

Light-assisted chemical deposition of highly (0001) oriented zinc oxide film

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Highly (0001) oriented zinc oxide (ZnO) films of smooth layer type and hexagonal columns have been prepared on quartz glass substrates at temperature as low as 323 K by UV light assisted chemical deposition from an aqueous solution containing hydrated zinc nitrate and dimethylamine–borane (DMAB).

Highly (0001) oriented zinc oxide (ZnO) films find use in numerous applications such as surface acoustic wave (SAW) and piezoelectric devices,¹ and have attracted increasing attention as room-temperature UV laser emitting devices.² Oriented ZnO films have been prepared on (0001) oriented single aluminum oxide (sapphire) and quartz glass substrates³ by using gas phase deposition techniques such as molecular-beam epitaxy, laser abrasion and radio-frequency magnetron sputtering techniques.

Electrochemical preparation of oxide films from aqueous solutions is a simple, environmentally friendly and low temperature technique, and may be an alternative to gas phase deposition techniques. Pauporte and Lincot reported that (0001) oriented ZnO films can be prepared on a conductive GaN coated sapphire substrate by electrodeposition from a zinc chloride aqueous solution saturated with dissolved oxygen, and showed the possibility for a UV laser emitting device application.⁴

The author proposed a chemical process for preparing oxide films and demonstrated preparations of ZnO,^{5–7} CeO₂,⁸ and Fe₃O₄⁹ films from aqueous solutions containing the nitrate salts and dimethylamine–borane (DMAB). In the chemical process, the reduction reaction plays an important role in oxide formation and DMAB acts as the reducing agent for nitrate ion.⁷ The cell used for the process has an uncomplicated design, and the film can be obtained by simple immersion of the substrate into the solution. Also, materials including metals, ceramics and polymers can be used as the substrate regardless of their conductivity and melting point. In the chemical process, a catalytic activation process,¹⁰ which leads to Pd particles on the substrate,⁷ is indispensable for initiating the deposition reactions. Although the chemically prepared ZnO films are composed of aggregates of hexagonal columnar grains, (0001) oriented ZnO film could not be obtained under the adopted preparation conditions. It was speculated that the existence of catalytic particles prevented the development of a (0001) preferred orientation.

The author found that the highly (0001) oriented ZnO film could be obtained even on a quartz glass substrate by irradiating UV light during the chemical deposition. The catalytic activation process was not needed for the light-assisted chemical deposition, since UV light at a wavelength of 300 nm induced the reduction reaction of nitrate ion to nitrite ion.¹¹ The solution temperature is very important, affecting the preparation of highly (0001) oriented ZnO films. The effect of the temperature on the preferred orientation and morphology of ZnO films was investigated by X-ray diffraction and atomic force microscopy (AFM).

The aqueous solution used for preparing ZnO films was composed of 0.1 mol L⁻¹ hydrated zinc nitrate (Zn(NO₃)₂·6H₂O) and 0.01 mol L⁻¹ DMAB ((CH₃)₂NH·BH₃). The solution was prepared with reagent grade chemicals and

distilled water purified using a Milli RX12 Plus system (Millipore Corporation). The freshly prepared solution was used for the film formation. The solution temperature and pH were 323–343 K and 6.0, respectively. A quartz glass sheet (25.4 mm × 25.4 mm × 1.1 mm) was used as the substrate. Prior to the film formation the substrate was rinsed in acetone and then rinsed with distilled water.

Fig. 1 shows a schematic view of apparatus used for the preparation. A glass beaker (a) with a cylindrical joint (b) at one side was used as the cell. The substrate (c) was adhered to the end of joint by using four clamps and was contacted to the aqueous solution (d) filled in the cell. Irradiation of UV light at wavelength below 325 nm was carried out in a direction normal to the substrate surface by using a high-pressure mercury lamp (USHIO Denki, USH-10D, 100 W) and optical filters (e) during the film formation. The cell was immersed into hot water (f) maintained at a preparation temperature of 323–343 K with a temperature control system (g).

The optical band gap energy evaluated from the absorption edge taken with a spectrophotometer was constant at 3.3 eV for the films prepared at 323 and 343 K. This energy is characteristic for non-doped wurtzite ZnO.⁵ Secondary ion mass spectrometry analysis with a ULVAC-PHI model 6650 and primary Cs⁺ ion source indicated that the film contained only a minute amount of boron impurity originating from the DMAB.⁶ The boron, however, could not be detected by inductively coupled plasma-atomic emission spectroscopy (ICP, Seiko Instruments, SPS-1500 VR). The boron content was estimated to be less than 0.002 mass% from the detection limit of ICP analysis. It was confirmed that wurtzite ZnO film with purity above 99.998% was obtained by the light-assisted chemical deposition.

Fig. 2 shows AFM images for morphologies of ZnO films prepared on a quartz glass substrate at 323 and 343 K for 1 and 2 h. At the solution temperature of 323 K, ZnO grains of hexagonal columnar shape grew in the direction normal to the substrate surface with the passage of time after irradiating with UV light. The grains formed after 1 h deposition had about the same width of 180 nm and height of 100 nm, as shown in Fig. 2(a). The density of ZnO grains was about 1.6 × 10⁹ cm⁻². Coalescences between adjacent ZnO grains were observed in

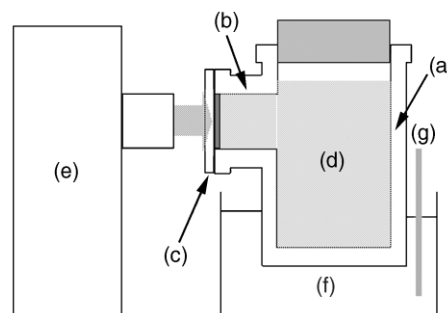


Fig. 1 Schematic view of the preparation cell used for light-assisted chemical deposition: (a) cylindrical beaker, (b) cylindrical joint, (c) substrate, (d) solution, (e) high pressure mercury lamp, (f) hot water bath, (g) temperature control system.

the image. Hexagonal facets corresponding to the (0001) plane in wurtzite ZnO crystal could be observed clearly and were parallel to the substrate surface. The grains had a smooth top surface (0.26 nm root-mean-square roughness (rms)) calculated from the AFM image. The height and width increased with an increase in deposition time. Formation of a continuous film was achieved by complete coalescence at a deposition time of 2 h corresponding to a film thickness of *ca.* 200 nm [Fig. 2(b)]. The ZnO film showed a smooth surface (*ca.* 1.0 nm rms).

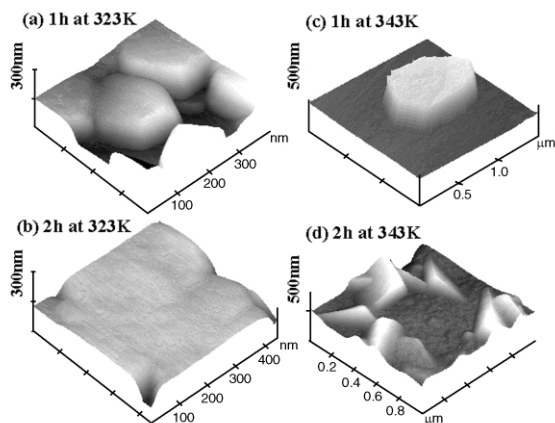


Fig. 2 AFM images for surface morphologies of ZnO films prepared by light-assisted chemical deposition for 1 and 2 h at 323 and 343 K. The images were taken with a tapping mode atomic force microscope (Digital Instruments, NanoScope IIIa, Dimension 3000).

At a solution temperature of 343 K hexagonal columnar grains with increased width of 600 nm and height of 250 nm were formed after 1 h deposition [Fig. 2(c)]. Hexagonal facets showed slightly increased irregularity (rms 7.39 nm) and were tilted somewhat. A continuous film with large surface irregularity (rms 31.9 nm) was formed upon coalescence of the ZnO grains at a deposition time of 2 h and tilted (0001) facets could be observed [Fig. 2(d)].

Fig. 3 shows X-ray diffraction spectra for ZnO films prepared for 1 h at 323 and 343 K. The profile of the X-ray diffraction spectrum strongly depended only on the solution temperature regardless of deposition time. The ZnO film prepared at 323 K showed only two peaks, which were assigned to (0002) and (0004) planes in wurtzite ZnO.¹² A broadened X-ray diffraction pattern originating from the quartz glass substrate could not be

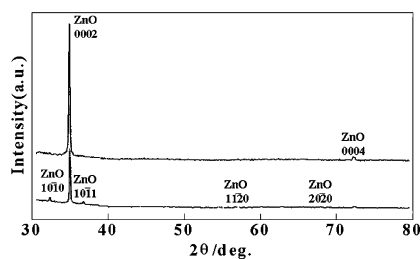


Fig. 3 X-Ray diffraction spectrum for ZnO films prepared by light-induced chemical deposition for 1 h at 323 and 343 K. Spectra were recorded using a MAC Science MXP18 diffractometer system with monochromated Cu-K α radiation operated at 40 kV and 100 mA. The diffraction angles were referenced to those for high purity Si powder.

observed on the spectrum owing to the very strong (0002) diffraction line. It was confirmed from the X-ray diffraction and AFM images that highly (0001) oriented ZnO film could be obtained onto quartz glass substrates at temperature as low as 323 K by UV light-assisted chemical deposition.

In addition to the (0002) and (0004) peaks, some weak peaks assigned to those for wurtzite ZnO crystal could be observed on the spectrum recorded for the ZnO film prepared at 343 K. The (0002) diffracted X-ray line was slightly less intense than for the 323 K sample, indicating that the (0001) preferred orientation weakened, compared with that at 323 K.

The fact that the isolated ZnO grains were formed on the substrate indicates that the film formation proceeds by a tridimensional mechanism. The smooth top surface and hexagonal columnar shapes of ZnO grains are a consequence of the growth of individual nuclei in the direction of $\langle 0001 \rangle$ orientation. In wurtzite ZnO crystals, the $\langle 0001 \rangle$ orientation is vertical to the (0001) plane. The (0001) plane is apt to be parallel to the top surface under conditions close to the equilibrium state, because of the lowest surface energy in wurtzite ZnO crystal.¹³ This suggests that the growth condition at 323 K is close to the equilibrium state. Therefore, the preferred orientation of the resultant ZnO grains is determined by the nucleation stage, which is closely related to the interfacial energy between the ZnO grain and quartz glass substrate. The change in preferred orientation of isolated ZnO grains is evidence of the importance of the interfacial energy, and indicates that the interfacial energy changes depending on the solution temperature.

In the chemical deposition *via* a catalytic activation process, (0001) oriented ZnO film could not be obtained, regardless of preparation conditions.⁶ This fact indicates that the catalytic particles formed on the substrate strongly affects the interfacial energy, central to the nucleation stage, and prevents the formation of (0001) oriented ZnO film.

In conclusion, highly (0001) oriented ZnO films with smooth surfaces have been prepared on a quartz glass substrates at temperatures as low as 323 K by UV light-assisted chemical deposition from an aqueous solution containing hydrated zinc nitrate and DMAB. Prior to coalescence ZnO hexagonal columnar grains were formed with a low density.

Notes and references

- 1 T. Mitsuya, S. Ono and K. Wase, *J. Appl. Phys.*, 1980, **51**, 2464–2470.
- 2 Y. Segawa, A. Ohotomo, M. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu and G. K. L. Wang, *Phys. Status Solidi B*, 1997, **202**, 669–672.
- 3 M. Kadota, *Jpn. J. Appl. Phys.*, 1993, **32**, 2341–2345.
- 4 Th. Pauporte and D. Lincot, *Appl. Phys. Lett.*, 1999, **75**, 3817–3819.
- 5 M. Izaki and T. Omi, *Appl. Phys. Lett.*, 1996, **68**, 2439–2440.
- 6 M. Izaki and J. Katayama, *J. Electrochem. Soc.*, 2000, **147**, 210–213.
- 7 M. Izaki, *J. Electrochem. Soc.*, 1999, **146**, 4517–4521.
- 8 M. Izaki, T. Saito, M. Chigane, M. Ishikawa, J. Katayama, M. Inoue and M. Yamashita, *J. Mater. Chem.*, 2001, **11**, 1972–1974.
- 9 M. Izaki and O. Shinoura, *Adv. Mater.*, 2001, **13**, 142–145.
- 10 M. Schlesinger, in *Modern Electroplating*, ed. M. Schlesinger and M. Paunovic, Wiley-Interscience, New York, 4th edn., 2000, p. 667.
- 11 M. Izaki, Y. Kobayashi, J. Katayama, H. Takahashi and H. Nakamura, *Electrochem. Soc. Proc.*, 1999, **99-34**, 390–394.
- 12 Joint Committee of Powder Diffraction Standard, Powder Diffraction File, No. 36-1451, International Center for Diffraction Data, Swarthmore, PA, 1992.
- 13 N. Fujimura, T. Nishihara, S. Goto, J. Xu and T. Ito, *J. Cryst. Growth*, 1993, **130**, 269–279.