Applied Surface Science 257 (2011) 8396–8401

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

ZnO nanoparticles produced by reactive laser ablation

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ARTICLE INFO

Article history:
Received 14 February 2011
Received in revised form 11 April 2011
Accepted 17 April 2011
Available online 27 April 2011

Keywords:
Nanopowders oxides
Cluster formation
Luminescence
Laser annealing
Gas sensors

ABSTRACT

The paper presents the results of theoretical and experimental researches of the analysis of nanopowder ZnO and ZnO-based structures formation mechanisms by means of pulse laser reactive technology ($\lambda = 1.06\,\mu m$, $\tau = 10^{-7}$ to 10^{-5} s). The developed 2D model combines non-stationary heat transfer and fluid motion along with the calculated profile of surface deformation. The characteristics of the dispersive and chemical compositions and structural parameters of the synthesized nanopowder together with the influence of the energy of laser impulse evaporation, its duration and gas pressure in the reaction chamber have been studied using X-ray diffractrometry (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM). Particle size distribution analysis of ZnO has shown that the majority of them range from 5 to 60 nm in size. The photoluminescence emission spectra of the initial ZnO nanopowder at room temperature have been identified.

1. Introduction

Zinc oxide is a wide-gap semiconductor material ($E_g = 3.37$ eV), the interest which has especially grown recently, because this material is considered to be the one of the most prospective ones both for creating light-emitting structures, lasers and for gas sensors [1]. As it is known, gas adsorption processes are associated with electronic transitions on the surface of the material, and this leads to various effects in luminescence [2], and these processes are particularly strongly pronounced in nanopowder materials which have a big effective surface. One of the prospective methods of creating wide-class nanopowder materials is pulse laser reactive technology [3]. There are a lot of methods of nanopowder synthesis including the synthesis using CO_2 laser during evaporation of metal oxide targets [4]. However, in this method there is no dosed control of pressure and reactive gas composition, which fact does not enable to form composite nanopowder materials and barrier structures on their basis during evaporation of metal targets. Besides, for evaporation of mainly transparent targets of metal oxides it is necessary to use CO_2 or eximer lasers, and that limits the use of accessible and low-price solid-state powerful lasers which work in visible or close infrared spectral regions for that purpose.

In this paper we suggest the method of formation of nanopowder materials and barrier structures on their basis by means of pulse laser reactive evaporation of material targets which can effectively be used for nanopowder production. The above method enables to regulate technological parameters of the process and, accordingly, the characteristics of synthesized nanopowders. And there takes place formation of disperse phase in the conditions of high rates of growth and speeds of the process which leads to the formation of non-equilibrium structure of ZnO material which possesses a clearly manifested self-defective structure [5]. On the other hand, properties of the material can additionally be modified by different laser-alloyed admixtures.

At present there is no generally accepted model of laser ablation of material from the target, that is why the issue of metal targets evaporation mechanism, in particular, at high density of laser impulse energy, remains unanswered. It is often considered that particles are mainly formed as a result of coagulation of clusters which are formed at early stages of evaporation [6]. Since during the evaporation products expansion process the liquid phase does not completely evaporate, the particle formation process can occur both with involvement of condensation and coagulation mechanisms. The establishment of the mechanism which dominates at nanoparticles formation is of fundamental and applied interest.

2. Mathematical modeling

The suggested model enables us to determine the ablated matter size and the character of substance distribution on the Zn-target (Fig. 1) [7] in oxygen ambient. To study this, we use the equations of the non-stationary heat transfer and the fluids mechanics. The process was simulated with a finite element method (FEM) by means of the software package Comsol 3.5 [8]. Analogical problem, without standard enthalpy of formation has been considered in ref. [9] (Table 1).

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doi:10.1016/j.apsusc.2011.04.084

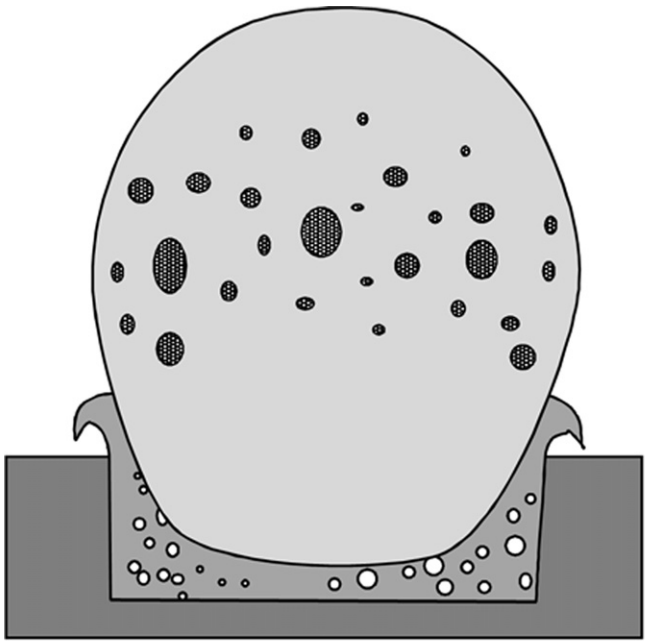

Fig. 1. Schematic representation of boiling process at pulsed laser ablation.

Table 1
Materials data of ZnO used in calculation [10].

Parameter	Symbol	Value
Latent heat of vaporization ($kJ\,kg^{-1}$)	L_v	25.499
Temperature of vaporization (K)	T_v	1179
Emissivity	ε	0.6
Latent heat of fusion ($kJ\,kg^{-1}$)	L_m	111
Temperature of fusion (K)	T_m	692.5
Surface tension ($N\,m^{-1}$)	σ	0.8
Density ($kg\,m^{-3}$)	ρ	7133
Conductivity ($W\,m^{-1}\,K^{-1}$)	k	110.95
Heat capacity ($J\,kg^{-1}\,K^{-1}$)	C_p	0.383
Thermal dilatation (K^{-1})	α	64×10^{-6}
Standard enthalpy of formation ($kJ\,mol^{-1}$)	q	350
Activation energy ($kJ\,mol^{-1}$)	E_a	361

We consider that during the irradiation phase the surface receives specific power with a Gaussian distribution:

$$\varphi = \frac{2\varepsilon P_C}{\pi r^2} e^{(2x^2/r^2)} \tag{1}$$

where P_c – specific power, ε – emissivity, r – beam radius.

However, the surface of the layer of molten metal quickly reaches the irradiation temperature. This vapour flow means that:

- the surface remains with the temperature of vaporization;
- the vapour ejected creates a recoil pressure on the liquid layer.

To model this effect, it is necessary to know the evolution of the recoil pressure generated by this vapour ejection.

Our purpose is to model a thermal cycle, i.e., the heating during 120 ns and then the cooling under the effect of the environment. In this paper we have developed a 2D model coupling the non-stationary heat transfer and the fluid motion.

We assume that this is a Newtonian fluid and incompressible. In this case, in order to model the movement of the liquid under the effect of recoil pressure, use the Navier–Stokes equation. The heat conductivity equation takes account of the fluid motion through an advection item.

$$\rho C\mathrm{p}\frac{\partial T}{\partial t} + \vec{\nabla}(-k\vec{\nabla}T) + \rho C_\mathrm{p}\vec{u}\vec{\nabla}T + q_\mathrm{chem} = \varphi \tag{2}$$

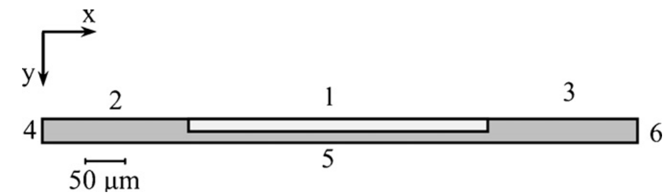

Fig. 2. Geometry and boundaries.

$$\rho\frac{\partial\vec{u}}{\partial t} - \vec{\nabla}[\eta(\nabla\vec{u} + \nabla\vec{u})^t] + \rho(\vec{u}\vec{\nabla})\vec{u} + \vec{\nabla}p = \vec{f} \qquad \vec{\nabla}\vec{u} = 0 \tag{3}$$

$$q_\mathrm{chem} = qK_0 e^{E_\mathrm{a}/KT} \tag{4}$$

where ρ – density, k – specific conductivity, Cp – heat capacity, q_chem – reaction heat, φ – power density, η – viscosity, q – standard enthalpy of formation, E_a – activation energy, $\vec{f}$ – volume force, $\vec{u}$ – liquid velocity.

The difference between the solid condition and liquid manifests itself in a very high value of viscosity when the material is in a solid state (temperature lower than the melting point). The effect of recoil pressure on the free part of the fluid layer is described in the Laplace's equation:

$$\Delta p = \sigma C \tag{5}$$

with Δp – difference in pressures, σ – surface tension factor, C – curvature of surface.

Boundary conditions (Fig. 2).

Thermal conductivity conditions.

For boundaries 1–3 we impose the following limiting conditions:

- constant flow on the surface until the temperature of the surface is $T = T_v$.
- stable temperature $T = T_v$ of the surface until the end of the pulse ($T < \tau_\mathrm{las}$).
- cooling by advection and radiation of air ($T = T_0$) for $T > \tau_\mathrm{las}$.

Hydrodynamic conditions.

Boundary 1 is subjected to the effect of two forces. The first one is due to recoil pressure formed by the ejected vapour, while the second one is due to surface tension force.

$$\left[-pI + \eta(\nabla\vec{u} + (\nabla\vec{u})^t)\right]\cdot\vec{n} = -P_r\vec{n} \tag{6}$$

$$P_r\vec{n} - \sigma\frac{\partial\vec{t}}{\partial s} = 0 \tag{7}$$

with, $\vec{n}$ – normal, $\vec{t}$ – tangential vectors and P_r – recoil pressure.

Boundaries 2 and 3 are subjected to neutral boundary conditions. For boundaries 4, 5 and 6 we impose a condition of displacement which results in the components of speed normal being equal to zero. Boundaries 1, 2 and 3 correspond to the free part of the material. In this case, because of free surface movement, it is necessary to set the surface speed normal components as equal to normal components of the material motion speed.

Fig. 3 shows the calculated profile of deformation of the surface.

It is noticed that the depth of the crater is weak at the end of the pulse. However, after the end of the pulse, the surface remains deformed. This phenomenon can also be observed in the experimental section of the crater after a series of impulses. Crater formation is accompanied drops ablation from crater edges. This confirms that in our case the effect of recoil pressure is definitely more important than the effect of surface tension. The offered model describes a partial version of possible formation of drops.