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Effect of thermal annealing on properties of polycrystalline ZnO thin films

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ABSTRACT

Electrical properties (density, carriers mobility, resistivity), optical absorption and photoluminescence spectra of ZnO, grown by MOCVD and hydrothermal methods, have been investigated depending on the annealing and treatment modes in a hydrogen plasma. It has been shown that the electrical and photoluminescent (PL) properties of ZnO are strongly dependent on gas atmosphere during annealing. The annealing in oxygen atmosphere causes a sharp drop of carrier mobility and films conductivity due to the absorption of oxygen on grain boundaries. The process of ZnO electrical properties recovery by the thermal annealing in inert atmosphere (nitrogen), in oil (2×10^{-2} mbar) and oil-free (1×10^{-5} mbar) vacuum has been investigated. The hydrogen plasma treatment influence on the intensity of near-band-gap emission (NBE) has been studied. The effect of annealing and subsequent plasma treatment on PL intensity depends on the gas atmosphere of preliminary thermal annealing.

KEYWORDS: A1. Thermal treatment, A1. Electrical properties, A1. Photoluminescence, A2. MOCVD, A2. Hydrothermal crystal growth, B2. ZnO thin films.

INTRODUCTION

Thin film zinc oxide (ZnO) and its alloys find an increasing use as low-cost transparent conductive oxide (TCO) layers, gas sensors, biosensors, transparent thin-film transistors (TFT), piezoelectric devices, dye-sensitized solar cells [1-6], light-emitting diodes (LED) [7]. The advantages of ZnO include a wide (about 3.37 eV) bandgap, high transparency in the visible range, low cost of the material, biological and environmental compatibility. Electrical parameters of zinc oxide can be varied widely by alloying and varying deposition process parameters.

Electronic and optical properties of polycrystalline ZnO thin films are largely determined by the conditions on grain boundaries and the presence of intrinsic defects, such as oxygen interstitial and zinc interstitial, zinc and oxygen vacancies and their complexes [8, 9].

Improvement of conductivity can be achieved by thermal treatments under oxygen-deficient and / or zinc-rich conditions. In contrast, the treatment in an oxidizing atmosphere would result in suppressed electron conductivity. Therefore, development of methods for controlling properties of ZnO by various treatments, such as annealing in oxidizing, reducing, and inert atmospheres, is of significant importance.

This paper presents the results of the electrical, optical and luminescent properties investigation of ZnO films, synthesized by MOCVD and hydrothermal method. A comparison of the effects of annealing in air, oil and oil-free vacuum, inert atmosphere on the electrical and photoluminescent properties is made.

EXPERIMENTAL DATA

Two series of boron-doped n-type ZnO films were investigated: i) films on glass substrates synthesized by metal-organic chemical vapor deposition (MOCVD-ZnO) at ~200^oC, ii) films on glass and crystalline silicon substrates synthesized by hydrothermal method (HT-ZnO).

Metal organic chemical vapor deposition was performed at low pressure. Diethylzinc ($(C_2H_5)_2Zn$), or DEZ, and deionized water were used as precursors. $[H_2O]/[DEZ]$ ratio of 5:6 was used. Diborane and hydrogen gas mixture ($2\%B_2H_6/98\%H_2$) was used in order to obtain boron doped ZnO. Hydrogen (H_2) dilution was used to maintain uniform temperature in the CVD chamber, while nitrogen (N_2) was used to maintain constant pressure in the reactor. The main variable parameters were the substrate temperature, the pressure and the ($2\%B_2H_6/98\%H_2$) /DEZ flow rate ratio.

In the second case, thin ZnO seed layer was initially grown on the substrate by sol-gel method. To obtain the seed layer 0.4 g zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$ were dissolved in 10 ml ethanol for 30 min at room temperature to yield a homogeneous and transparent sol using a magnetic stirrer. Uniform sol distribution on the substrate surface was achieved by depositing of several sol drops on the substrate, fixed at the horizontal table with followed table rotating about 2000 cycle/min for 5 minutes. Finish annealing at 450^oC for 60 minutes in a muffle furnace led to the formation of uniform seed layer.

An equimolar (0.3 M) aqueous solution of zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ and hexamethylenetetramine $(CH_2)_6N_4)$ was prepared under continuous stirring. The hydrothermal synthesis was carried out in the fluoroplastic cup for 2 hours under stirring at 90°C. The samples were placed vertically and faced to the walls of the cup. Boric acid H_3BO_3 at 0.6 at.% to 3 at.% was added to the solution to obtain p-type ZnO films doped with boron. Aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ or aluminum chloride $AlCl_3{\cdot}6H_2O$ of 0.6 at. % to 3 atm. % was added to the solution to obtain n-type ZnO films doped with aluminum. After growth, the resultant samples were removed from the vessel, washed with distilled water in ultrasound for 10 minutes to remove any residual salt from the surface and dried in an oven at 100-110 ^oC for 5 minutes.

Typical thickness of the HT-Zn films doped with boron or aluminum after synthesis for 2 hours was 0.8-1 microns, provided that the impurity concentration in the solution was less than 1 at. %. Increasing the concentration of impurities in the solution resulted in a slower growth rate.

The samples were annealed in a quartz tube furnace. The annealing at atmospheric pressure was carried out in air or in a stream of nitrogen with a purity of 99.999%. Annealing in a vacuum of $\sim 2\times10^{-2}$ mbar was carried out at the pumping of conventional rotary pump.

Annealing in oil-free vacuum of $\sim 1\times10^{-5}$ mbar was conducted in alundum furnace using turbo-molecular pump. Plasma treatment was carried out in a quartz reactor in hydrogen atmosphere at 0.5 mbar at 30 W RF (27.12 MHz) power. Measurements showed that during H-treatment for 5 minutes, the temperature of samples rose to an average of 50-70^oCdue to microwave absorption.

The morphology of the samples was investigated by scanning electron microscopy (SEM) using Quanta 200i 3D (FEI) microscope. The crystal structure was studied by X'pert MPD PRO X-ray diffractometer. The optical transmission spectra in 190-1100 nm range were measured with Lambda 35 (Perkin Elmer) spectrophotometer. The photoluminescence (PL) spectra were studied by Cary Eclipse (Agilent) spectrophotometer in 300-850 nm wavelength range under the excitation of xenon flash lamp through FF01-292/27-25 (Semrock) band pass filter. An additional edge filter BLP01-325R-25 (Semrock) was used to cut off scattered radiation from the xenon lamp. The carrier concentration, the mobility, and the resistivity of the films were measured at room temperature by Van der Pauw four-probe method using HMS-3000 (Ecopia) setup with 0.56 T magnet.

RESULTS AND DISCUSSIONS

Figure 1 shows typical morphology of investigated polycrystalline ZnO films synthesized by MOCVD (a) and hydrothermal method (b). Figure 2 shows XRD patterns of the HT-ZnO and

MOCVD-ZnO thin films, indicating that the all ZnO samples present a hexagonal wurtzite structure. The HT-ZnO samples are polycrystalline with a (002) preferential orientation, and the MOCVD-ZnO sample is also polycrystalline with a (110) preferential orientation.

Figure 3 shows the carrier concentration and the mobility in MOCVD-ZnO films annealed for 40 minutes in air, in nitrogen atmosphere, and in oil vacuum. Typical room temperature parameters of as-deposited MOCVD-ZnO films with thickness of 1.7 microns are as follows: the free electron concentration ~5×10^{19} cm^{-3}, carriers mobility 22-24 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$, resistivity ~0.005 $\mathrm{Ohm{\cdot}cm}$. The deviation of these parameters in batches of samples cut from 100 mm×100 mm glass substrate did not exceed 10%.

Electrical parameters of the film did not change after annealing in air at temperatures below 200°C. At higher annealing temperature, the carrier concentration gradually decreases, reaching ~7×10^{17} cm^{-3} after annealing at 550°C. Similarly, the carrier mobility decreases to 0.2-0.4 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$. It can be concluded that a strong grain boundary scattering emerges. In addition, carriers are captured by oxygen in the grain boundaries, and the concentration of free electrons in the ZnO film is decreased. It explains the drop in the carrier mobility and concentration.

In contrast, annealing temperature dependences of carrier concentration and mobility of MOCVD-ZnO films annealed in oil vacuum and in nitrogen are significantly different (Fig. 3). Mobility increases from 22-24 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ to 32-36 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ at annealing temperatures of 150-160°C, carrier concentration also slightly increases. At higher annealing temperatures, carrier concentration decreases and reaches $4\ldots8\times10^{18}$ cm^{-3} at 350-550°C annealing whereas carrier mobility is restored to the initial value.

Such a behavior may be due to the fact that annealing in oil vacuum and in an inert atmosphere causes surface regions to be oxygen deficient. This contributes to the formation of oxygen vacancies and interstitial atoms of zinc in ZnO [10]. Interstitial Zn atoms, which have high mobility and low migration barrier energy, can diffuse into the sample, so they may be responsible for observed change of electrical properties. The decrease of the electron concentration upon annealing may be due to compensation of boron donors by interstitial zinc atoms [11].

Figure 4a shows the absorption spectra for ZnO samples annealed in oil vacuum. Respective Fermi energy positions calculated from the carrier concentration of these samples are shown in Figure 4b as a function of annealing temperature. It can be seen that at low annealing temperatures (100 and 150°C), the absorption is increasing at higher photon energies, and at higher annealing temperature, absorption edge shifts towards low photon energies. These shifts are accompanied by the Fermi energy position shift towards conduction energy starting after annealing above 150°C, and by a decrease of the energy E_α corresponding to the optical absorption $\alpha=5\times10^{5}$ cm^{-1} to 3.31 eV. This can be attributed to the formation of oxygen vacancy states near the bottom of the bandgap, and the main contribution to the shift of the optical absorption edge upon annealing is due to Fermi level motion.

Figure 5 shows the effect of annealing on the electrical parameters of two sets of ZnO samples. The first 12 samples were subjected to preliminary annealing in air (curve 1) at 200-550°C. Then they were annealed in oil vacuum for 1 hour at 500°C (curve 2). It is seen that after annealing all the samples including the reference sample not annealed in air have approximately the same parameters: the mobility of ~23 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$, the resistivity of 0.044 $\mathrm{Ohm{\cdot}cm}$, the carrier density about 6×10^{18} cm^{-3}. Thus, annealing in oil vacuum eliminates the effect of pre-annealing in air.

Second group of 5 samples were annealed in air at 200-550°C (electrical parameters of the samples were the same as those for the first group), and then annealed in high oil-free vacuum for 1 hour at 500°C (Figure 5, curve 3). It can be seen that the effect of annealing in oil-free vacuum on electrical parameters of samples significantly differs from annealing in vacuum oil. Then the samples were processed in a hydrogen plasma (Figure 5, curve 4), and their electrical parameters returned to the same values as after annealing in oil vacuum.

In both groups, oxygen deficiency exists on the surface of ZnO. However, during annealing in oil-free vacuum, excess zinc atoms can evaporate from the surface and the formation of non-equilibrium interstitial zinc atoms on the surface region becomes difficult. During the annealing in oil vacuum, oil molecules may absorb on catalytically active surface of zinc oxide and initiate carbothermic reduction of zinc oxide. Previously, it was shown [12] that oxygen exchange with the gas phase affects ZnO surface states and plays an important role in its electrical conductivity.

Thus, in the case of annealing in oil vacuum, recovery of ZnO on the surface by organic molecules creates an excess of zinc atoms, which can diffuse into the film bulk and recombine with zinc vacancies created under oxygen-rich conditions. Probably, the carrier concentration of $(4\text{-}8)\times10^{18}$ cm^{-3} achieved through the annealing is correspond to equilibrium established by zinc diffusion from the surface into the volume.

Typical resistivity of as-synthesized hydrothermal samples was about 50 Ohm*cm, so the behavior of the electrical parameters during annealing in air has not been studied. Figure 6 shows the variation of the electrical parameters HT-ZnO samples doped with boron and aluminum during annealing in vacuum. The films typically show carrier concentration about 2×10^{18} cm^{-3}, mobility of 25-27 cm^2/V×s, and resistivity of 0.1 Ohm×cm after annealing at 450°C for 1 h.

It should be noted that the undoped HT-ZnO samples also showed similar behavior of the mobility and resistivity under vacuum annealing, but a low value of resistivity after annealing in oxygen deficit conditions was unstable. The resistivity of the samples, which were stored at room temperature in air for 1-2 weeks, increased significantly due to exposure to oxygen. In contrast, the electrical parameters of the HT-ZnO sample doped with B or Al were stable after annealing. It can be concluded that the annealing of HT-ZnO leads to activation of the electrical activity of boron and aluminum impurity donor atoms.

Fig. 7 shows PL spectra of HT-ZnO samples annealed in oil vacuum. The intensity of the near-band-gap emission (NBE) band increases after annealing at temperatures of 250-400°C and decreases after annealing above 400°C like in the MOCVD-ZnO samples. The dependence of the intensity of the deep-level emission (DLE) band is non-monotonic during annealing at 250-400°C and decreases during annealing above 400°C. The intensity at first falls and then a few increases, and a peak of the band is shifted to longer wavelengths. Note that the increase in DLE intensity during annealing is characteristic of ZnO samples grown at low (<200°C) temperatures [13, 14].

It is known that hydrogen easily diffuses into ZnO during low-temperature plasma treatments (e.g., 30 minute hydrogen plasma treatment at 100°C yields penetration depth of about 10 micron [15]) and efficiently passivates electrically active defects. The hydrogen plasma treatment has strong effect on electrical properties of ZnO samples grown by MOCVD and annealed in air. As can be seen from Figure 5, hydrogen treatment completely eliminates grain boundary scattering, that is, the treatment eliminates the effect of oxygen adsorption.

Hydrogen treatment was also carried for ~2 micron thick ZnO films grown by the hydrothermal method. Upon short (4-5 minutes) hydrogen plasma treatment at room temperature, carrier density reached 5.5×10^{18} cm^{-3}, mobility grew to ~30 cm^2/V*s, resistivity was in the range of 0.035-0.040 Ohm*cm.

We investigated the effect of treatment in hydrogen plasma on the photoluminescence of the samples grown by MOCVD and hydrothermal methods. The room temperature PL spectra of ZnO samples prior to the treatment consisted of a narrow (~0.25 eV) NBE at ~380 nm, and broad deep-level emission (DLE) in the range from 450 to 800 nm with a maximum around 500 nm. Typical PL spectra of as-synthesized ZnO samples, as well as samples annealed at 400°C and treated in hydrogen plasma are shown in Figure 8 along with NBE intensity dependence on the annealing temperature which shown in the inset of the Fig. 8. One can see that at higher annealing temperatures, the NBE intensity increases, passes through a maximum at about 300°C, and begins to decrease. At the same time, DLE intensity starts to grow above 200-300°C. This is consistent with the results of [16].

The hydrogen plasma treatment increases NBE intensity and causes DLE band to disappear. DLE band passivation occurs at room temperature and in short time. Such effect was reported in a number of studies [17-19]. The average increase in NBE band intensity after hydrogen plasma treatment was 25-35 times in samples grown by hydrothermal method and by MOCVD method.

It was found that the effect of hydrogen plasma treatment depends on the prior annealing temperature in air and the NBE band intensity increases more in previously annealed samples. The inset in Figure 8 shows that while the NBE band intensity varies slightly with increasing annealing temperature, it is very much increased after hydrogen treatment in both HT and MOCVD samples. If PL intensity increase after hydrogen treatment is 50-60 times in the initial samples, then for the samples after annealing, the PL intensity increase after hydrogen treatment was up to three orders of magnitude.

The preliminary annealing in air has little effect on the intensity of NBE band at annealing temperature below 200^{o}C. At higher annealing temperatures, PL intensity increases, reaching a maximum at 400-550^{o}C. In case of annealing in vacuum and nitrogen, PL intensity dependencies are similar and differ from that in air. Preliminary annealing at 100-160^{o}C has significant effect on the dependencies. The maximum impact of preliminary annealing in vacuum and nitrogenon NBE band intensity is observed at ~250^{o}C, whereas above 350^{o}C, PL intensity changes only slightly.

CONCLUSION

Electrical properties (carrier concentration and mobility, resistivity), spectra of optical absorption and photoluminescence of polycrystalline ZnO films have been investigated as a function of the thermal and plasma treatments. It has been shown that annealing of MOCVD-ZnO films in oxygen atmosphere leads to decrease of free carrier concentration due to oxygen chemisorption and formation of depletion layers in the grain-boundary regions. The carrier mobility decreases due to grain boundary scattering. The electrical properties of ZnO samples can be significantly recovered by the subsequent annealing, and result of recovery annealing depends on the gas atmosphere during the annealing. Annealing in nitrogen atmosphere as well as in oil vacuum of 2×10^{-2} mbar allows to fully recover the carrier mobility, and the carrier concentration stabilizes at a level of $(6\text{-}8)\times10^{18}$ cm^{-3}. In contrast, annealing in oil-free vacuum of 1×10^{-5} mbar improves the electrical properties insignificantly. Short-term treatment in hydrogen plasma dramatically improves the electrical and photoluminescent properties, and the effect of plasma treatment on the PL intensity depends significantly on the preliminary treatments of both MOCVD-ZnO and HT-ZnO films. Preliminary annealing in vacuum, as well as in inert atmosphere leads to a minor improvement of efficiency of hydrogen treatment, however, the annealing in oxidizing atmosphere at 400-500^{o}C followed by treatment in hydrogen plasma results in the greatest intensity of NBE. A correlation between the Fermi level and shift of optical absorption edge during the thermal annealing was found.

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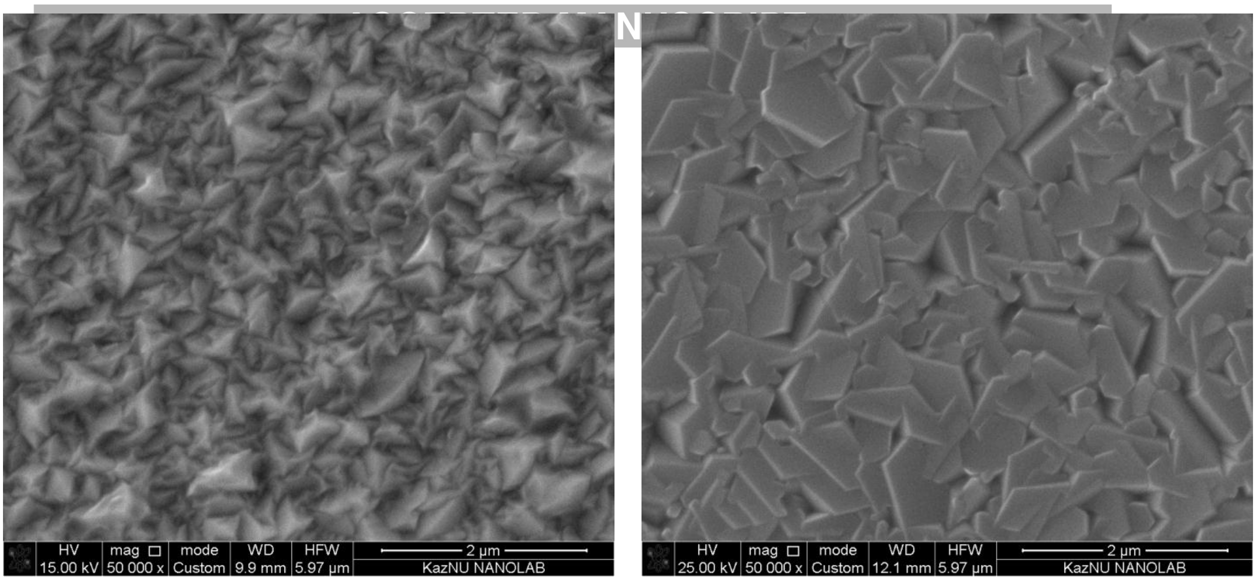

a **b**

Figure 1 – SEM images of (a) MOCVD-ZnO and (b) HT-ZnO(B) films.

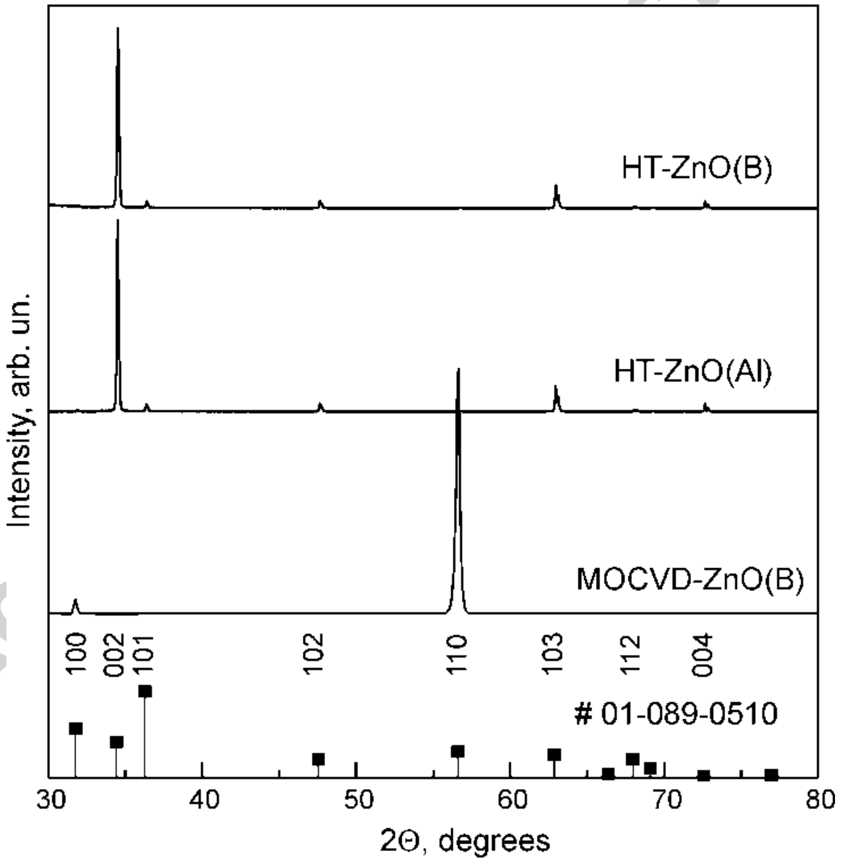

Figure 2 – XRD patterns of HT-ZnO samples doped with boron or aluminum and MOCVD-ZnO(B) sample. The line pattern at the bottom of the figure shows JCPDS card # 01-089-0510 for ZnO with the hexagonal wurtzite type structure.

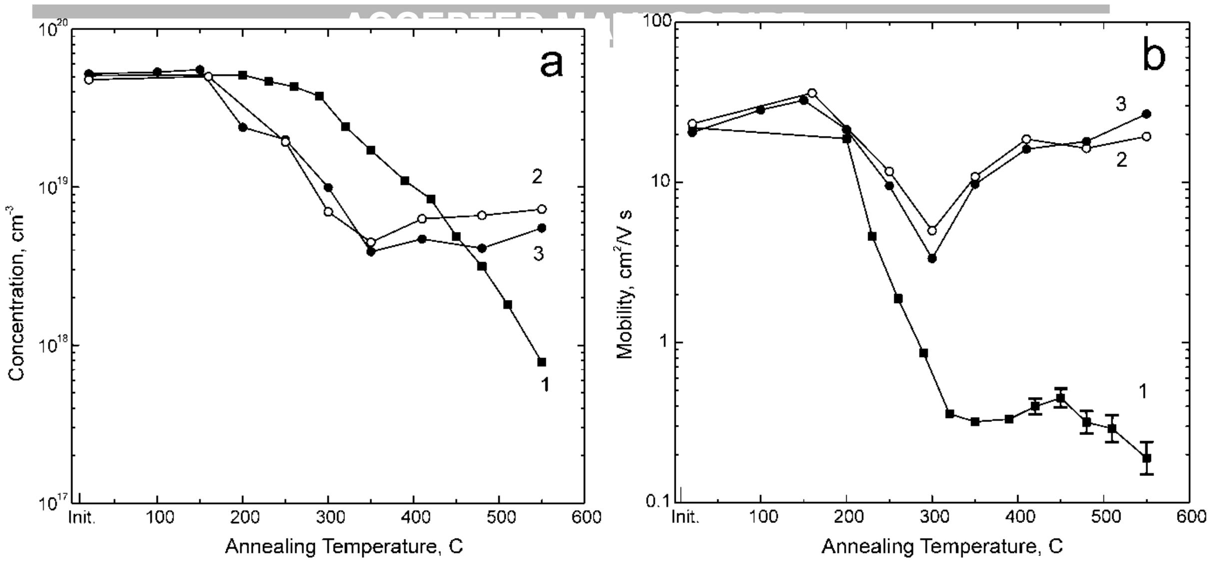

Figure 3 − Carrier concentration and mobility in MOCVD-ZnO films vs annealing temperature in air (1), in nitrogen atmosphere (2), and in oil vacuum (3).

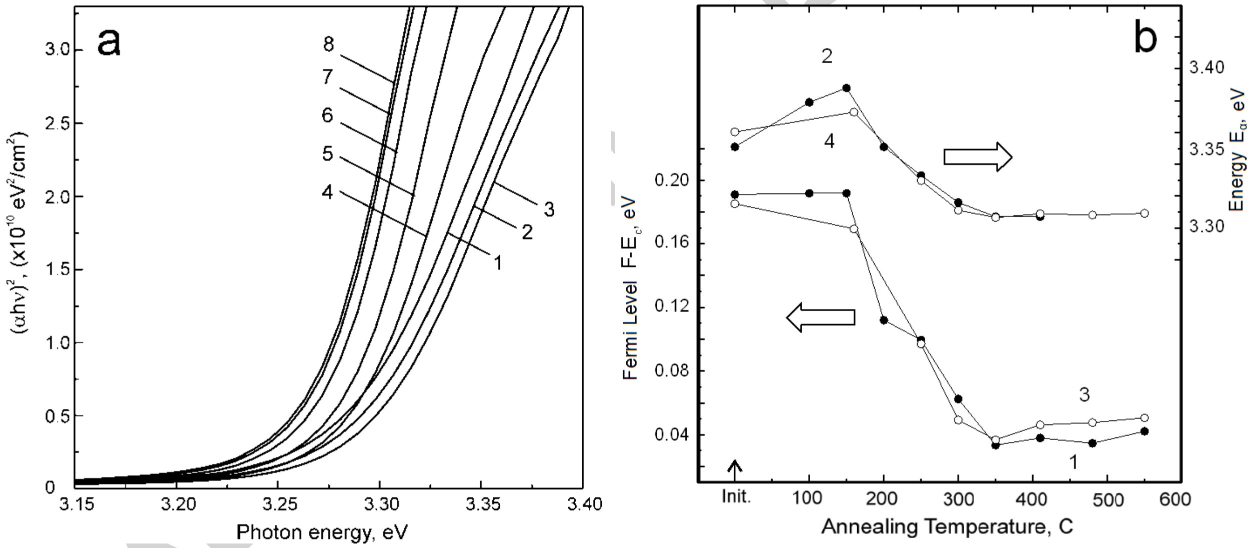

Figure 4 − (a) Absorption spectra of MOCVD-ZnO samples: 1– initial, and after annealing in vacuum for 40 min at temperature 100 (curve 2), 150 (3), 200 (4), 250 (5), 370 (6), 350 (7) and 410^{o}C (8); (b) Dependence of Fermi level (F-E_c) on the annealing temperature in ZnO samples at the annealing in oil vacuum (1) and nitrogen (3), calculated from measured Hall, and energy E_α, which corresponds to the optical absorption α=5×10^5 cm^{-1}, upon annealing in oil vacuum (2) and nitrogen (4).

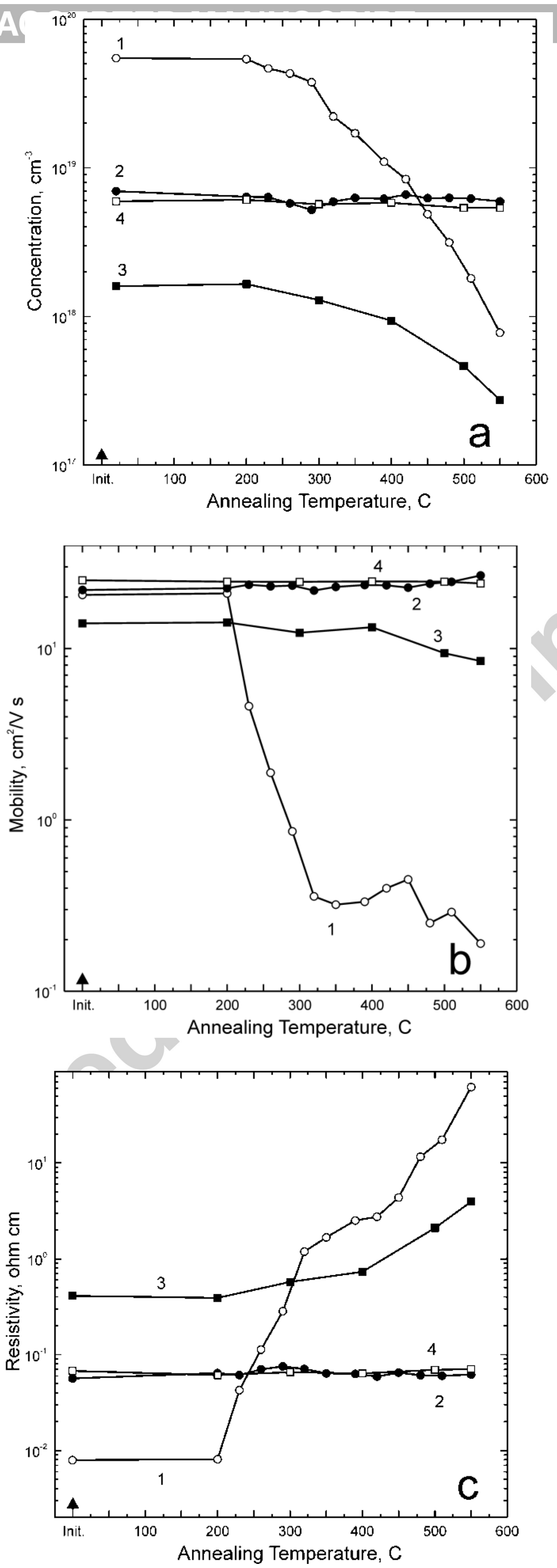

Figure 5 − Carrier concentration (a), mobility (b) and resistivity (c) in MOCVD-ZnO films, annealed for 40 minutes in air (1) and in oil vacuum at 2×10^{-2} mbar, 1 hour at 500^{o}C (2), ZnO films, annealed in air for 30 minutes and in oil-free vacuum 1×10^{-5} mbar for 1 hour at 500^{o}C (3), with further treatment in hydrogen plasma for 4 minutes at the room temperature (4).

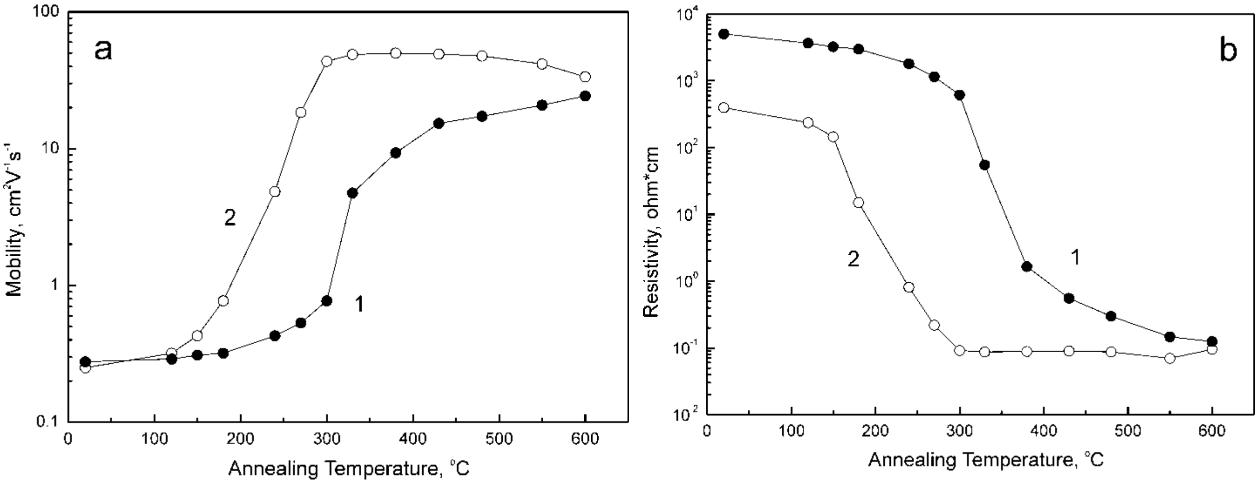

Figure 6 − Carrier mobility and resistivity in HT-ZnO films doped with B (1) and Al (2) vs annealing temperature in oil vacuum.

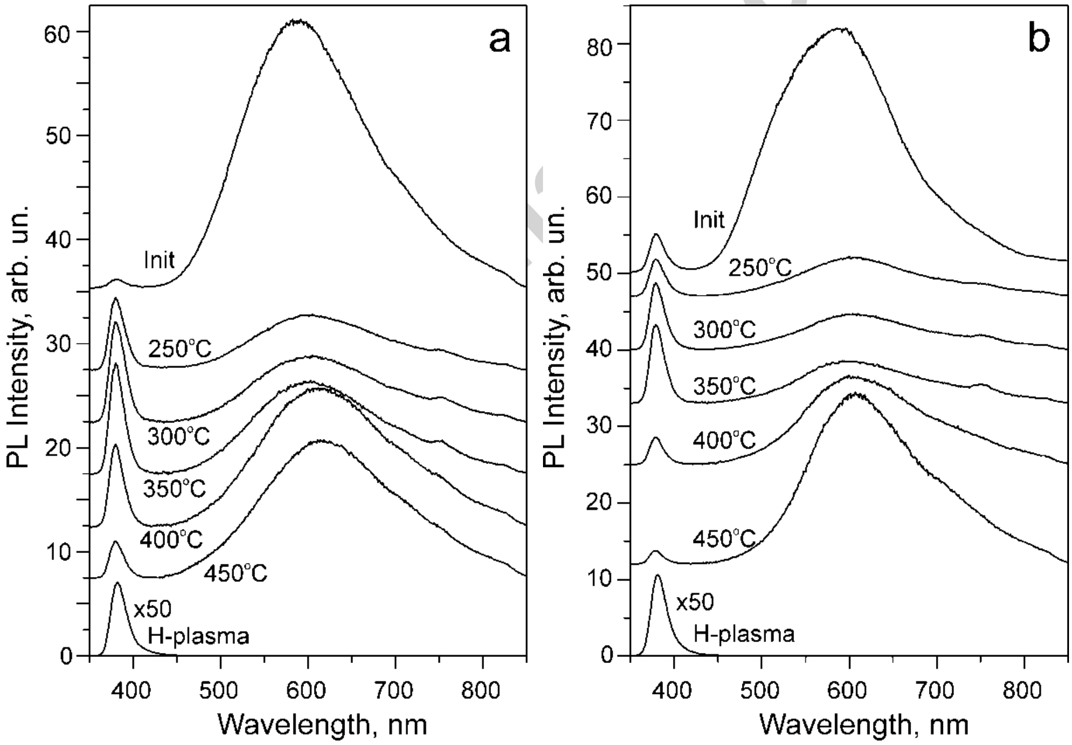

Figure 7 − The PL spectra of the initial samples of HT-ZnO films doped with boron (a) and with aluminum (b), and HT-ZnO samples annealed in oil vacuum. The spectra of the samples after annealing at 450°C followed by plasma treatment in hydrogen are also shown; the intensity of the spectra has been 50 times multiplied for comparison.

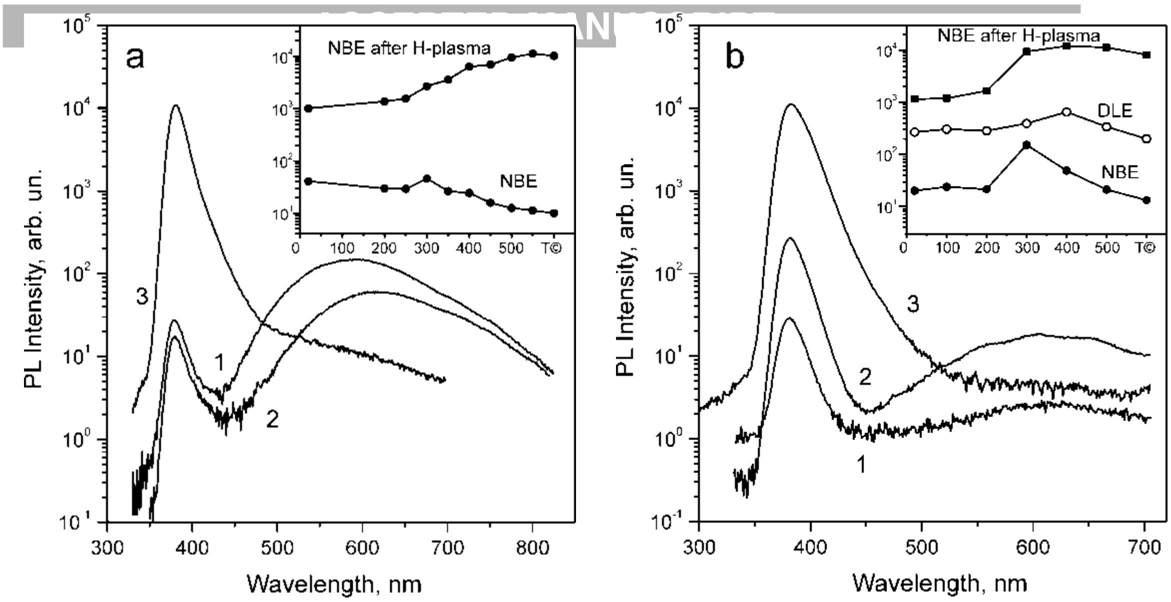

Figure 8 − The PL spectra of HT-ZnO (a) and MOCVD-ZnO (b) samples: 1 –initial spectra, 2 - after annealing in air at 400^{o}C for 30 min and 3 - after treatment in a hydrogen plasma at the room temperature for 4 min. The inset shows the intensity dependence of the NBE band on T_{ann} in samples, annealed in air for 30 minutes at the appropriate annealing temperature and after processing these samples for 4 minutes in hydrogen plasma.

Highlights

Effect of thermal annealing on properties of polycrystalline ZnO thin films

- An annealing of ZnO films in oxygen leads to decrease of free carrier concentration.
- A hydrogen plasma treatment improves the electrical and photoluminescent properties.
- The effect of plasma treatment on the PL intensity depends on preliminary treatments.
- A correlation between the Fermi level and shift of optical absorption edge was found.