Optical and electrical properties of Vanadium doped Indium oxide thin films

Huibin Li, Ning Wang, and Xingyuan Liu*

Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P.R. China.
**Corresponding auhor: holiday00017@mail.jl.cn*

Abstract: A new transparent conducting indium vanadium oxide (IVO) thin film is developed by using a modification-specific reactive thermal co-evaporation method. Electrical and optical characteristics of IVO films were studied with different vanadium doping concentration, which shows good optical transmittance in the visible spectra range and a minimum electrical resistivity of 7.95×10^{-4} Ω·cm corresponding to a carrier density of 2.28×10^{20} cm^{-3} and a Hall mobility of 34.5 $cm^2 V^{-1} s^{-1}$, respectively. Using IVO film as the anode, OLED shows a reduced turn-on voltage and significantly enhanced luminance and electroluminescence efficiency with respect to the device with an ITO anode. Our results indicate that IVO is a promising transparent conducting oxide material, and a suitable electrical contact for hole injection in OLEDs.

OCIS Codes: (310.7005) Transparent conductive coatings; (310.6860) Thin films, optical properties; (230.3670) Light-emitting diodes.

References and links

1. T. Minami, "New n-type transparent conducting oxides," MRS Bulletin **25**, 38-44 (2000).
2. S. Major, A. Banerjee, and K. L. Chopra, "Annealing studies of undoped and indium-doped films of zinc oxide," Thin Solid Films **122**, 31-43 (1984).
3. K. Bädeker, "Über die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbindungen, " Ann. Phys. (Leipzig) **22**, 749-766 (1907).
4. D. D. Edwards, T. O. Mason, F. Goutenoire and K. R. Poeppelmeier, "A new transparent conducting oxide in the Ga_2O_3–In_2O_3–SnO_2 system," Appl. Phys. Lett. **70**, 1706-1708 (1997).
5. G. J. Exarhos and X. D. Zhou, "Discovery-based design of transparent conducting oxide films," Thin solid films **515**, 7025-7052 (2007).
6. R. B. H. Tahar, T. Ban, Y. Ohya, and Y. Takahashi, "Tin doped indium oxide thin films: Electrical properties," J. Appl. Phys. **83**, 2631-2645 (1998).
7. A. L. Dawar and J. C. Joshi, "Semiconducting transparent thin films: their properties and applications," J. Mater. Sci. **19**, 1-23 (1984).
8. B. G. Lewis and D. C. Paine, "Applications and processing of transparent conducting oxides," MRS Bulletin **25**, 22-27 (2000).
9. Y. Park, V. Choong, Y. Gao, B. R. Hsieh, and C. W. Tang, "Work function of indium tin oxide transparent conductor measured by photoelectron spectroscopy," Appl. Phys. Lett. **68**, 2699-2701 (1996).
10. J. Kido, M. Kimura, and K. Nagai, "Multilayer white light-emitting organic electroluminescent device," Science **267,** 1332-1334 (1995).
11. H. Kim, C. M. Gilmore, J. S. Horwitz, A. Piqué, H. Murata, G. P. Kushto, R. Schlaf, Z. H. Kafafi, and D. B. Chrisey, "Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices," Appl. Phys. Lett. **76**, 259-261 (2000).
12. W. Chen, C. Huang, X. Y. Gao, L. Wang, C. G. Zhen, D. Qi, S. Chen, H. L. Zhang, K. P. Loh, Z. K. Chen, and A. T. S. Wee, "Tuning the hole injection barrier at the organic/metal interface with self-assembled functionalized aromatic thiols, " J. Phys. Chem. B **110**, 26075-26080 (2006).
13. S. Kato, "Designing interfaces that function to facilitate charge injection in organic light-emitting diodes," J. Am. Chem. Soc. **127**, 11538-11539 (2005).
14. Z. Z. You, and J. Y. Dong, "Surface properties of treated ITO anodes for organic light-emitting devices," Appl. Surf. Sci. **249**, 271–276 (2005).
15. L. S. Hung, and C. H. Chen, "Recent progress of molecular organic electroluminescent materials and devices," Mater. Sci. and Eng. R **39**, 143–222 (2002).

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008

16. J. Li, M. Yahiro, K. Ishida, H. Yamadab, and K. Matsushige, "Enhanced performance of organic light emitting device by insertion of conducting/insulating WO3 anodic buffer layer," Synth. Met. **151**, 141–146 (2005).
17. J. J. Ho, C. Y. Chen, R. Y. Hsiao, and O. L. Ho, "The work function improvement on indium-tin-oxide epitaxial layers by doping treatment for organic light-emitting device applications," J. Phys. Chem. C **111**, 8372-8376 (2007).
18. H. Kim, C. M. Gilmore, J. S. Horwitz, A. Piqué, H. Murata, G. P. Kushto, R. Schlaf, Z. H. Kafafi, and D. B. Chrisey, "Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices," Appl. Phys. Lett. **76**, 259-261 (2000).
19. C. M. Hsu, J. W. Lee, T. H. Meen, and W. T. Wu, "Preparation and characterization of Ni–indium tin oxide cosputtered thin films for organic light-emitting diode application," Thin Solid Films **474**, 19-24 (2005).

1. Introduction

Transparent conducting oxides (TCOs) are attractive wide band-gap semiconductor materials that can be doped to relatively high levels and fabricated into thin films exhibiting both high optical transparency and reasonable electrical conductivity [1-7]. Indium tin oxide (ITO) is the most frequently used TCO film in optoelectronic technology such as solar cells, photodetectors, liquid crystal display, and organic light-emitting devices (OLEDs) [7-11]. Generally, ITO is used as a transparent anode for hole injection in OLEDs. However, the chemical and electronic properties of ITO films are far from optimum for OLEDs. There exists a hole injection barrier between ITO/organic layer, which plays an important role on OLED performance such as operation voltage, electroluminescence (EL) efficiency and stability [12-13]. Considerable efforts, including surface treatment on ITO layer and the insertion of buffer layer between ITO and organic layers, have been made to lower the hole injection barrier and improve interface stability [14-17]. Moreover, some TCOs such as Aluminum-doped zinc oxide, Ni–indium tin oxide have been tested in OLEDs as an anode contact, which showed comparable performance to ITO anode [18-19]. In this paper, we have developed a novel TCO film based on a binary compound of indium oxide (In_2O_3) doped with vanadium oxide (V_2O_5). As the dopant, V_2O_5 is a transition metal oxide, which attracts extensive interest for many practical applications such as photochromism devices alternative, catalyst material in chemical reactions, cathode material for lithium batteries, and buffer layer material for OLEDs. The preparation and basic optical and electrical characteristics of indium vanadium oxide (IVO) were reported. The effect of the IVO anode contact on the EL performance of OLEDs was investigated and compared with an ITO anode. Our results suggest that the IVO film can serve as a very effective electrical contact in OLEDs for hole injection.

2. Experimental

Source materials, indium (In) pellets and V_2O_5 powder were placed in tungsten and molybdenum boats, respectively. Substrates were kept 25 cm above the center between the two boats. The chamber was evacuated at a base pressure of 1×10^{-3} Pa, and the films were deposited in a reactive oxygen atmosphere which was introduced into the deposition chamber through a calibrated valve at constant pressure ~2×10^{-2} Pa. A chamber temperature of 250°C was provided by an infrared halogen lamp. The film thickness was monitored in situ by quartz crystal oscillator. The IVO samples with different vanadium doping content were obtained by controlling the deposition rates of the two source materials with two independent quartz monitors. The room temperature carrier concentrations, resistivities and Hall carrier mobilities of the IVO coatings were estimated from Hall measurements. Transmittance spectra were measured with a Shimadzu UV-3101PC spectrophotometer. A field emission scanning electron microscopy (SEM) Hitachi S-4800 and GENE SIS2000 XMS 60S (EDAX Inc.) were used to investigating the morphology and ingredient of the IVO films, respectively. In the OLED structure, N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1Vbipheny1-4,4V-diamine (NPB) and tris(8-hydroxyquinoline)aluminum (Alq_3) were used as the hole transport layer and light-emitting layer, respectively. The cathode used is a buffer layer of lithium fluoride (LiF)

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008

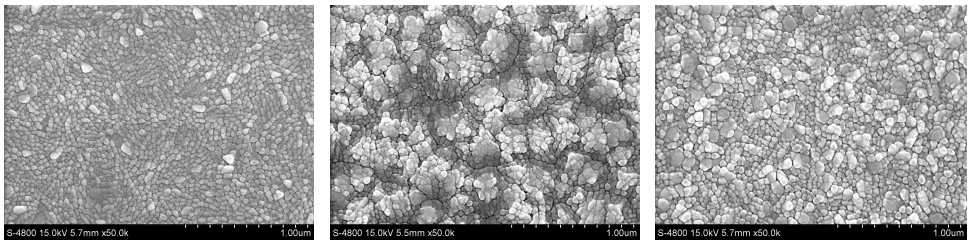
capped with aluminum (Al). The organic and metal layers were deposited with a deposition rates about 0.1-0.2 nm/s by thermal evaporation in a high vacuum of 5×10^{-4} Pa. Current density-voltage-luminance characteristics were measured with a Keithley 2400 source meter and a Photo Research PR705 spectrascan system. All measurements were carried out in air at room temperature.

3. Results and discussion

Table 1. Resistivity, carrier density and Hall mobility of IVO samples with different V doping content

IVO Samples	Wt %		Resistivity	Carrier Density	Hall Mobility
	In	V	Ω·cm	cm^{-3}	$cm^2 V^{-1}s^{-1}$
A	98.20	1.80	7.95E-4	2.28E20	34.5
B	97.89	2.11	9.62E-4	2.54E20	25.5
C	96.95	3.05	8.05E-4	2.98E20	25.9

IVO films were deposited on polished glass substrates by a modification-specific reactive thermal co-evaporation technique without postdeposition anneal. It is well known that indium has a valence of three, and vanadium has a valence of five. In IVO samples, vanadium acts as a cationic dopant in the In_2O_3 lattice and substitutes the indium, which results in n doping of the lattice by providing one or two electrons to the conduction band. Table 1 shows the resistivity, carrier density and Hall mobility of three IVO samples with different vanadium content (V/(V +In) weight ratio). Hall measurements indicate that these IVO films are *n*-type degenerated semiconductors, with carrier concentrations of the order of 10^{20} cm^{-3} provided by native donors such as oxygen vacancies and substitutional vanadium dopants. The electrical properties of IVO films depend on the film composition and deposition conditions such as oxygen pressure, substrate temperature, and film thickness. The IVO sample A, sample B and sample C were grown under the same oxygen pressure of 2×10^{-2} Pa and substrate temperature of 250°C, and controlled in nearly the same thickness of about 140 nm. Therefore, it can be inferred that the increased carrier density with the vanadium content is mainly due to the donor electrons from vanadium dopants.



(a) (b) (c)

Fig. 1. SEM images of IVO films. Part (a) to (c) corresponding to sample A, sample B and sample C.

Figure 1 shows the SEM images of the three IVO samples. The SEM images show clearly that the deposited IVO films have a polycrystalline structure or domain-grain structure with distinguishable grain size. A large number of the aggregation of small particles and rough surface morphology can be observed. The surface morphology of IVO films with different vanadium content is quite different due to the substitutional incorporation of V^{5+} ions into In^{3+} locations and the incorporation of V ions in the interstitial positions. The IVO sample A that

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008

having a lower doping concentration shows a homogeneous surface compared with the other two samples. The increased disorder of grains can be observed in IVO samples with higher vanadium content, which leads to a decrease in mobility as a result of scattering by ionized dopants, acoustical phonons and grain boundary. A minimum resistivity of 7.95×10^{-4} Ω·cm was obtained at the IVO sample A corresponding to the carrier density of 2.28×10^{20} cm^{-3} and the Hall mobility of 34.5 $cm^2V^{-1}s^{-1}$, respectively. An improvement in the electrical characteristics might be expected in IVO films by optimizing vanadium doping content, deposition parameters, film thickness, as well as postdeposition anneal.

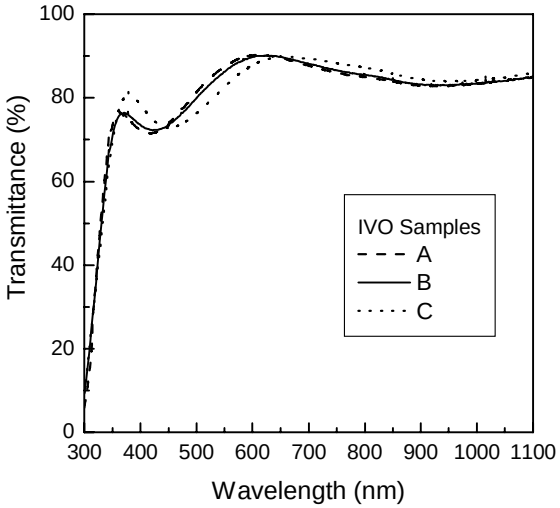


Fig. 2 . The transmittance spectra of IVO films.

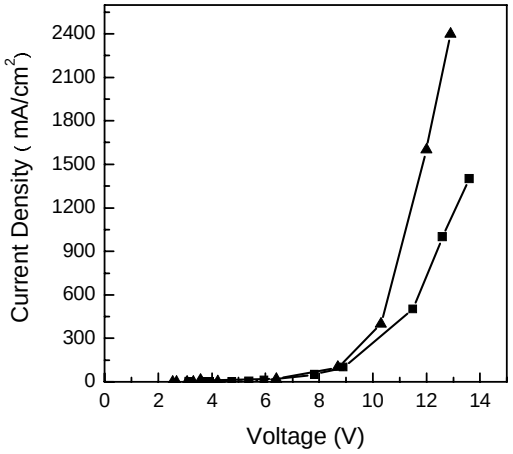


Fig. 3. The current density-voltage characteristics of the OLEDs based on IVO anode (triangle) in comparison with ITO anode (square).

The measured UV/VIS/NIR optical transmission spectra of three IVO samples are shown in Fig. 2. The transmittance curves are determined by the optical constant and thickness of the IVO films. The thickness of all samples is around 140 nm. All the curves exhibited low absorption in the VIS/NIR range and a sharp fundamental absorption edge in UV region. It

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008

shows that the three IVO samples have an average transmittance of better than 84% over the spectrum range from 400 nm to 1000 nm. Optical transmission spectra reveal a maximum transmittance of 90.4% in the IVO sample A and sample B, and a slightly decreased peak transmittance of 89.8% in the sample C, which might result from an increased carrier density in the sample C.

The IVO sample B was employed as an anode contact in a standard OLED with the following structure: Glass/IVO/NPB (74 nm)/Alq_3 (63 nm)/LiF (1 nm)/Al (60 nm). A control device was also fabricated for comparison studies with identical device architecture on a commercial ITO anode. The used IVO and ITO anodes have the similar resistivity. The two kinds of OLEDs were fabricated under the same processing conditions, and had an active emitting area of 2 mm×2 mm. Figure 3 gives the current density (J) and operating voltage (V) characteristics of the OLEDs based on IVO (triangle) and ITO (square) anodes under forward bias. It shows that the IVO-anode device has a turn-on voltage of 2.6 V, which is 0.5 V lower than the conventional ITO-anode device. Moreover, current densities of the IVO-anode OLED are increased with respect to the device with an ITO anode under the same voltage. These results suggest that the hole injection is enhanced when using IVO film as anode, which might be owing to an appropriate work function of the IVO film that can facilitate hole injection.

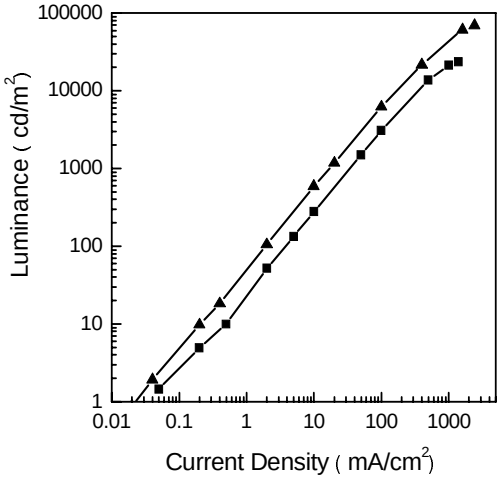


Fig. 4. The luminance-current density curves of the OLEDs fabricated on the IVO (triangle) and ITO (square) glass substrates.

As shown in Fig. 4, the luminance (L) is linearly dependent on the current density (J) for the two devices. The ITO-anode OLED shows a maximum luminance of 23580 cd/m^2 at the current density of 1400 mA/cm^2. For the comparison, the IVO-anode device exhibits a high luminance of 69300 cd/m^2 at 2400 mA/cm^2. Figure 5 shows the EL efficiency of the OLEDs as function of current density. The maximum EL efficiencies of the IVO and ITO based devices were achieved at the same current density of 100 mA/cm^2, which are 6.2 cd/A and 3.0 cd/A, respectively. Moreover, at the highest current density of 2400 mA/cm^2, the IVO-anode device still demonstrated an EL efficiency of 2.9 cd/A. Since the two kinds of OLEDs have the same device architecture except the anode used, the lower turn-on voltage and higher EL efficiency of the device with IVO anode should result from reduced hole injection barrier and enhanced hole injection, which leads to balanced injection between electron and hole.

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008

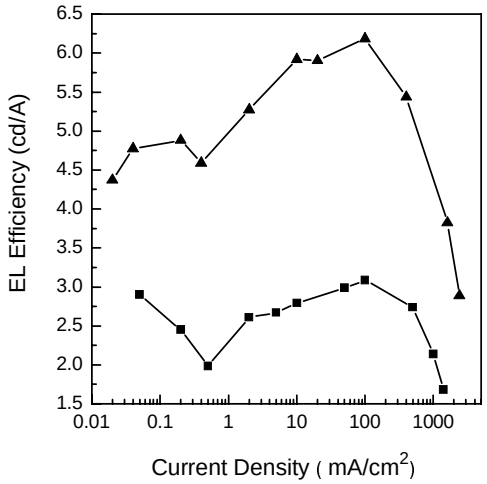


Fig. 5 The EL efficiency-current density characteristics of the OLEDs fabricated on the IVO (triangle) and ITO (square) glass substrates.

4. Conclusions

In summary, we carried out the first investigation on a novel transparent conducting indium vanadium oxide thin film. The IVO films were fabricated on polished glass substrate by using a modification-specific reactive thermal co-evaporation method. Optical and electrical characteristics of IVO films with different vanadium doping content were studied. In the 140-nm-thick IVO film with a vanadium content of 1.8 Wt%, a minimum electrical resistivity of 7.95×10^{-4} Ω·cm was obtained corresponding to a carrier density of 2.28×10^{20} cm^{-3} and a Hall mobility of 34.5 cm^2 V^{-1} s^{-1}, respectively. The IVO films show an average optical transmittance of better than 84% over the spectrum range from 400 nm to 1000 nm. The OLED utilizing IVO film as an anode was fabricated. The maximum luminance of 69300 cd/m^2 and the maximum EL efficiency of 6.2 cd/A were achieved. Compared with a conventional device with an ITO anode, the maximum luminance and EL efficiency were improved by 1.9 times and 1.1 times, respectively. Much better EL performance of the OLED with an IVO anode can be attributed to an appropriate work function and an improved hole injection from the IVO film. These results indicate that IVO thin films can be promising TCO films and efficient electrical contact for hole injection in OLEDs.

Acknowledgments

This study is supported by the National Natural Science Foundation of China under Grant No. 60376029 and 10174077, Jilin Province Science and Technology Research Project No. 20050108, and CAS Innovation Program.

#89138 - $15.00 USD Received 29 Oct 2007; revised 5 Dec 2007; accepted 16 Dec 2007; published 2 Jan 2008