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Photoluminescence of ZnO films excited by femtosecond laser

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Photoluminescence of ZnO films deposited by various technologies including magnetron sputtering and PEMOCVD on different substrates was studied at room temperature by femtosecond Ti:sapphire laser. The effect of film texture on PL spectra was revealed. The influence of annealing on ultraviolet and green photoluminescence was also considered. The most intensive ultraviolet excitonic photoluminescence was observed for ZnO films deposited on SiN_x/Si substrate.

Key words: ZnO, magnetron sputtering, PEMOCVD, photoluminescence, femtosecond laser

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Introduction

ZnO as wide band gap semiconductor (E_g = 3.37 eV) which has extremely large exciton binding energy (60 meV) is a prospective material for optoelectronic devices in ultraviolet range. Room temperature optically pumped ultraviolet photoluminescence (UV PL) has been demonstrated by several researcher groups in polycrystalline and epitaxial ZnO films [1, 2]. Some researches even observed so-called lasing in high quality micro- and nanocrystalline structures as well as in epitaxial ZnO films [3, 4]. It is well-known that ZnO films can emit in UV as well as in green and red optical regions. UV photoluminescence arises as a result of free exciton recombination process. At optical pumping increasing it is also due to exciton-exciton scattering process as well as electron-hole plasma recombination process. The deep-level emission can originate from different defects: oxygen vacancies, zinc or oxygen ions in interstitial position as well as from deep impurity levels such as copper. In order to obtain high quality material displaying strong UV emission we must exclude forming such deep-level recombination centers as well as we need also improving of film-substrate interface. The bad interface as well as rough surface morphology can be a reason for a large amount of non-radiative recombination centers which result in suppression of UV PL. Thus, it is obvious that UV PL strongly depends on parameters of growth method, conditions of further annealing and a nature of a substrate. In present work we report on PL of ZnO films deposited by reactive thermal evaporation (RTE), magnetron sputtering (MS), and plasma enhanced metalorganic chemical vapor deposition (PEMOCVD) on different substrates. We consider also the influence of annealing on UV and green PL. Information on structure and morphology of ZnO films deposited by RTE, MS and PEMOCVD can be found in our earlier paper [5]. For short review devoted to promising properties of ZnO films and for technology of transparent ZnO thin films the reader can be referred to [6].

I. Experimental details

ZnO films were deposited by reactive thermal evaporation (RTE), magnetron sputtering (MS) and PEMOCVD on Al_2O_3 (0001) and SiN_x/Si (110). RTE deposition of ZnO films was carried out in a vacuum chamber. Zn in the form of a metal granules was evaporated out of heated cell in oxygen atmosphere at the pressure Po_2 = 0.01 Pa. The temperature of substrate was held at 300 °C. Also, ZnO films consisted of micro- and nanocrystallites were grown from mixture of ZnO and carbon powder in quartz tube heated up to 1100 °C. Deposition by magnetron sputtering was carried out in argon-oxygen (4:1) media from Zn target on Al_2O_3 (0001) substrates. Total gas pressure was 1 Pa. The

substrate temperature was ranged from 300 to 500 °C. In PEMOCVD technology we used the Zn acetylacetonate as a precursor which vapor was transported to a chamber by Ar as gas carrier. Applied radio frequency voltage causes the discharge in Ar-O_2 atmosphere which activate the introduced precursor vapor forming the ZnO film. The substrate temperature of deposition was in the range 150-500 °C. Annealing of ZnO films was carried out in air at 600-1000 °C during 2-9 h. Photoluminescence of as-grown and annealed ZnO films was studied at room temperature by an Acton 2500i monochromator with a CCD camera. The third harmonic of a femtosecond Ti:sapphire laser (266 nm, 37 mW, 170 fs, 76 MHz) was used as excitation source. At this study energy pumping density per pulse **P** changes from 2.5 to 250 nJ/cm^2 by varying the size of a spot.

II. Results and discussion

Fig.1 represents PL spectra of ZnO/Al_2O_3 films deposited by RTE. As one can see PL spectra consist of two bands: near-band edge (NBE) and green-yellow band (GYB). It is considered that, NBE emission peaked at 3.27 eV originates from recombination of free excitons while GYB emission is obliged to intrinsic defects such as oxygen vacancies or interstitials [7]. More intense broad GYB and a small UV PL indicate an oxygen deficiency in ZnO crystal structure. It is clearly seen that annealing of sample suppresses GYB emission without significant enhancing in UV PL. Increasing the excitation fluence leads to weak raising of UV PL. This behavior confirms the presence of a large amount of defects and nonradiative recombination centers.

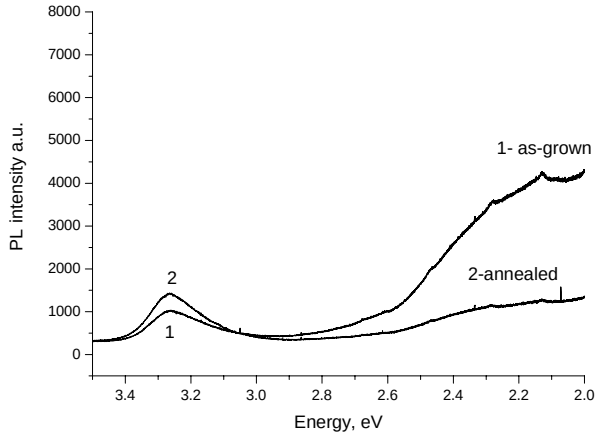

Fig. 1. PL spectra of ZnO film deposited by RTE as-grown and annealed at 600 °C, 2 h.

The similar PL spectra were obtained from micro- and nanocrystalline ZnO films grown from vapour phase (Fig.2). However, in this case GYB emission was significantly larger then UV one. Increase of optical pumping leads to increasing of green PL. Even annealing at 600 °C during 2 hours does not suppress this green band. This behavior can be explained by the great number of oxygen vacancies which cannot be sufficiently lowered at applied annealing regime.

As-grown ZnO films deposited by MS exhibit no UV PL. However, short annealing during 2-3.5 h at moderate temperature range (600-800 °C) leads to an appearance of UV PL (see Fig.3). We revealed the influence of film texture on PL spectra. ZnO films deposited by MS on sapphire at substrate temperature T_s = 200 °C and discharge power W=200 W have (002) texture. The C-axis of ZnO films, deposited at T_s = 200 °C and W=300 W, was arranged in film plane and its orientation was (110). PL spectra of these textured films have different dependence on optical pumping (Fig.3). At increasing optical excitation PL intensity of ZnO films with (002) texture strongly increases, while for ZnO films with (110) texture weak increase was observed. This feature of PL spectra can be explained by different quality of interface between film and substrate. It is well-known that growth of ZnO (002) on c-plane Al_2O_3 results in a large lattice misfit (at least ~ 18 %) [8]. At the same time growth of ZnO (110) on c-plane Al_2O_3 results in a relatively small lattice mismatch ~ 8.8 %. Thus, at growth of ZnO with (002) texture on c-sapphire both interface and growing ZnO layer has a poor crystal and optical quality due to forming of threading dislocations and point defects. They can promote a creation of nonradiative centers. That is the reason why PL of ZnO films with (002) texture insufficiently develops with increasing of optical pumping.

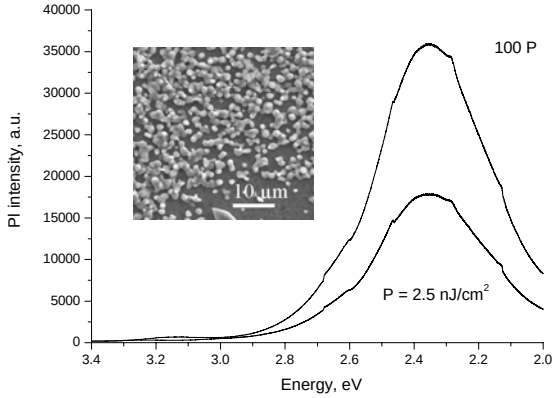

Fig. 2. PL spectra of ZnO micro- and nanocrystalline films grown from vapor gas phase. The inset shows SEM image of investigated ZnO/Si micro- and nanocrystals.

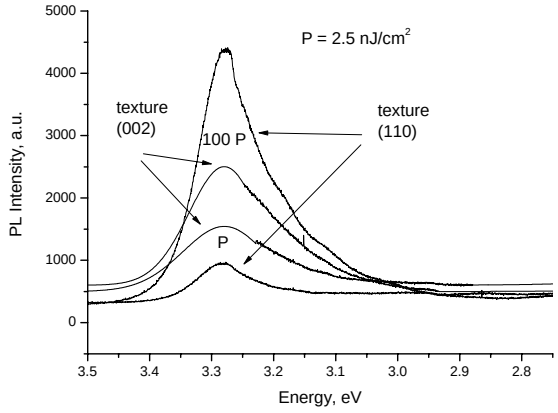

Fig. 3. PL spectra of textured ZnO films deposited by MS. The samples were annealed at 600 °C, 3.5 h.

However, it should be noted that photons with λ=266 nm (hν = 4.67 eV) at excitation by the third harmonic of Ti:sapphire laser is strongly absorbed in ZnO. Assuming that the penetration depth is ~ 50 nm observed PL characterizes PL of film region near surface. Therefore, high intensity of UV PL characterizes the high quality of ZnO films surface free of non-radiative recombination centers. Thus, different behavior of PL spectra at increasing optical excitation of studied ZnO films with (002) and (110) texture can be also explained by different density of surface states which are considered to be active centers of non-radiative recombination.

On Fig.3 one can see a low energy tail in ZnO films deposited by MS. This tail can be obliged to LO phonon replica due to strong exciton-phonon coupling in ZnO. In order to enhance UV PL from ZnO films deposited on Al_2O_3 (0001), we must find out the technological conditions (by increasing substrate temperature or by introducing low temperature ZnO buffer layer) which improve interface quality resulting in high UV PL. It should be noted that durable annealing of samples in air (9 h) especially at higher temperatures (900-1000 °C) suppress UV PL and give rise to visible GYB emission.

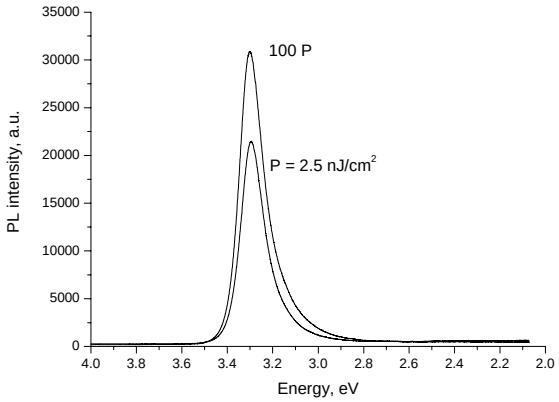

Fig. 4. PL spectra of as-grown ZnO film deposited by PEMOCVD on SiN_x/Si at T_s=500 °C.

Finally, we investigated PL of ZnO films deposited by PEMOCVD. PL spectra are various and depend on the type of substrate and annealing conditions. As-grown ZnO films deposited by PEMOCVD at 350 °C on SiN_x/Si revealed the most intensive NBE photoluminescence peaked at 3.27 eV (Fig.4). The increasing of optical excitation density enlarges the UV PL without changing its band form. There is no low energy tail as in ZnO films deposited by MS. The high UV PL with symmetric shape of peak and an absence of any visible emission testify the high optical quality of films deposited on nitridized silicon buffer layer. However deposition at low temperature 150-200 °C as well as at high temperature 500 °C by PEMOCVD on SiN_x/Si substrates does not lead to strong UV emission. Films, deposited at lower temperatures, possess worthy crystallinity (proved by XRD spectra, not shown here) and hence, have more non-radiative centers, which lead to low-quality UV PL in turn. In case of high growth temperatures (500 °C) ZnO films show GYB emission that indicate on forming of oxygen vacancies at film growth, in particularly, due to formation of SiN_xO_y layer at interface. The high temperature annealing (800 °C) of ZnO films increase the number of defects in oxygen sublattice enhancing GYB emission.

ZnO films deposited on Al_2O_3 (0001) and SiO_2/Si substrates by PEMOCVD were characterized both NBE and broad deep-level luminescence. Moreover, observed NBE emission was weaker than GYB emission. In these cases, annealing of ZnO samples leads also to increasing of deep-level GYB luminescence peaked at 2.39 eV. These experiments clearly demonstrate the influence of nature of substrate on PL properties of ZnO films.

Conclusion

PL investigation of ZnO films grown on different substrates by various technologies were carried out by femtosecond Ti:sapphire laser. The best UV PL was obtained in ZnO films deposited by PEMOCVD on SiN_x/Si substrates. Good PL results were obtained also on ZnO films processed by MS. In this case the influence of ZnO texture on PL intensity was revealed. The most intense PL was observed in samples with c-axis situated in plane of Al_2O_3 substrate. Stresses arising in films at growth and annealing as a result of large misfit between ZnO and Al_2O_3 in periods of crystal lattice introduce defects responsible for suppression of UV PL. The influence of ZnO film texture on PL intensity was discovered and can also be explained by different amount of non-radiative centers of surface recombination.

Right choice of technological conditions can provide growth of ZnO films with high optical and crystal quality enough for optoelectronic applications. PEMOCVD techniques can be used for growth of ZnO films showing only NBE emission without post-growth annealing in case of SiN_x/Si substrate.

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Фотолюмінісценція плівок ZnS збуджена фемтосекундним лазером

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Фотолюмінесценція плівок ZnO, осаджених на різні підкладки чотирма технологічними методами включаючи магнетронне розпилення та PEMOCVD, була досліджена при кімнатній температурі при збудженні фемтосекундним лазером сапфір:Ti. Виявлено вплив текстури плівки на спектр фотолюмінесценції. Досліджено вплив відпалу на ультрафіолетову та зелену фотолюмінесценцію. Найбільш інтенсивна ультрафіолетова екситонна фотолюмінесценція була виявлена в плівках ZnO осаджених на SiN_x/Si підкладки.