Exciton Photoluminescence of ZnO Thin Films Grown by ALD-Technique


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Abstract

The low-temperature exciton photoluminescence of thin ZnO films grown by atomic layer deposition (ALD) on (100) and (111) Si substrates under He-Cd (λ = 325 nm) and N2 (λ = 337 nm) laser excitation is studied. The structure of the films is analyzed by XRD and SEM methods. The effects of excitation intensity and laser irradiation on the photoluminescence spectra are investigated. A wide asymmetric emission band attributed to excitons localized in the near surface potential fluctuations has been observed in photoluminescence spectra of the film and powder samples.

Keywords: Atomic layer deposition metod; ZnO thin films; photoluminescence; localised exitons; suface states

Introduction

As known the crystalline zinc oxide is one of model objects for the exciton state studies. The photoluminescence studies of this compound provided valuable information on polariton states, exciton-impurity complex nature, the exciton-phonon interaction and exciton density effects [1, 2]. On the other hand, the semiconducting ZnO crystals...
with a wide band gap (3.37 eV) and a large exciton binding energy of 60 meV find wide range of practical applications. It is a promising material for the short-wavelength (blue and UV) light emitting and laser devices. Nowadays the ZnO films are used as elements of dye-sensitized solar cells with over 12% photoelectric conversion efficiency [3], as sensitive detectors of various gases (NH₃, CO, H₂ etc.) [4]. The ZnO powder is used as a catalyst of water photolysis.

In this work we study photoluminescence (PL) spectra of thin ZnO films obtained ALD technique on silicon substrates. The spectra of the films are compared with the spectra of undoped single crystals and powder samples.

1. **Experimental procedure**

ALD method [5] included four steps: injection of dietilzinc, cleaning of the reactor by the N₂ flow, injection of the water vapor and the second cleaning of the reactor by the nitrogen flow. The process was repeated in 0.1-0.2 sec cycles with the intervals of 0.5-2.0 sec. between them. The precursor vapors – dietilzinc of 99.999% purity, O₂, N₂ and deionized water - were consequently introduced onto the surface of a Si plate at 200º C. Silicon plates oriented to the (100) face and to the (111) face were used.

The structure of the films was analyzed by XRD and SEM methods. Images of ZnO films grown by ALD method on (100)- and (111)-Si plates, obtained with SEM-FIB Zeiss 1540-XB Cross Boam (1 nm resolution power) are given in Fig.1. As SEM images show, the films are composed of rather tightly packed slightly prolonged ZnO particles with a characteristic size of 20-30 nm. The thickness of ZnO films under study determined by the ellipsometry method varies from 3.5 nm to 100 nm. All the films display the hexagonal structure.

The PL spectra in the temperature range from 5K to 80 K were performed with the use of continuously operated He-Cd laser (λ = 325 nm, W= 5 mW) and the pulse N₂ laser (λ = 337 nm, W(pulse)= 150 kW, τ =10 nsec). The samples were kept in the helium closed cycle cryostat and were fixed on a cold finger.

![Fig. 1 SEM images of ZnO films grown by ALD method on (111)-Si face (a) and on (100)-Si face (b).](image)

2. **Results and discussion**

The PL spectra of ZnO films of thickness of 100 nm grown on variously oriented Si plates (curves 3 and 4), of the single crystal (curve 1) and of the powder (curve 2) are shown in Fig.2. The spectra are recorded at T = 5K with the He-Cd laser. It is seen that the spectra of the film grown on (111) Si face, the bulk crystal and the powder samples do not differ structurally. All these spectra include two spectral fetures - the lines attributed to the donor bound excitons (370 nm) which are most prominent in the spectrum of the bulk crystal and the bands attributed to the first and second order LO-phonon replicas of the free (374.5 nm, 383.0 nm) and bound (376 nm, 385 nm) excitons.

In PL spectra of several samples at ~367 nm a faint shoulder due to free exciton radiative recombination can be observed. It becomes more clear as temperature increases. But the clearly defined distinctions between PL spectra of films deposited on Si plates variously oriented are observed. The spectrum of the films on (100)-Si face, unlike
the spectrum of films on (111)-Si face and the spectra of the bulk and powder samples, has the shape of an asymmetric wide band with the rather abrupt short-wave edge in the region of the free and bound exciton lines and a more flat long-wave tail.

A dramatic effect of the excitation intensity on the shape of PL spectra was observed in the present study. The evolution of the spectra of the film grown on (111)-Si face and powder samples with increasing excitation intensity at \( T = 77 \) K is shown on Fig. 3 (a) and (b), correspondingly. The curves are numbered in order of increasing excitation. As the excitation intensity increases PL spectra acquire the shape of an asymmetric wide band with hardly noticeable peculiarities due to the emission of free and bound excitons and their phonon replicas.
So, we see that the PL spectra of both films on (111)-Si face and powders under some excitation intensity become similar to the spectra of the films on (100)-Si plates - that is the spectra take the shape of a wide asymmetric band with flat long-wave tail extending to ~ 420 nm.

It is believed that the transformations of the spectra with excitation intensity increase as well as the different PL spectra of films grown on Si plates variously oriented are connected with the presence of charged surface defects, intrinsic and adsorbed, the number of which is obviously dependent on the processes of the growth and varies under laser light. In both cases the inhomogeneous electric fields due to spatially random distribution of these charges inhomogeneous electric fields due to spatially random distribution of these charges are produced and the fluctuations of electron potential arise, besides the change of the average potential. As consequence, the exponent tails of band states are formed which results in localization of carriers and excitons. Inhomogeneously broadened bands with long-waved tails formed by localized exciton states appear in the exciton optical absorption and the luminescence spectra. In high electrical fields the exponential tail extending from the exciton energy to low-energy side is the characteristic feature of exciton absorption spectra [6]. We observe the similar effect in the photoluminescence spectra.

It is worth noting, that in the PL spectra of ZnO single crystals the similar effects are not observed. It appears natural that the number of the surface states in powder samples and polycrystalline films is larger than in single crystals.

A further effect of surface states on PL spectra has been revealed in the present study. The PL intensity has been found to increase under irradiation of the films by the He-Cd laser (sensitization of luminescence). In Figures 4 and 5 the temporal changes of PL spectra of the films under the irradiation at T= 5 K are shown. The total half-width (Δ) of PL band decreases along with an increase of the PL integrated intensity (Fig. 4, curve (a)).

![Image](https://via.placeholder.com/150)

Fig. 4 The influence of the irradiation by He-Cd laser at T=5K on photoluminescence spectra of the ZnO film on (100)-Si (d=40 nm). The curves present the spectra before additional irradiation and after the irradiation during 15 min, 30 min and 45 min, correspondingly. Insert - the dependences of the luminescence intensity and halfwidth of luminescence band on the irradiation time.

After the long persistence of the irradiation the PL intensity enhancement is saturated (Fig. 5, curve (b)). It has been established that the prolongation of the vacuum deposition of the films augments the photoluminescence intensity whereas the storage of the films in the open air results in the irreversible degradation. We suppose that the phenomena of sensitization may be caused by elimination of the recombination centers (primarily due to
photodesorption of oxygen) from the film surface. The sensitization may last ten minutes. According to the mass spectroscopy researches, the CO₂ and H₂O molecules are removed too [7].

Summary

Thin ZnO films (thickness of 3.5 - 100 nm) on variously oriented silicon substrate have been grown by atomic layer deposition method. The morphologic researches of surfaces by scanning electron microscopy method and the mass spectroscopy study of desorption of gases from surface of films in high vacuum have been carried out. The comparative study of low-temperature PL spectra of the ZnO films, undoped single crystals and powder samples allow us to draw the conclusion about a high quality of the films on (111) - Si face obtained by ALD method. The manifestation of effects of inhomogeneous electric fields caused by charged surface states in photoluminescence spectra of ZnO films has been revealed.

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References