Obtaining of nanostructured ZnO coatings using mechanoactivated oxidation

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Abstract. The concept to use nanostructured state of metal at the instant of destruction in air environment was used to obtain nanostructured Zn-ZnO coatings on glass and quartz by mechanical method. Subsequent annealing in the ambient atmosphere, annealing in vacuum and irradiation with 532-nm YAG:Nd laser were used to obtain completely oxidized, transparent ZnO coatings. The saturated with oxygen nanostructured coatings were transformed into nanostructured ZnO coatings after annealing above 773K or irradiation with laser (allowing to reach 673K) in ambient atmosphere. AFM and SEM images show that after annealing ZnO coatings have multi-shaped structure. The formation of ZnO needle-like whiskers (d=100nm, l=2 μm) was observed after laser irradiation. Obtained ZnO coatings have high microhardness (10-12GPa), strong adhesion with substrates and show green and blue luminescence at room temperature. The oxidation process is mechano activated due to the facilitated oxygen diffusion along deformation defects: vacancies, dislocation, microcracks, and developed network of grain boundaries.

1. Introduction

Nanostructured oxide coatings can be used as functional materials for different applications: for laser diodes, optical waveguides, acousto-optic devices, as transparent conducting films for solar cells etc. Usually to obtain such nanostructured coatings reactive sputtering, CVD, PVD or multistage oxidation methods are used [1-5]. At the same time, little attention has been paid to the obtaining of nanostructured oxide coatings using mechanoactivated oxidation of nanostructured metals. As it is known, during severe plastic deformation generation of various structural defects (mainly point defects, dislocations) and formation of small-grained structure occurs. At the moment of destruction metals are nanostructured and contain a net of microcracks [6]. These elements of structure as well as high level of internal pressure promote diffusion and reactive processes.

From our previous work [7] it follows, that during plastic deformation of metals with high affinity to oxygen (Al, Mg, In) on the surface of oxides (glass, SiO\(_2\), Al\(_2\)O\(_3\), MgO, etc.) a level of chemical adhesion in the regions of the maximum shear stresses could be reached even at room temperature. Based on these concepts, we have shown that nanostructured metal-oxide composite coatings on glass can be obtained at room temperature by the mechanical method using quickly rotating steel wire brush [8]. Coatings obtained in this way have small-grained (30-500nm) structure, high microhardness.
values, good adhesion to the glass and are saturated with oxygen, which can act as barrier for grain growth in the coatings.

By the subsequent annealing, metal-oxide coatings could be modified into completely oxidized, stoichiometric oxide coatings. In the present work this method was applied for the obtaining of nanostructured Zn coating on glass and quartz substrates with the subsequent formation of nanostructured ZnO coating, because Zn is relatively easily oxidized ($\Delta G_{293} = -318\text{kJ/mol}$) and diffusion of oxygen through ZnO is not complicated. The choice of materials was dictated by the fact, that ZnO has become an important functional semiconductor with plenty of promising properties and is an important potential material for blue and ultraviolet light-emitting diodes, for transparent electrodes for the solar cells etc. Moreover, in the nanostructured state ZnO coating exhibits new mechanical and optical properties, so the obtaining of ZnO nanostructured coating is an actual problem.

2. Experimental

Polycrystalline Zn of technical purity (99.9%) was chosen as a material for coatings, sodium-silicate glass and quartz were used as substrates. Zn coatings on glass and quartz were obtained by mechanical method described in [8]. Actually in this method the phenomenon of microscopic mass transfer by wear in the air environment is used. The process of coating formation occurs in three main stages. During the first one, metal particles are cut out from a bulk metal specimen with steel wires. The second stage is intensive oxidation of the cut metal particles due to the favoured penetration of atmospheric oxygen along the developed net of grain boundaries and microcracks. And the third stage is the transfer of oxidized metal particles to the substrate and formation of welded junctions between substrate and metal particles under dynamic shear stresses action. As the steel wire brush rotates with frequency 1400rpm all these three stages are repeated several times and the material of obtained coating is heavily deformed. The mean time to obtain a Zn-ZnO coating with a thickness 2-2.5 $\mu$m was less than 5 minutes without the expensive complex equipment.

In this work several methods to obtain transparent ZnO from Zn-ZnO precursor coating were used: annealing in ambient atmosphere, annealing in vacuum (when only redistribution of oxygen in coating can take place) and irradiation with laser. Annealing experiments were made at temperatures 373-823K (40 min) in muffle furnace in ambient atmosphere and in high vacuum ($10^{-6}$Pa). Direct chemical reaction stimulation was provided at irradiation by 532nm YAG:Nd laser in ambient atmosphere at 673K during 4 hours.

Micromechanical properties were measured using the microhardness tester PMT-3M with a Vickers diamond pyramid. A modified precision loading device allowed accurate measurements to be performed over a wide load range from $1.12 \times 10^{-3}$N to 2N. Structure and chemical composition of coatings were investigated using optical microscope, AFM, XRD, SEM (with EDX) techniques. Optical properties were controlled by adsorption spectra using Specord M-40, luminescence was excited using YAG:Nd laser (266nm) at room temperature.

3. Results and discussion

3.1. Properties of Zn-ZnO coatings on glass and quartz in as-obtained state

As-obtained coatings were non-transparent with typical metallic shine, but already had diffraction peaks characteristic for ZnO in the XRD patterns (Fig.1). Due to the relatively low energy of oxide formation ($\Delta H_{293}=318\text{kJ/mol}$) and quick diffusion of oxygen through ZnO the oxidation of zinc takes place very quickly. As it is known, during strong deformation of metal the high density of dislocations is formed, along which pipe-diffusion is possible [9]. More over, grain boundaries have the bigger fraction of free volume. As it was shown in [10], it can cause an increase of grain boundary diffusivity by a factor of two. Besides, the Zn coating contains a network of microcracks and open pores, along which a quick redistribution of oxygen is possible.
Coatings showed strong adhesion to the glass and SiO$_2$ without detachment at high normal load or during heating till Zn melting point. Coatings have high microhardness values (2.5GPa), as will be shown below.

The micrographs show relatively smooth relief of the coatings surface (Fig.2,a). SEM image shows the presence of quasi-brittle phases (Fig.2,b) and AFM images reveal nanostructure in the form of the terraces with size $\approx$ 100-300nm and thickness about 10-50nm.

### 3.2. Annealing experiments

After annealing in vacuum SEM images show that the surface relief has changed (Fig.3,a). There are practically no smooth sites at the surface. It is possible to assume, that modification of structure occurs due to the redistribution of oxygen during annealing in vacuum.

Annealing at ambient atmosphere led to the essential changes in structure and in microhardness of coatings. With an increase of annealing temperature till 773K new small phases with hexagonal sides of planes (d=200-500nm) appear in the structure, that is typical for ZnO phases (Fig.3, b, c).
During annealing above 773K in air, transformation of coatings to transparent state was observed. It is possible to assume, that all coating at this temperature has altered to transparent ZnO phase. To show it, XRD, optical absorption (Fig.4,a) and luminescence spectra (Fig.4,b) were made on the samples after annealing at 773K and at 873K.

As it is seen the edge of absorption spectrum is typical for ZnO [11]. Photoluminescence spectrum was measured at the room temperature and obtained two strong bands: green at 2.5eV (associated with defects states) and blue at 3.26eV (associated with free exitons). These data testify presence of high-quality ZnO crystals [12,13].

It is known, that ZnO monocrystals have high microhardness (typically, 1.5GPa-3GPa). It was possible to expect microhardness value of the same order of magnitude for coatings. The results of microhardness testing for after obtaining and after annealing samples are shown in Fig.5.
In as-obtained state coatings have microhardness values 2.5GPa, near the surface microhardness was higher \( H \approx 3.2 \text{GPa} \). These values are close to ZnO monocrystal hardness. As in the initial state coatings consist of mechanical mixture of Zn and ZnO, it is possible to explain so high values of microhardness with the nanocomposite structure of the coating. ZnO layers are barrier for grain growth, but on the other side they bring own contribution to hardening of coatings. Annealing leads to the increase of microhardness up to 10-12GPa.

These data and non-homogeneity of microhardness data through depth specify structural transformations during annealing. SEM images show that at high annealing temperature (above 773K) formation of the separate needle-like whiskers (\( l=2-10 \mu m, d=50-100 \text{nm} \)) occurs on the hexagonal grains (Fig.3,c, 6,a). The presence of these whiskers is the cause of the high microhardness.

From [12,13] it follows that ZnO whiskers can be obtained by laser stimulation of ZnO powders. On the Fig. 6(b,c) is shown SEM image of the laser irradiated Zn-ZnO coatings. The formation of needle-form ZnO crystals is seen over the whole surface. The length of microcrystals is smaller (\( l=2-3 \mu m \)) than in annealed samples, probably, because the growth occurs from the many centres of
crystallization. As it is known these ZnO microcrystals have excellent optical properties and are promising materials for laser diodes. Based on the obtained results, mechanoactivated oxidation could be a simple and effective method to produce ZnO in different forms.

**Conclusions**

1. ZnO-Zn coatings after obtaining are saturated with oxygen, show high adhesion to the glass, have high microhardness values and nanocomposite structure.
2. Annealing at ambient atmosphere leads to the changes in structure and to the increase of microhardness (10-12GPa). The origin and growth of separate ZnO whiskers on the surface is seen after annealing. The formation of the transparent ZnO coating occurs above 773K.
3. The transformation of all structure in form of needle-like ZnO whiskers occurs after irradiation by laser.
4. ZnO coatings show green and blue luminescence after annealing at 873K, or after irradiation by laser.
5. The oxidation process is mechanoactivated by the presence of stresses in coatings, and due to the facilitated oxygen diffusion along deformation defects: vacancies, dislocation, microcracks, developed network of grain boundaries.
6. As it is known ZnO microcrystals are promising materials for laser diodes and for solar cells. Based on the obtained results, mechanoactivated oxidation could be a simple and effective method to produce ZnO in different forms.

**References**

[1] Tanaka H, Ihara K, Miyata T, Sato H, and Minammi T 2004 *J.Vac. Technol. A* **22** 1757.
[2] Minami T, Ida S, and Miyata T 2002 *Thin Solid Films* **416** 92.
[3] Calderon C, Gordillo G, and Olarte J 2005 *Phys. Stat. Sol. (b)* **242** 1915.
[4] Suchea M, Christoulakis S, Moschovis K, Katsarakis N, Kiriakidis G 2006 *Thin Solid Films* **515** 551.
[5] Wang Y G, Lau S P, Lee H W, Yu S, Tay B K, Zhang X H, Hung H H 2003 *J. Appl. Phys.* **94** 354.
[6] Valiev R Z, Alexandrov I V and Islamgaliev R K : in Nanostructured materials, G.M. Chow and N.I. Noskova, eds. (Kluwer Academic Publishers 1998), p. 121.
[7] Muktepavela F, Bakradze G, Tamanis E, Stolyarova S, and Zaporina N 2005 *Phys. Stat. Sol. c* **2** 339.
[8] Muktepavela F, Bakradze G, and Stolyarova S 2007 *Phys. Stat. Sol. c* **4** 740.
[9] Gupta D 1973 *Phys. Rev.* **B7** 583.
[10] Paritskaya L, Kaganovskii Yu, and Bogdanov V 2005 *Sol. St. Phen.* **101-102** 123.
[11] Murth J F, Kolbas R M, Sharma A K, Oktaybrsky S and Narayan J 1999 *J. Appl. Phys.* **85** 7884.
[12] Grigorjeva L, Millers D, Smits K, Monty C, Kouam J, and Mir LE 2007 *Sol. St. Phen.* **128** 135.
[13] Cao W, and Du W 2007 *J. Luminescence* **124** 260.