

An Au buffer layer for the growth of a ZnO sol–gel film on a Si substrate

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2011 Phys. Scr. 84 045402

(<http://iopscience.iop.org/1402-4896/84/4/045402>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 132.174.255.116

This content was downloaded on 01/10/2015 at 17:29

Please note that [terms and conditions apply](#).

An Au buffer layer for the growth of a ZnO sol–gel film on a Si substrate

Yidong Zhang¹, Guofu Sun², Hongxiao Zhao¹, Jing Li¹ and Zhi Zheng¹

¹ Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang 461000, People's Republic of China

² College of Chemistry and Chemical Engineering, Xuchang University, Xuchang 461000, People's Republic of China

E-mail: zyd630@126.com (Y Zhang)

Received 14 May 2011

Accepted for publication 24 August 2011

Published 20 September 2011

Online at stacks.iop.org/PhysScr/84/045402

Abstract

In this work, we demonstrate the influence of an Au buffer layer on the structure and photoluminescence (PL) properties of ZnO sol–gel thin films on Si substrates. An Au layer was deposited on the silicon substrate by the evaporation deposition method from highly pure Au (99.99%) wires. Then, a ZnO film was prepared by the sol–gel method with spin-coating technology, followed by calcinations in air at 600 °C for 1 h. The structures and morphologies of the prepared films were characterized by x-ray diffraction, energy dispersive spectrum analysis, atomic force microscopy and PL. The results show that the prepared ZnO thin film with an Au buffer layer exhibits good crystallinity and surface morphology compared with that without an Au buffer layer. Interestingly, different from other previous reports on buffer layers with PL-enhanced properties, the ZnO thin film with Au buffer layer showed an obvious violet PL-quenched property.

PACS number: 42.79.Wc

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Zinc oxide (ZnO) is widely used in UV light-emitting devices [1], surface acoustic wave devices [2], transparent electronics [3], photo-detectors [4], dye-sensitized solar cells [5], thin film transistors [6] and random lasers [7] because of its direct wide band gap (3.37 eV), large exciton binding energy (60 meV at room temperature (RT)), exciton Bohr radius in the range 1.4–3.5 nm, high breakdown voltage, good piezoelectric characteristics, good compatibility with many organic compounds, high transparency in the visible region, and high mechanical, thermal and chemical stability. Moreover, the generation of high-quality ZnO thin films is expected to improve the photoluminescence efficiency of electro-optic devices and the sensitivity of chemical sensors.

A great deal of research shows that the optical and electrical properties of ZnO thin films have a direct connection with their crystalline quality. However, the quality of ZnO thin films is closely related to the substrate materials. Until now,

ZnO thin films have been prepared on various substrates such as sapphire [8], silicon [9] and glass [10]. In particular, silicon is a promising candidate because of its low cost, excellent thermal conductivity, high crystallinity, availability of large size and all types of conductivity. Furthermore, silicon is the cornerstone of the current semiconductor microelectronics industry. If high-quality ZnO thin films are prepared on Si substrates, it will be beneficial for effective intergration of optoelectronic devices with Si integrated circuit (IC) technology. However, when ZnO thin films are deposited on Si substrates and annealed at high temperature, Si atoms on the substrate surface easily 'capture' oxygen atoms from ZnO thin films [11]. As a result, oxygen vacancies in the bulk of ZnO increase greatly and consequently deteriorate the quality of ZnO thin films. Therefore, some buffer layers, such as Zn [12], Ti [13], Pt [14], Ru [15], SiC [16], TiO₂ [17], CaO [18], MgO [19], CaF₂ [20], ITO [21], SiO₂ [22], Al₂O₃ [23], ZnS [24], AlN [25] and GaN [26], have been introduced to prevent the Si substrate surface from being oxidized by the ZnO thin films during the annealing process. However, to



Figure 1. Schematic diagram of ZnO/Au/Si thin films.

the best of our knowledge, few reports have mentioned the influence of an Au noble metal buffer layer on the structure and photoluminescence (PL) properties of a ZnO thin film.

In this work, ZnO sol-gel film was deposited on an Au buffer layer fabricated on silicon substrates by the evaporation method. The effects of an Au buffer layer on the structure and PL properties of ZnO thin films were investigated.

2. Experimental procedure

All the reagents used in the experiments were of analytic grade (purchased from Shanghai Sinopharm Chemical Reagent Co.) and used without further purification.

2.1. Preparation of Au buffer layers and ZnO thin films

An Au buffer layer was fabricated by the evaporation method using a pure Au wire as a precursor on a Si substrate. The thickness of the buffer layers was 50 nm, which was controlled by the working currents and times of the instruments. The silicon substrates had been ultrasonically cleaned by ethanol, acetone and distilled water for 30 min, respectively. ZnO sol was fabricated by the sol-gel method using zinc acetate, anhydrous ethanol and diethanolamine (DMA) as the solute, solvent and sol stabilizer, respectively, which have been reported in our previous work [27]. ZnO thin films were prepared by a spin-coating method on Si substrates for 30 s with a spinning speed of 3000 rpm. The resulting thin films without a buffer layer (ZnO/Si), and with an Au buffer layer (ZnO/Au/Si) were annealed at 600 °C in air for 1 h, which were marked (a) and (b), respectively. Figure 1 shows the schematic structure of a ZnO thin film based on an Au buffer layer on a Si substrate.

2.2. Characterization of ZnO thin films

The crystal structure of the prepared samples was determined by x-ray diffraction (XRD; Bruker D8 Advance) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scan rate of $0.01 \text{ } 2\theta \text{ s}^{-1}$. The elemental distributions of ZnO/ZnO-buffer/Si were analyzed by an energy dispersive spectrum (EDS; Bruker). The surface morphology of ZnO/ZnO-buffer/Si was observed by an atomic force microscope (AFM; Veeco Digital Instruments, Nanoscope 3d) in tapping mode at a scan rate of 1.0 Hz with a commercial silicon micro-cantilever probe under ambient conditions ($24 \pm 2 \text{ } ^\circ\text{C}$). The tip radius, spring constant and resonance frequency of the probe are less than 10 nm, 42.5 N m^{-1} and 243.54 kHz, respectively.

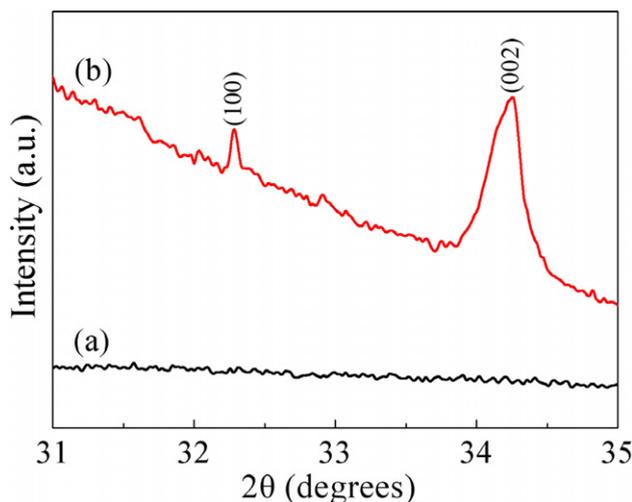


Figure 2. XRD patterns of (a) ZnO/Si and (b) ZnO/Au/Si.

The PL spectra were recorded by a PL spectrophotometer (GILDEN—photonics fluoro SENS) with a wavelength region from 335 to 800 nm. The excitation wavelength was 325 nm with a Xe lamp excitation source.

3. Results and discussion

Figure 2 shows the XRD patterns of ZnO thin films deposited on Au/Si templates and Si substrates. Considering the interference of a strong diffraction peak of the Si substrate in the analysis of ZnO peaks, a small 2θ scope from 31° to 35° is chosen. There are no obvious peaks in curve (a) due to the poor crystallinity. However, after introducing the Au buffer layer, the (100) and (002) peaks can be observed, indicating that the sample was a polycrystalline hexagonal wurtzite structure (Zincite, JCPDS 36-1451), i.e. introducing an Au buffer layer could effectively prevent Si atoms on the substrate surface from capturing oxygen atoms from ZnO thin films causing the crystallinity of ZnO to be enhanced. The size of the nanocrystals (D) was calculated on the basis of the Scherrer formula, $D = k\lambda/\beta\cos\theta$, where k (0.9) is the shape factor, λ is the x-ray wavelength of Cu-K α radiation (1.5418 \AA), θ is the Bragg diffraction angle and β (0.36°) is the full-width at half-maximum (FWHM) of the (002) peak. The average nanocrystallite size in ZnS microspheres was $\sim 23 \text{ nm}$. The intensity of the (002) peak was much stronger than that of the (100) peak in sample (b). This indicated that the ZnO thin film with an Au buffer layer had a high preferential orientation to the c -axis orientation, which is perpendicular to the substrate surface.

Figure 3 shows the EDS analysis of the samples. Obviously, the relative intensity of oxygen was increased after introducing an Au buffer layer. The mol contents of all the elements of the samples are shown in table 1. The oxygen mol content was increased from 23.1 to 41.5% due to the oxidation enhancement effect based on an Au buffer layer.

Figure 4 shows two-dimensional (2D) AFM surface height morphologies and cross section profiles of the ZnO films on the Si substrate and the Au buffer layer. The scanning area is $500 \times 500 \text{ nm}^2$. Compared with the ZnO thin film grown on the Si substrate, the ZnO thin film grown on the

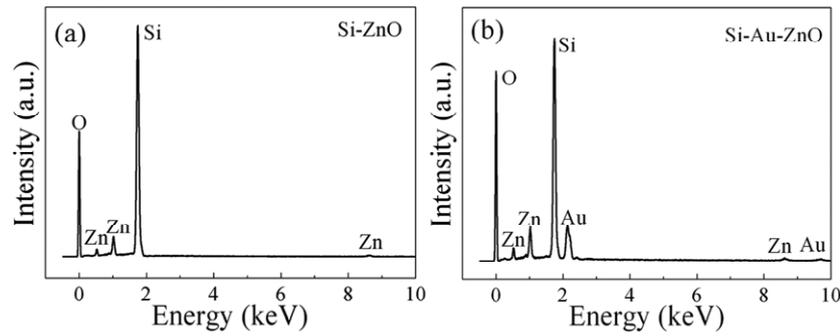


Figure 3. EDS analysis of (a) ZnO/Si and (b) ZnO/Au/Si.

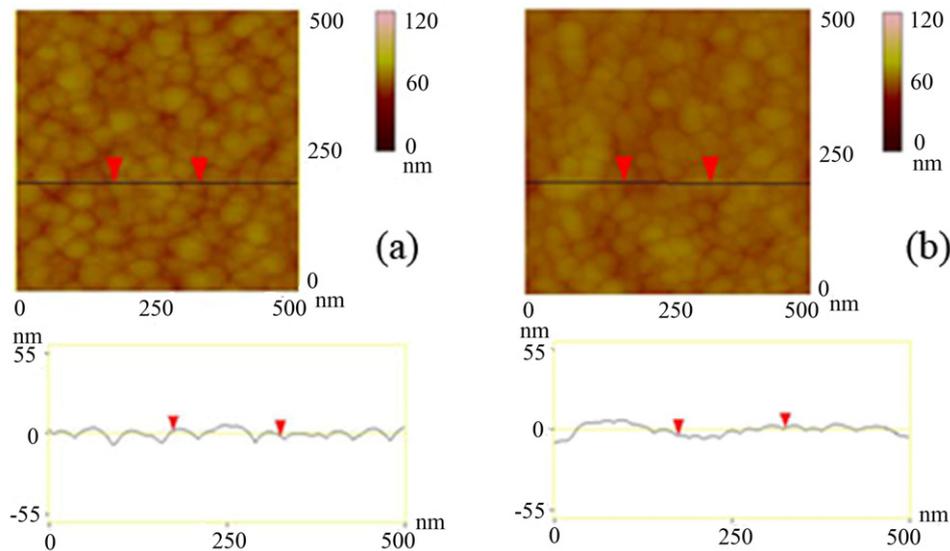


Figure 4. Two-dimensional AFM height morphologies and cross section profiles of (a) ZnO/Si and (b) ZnO/Au/Si.

Table 1. Element content of ZnO/Si and ZnO/Au/Si.

	Content (mol.%)			
	Zn	O	Si	Au
ZnO/Si	45.4	23.1	18.7	0
ZnO/Au/Si	48.6	41.5	4.6	8.5

Au buffer layer has a smooth surface and compact grains. On the right of each image, an intensity strip is shown, indicating the depth and height along the z -axis. The root mean square (rms) roughness, calculated using the equipment's software, of ZnO thin film samples (a) and (b) was 18.4 and 9.5 nm, respectively. The average size of samples (a) and (b) was 30 and 25 nm, respectively, which is consistent with the XRD analysis. Obviously, the rms roughness values decreased after introducing the Au buffer layer. This is due to the fact that the Au buffer layers can effectively prevent the Si substrate from capturing oxygen from ZnO thin films and, as a result, the crystal quality of the ZnO thin film was improved, leading to a flat and compact surface.

The PL spectrum is a powerful tool for characterizing the optical quality of semiconductor materials, such as the PL peak intensity correlating directly with the defect densities in materials. Figure 5 shows the PL spectra of ZnO films at RT. The spectra show only one strong violet emission

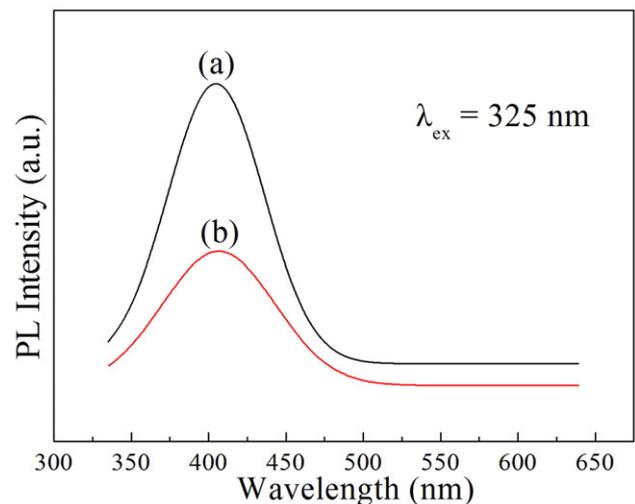


Figure 5. PL spectra of (a) ZnO/Si and (b) ZnO/Au/Si.

at 415 nm for the samples. The ZnO excitonic emission is probably related to oxygen vacancies [28]. A violet emission in ZnO films has actually been reported by some research groups. The Im group [29] observed a violet emission at 420 nm in ZnO films prepared by pulsed laser deposition

(PLD) under an oxygen pressure of 1 mtorr at RT grown on a sapphire (001) substrate. They indicated that the violet luminescence was probably emitted from the grain boundaries of an oxygen-deficient ZnO_x film. The Jayaraj group [30] also reported that violet luminescence was observed from ZnO nanorods grown by RT PLD. The Lian group [31] found a single violet emission at 413–424 nm in the ZnO films prepared by oxidation of a Zn film on quartz glass deposited by PLD. The violet emission peak position shifted slightly from 424 nm (2.91 eV) to 413 nm (3.0 eV) when the oxygen pressure increased from 50–500 Pa to 5000–23 000 Pa during the process of oxidation. They deduced that the variation of the position of the violet emission peak may be attributed to defects or stoichiometry in ZnO films, the interstitial zinc (Zn_i) defects in the ZnO films were responsible for the violet emission of ZnO films obtained by oxidation under low oxygen pressure, and the zinc vacancy (V_{Zn}) defects in the ZnO films were responsible for the violet emission of ZnO films obtained by oxidation under high oxygen pressure. In this work, the strong violet emission intensity of ZnO thin films on a silicon substrate is due to the high oxygen vacancy concentration obtained during calcination at 600 °C. The decreasing violet emission intensity of ZnO films deposited on an Au buffer layer is probably related to the enhanced oxidation of the film, which will result in improvement of the oxygen deficiency of ZnO crystals. The enhanced oxidation process can be proved by the previous EDS analysis.

4. Conclusions

In summary, an Au buffer layer was deposited on a Si substrate by the evaporation method and then a ZnO thin film was deposited on an Au buffer layer by the sol–gel method. The analyses of structures show that the ZnO thin film on an Au buffer layer is preferentially oriented along the *c*-axis perpendicular to the substrate surface with a compact hexagonal wurtzite structure. An Au buffer layer can increase the intensity of (002) peaks, and improve the crystal quality of a ZnO thin film. The ZnO film deposited on an Au buffer layers has a smoother surface and uniform grains. The PL spectra indicate that the ZnO thin film deposited on an Au buffer layer has a weaker violet emission (PL quenching) compared with that on a Si substrate. It is probably due to the decreasing oxygen deficiency of ZnO crystals caused by the enhanced oxidation of the film.

Acknowledgments

This work was financially supported by the Natural Science Project in Education of Henan Province, China (grant no. 2011A150026) and the Foundation of Xuchang University (no. 2011B018).

References

- [1] Liu J P, Qu S C, Zeng X B, Xu Y, Gou X F, Wang Z J, Zhou H Y and Wang Z G 2007 *Appl. Surf. Sci.* **253** 7506
- [2] Krishnamoorthy S and Iliadis A A 2008 *Solid State Electron.* **52** 1710
- [3] Logothetidis S, Laskarakis A, Kassavetis S, Lousinian S, Gravalidis C and Kiriakidis G 2008 *Thin Solid Films* **516** 1345
- [4] Kim H Y, Kim J H, Kim Y J, Chae K H, Whang C N, Song J H and Im S 2001 *Opt. Mater.* **7** 141
- [5] Rani S, Suri P, Shishodia P K and Mehra R M 2008 *Sol. Energy Mater. Sol. Cells* **92** 1639
- [6] Lee K, Choti J M, Hwang D, Oh M S, Kim J K, Jung Y, Oh K and Im S 2008 *Sensors Actuators B* **144** 69
- [7] Miao L, Tanemura S, Ieda Y, Tanemura M, Hayashi Y, Yang H Y, Lau S P, Tay B K and Gao Y G 2007 *Surf. Sci.* **601** 2660
- [8] Wang Y Z, Chu B L and He Q Y 2008 *Vacuum* **82** 1229
- [9] Kar J P, Kumar M, Choi J H, Das S N, Choi S Y and Myoung J M 2009 *Solid State Commun.* **149** 1337
- [10] Kumar P S, Raj A D, Mangalaraj D and Nataraj D 2010 *Thin Solid Films* **518** 183
- [11] Nakamura T, Yamada Y, Kusumori T, Minoura H and Muto H 2002 *Thin Solid Films* **411** 60
- [12] Lee C, Park A, Cho Y J, Lee W I and Kim H W 2008 *Vacuum* **82** 1363
- [13] Li F, Li D M, Dai J N, Su H B, Wang L, Pu Y, Fang W Q and Jiang F Y 2006 *Superlatt. Microstruct.* **40** 56
- [14] Yamada H, Ushimi Y, Takeuchi M, Yoshino Y, Makino T and Arai S 2004 *Vacuum* **74** 689
- [15] Kim E K, Lee T Y, Hwang H S, Kim Y S, Park Y and Song J T 2006 *Superlatt. Microstruct.* **39** 138
- [16] Zhao C Y, Liu Z R, Sun B, Tang J, Xu P S and Xie J C 2009 *Physica E* **41** 479
- [17] Xu L H, Shi L X and Li X Y 2008 *Appl. Surf. Sci.* **55** 3230
- [18] Lim Y S, Jeong J S, Bang J and Kim J 2010 *Solid State Commun.* **150** 428
- [19] Chen Y F, Ko H J, Hong S K, Inaba K, Segawa Y and Yao T 2001 *J. Cryst. Growth* **227** 917
- [20] Koike K, Komuro T, Ogata K, Sasa S, Inoue M and Yano M 2004 *Physica E* **21** 679
- [21] Vinodkumar R, Lethy K J, Beena D, Detty A P, Navas I, Nayar U V, Pillai V P M, Ganesan V and Reddy V R 2010 *Sol. Energy Mater. Sol. Cells* **94** 68
- [22] Chen X and Liu D L 2009 *Sensors Actuators A* **156** 317
- [23] Kim C R, Lee J Y, Heo J H, Shin C M, Lee T M, Park J H, Ryu H, Chang J H and Son C S 2010 *Curr. Appl. Phys.* **10** S298
- [24] Wang D W, Zhao S L, Xu Z, Kong C and Gong W 2011 *Org. Electron.* **12** 92
- [25] Wang L, Pu Y, Chen Y F, Mo C L, Fang W Q, Xiong C B, Dai J N and Jiang F Y 2005 *J. Cryst. Growth* **284** 459
- [26] Sahoo T, Jeon J W, Kannan V, Lee C R, Yu Y T, Song Y W and Lee I H 2008 *Thin Solid Films* **516** 8244
- [27] Zhang Y D, Jia H M, Li P J, Yang F L and Zheng Z 2011 *Opt. Commun.* **284** 236
- [28] Huang Y Q, Lin J R, Du H Y, Gao L F and Hu Y 2006 *Mater. Lett.* **60** 3818
- [29] Jin B J, Im S and Lee S Y 2000 *Thin Solid Films* **366** 107
- [30] Ajimsha R S, Manoj R, Aneesh P M and Jayaraj M K 2010 *Curr. Appl. Phys.* **10** 693
- [31] Fan X M, Lian J S, Zhao L and Liu Y H 2005 *Appl. Surf. Sci.* **252** 420