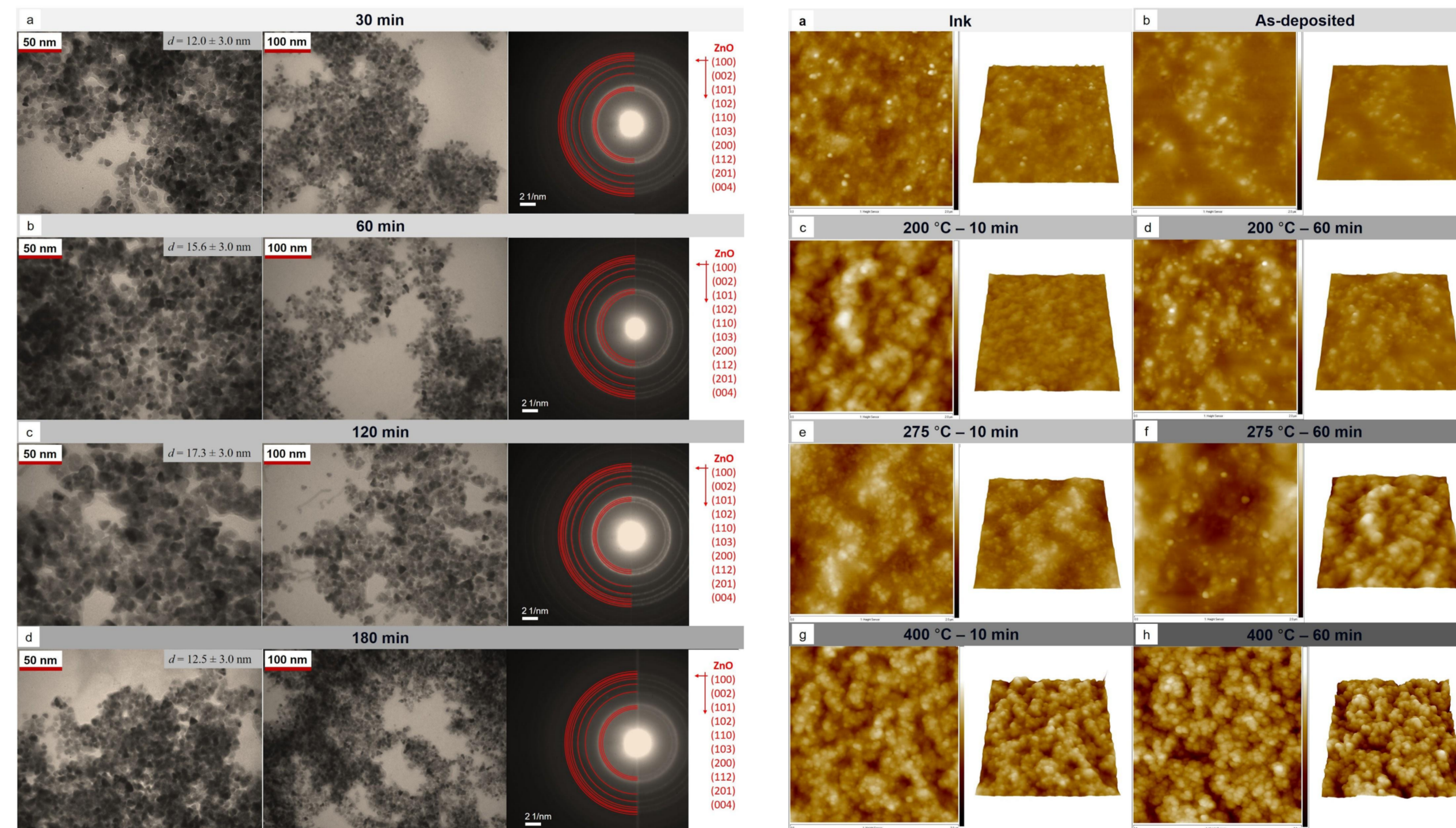


Fig. 3. Electron microscopic images obtained by TEM and SAED from synthesized ZnO nanocrystals at the different growth times (a-d).

Fig. 4. Atomic force microscope images of ZnO nanoink (a), deposited (b) and annealed (c-h) ZnO films. The scan area was set to 2 x 2 μm. The bar height was set to 200 nm.

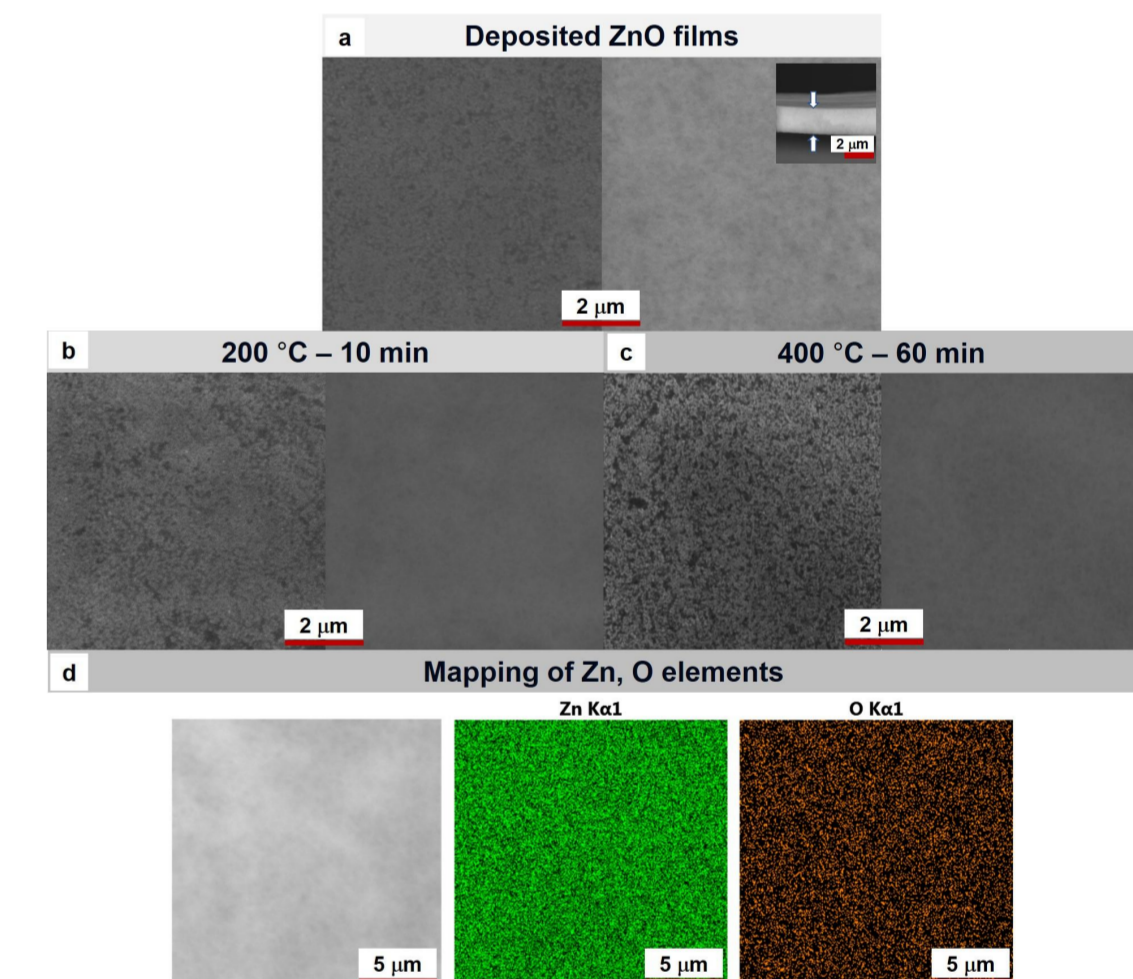


Fig. 5. Electron microscopic images of the surface of deposited (a) and annealed (b, c) ZnO films and elemental mapping of ZnO films (d).

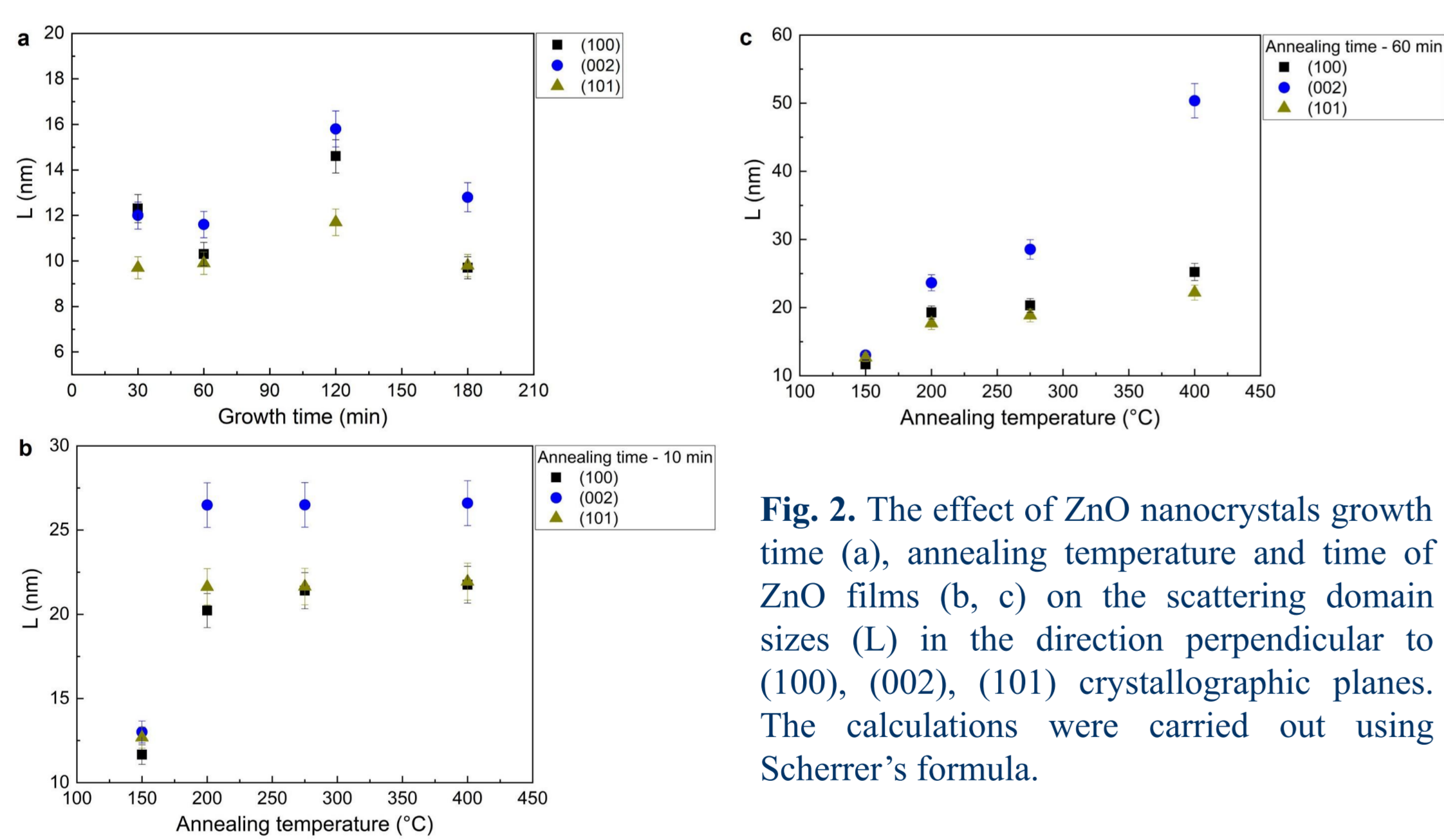


Fig. 2. The effect of ZnO nanocrystals growth time (a), annealing temperature and time of ZnO films (b, c) on the scattering domain sizes (L) in the direction perpendicular to (100), (002), (101) crystallographic planes. The calculations were carried out using Scherrer's formula.

Table 2. Average chemical composition, surface roughness and optical characteristics of ZnO nanocrystals, deposited and annealed films.

Samples	C _{Zn} , at. %	C _O , at. %	Y _{ZnO}	Surface roughness		E _g , eV	T, %	
				R _{ms} (nm)	R _s (nm)			
Nanocrystals	42.50	57.50	0.74	10.5	8.8	3.3 ± 0.1	60-80	
Deposited films	31.50	68.50	0.46	12.6	9.5			
Annealed films, T _a , °C; t _a , min	200, 10	32.50	67.50	0.48	20.5			14.8
	200, 60	33.50	66.50	0.50	18.4			15.7
	275, 10	33.50	66.50	0.50	23.2			18.1
	275, 60	34.60	65.40	0.53	25.1			19.3
	400, 10	35.60	64.40	0.55	38.2	31.2		
400, 60	36.50	63.50	0.57	43.2	32.7			

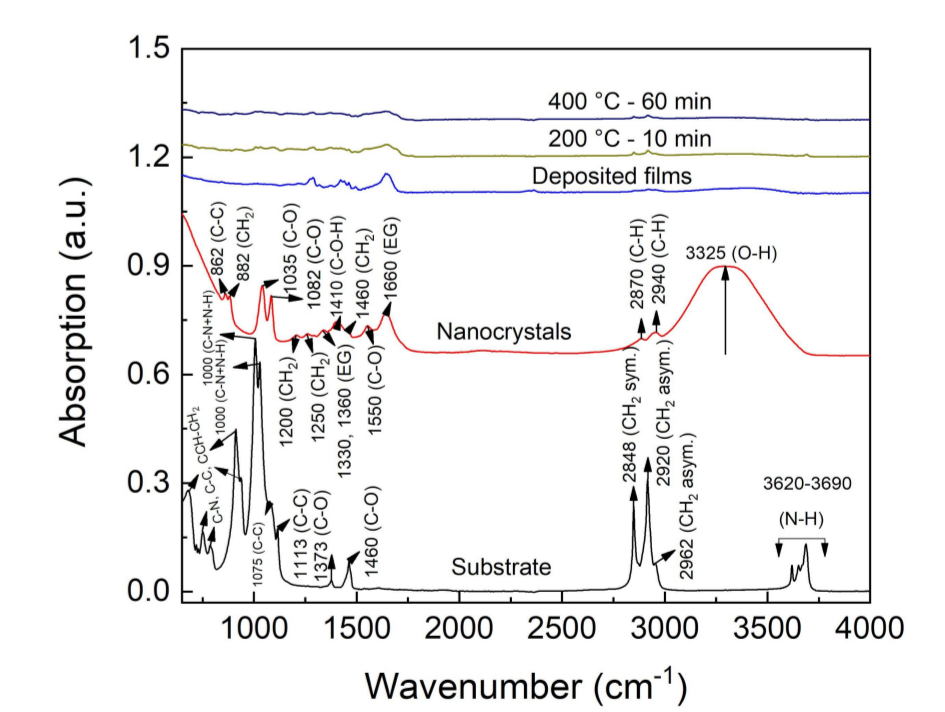


Fig. 6. FTIR spectra of polyamide substrate, synthesized ZnO nanocrystals, deposited and annealed films.

Conclusions

- In this work, ZnO films were developed onto flexible polyamide substrates by spraying nanoinks containing nanocrystals synthesized by polyol method;
- We studied the effect of annealing temperature (200-400 °C) and time (10 min, 60 min) of films on the structural, substructural properties and chemical composition;
- ZnO nanocrystals had single-phase and changed size in the range of $d = (12-17) \pm 3$ nm depending on the growth time $t_g = (30-180)$ min;
- Content of organics decreased with increasing temperature and annealing time which was confirmed by results of AFM and FTIR spectroscopies;
- Lattice parameters of ZnO materials changed with time/temperature in the range of $a_{ZnO} = (0.32454-0.32588)$ nm, $c_{ZnO} = (0.52105-0.52221)$ nm, $c/a_{ZnO} = (1.6000-1.6080)$ and were close to the stoichiometric values;
- Structural and substructural properties of ZnO nanocrystals and films have been improved with increasing growth time t_g and annealing time T_a . The obtained materials are characterized by excess of oxygen ($Zn/O = 0.46-0.57$) and regular distribution of chemical elements over the surface. ZnO films were continuous with a good adhesion to the substrate surface and had a thickness of 2.0 ± 0.4 μm;
- ZnO films had high optical properties (transmission coefficient of $T = 60-80\%$) and band gap $E_g = 3.3 \pm 0.1$ eV;
- ZnO films studied in this work possess the properties suitable for application in the microelectronics devices, flexible solar cells and thermoelectric generators.

Acknowledgments

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