

Growth of highly oriented (110) γ -CuI film with sharp exciton band

Zhi Zheng,^{*ab} Airuo Liu,^a Shumin Wang,^a Baojun Huang,^a Ka Wai Wong,^b Xitian Zhang,^b Siu Kong Hark^b and Woon Ming Lau^{*bc}

Received 17th December 2007, Accepted 3rd January 2008

First published as an Advance Article on the web 10th January 2008

DOI: 10.1039/b719452h

The growth of highly oriented (110) γ -CuI films on copper substrates with the best photoluminescence properties among all known CuI films are demonstrated, in the context of improving the current techniques in the preparation of CuI films for electronic and optoelectronic applications. The comparison of the photoluminescence spectra of CuI films with different growth orientations shows that the highly oriented (110) films prepared are less defective and give only a sharp exciton band.

Cuprous iodide (CuI) is a versatile compound drawing rapidly expanding attention in many materials research fields. The most interesting and important nature of this compound is that on one hand, it is an inorganic semiconductor and on the other, its coordination chemistry lets it readily couple with many inorganic and organic ligands. Hence, from the perspective of solid-state physics, one sees applications in electronics and optoelectronics. In fact, the γ -phase of CuI, the common product of prevalent solvothermal/hydrothermal crystal growth at low temperature, is a semiconductor with a direct band gap of ~ 3.1 eV.^{1,2} These as-grown γ -CuI semiconductor films are typically p-type in nature and are applicable in collecting and transporting holes, in the fabrication of devices, such as solar cells,³⁻⁵ light/chemical sensors, and optical display products,⁶ and also in the preparation of conducting transparent films.^{7,8} Their scope of applicability in optoelectronics is further extended when organic dye molecules are coupled to them.⁹ From the perspective of chemistry and biochemistry, one sees novel applications in catalysis, in which CuI can be used as a catalyst for hydrophosphinylation¹⁰ and arylation.¹¹ One also sees novel applications in synthesis with CuI coordination chemistry, including the formation of both inorganic and biochemical supramolecular compounds.^{12,13}

The following common thin film techniques have been adopted for the preparation of CuI films: vacuum evaporation,¹⁴ magnetron sputtering,⁸ pulsed laser deposition (PLD),^{3,7} and hybrid electrochemical/chemical synthesis.¹⁵ Among them, the direct synthesis of a CuI thin film on a copper substrate by iodination is particularly attractive and the development of new means to improve the results of this approach has become an active research subject.¹⁶ Common to all known data on the grain-orientation behavior of γ -CuI films, they show the preferred growth of grains with their (111) axis aligning with the growth direction. This interesting consistency likely arises from the following

reasons: (a) general consideration of the stability energy at the growth front predicts the growth rate along (111) being the fastest;¹⁷ (b) γ -CuI is a zinc-blende structure with a lattice constant of 0.608 nm and copper is a face-centred cubic structure with a lattice constant of 0.348 nm; as such, γ -CuI can nucleate on a copper grain with a pseudomorphic heteroepitaxial relationship ($3 a_{\text{CuI}} \approx 5 a_{\text{Cu}}$); (c) several surface science groups¹⁸ have shown the formation of a commensurate hexagonal atomic lattice of iodine on Cu (111), an ordered lattice which can conceivably lead to the formation of (111) oriented γ -CuI nuclei. The recent extension of this research to Cu (100) has also shown the evidence of ordered atomic lattice formation with which the growth of (111) oriented γ -CuI nuclei was inferred.¹⁹

To further exemplify this growth habit, we show in Fig. 1(a) the X-ray diffraction data of a typical γ -CuI film grown on a copper substrate surface comprising highly oriented Cu (111) grains and in Fig. 1(b) the data of another film grown on a copper substrate surface comprising highly oriented Cu (100) grains. Both films were grown with a solvothermal approach of supplying iodine in an organic solvent in a Teflon-lined autoclave at 160 °C and the required crystal structures of the copper substrates were confirmed with XRD. Clearly, the growth of (111) oriented γ -CuI grains along the film

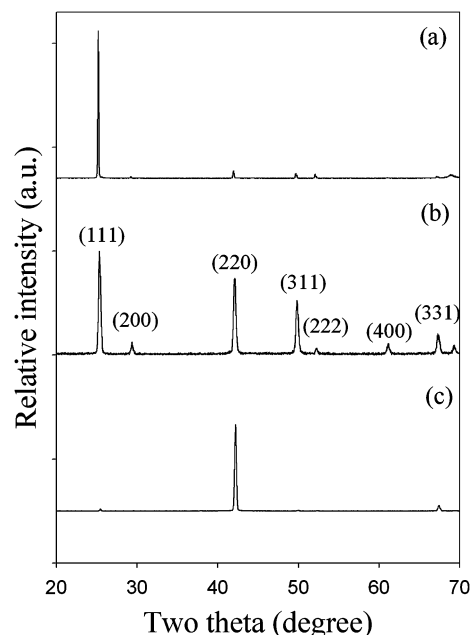


Fig. 1 Representative XRD patterns of the CuI films generated from (a) growth on a copper substrate comprising (111) grain orientation along its surface normal direction with ethanol as the growth solvent; (b) growth on a copper substrate comprising (100) grains with hexane as the growth solvent; and (c) the same as (b) but with ethyl acetate as the growth solvent.

^aInstitute of Surface Micro and Nano Materials, Xuchang University, Henan Province, Xuchang, 461000, China. E-mail: zhengzhi9999@yahoo.com.cn; Fax: +86-374-4369209; Tel: +86-374-4369209

^bDepartment of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, P.R. China

^cSurface Science Western, The University of Western Ontario, London, Ontario, Canada. E-mail: llau22@uwo.ca

growth direction is almost the only growth process on Cu (111). On Cu (100), it is also the main growth process accompanied by the formation of some (110) oriented γ -CuI grains.

From the perspective of crystal growth design for yielding the best γ -CuI properties, growth in its (111) direction is not desirable because while copper has a small ionic radius of 0.074 nm, iodine has a huge ionic radius of 0.206 nm and squeezing iodide into the tightly packed (111) plane during growth can lead to a high probability of iodide vacancy formation. Indeed, Fig. 2(a) and (b) give the photoluminescence spectra of the films shown in Fig. 1(a) and (b), spectra which show that, for both films, the exciton band of an ideal γ -CuI crystal at ~ 410 nm is weak and the broad defect band at ~ 420 nm is very intense. This phenomenon generally exists in CuI films mainly with (111) crystals.^{14,20} Although excess iodine has been associated with the presence of hole traps near the valence band maximum (VBM) of γ -CuI and the consequential fluorescence emission at ~ 420 nm, a recent first principles study shows that the introduction of iodide vacancies also gives new energy states slightly above the VBM of the stoichiometric crystal.²¹ In addition, it has been consistently shown that photodecomposition of γ -CuI leads to an increase of the defect band at ~ 420 nm.^{20,22} The spectral change was previously attributed to the surface states associated with excessive iodine due to iodine leaving the bulk and segregating to the surface.²² In our opinion, fluorescence emission is bulk instead of surface sensitive; hence, the defect band at ~ 420 nm is more likely to arise from bulk iodide vacancies than surface segregation/accumulation of iodine.

The above consideration drives the new crystal growth design to suppress (111) grain growth and enhance (110) grain growth, with the objective of growing γ -CuI with the (110) face, which is more open than the (111) face, as its growth front. The design strategy makes use of the well-known effects of solvent polarity on the growth habit in the solvothermal/hydrothermal formation of crystals.²³ In

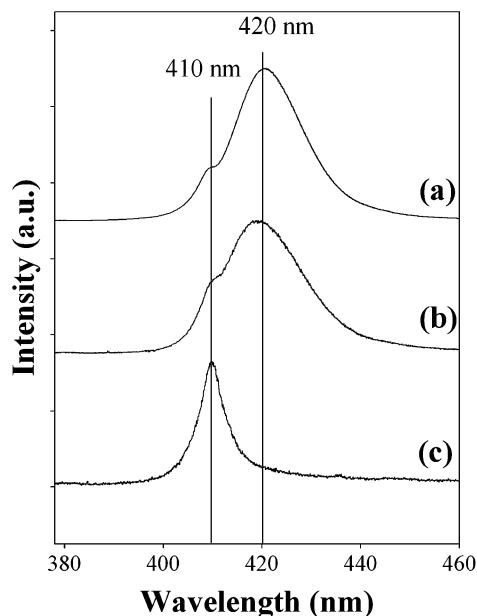


Fig. 2 Photoluminescence spectra of the CuI films having (a) highly oriented (111) grains corresponding to the same film as that in Fig. 1(a); (b) mixed (111) and (110) grains corresponding to the same film as that in Fig. 1(b); and (c) highly oriented (110) grains corresponding to the same film as that in Fig. 1(c).

essence, because the (111) face is polar and the (110) face is nonpolar, the adoption of a polar solvent in the growth process can be effective in suppressing (111) grain growth relative to (110) grain growth. The effectiveness of this design is demonstrated by the XRD data of a γ -CuI film showing virtually only highly oriented (110) grains in Fig. 1(c). The film was grown with the same conditions† as those showing the mixed grain orientations of (111) and (110) in Fig. 1(b), except that the solvent for the former was ethyl acetate whose dipole polarity is 1.78 D and that for the latter was hexane. It is evident from the XRD results that the use of ethyl acetate (polar) led to the formation of an almost entirely CuI (110) film; while the use of hexane (nonpolar) resulted in a film comprising both CuI (110) and CuI (111) grains. For the accomplishment of this “unconventional” growth habit in γ -CuI research, the use of a copper substrate with (100) grains appears to be important. We speculate that in the initial growth process, some γ -CuI (111) nuclei are grown on the step facets of the Cu (100) surface grains. These γ -CuI (111) nuclei then provide some γ -CuI (110) facets with the (110) direction along the surface normal direction of the substrate. As the growth conditions favor the γ -CuI growth in the (110) direction, once these (110) nuclei are formed, they can take over the film growth by covering and eliminating those nuclei with their (110) direction pointing away from the growth direction. In fact, the XRD data indicate the evolution from a mixed grain orientation growth habit to the growth of nearly pure (110) oriented film when the film grows from less than 1 micron to over 10 microns.

As expected, the advantage of suppressing (111) oriented grains and selectively growing highly oriented (110) grains is the improvement of crystallinity. This is demonstrated in Fig. 2(c) where the photoluminescence spectrum of the highly oriented (110) film is shown. Clearly the film only shows a sharp exciton band at ~ 410 nm with a full-width-at-half-maximum (FWHM) of only 5.8 nm, while the commonly reported FWHM value of the exciton band at ~ 410 nm is ~ 14 nm.²⁴

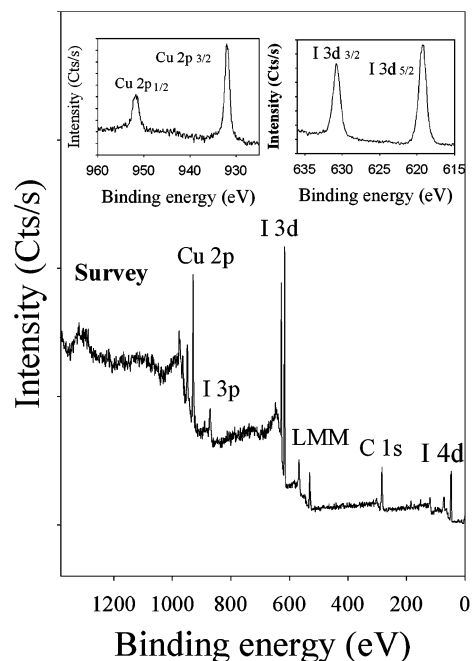


Fig. 3 Typical XPS survey spectrum and Cu 2p and I 3d core level spectra (inset) of the CuI crystal/film generated from I₂/solvothermal system.

We also conducted X-ray photoelectron spectroscopy analysis to check the surface composition of the resulting films. Fig. 3 shows the typical XPS survey and core level spectra of the CuI film obtained from the I₂/ethanol system. The I 3d_{5/2} and Cu 2p_{3/2} core levels appear at the binding energies of 619.4 and 932.1 eV respectively, which match the literature well with values of 619.5 and 932.3 eV for the pure CuI material.²⁵ Also, we confirmed the absence of any other by-product such as CuO or Cu(OH)₂ from the Cu 2p core level spectrum, even on the top surface.

In summary, the objective and strategy of the crystal growth design of highly oriented (110) γ -CuI films are explained. By selecting copper having (100) surface grains as the growth substrate and optimizing the solvent polarity effect on growth habit, the (111) grains commonly observed in all known growth data in the literature can be virtually completely suppressed and highly oriented (110) γ -CuI films can be formed. These films have no defect bands in their photoluminescence spectra and are expected to yield improved performance in their applications.

This work was supported by National Natural Science Foundation of China (Grant No. 20574058); Program for Science&Technology Innovation Talents in Universities of Henan Province (HASTIT-16, 2008) and Natural Science Foundation of Henan Province, China (Grant No. 611021900).

Notes and references

† In a typical procedure, a piece of copper foil (Sinopharm Chemical Reagent Co., Ltd, purity: >99.9%, used after rinsing with ethanol), 0.1 g of iodine powder (Sinopharm Chemical Reagent Co., Ltd, purity: >99.9%) and 15 mL of ethanol, hexane or ethyl acetate were placed in a 20 mL Teflon-lined autoclave. The autoclave was maintained at 160 °C for 24 h and then air cooled to room temperature. The products were taken out of the solution and washed with ethanol several times, and finally air-dried for characterization. X-Ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance XRD diffractometer equipped with a Göbblé mirror, using Cu K α radiation. A Kratos AXIS-HS X-ray photoelectron spectrometer (XPS) equipped with a standard and monochromatic source (Al K α) operated at 150 W (15 kV, 10 mA) was employed for surface analysis. The binding energy (B.E.) scale was calibrated against the B.E. of Au 4f_{7/2} at 84.0 eV. The photoluminescence (PL) studies of CuI films were performed with a 1000B Renishaw Micro-Raman system, and the excitation source was the 325 nm line of an He-Cd laser.

1 A. Chahid and R. L. McGreevy, *Physica B*, 1997, **234**, 87.

2 W. Sekkal and A. Zaoui, *Physica B*, 2002, **315**, 201.

3 M. Rusop, T. Soga, T. Jimbo and M. Umeno, *Surf. Rev. Lett.*, 2004, **11**, 577.

- 4 B. R. Sankapal, A. Ennaoui, T. Guminskaya, T. Dittrich, W. Bohne, J. Rohrich, E. Strub and M. C. Lux-Steiner, *Thin Solid Films*, 2005, **480**, 142.
- 5 G. R. A. Kumara, S. Kaneko, M. Okuya and K. Tennakone, *Langmuir*, 2002, **18**, 10493.
- 6 I. Tanaka and M. Nakayama, *J. Appl. Phys.*, 2002, **92**, 3511.
- 7 P. M. Sirimanne, M. Rusop, T. Shirata, T. Soga and T. Jimbo, *Chem. Phys. Lett.*, 2002, **366**, 485.
- 8 T. Tanaka, K. Kawabata and M. Hirose, *Thin Solid Films*, 1996, **281–282**, 179.
- 9 B. Mahrov, G. Boschloo, A. Hagfeldt, L. Dloczik and T. Dittrich, *Appl. Phys. Lett.*, 2004, **84**, 5455.
- 10 M. Niu, H. Fu, Y. Y. Jiang and Y. F. Zhao, *Chem. Commun.*, 2007, 272.
- 11 X. A. Xie, Y. Chen and D. W. Ma, *J. Am. Chem. Soc.*, 2006, **128**, 16050.
- 12 (a) A. Pfitzner, S. Reiser and T. Nilges, *Angew. Chem., Int. Ed.*, 2000, **39**, 4160; (b) A. Pfitzner, M. F. Brau, J. Zweck, G. Brunklaus and H. Eckert, *Angew. Chem., Int. Ed.*, 2004, **43**, 4228.
- 13 C. G. Oliveri, N. C. Gianneschi, S. T. Nguyen, C. A. Mirkin, C. L. Stern, Z. Wawrzak and M. Pink, *J. Am. Chem. Soc.*, 2006, **128**, 16286.
- 14 D. Kim, M. Nakayama, O. Kojima, I. Tanaka, H. Ichida, T. Nakanishi and H. Nishimura, *Phys. Rev. B*, 1999, **60**, 13879.
- 15 G. S. Hsiao, M. G. Anderson, S. Gorer, D. Harris and R. M. Penner, *J. Am. Chem. Soc.*, 1997, **119**, 1439.
- 16 (a) Z. Zheng, A. R. Liu, S. M. Wang, Y. Wang, Z. S. Li, W. M. Lau and L. Z. Zhang, *J. Mater. Chem.*, 2005, **15**, 4555; (b) Z. Zheng, S. M. Wang, D. P. Li, A. R. Liu, B. J. Huang, H. X. Zhao and L. Z. Zhang, *J. Cryst. Growth*, 2007, **308**, 398; (c) X. Li and M. X. Wan, *Cryst. Growth Des.*, 2006, **6**, 2661.
- 17 W. J. Li and E. W. Shi, *Cryst. Res. Technol.*, 2002, **37**, 1041.
- 18 See for example: (a) J. Inukai, Y. Osawa and K. Itaya, *J. Phys. Chem. B*, 1998, **102**, 10034; (b) B. Y. Andryushechkin, K. N. Eltsov and V. M. Shevlyuga, *Surf. Sci.*, 2001, **472**, 80; (c) B. Obliers, P. Broekmann and K. Wandelt, *J. Electroanal. Chem.*, 2003, **554**, 183.
- 19 P. Broekmann, N. T. M. Hai and K. Wandelt, *Surf. Sci.*, 2006, **600**, 3971.
- 20 Y. Yang and Q. M. Gao, *Langmuir*, 2005, **21**, 6866.
- 21 H. Feraoun, H. Aourag and M. Certier, *Mater. Chem. Phys.*, 2003, **82**, 597.
- 22 V. P. S. Perera and K. Tennakone, *Sol. Energy Mater. Sol. Cells*, 2003, **79**, 249.
- 23 (a) G. Clydesdale, K. J. Roberts, G. B. Telfer, V. R. Saunders, D. Pugh, R. A. Jackson and P. Meenan, *J. Phys. Chem. B*, 1998, **102**, 7044; (b) C. S. Strom, *J. Phys. Chem. B*, 1999, **103**, 11339; (c) J. M. Liang, Y. Ma, Y. Zheng and H. T. Davis, *Langmuir*, 2001, **17**, 6447; (d) S. P. Anthony, P. Raghavaiah and T. P. Radhakrishnan, *Cryst. Growth Des.*, 2003, **3**, 631.
- 24 Y. Yang, X. F. Li, B. Zhao, H. L. Chen and X. M. Bao, *Chem. Phys. Lett.*, 2004, **387**, 400.
- 25 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy*, ed. J. Chastain and R. C. King, Physical Electronics, Inc., Eden Prairie, Minnesota, 1995.