Orientation Controlled Electrodeposition of Zinc Oxide Thin Films

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Cathodic electrodeposition of zinc oxide (ZnO) thin films in aqueous zinc nitrate solutions has been studied using various conductive substrates. While the deposited films did not possess specific crystallographic orientation on random structured substrates such as indium-tin-oxide-coated conductive glass or polycrystalline Au electrodes, the films were oriented in a ZnO(002) // substrate direction when deposited on ordered surfaces such as Au(111), Si(100), Si(111) and basal-planes of oriented pyrolytic graphite (OPG), despite of the difference in atomic geometry or large lattice misfit at the substrate/ZnO boundary. In particular, the ZnO film deposited on a basal-plane of OPG was highly oriented with its c-axis perpendicular to the substrate, whereas the film deposited on an edge-plane of OPG had a random structure. Because the basal-plane of OPG is a Van der Waals surface which is covered with anti-bonding π-electrons, it should not exhibit a notable template effect to the ZnO adlayer, so that ZnO is self-oriented as growing in a direction to expose the most stable (002) planes to the electrolyte. The direction of the crystal growth was altered by 90° into a ZnO(100) // substrate orientation by adding 2,9,16,23-tetrasulfo-phthalocyaninatosilicon(IV) (TSPcSi) to the deposition bath, because of preferential adsorption of TSPcSi onto the (002) crystal faces to hinder the crystal growth along the c-axis.
Key words: zinc oxide, electrodeposition, epitaxial, Van der Waals surface, phthalocyanine

1.INTRODUCTION

Chemical and electrochemical deposition of compound semiconductor thin films in solutions [1,2] enjoys its advantages in reducing the cost as well as the environmental stress upon processing as compared to thin film processing in gas phases such as vacuum evaporation or CVD. However, these methods have to be developed to realize precise control of the film structure during the processing. Because the function of a device is the sum of the phenomena occurring at atomic and ionic levels, achieving crystallographic uniformity of the materials should result in a drastic improvement of the device performance.

It has been generally believed that film growth in solution results in structurally and chemically inhomogeneous products because of the strong chemical interactions among precursor molecules, ions and solvent molecules. However, ordered growth of compound thin films with controlled crystal structure, orientation and size has been successfully achieved in recent active studies on solution phase film processing. One of the most promising approaches to control the crystallographic orientation of the film is to achieve heteroepitaxial growth by using a single crystal substrate having an atomic geometry matched to that of the material to be deposited. Several groups have succeeded in deposition of single crystal thin films of cadmium chalcogenides by this approach [3-8], while only very few examples can be found for metal oxides [9-11]. However, growth control by this strategy automatically limits the choice of the substrate materials. Single crystal materials are also very expensive. Therefore, achieving ordered growth of thin films by use of single crystal substrate virtually finds no use in practical applications. Interestingly, there have been several reports in which thin films with high crystallographic orientation were obtained on amorphous or even random structured polycrystalline substrates [12-14]. It is because the crystallographic orientation of the deposited films is not only controlled by the geometrical and chemical matching between the substrate and the deposits but also strongly influenced by anisotropic stability of the deposited materials at the deposit/solution interfaces. It is supposed that such influence from the chemical stability of the growing surface of the deposits prevailed to that from the substrate materials in the above examples. The surface chemistry influences not only orientation of the crystals but also the crystal structure and size. In our recent studies on electrochemically induced chemical deposition (EICD) of CdS thin films, changing co-existing anion from Cl^- to SO_4^{2-} was found to change the crystal structure of CdS from hexagonal into cubic [15,16]. Presence of surface adsorbates during the film growth has also found a significant effect on the crystal growth as exemplified in our recent studies on the formation of nano-particulate CdS thin films by introducing thiols in the EICD process [16] and electrochemical self-assembly of ZnO/dye mixed thin films [17].

In the present study, we have attempted to control crystallographic orientation in the cathodic electro-deposition of zinc oxide thin films from aqueous zinc nitrate bath. Pauporté and Lincot have recently succeeded in heteroepitaxial electrodeposition of ZnO thin film by electrochemical reduction of dissolved oxygen in an aqueous $ZnCl_2$ bath and using an n-GaN electrode which imposes very small lattice mismatch of only 2.4 % to ZnO [11]. Here, we have purposely employed cheap single crystals such as Au, Si and graphite, even though large lattice mismatches are expected for ZnO deposition. We have also prepared ZnO thin films in the presence of organic dyes which are expected to get adsorbed onto specific crystal faces and alter the direction of crystal growth. The purpose of this study is to establish economical and versatile methods to obtain orientation-controlled ZnO thin films with the above-mentioned strategies.

2.EXPERIMENTAL

An oriented pyrolytic graphite (OPG, Union Carbide) or an STM-grade highly oriented pyrolytic graphite (HOPG, Advanced Ceramics) was cleaved to expose their basal-planes (graphite(002)). While OPG is poly-crystalline, made up with graphite crystals aligned only along their c-axis but twisted around the c-axis, HOPG is a single crystal, as found in our analyses by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Edge-planes of OPG were polished by SiC

abrasive paper and 0.5 µm alumina powder. A commercial Au single crystal film deposited on a plastic substrate (Auro Sheet, Tanaka Precious Metals) served as a Au(111) substrate. A poly-crystalline random-structured Au electrode was etched in aqua regia for 10 s and rinsed by pure water prior to the film deposition. Ohmic contacts to n-Si(100) and n-Si(111) were made by connecting Cu wire with an In-Ga alloy. Si electrodes were etched in a 5% HF aqueous solution for 2 min, rinsed by pure water and immediately dipped in the deposition bath. An ITO coated glass electrode (10Ω/sq.) was ultrasonically cleaned in acetone, 2-propanol and water, each for 15 min.

The electrodeposition of ZnO films was performed according to the method developed by Izaki and Omi, that is, cathodic electrolysis under potentiostatic conditions with the electrode potential of –0.8 or –0.9 V (vs SCE) and for 60 min in a 0.1 M $Zn(NO_3)_2$ aqueous solution maintained at 70 °C [18]. Sodium salt of 2,9,16,23-tetra-sulfophthalocyaninatosilicon(IV) (TSPcSi) was provided by Professor Dieter Wöhrle of university of Bremen. TSPcSi was added to the deposition bath at 50 µM to study its effect on the crystal growth [17]. The deposited films were rinsed by water and dried in air at room temperature.

The crystallographic orientation of the deposited films has been studied by measuring their XRD patterns on a RIGAKU RAD-2R X-ray diffractometer using Cu-Kα radiation. Surface morphologies of the films were observed by a TOPCON ABT-150FS scanning electron microscope (SEM).

3.RESULTS AND DISCUSSION

Deposition of ZnO thin films has been carried out on various conductive substrates under the same conditions and their XRD patterns are shown in Fig. 1 for the three major diffraction peaks arising from the (100), (002) and (101) planes of hexagonal ZnO. While all of the peaks are assigned to those of ZnO, the relative peak intensities
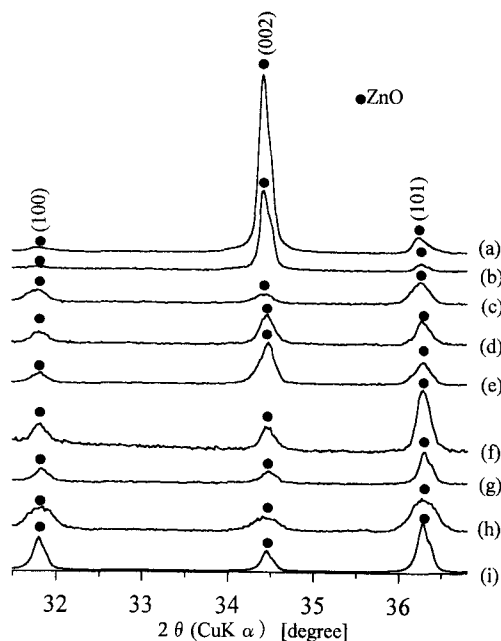
Fig.1 XRD patterns of ZnO thin films electrodeposited at -0.9V vs SCE and for 1h on HOPG basal-plane (a), OPG basal-plane (b), OPG edge-plane (c), Si(111) (d), Si(100) (e), Au(111) (f), polycrystalline Au (g) and ITO glass (h) in a 0.1M $Zn(NO_3)_2$ aqueous solution at 70°C. XRD pattern of ZnO powder sample (i) also shown for comparison.

significantly varies for the films deposited on different substrates, as noticed by comparison to the XRD pattern of standard ZnO powder sample also shown in the figure. Such differences in the relative peak intensity indicate the differences in the alignment of crystallographic orientations. In order to evaluate the crystallographic orientation quantitatively, orientation indices (X_{hkl}) were calculated for each diffraction peak in Fig. 1 according to the method described in our previous report [17] and the results are listed in Table 1. For crystal planes not oriented in specific directions, the X_{hkl} equals to 1. Any crystal faces whose X_{hkl} values exceed 1 tend to be parallel with the substrate, while those with X_{hkl} values smaller than 1 have a tendency to be not parallel with the substrate. All of the X_{hkl} values are almost 1 for the films deposited on ITO coated glass and polycrystalline Au electrodes which have randomly oriented polycrystalline surfaces, suggesting that ZnO deposited on these substrates also has random structure. Examination of the X_{hkl} values for the films deposited on the ordered surfaces of Au(111), Si(100), Si(111) and the basal-plane of OPG and HOPG reveals a preferential orientation of ZnO(002) planes parallel with the substrate surface, as recognized from the X_{002} values being larger than 1. The crystallographic orientation in this preference becomes most prominent for the films deposited on the basal-planes of graphite for which X_{002} becomes as large as 4, at the expense of the other two parameters, especially of X_{100}, indicating that ZnO(100) planes are almost vertical to the substrate and the ZnO(002) planes are almost perfectly aligned parallel with the substrate. Comparison of the X_{hkl} values for the films deposited on the basal-planes of OPG and HOPG finds a higher order in the crystallographic orientation for the latter, indicating that the higher order of the substrate surface contributes to the more perfect crystallographic alignment of the deposits. The film deposited on the edge-plane of an OPG, in contrast, has a random structure, confirming the special role of the basal-plane for the ordered growth of ZnO.

Surface morphologies of ZnO thin films deposited on various graphite surfaces were observed by SEM (Fig. 2). It can be seen that the films are made of hexagonal particles in all cases. However, it should be noticed that the hexagonal faces of the particles are more clearly perceived for the film deposited on the basal-plane of OPG (b) than that deposited on the edge-plane of OPG (a), and it gets even more distinctive for the film deposited on HOPG (c). It is therefore reasonable to consider that the hexagonal faces of the particles correspond to the (002) planes of ZnO crystals and the rectangular sides to the (100) planes. These observations quite nicely match with the crystallographic orientation of the films found in the XRD analysis. Careful inspection of Fig.3(c), however,

Table1 Orientation indices determined from the XRD data in Figure1 and using the method described in ref.17.*

substrates	orientation indice		
	X_{100}	X_{002}	X_{101}
ITO	1.13	0.93	0.95
polycrystal Au	0.88	1.02	1.06
Au(111)	0.65	1.30	1.07
Si(100)	0.53	2.48	0.62
Si(111)	0.84	1.83	0.72
OPG edge-plane	1.04	1.09	0.93
OPG basal-plane(002)	0.66	2.51	0.53
HOPG basal-plane(002)	0.09	4.07	0.17

*Data of ZnO powder sample (JCPDS,36-1451) has been used as the standard for calculation.

reveals that the rotation of each crystallite around the c-axis is not uniform, indicating a random structure of the film for the in-plane crystallographic orientation. It is therefore understood that the ZnO film deposited on HOPG is not single crystal but is highly oriented only along the c-axis.

The lattice mismatch at the substrate/ZnO(002) boundary has to be considered in an attempt to understand the observed differences in the crystallographic orientations of the ZnO thin films deposited on various ordered surfaces. For the (002) planes of ZnO with 6-fold atomic symmetry to be deposited, several adlayer structures can be expected on the 6-fold symmetrical planes of the substrate as illustrated in Fig. 3. The difference between the interatomic distance in ZnO(002) planes (a_{ZnO}) and site to site distance (a_{site}) imposed from the substrate has to be as small as possible for the epitaxial growth to take place. The misfit defined as $\{(a_{ZnO} - a_{site})/a_{site}\} \times 100$ (%) was calculated for each substrate and for each adlayer structures (Table 2). The value of lattice mismatch usually has to be smaller than 10 % to expect an epitaxial alignment of the deposit to the substrate. As can be seen from Table 2, all of the substrates used in this study enforce large misfit in any adlayer structures. Among all, the (1×1) sites of Au(111) surface impose relatively small misfit of 12.66%. The observed ZnO(002)//substrate preference on Au(111) as compared to that of poly-Au (Table 1) could be attributed to the formation of epitaxial ZnO seeds on Au(111), because epitaxial electrodeposition of CdS(002) onto (√3×√3)R30° sites of Au(111) has been reported in spite
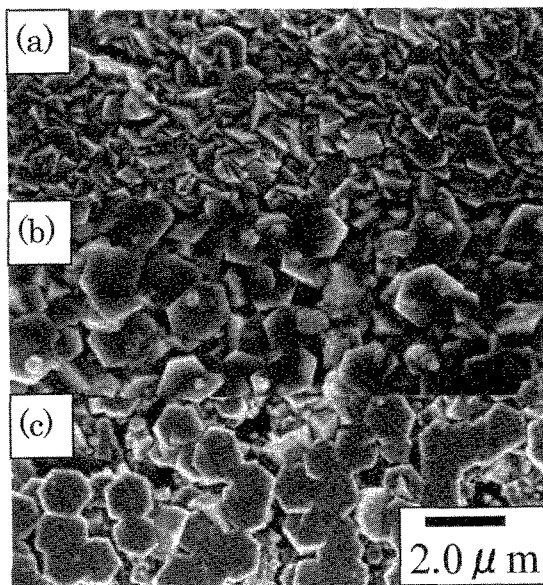

Fig.2 SEM photographs of ZnO thin films electrodeposited at –0.8V vs SCE and for 1h on OPG edge-plane (a), OPG basal-plane (b) and HOPG basal-plane (c) in a 0.1M Zn(NO₃)₂ aqueous solution at 70°C.
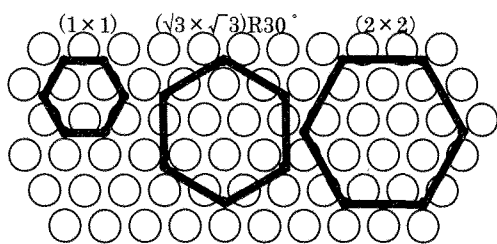

Fig.3 Possible adlayer structures in 6-fold symmetry.

of their large lattice mismatch of 17.2 % [19]. However, the preferential orientation of ZnO films on Au(111) is actually less significant than those of the films deposited on other substrates which have larger mismatches. The film deposited on the 4-fold symmetrical Si(100) surface indeed results in a high order in c-orientation than that on the 6-fold symmetrical Si(111), despite of the fact that Si(100) does not provide any geometrical matching to ZnO(002). It is therefore concluded that heteroepitaxial deposition of ZnO onto these conductive substrates with unmatched geometry is not possible unlike the case with n-GaN [11], yet use of these different substrates does contribute to the control of the crystallographic orientation of ZnO. The reason of highly ordered growth of ZnO on basal-planes of graphite can be explained by considering the fact that they are Van der Waals surfaces covered by anti-bonding π-electrons of sp^2 carbon, which probably exhibit no significant template effect to the adlayer structure. The deposited ZnO crystallites are therefore self-oriented to expose the closest packed (002) planes to the electrolyte due to its highest chemical stability. The direction of crystal growth during film deposition is determined by the energetic balance between the substrate/deposit and deposit/solution interfaces. In the electrodeposition process in solution, as in this study, the effect of the latter is supposed to be significant because of strong ionic interactions in solutions, as compared to the processes in vacuum phase. Because a Van der Waals surface such as the basal-plane of graphite brings about very moderate template effect to the structure of the deposits, the direction of the crystal growth is controlled by the anisotropic stability of the deposits toward solution, leading to growth of ZnO along c-axis in case of the present study. Ordered growth of hexagonal CdS onto Van der Waals surfaces of layered compounds such as WSe₂ and MoTe₂ by vacuum evaporation has also been observed despite of their large lattice mismatch, called as "Van der Waals epitaxy" by Löher et al. [20]. The electrodeposition of ZnO on basal-planes of graphite in this study could be regarded as "electrochemical Van der Waals epitaxy" by analogy.

Because the crystallographic orientation of the deposited films is largely dependent on the chemical stability of the deposit/solution interface, addition of such chemical species that directly affect the interfacial chemistry should influence the direction of the film growth. Indeed, addition of TSPcSi to the deposition bath at a very low concentration significantly changed the crystallographic orientation of the deposited film. TSPcSi is a dye molecule, which is expected to be useful as a photo sensitizer to ZnO for photoelectrochemical application [21] and has been found to give a significant influence on ZnO crystal growth in our recent study [17]. The XRD pattern of the ZnO film deposited on the basal-plane of OPG and in the presence of TSPcSi is shown in Fig. 4. It is evident that the diffraction peak from (002) planes diminishes, while the peak from (100) planes is significantly enhanced, making a clear contrast to the XRD pattern of ZnO film deposited on the same substrate but in the absence of TSPcSi (Fig. 1b). Calculation of orientation indices from Fig. 4 reveals X_{100}, X_{002} and X_{101} values of 1.62, 0.47 and 0.88, respectively, clearly indicating a ZnO(100)//substrate alignment of the deposited ZnO crystallites. The degree of this alignment is more significant than that of the same film deposited on an ITO coated glass for which the orientation indices were 1.394, 0.680 and 0.914 [17]. The observed switching of the crystallographic orientation by 90°, i.e., from c-axis ⊥

Table2 Atomic symmetry and interatomic distance for each substrates used in this study, and calculated lattice mismatch for deposition of Zn(002) (a_{ZnO}=3.249Å) in each adlayer structure

substrates	symmetry	interatomic distance(Å)	lattice mismatch		
			(1×1)	$(\sqrt{3}\times\sqrt{3})R30°$	(2×2)
Au(111)	6-fold	2.884	12.66	38.96	43.37
Si(111)	6-fold	3.840	15.39	51.15	57.70
Si(100)	4-fold	3.840	–	–	–
Graphite(002)	6-fold	2.470	31.54	24.06	34.23

substrate into c-axis//substrate direction is explained from preferential adsorption of TSPcSi molecules onto the (002) crystal faces of ZnO to hinder the crystal growth along the c-axis. As a result, crystal growth of ZnO takes place preferentially into (100) direction, thus the (100) crystal planes is exposed to the electrolyte to build up a film with (100)//substrate orientation [17]. The SEM picture of this film is shown in Fig. 5, which shows a unique morphology of disk-like deposits of which disk plane aligns perpendicular to the substrate. Similar morphology has been found for the film deposited on an ITO glass substrate, where the edge and plane of the disks were found to correspond to (100) and (002) crystal faces of ZnO, respectively, by TEM [17]. Careful observation of Fig. 5 finds that the disk-like deposits are assemblies of fine crystals. Since each disk stack has been found to consist of single crystals of ZnO in electron beam diffraction analysis [17], these small crystals should have perfect crystallographic alignment with each other within the disk-like assemblies. The fact that the addition of surface modifying organic molecules can effectively alter the crystallographic orientation further supports that ZnO crystal growth on the basal-plane of graphite in the present system is not under control of the substrate/deposit interface energy but is dominated by chemical events taking place at the growing surface of ZnO.

4.CONCLUSION

The present study has found that the direction of the crystal growth and hence film growth is strongly influenced by the chemistry at the deposit/solution interface in the electrodeposition of ZnO. While use of single crystal substrate with matched structure such as n-GaN for ZnO still enables heteroepitaxial growth of
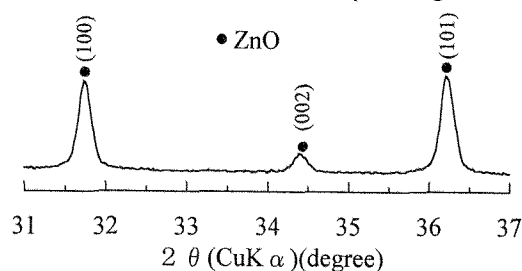

Fig.4 XRD pattern of a ZnO thin film electrodeposited at -0.9V vs SCE and for 1h on basal-plane of an OPG in a 0.1M Zn(NO$_3$)$_2$ + 50 μ M TSPcSi mixed aqueous solution at 70°C.
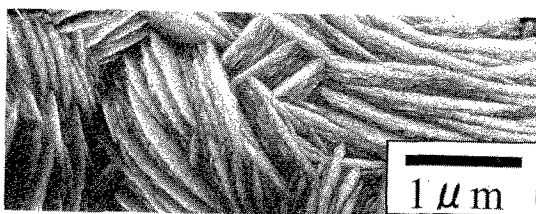

Fig.5 SEM photograph of a ZnO thin film electrodeposited at -0.9V and for 1h on basal-plane of an OPG in a 0.1M Zn(NO$_3$)$_2$ + 50 μ M TSPcSi mixed aqueous solution at 70°C

ZnO [11], use of other substrates with unmatched structures does influence the crystallographic orientation of the deposited film. "Electrochemical Van der Waals epitaxy" using substrates with van der Waals surfaces and modification of crystal growth by use of surface adsorbates are also expected to be useful for orientation control in the chemical and electrochemical deposition of other compound thin films.

REFERENCES
1) D. Lincot, M. Froment and H. Cahet, *Advances in Electrochemical Science and Engineering*, R.C. Alkire and D.M. Kolb (eds.), vol. 6, WILEY-VCH, 165 (1999).
2) G. Hodes, *Physical Electrochemistry: Principles, Methods and Applications*, I. Rubinstein (ed.), Marcel Dekker Inc., New York, 515 (1995).
3) M. Froment, M.C. Bernard, R. Cortes, B. Mokili and D. Lincot, *J. Electrochem. Soc.*, **142**, 2642 (1995).
4) D. Lincot, M.J. Furlong, M. Froment, R. Cortes and M.C. Bernard, *Mat. Res. Soc. Symp. Proc.*, vol. **451**, 223 (1997).
5) Y. Golan, G. Hodes and I. Rubinstein, *J. Phys. Chem.*, **100**, 2220 (1996).
6) Y.F. Nicolau, M. Dupuy and M. Brunel, *J. Electrochem. Soc.*, **137**, 2915 (1990).
7) I. Villegas and J.L. Stickney, *J. Electrochem. Soc.*, **138**, 1310 (1991).
8) S. Gorer, J.A. Ganske, J.C. Hemminger and R.M. Penner, *J. Am. Chem. Soc.*, **120**, 9584 (1998).
9) Y. Matsumoto, M. Fujisue and J. Hombo, *J. Electroanal. Chem.*, **314**, 323 (1991).
10) E.W. Bohannan, M.G. Shumsky and J.A. Switzer, *Chem. Mater.*, **11**, 2289 (1999).
11) Th. Pauporté and D. Lincot, *Appl. Phys. Lett.*, **75**, 24 (1999).
12) S. Lindroos, T. Kanniainen and M. Leskelä, *Appl. Surf. Sci.*, **75**, 70 (1994).
13) T. Kanniainen, S. Lindroos, J. Ihanus and M. Leskelä, *J. Mater. Chem.*, **6**, 161 (1996).
14) T. Yoshida, K. Yamaguchi, T. Kazitani, T. Sugiura and H. Minoura, *J. Electroanal. Chem.*, **473**, 209 (1999).
15) K. Yamaguchi, T. Yoshida, T. Sugiura and H. Minoura, *J. Phys. Chem. B*, **102** (48), 9677 (1998).
16) K. Yamaguchi, T. Yoshida, N. Yasufuku, T. Sugiura and H. Minoura, *Electrochemistry*, **67**, 1168 (1999).
17) T. Yoshida, M. Tochimoto, D. Schlettwein, D. Wöhrle, T. Sugiura and H. Minoura, *Chem. Mater.*, **11**, 2657 (1999).
18) M.Izaki and T.Omi, *Appl.Phys.Lett.*, **68**, 2439 (1996).
19) U. Demir and C. Shannon, *Langmuir*, **10**, 2794 (1994).
20) T. Löher, Y. Tomm, C. Pettenkofer, M. Giersig and W. Jaegermann, *J. Cryst. Growth*, **146**, 408 (1995).
21) D. Schlettwein, T. Oekermann, T. Yoshida, M. Tochimoto and H. Minoura, *J. Electroanal. Chem.*, **481**, 42 (2000).