GROWTH OF ZnO CRYSTALS BY CVT METHODS

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Abstract

Features of the growth of ZnO single crystals by chemical vapor transport with the use of H_2, HCl, H_2 + HCl mixture, and CO as transport agents and dopant sources are discussed in the present paper. Based on the investigation of electrical, luminescent, and optical properties of these samples with various doping level, the prospects of the used techniques for the obtaining of large-area substrates with controlled parameters are estimated.

1. Introduction

Zinc oxide (ZnO) crystals draw attention due to relatively low price and the prospects of their utilization in various applications. Commercially available crystals and corresponding substrates are usually obtained by hydrothermal methods. However, the presence of mobile Li or K ions in these materials limits their utilization in electronics [1]. In this respect, the elaboration of growth technology for ZnO single crystals with controlled parameters and impurity composition by means of chemical vapor transport in sealed chambers is of great interest.

2. Experimental techniques

ZnO single crystals were grown in evacuated sealed quartz ampoules at 1000°C and undercooling of 10-20°C by means of a chemical vapor transport method. H_2, HCl, H_2+HCl mixture, and CO were used as transport agents. The density of loaded HCl was varied from 0.07 up to 1.3 mg/cm^3. Hydrogen pressure was maintained at a level of 1 atm. An atmosphere of CO was obtained as a product of reaction between ZnO and carbon. The material synthesized by means of annealing of high pure Zn in an atmosphere of O was used as a source for crystal growth.

Electrical parameters were determined from the Hall effect measurements using a six-probe method. Photoluminescence (PL) was excited by a nitrogen laser ($E_{excit} \approx 3.68$ eV, ~ 10 mW/mm^2). PL and transmission spectra were registered in a range between 350 and 800 nm using a monochromator with a reciprocal dispersion of 1.4 nm/mm.

3. Experimental results

A ZnO saturated vapor pressure is extremely low even at a temperature close to the softening point of quartz (~1150ºC) and is no more than 10^{-2} torr. Due to this fact, the growth of these crystals by the physical transport method is impossible. HCl, H_2, and CO substances can be

used as chemical transport agents. An elementary calculation based on thermodynamic constants (namely, formation enthalpy and entropy) of reaction substances [2]:

$$ZnO + H_2 \leftrightarrow H_2O(gas) + Zn(gas), \quad (1)$$

$$ZnO + 2HCl \leftrightarrow H_2O(gas) + ZnCl_2(gas), \quad (2)$$

$$ZnO + CO \leftrightarrow CO_2 + Zn(gas) \quad (3)$$

indicates high pressure of the products of reactions (1)–(3), which reach the values of $1.7\cdot(p(H_2))^{1/2}$, $14\cdot p(HCl)$ and $0.8\cdot(p(CO))^{1/2}$ (all values of pressure are expressed in atm) at 1000ºC, respectively. The high pressure is favorable for crystal growth by the chemical transport method. The factor determining the high rate of mass transport by opposing chemical reactions is a high value of reaction enthalpy [2], which is 54, 5, and 45 kcal/mol for reactions (1)–(3), respectively.

3.1. H_2 transport agent

The use of H_2 as a transport agent provides a high growth rate of the crystals (1-2 mm/day), which compactly fill the growth chamber volume. However, these crystals are characterized by pore formation; the strong mechanical contact between ZnO:H and the quartz walls of the growth chamber leads to the destruction of both ampoules and grown crystals during a post-growth cooling. The effective low-temperature edge PL of these materials exhibits exciton emission caused by shallow hydrogen donors [3, 4] (Fig. 1).

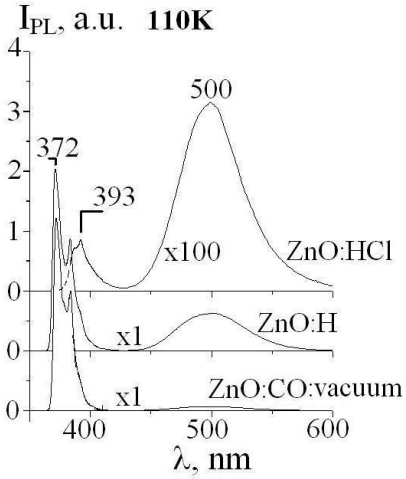

Fig. 1. Low-temperature PL spectra of crystals grown with the use of various chemical agents. ZnO:CO crystals were annealed in vacuum.

3.2. HCl transport agent

The use of HCl as a chemical transport agent is favorable for a growth of individual single crystals in sealed quartz ampoules, which have a minimal surface area contacted with the walls of growth chamber. As a result, the crystals are not subject to deformations during a post-growth cooling (Fig. 2a). The growth of the individual and well faceted crystals is caused by high density of the products of gas-transport reaction (2) (see the beginning of Section 3). Disadvantages of the method are the large ratio between the crystal length and diameter and the low growth rate at a high temperature gradient (~10º/cm). The low growth rate is expected because of the low value of the enthalpy of reaction (2).

Modification of density of loaded HCl, which is a source of shallow Cl and H donor

impurities in ZnO crystals [3-5], in a range of 0.07-1.3 mg/cm^3 allows obtaining the samples with controlled parameters such as free electron concentration (n) and electrical conductivity (σ) varied in ranges of (2–6) · 10^{17} cm^{-3} and 0.5–9 (Ω·cm)$^{-1}$ (Fig. 2c), respectively.

Low-temperature PL spectra of ZnO:HCl crystals consist of long-wavelength emission that can be attributed to intrinsic defects of zinc vacancies (V_{Zn}) [3], which are generated by compensation effect in the presence of shallow H and Cl donors (Fig. 1). Increasing temperature up to 300 K promotes a decrease in the long-wavelength emission contribution to near zero and an increase in the edge radiation contribution. The edge PL intensity decreases with increasing doping level (Fig. 2d). ZnO single crystals are less subject to self-compensation since the additional annealing in the medium enriched with Zn vapors has no strong influence on electrical conductivity, concentration and mobility (μ) of charge carriers (Fig. 3b).

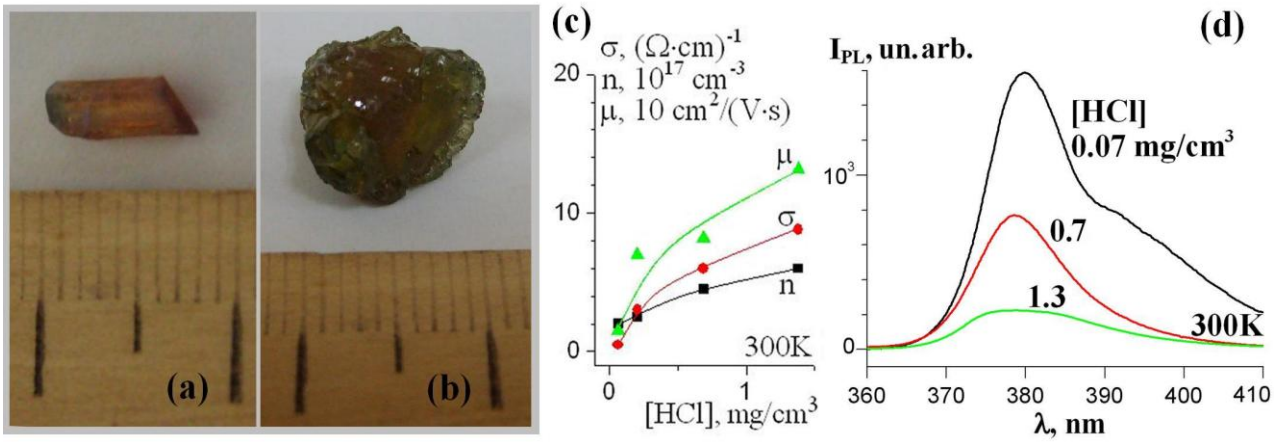

Fig. 2. ZnO:HCl crystals grown with the use of HCl (a) and H_2+HCl mixture (b), electrical parameters versus HCl contents in the growth medium (c) and edge PL spectra of ZnO:HCl crystals with various HCl contents in the growth medium.

3.3. H_2+ HCl transport agent

It is established that the use of H_2 + HCl mixture as a transport agent has the advantages, such as a high growth rate (1–2 mm/day) and compact filling of the ampoule volume with high-conductive n-ZnO:H:Cl crystals, which are not subject to any substantial destruction during post-growth cooling (Fig. 2b). The electric properties of these crystals are comparable to the crystals grown with the use of solely HCl vapors.

3.4. CO transport agent

The rate of mass transport for ZnO is independent on location of loaded carbon in the ampoule; chemical transport agent can be in close vicinity to the source of crystal growth (I) or spatially separated from both the source and the growing crystal (II). If the interaction between ZnO and C was solely limited by the reaction

$$ZnO + C \leftrightarrow CO + Zn(gas), \quad (4)$$

the rate of ZnO mass transport by chemical reactions in case II would be even lower than that by the physical transport method because of a long period of time necessary for ZnO vapors to reach the distant source of carbon (the carbon pressure at the experiment temperatures can be neglected). Effective transport of ZnO in the presence of carbon for various configurations of

growth volume indicates reaction (3) with participation of CO and CO_2. The complete equation for ZnO chemical transport reaction in the presence of C is as follows:

$$\{ZnO + C \rightarrow CO + Zn(gas)\} + ZnO \leftrightarrow CO_2 + 2 \cdot Zn(gas). \quad (5)$$

Reaction (5) differs from reaction (3) by higher concentration of Zn vapors that influences the properties of grown crystals, as seen below.

ZnO crystals grown in the presence of CO have the best structural perfection (they exhibit the absence of microscopic cavities) (Fig. 3a). However, their optical density within the visible spectrum range and PL intensity are extremely low, that can be caused by deep centers based on intrinsic defects of oxygen vacancies (V_O) [3] appeared due to a high Zn vapor pressure in the growth medium. These properties are characteristic for the crystals obtained by other methods and subsequently annealed in a high-density atmosphere of Zn vapors.

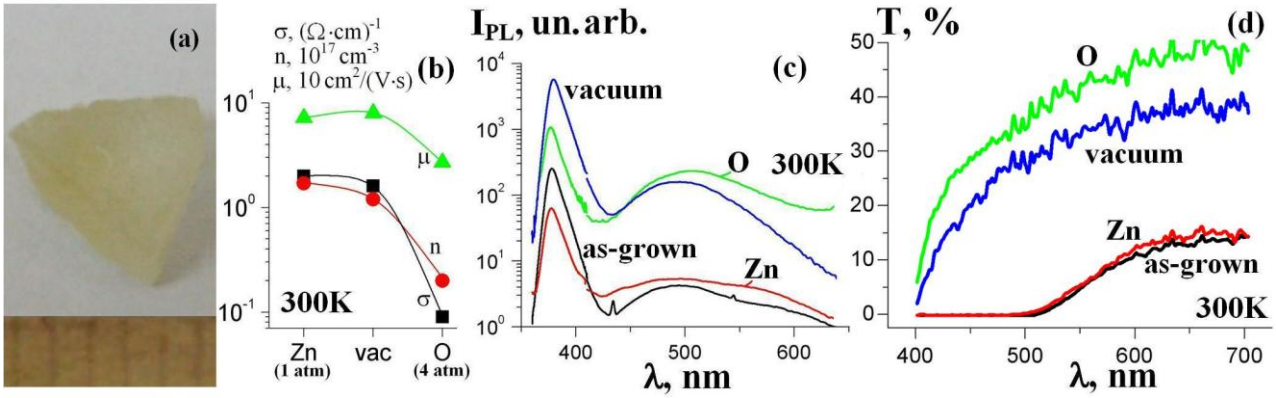

Fig. 3. ZnO:CO:vacuum crystal (a), electrical parameters (b), PL spectra (c), and transmission spectra (d) for ZnO:CO crystals before and after annealing in various media.

The optical, PL and, to a certain degree, electrical properties of ZnO:CO crystals can be varied by the deviation from stoichiometry (Fig. 3). Annealing in Zn vapors at the pressure of 1 atm has no essential influence on the properties of ZnO:CO crystals initially saturated with zinc. At the same time, the annealing in vacuum or oxygen leads to an increase of optical transparency and PL intensity (Figs. 3c, 3d); therefore, ZnO:CO:vacuum crystals predominate in these parameters over the crystals grown by other methods. In particular, these crystals are characterized by the greatest contribution of the edge radiation into the low-temperature PL spectra (Fig. 1). An essential decrease in the conductive properties of the samples due to changing concentration of V_O, V_{Zn} intrinsic defects occurs only in the case of oxygen enrichment of the crystals (Fig. 3b).

4. Conclusions

The use of hydrogen as the chemical transport agent for growing ZnO crystals is limited by low structural perfection of obtained crystals and their destruction during a post-growth cooling because of a strong mechanical contact between the grown material and the quartz walls of the growth chamber.

The use of HCl is limited by a low growth rate at high temperature gradients and the large ratio between the crystal length and diameter.

The use of H_2 + HCl mixture and of CO as transport agents provides the growth of n-ZnO

single crystals characterized by a high growth rate (1-2 mm/day) and compact filling of ampoule volume. Optical, PL and, to a certain degree, electric properties of these crystals can be varied in wide ranges by changing the impurity concentration or the deviation from stoichiometry.

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